

STRUCTURAL STUDIES OF AMINO ACID COMPLEXES

By

SHUI-TSE CHOW, B.Sc. (NANYANG)

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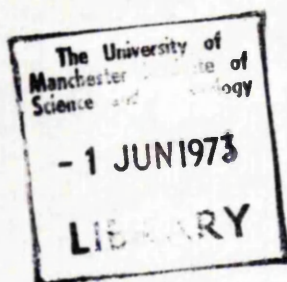
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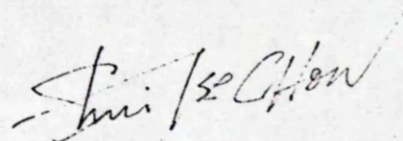
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TO

MY PARENTS

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January, 1973

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ABBREVIATIONS

| | | |
|---------------------|---|---------------------------------|
| AlaH ^(a) | = | alanine |
| ArgH | = | arginine |
| AspH | = | aspartic acid |
| ButH | = | butyric acid |
| DabaH | = | 1,4-diaminobutyric acid |
| DapH | = | 1,3-diaminopropanic acid |
| EDTA | = | ethylenediaminetetraacetic acid |
| en | = | ethylenediamine |
| GluH | = | glutamic acid |
| GlyH | = | glycine |
| HisH | = | histidine |
| LyH | = | lysine |
| OrH | = | ornithine |
| PenH | = | 1-aminocyclopentanic acid |
| ProH | = | proline |
| Py | = | pyridine |
| SerH | = | serine |
| ThrH | = | threonine |
| TyrH | = | tyrosine |
| b | = | broad |
| m | = | medium |
| s | = | strong |
| sh | = | shoulder |
| sp | = | sharp |
| w | = | weak |

(a) The anionic form of the amino acid will be represented without "H", e.g. ala = alaninate.

SUMMARY

Metal complexes of a potentially tridentate α -amino acid, L-arginine, were prepared and characterized by means of infrared and electronic spectroscopic, and magnetic susceptibility techniques. L-Arginine was found to act as a monodentate or bidentate ligand in the zwitterion form (such as $[\text{Cu}(\text{L-ArgH})_2(\text{ClO}_4)_2]$, $[\text{Ni}(\text{L-ArgH})_3(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, and $[\text{Cu}(\text{L-ArgH})_2(\text{H}_2\text{O})_2]\text{NO}_3$), and as a tridentate bridging ligand in the anionic form (such as $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_3]\text{NO}_3$).

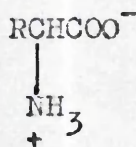
A unique "pressure rearrangement" in the solid state for the perchlorate group was found in the metal(II)-L-arginine-perchlorate systems.

Metal complexes of a Schiff base derived from L-arginine and salicylaldehyde have also been studied. The anomalous magnetic moments found for the copper(II)-N-salicylidenearginine complexes were explained as resulting from direct copper-copper interaction and super-exchange interaction through a tetrametallic structure. The anomalous magnetic moments found for the nickel(II)-N-salicylidenearginine complexes may be due to existence of an octahedral-square planar equilibrium in the solid state.

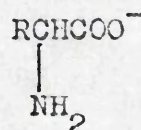
INTRODUCTION

(i) Introductory Section

Simple amino acids exist in the solid state as zwitterions, LH (i), but almost invariably coordinate as the

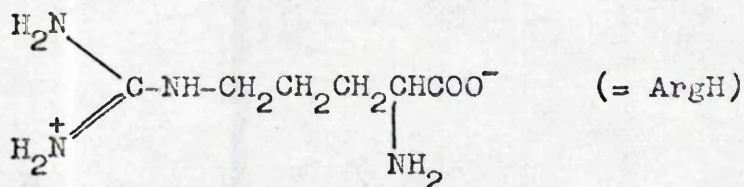


(i)



(ii)

anionic species, L⁻, (ii). In this present investigation coordination complexes of the unusual amino acid, L-arginine, (iii), have been synthesised and studied. Arginine differs from other simple amino acids in that the protonated site is the guanido group and not the α-amino group. Thus, because



(iii)

of the large charge separation between the positive and negative centres in the molecule, arginine may be expected to complex either as the neutral zwitterionic species (ArgH) or, by deprotonation of the guanido group, as an anion (Arg⁻).

The in vivo interaction of transition metal ions with amino acids and peptides is of immense biological importance (e.g. methionine biosynthesis from methylcobalmin and homocysteine;^(1,2) or the treatment of Wilson's disease by L-penicillamine⁽³⁾). There have been numerous reviews on the biochemistry of metal-amino acid complexes which show the

biological significance of this type of chemistry. Such reviews centre around the catalytic functions of metal ions and their complexes,⁽⁴⁾ the biochemistry of copper,⁽⁵⁾ the discriminating behaviour of metal ions and ligands with regard to their biological significance,⁽⁶⁾ the roles of transition metal ions in biological processes,⁽⁷⁾ chromium occurrence and function in biological systems,⁽⁸⁾ biochemical aspects of molybdenum coordination chemistry,⁽⁹⁾ and structural studies of iron-sulphur proteins.⁽¹⁰⁾

Although many simple amino acids have been complexed with numerous transition metal ions, it may be argued that such studies are far from the actual in vivo interaction between metal ions and body protein. In this study, therefore, a more complicated amino acid was chosen for examination, as arginine is much nearer to multidentate protein systems.

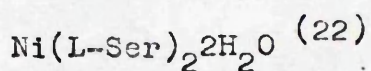
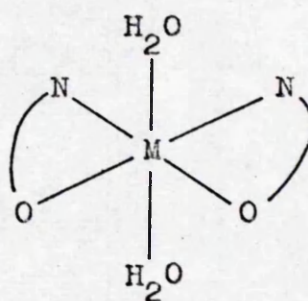
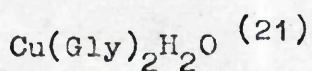
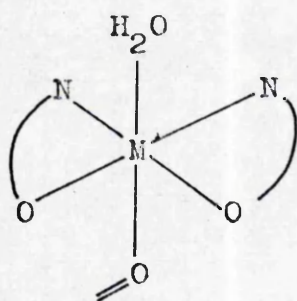
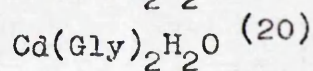
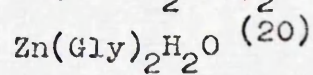
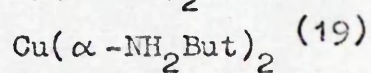
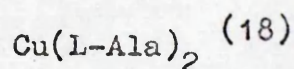
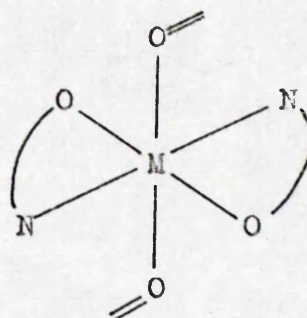
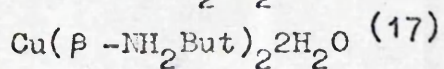
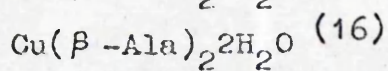
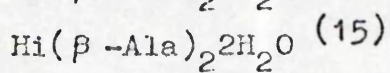
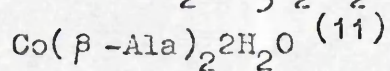
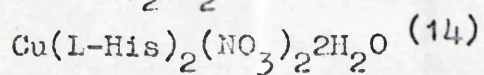
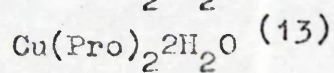
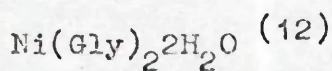
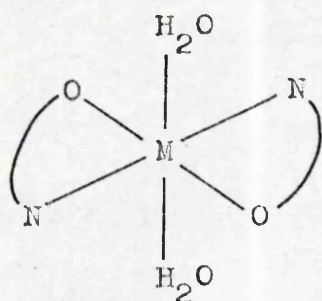
Before describing the work carried out in this study it is, perhaps, important to review the techniques which have been used to study other such systems.

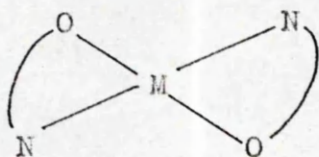
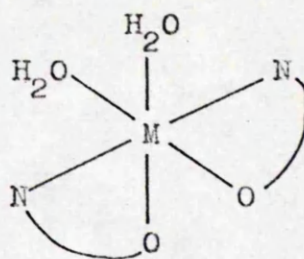
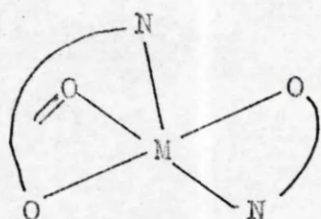
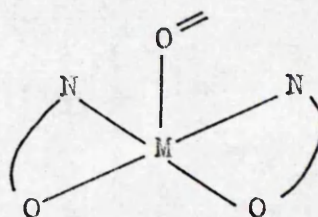
(ii) Crystal Structures of Metal-Amino Acid Complexes

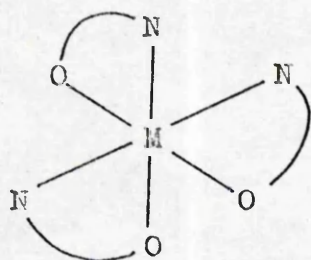
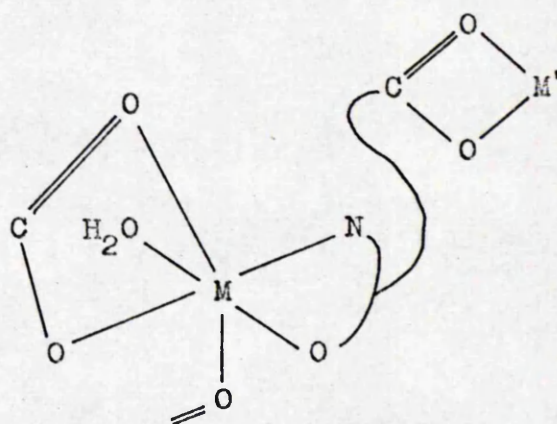
Three-dimensional X-ray crystallography techniques offer the best means for determination of the absolute structures of crystalline compounds. Although to correlate the structure of a compound in the solid state to that in the solution requires some empirical assumptions, the value of knowing the crystal structures of metal-amino acid complexes in order to serve as model compound to the much more complicated metal-protein system should not be ignored.⁽¹¹⁾

Figure I contains all the known crystal structures of metal-amino acid complexes. To simplify the drawings, the

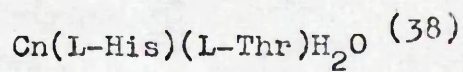
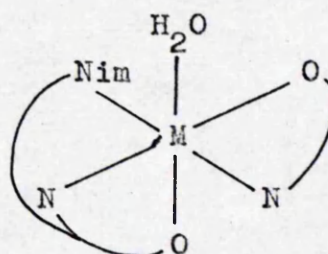
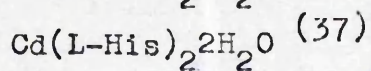
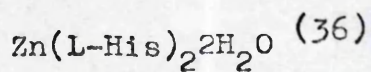
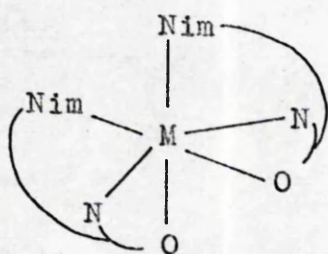
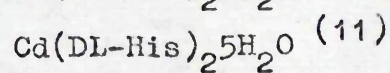
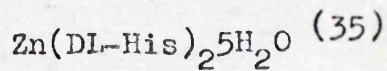
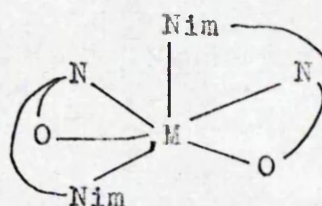
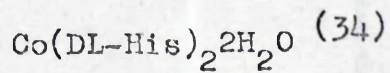
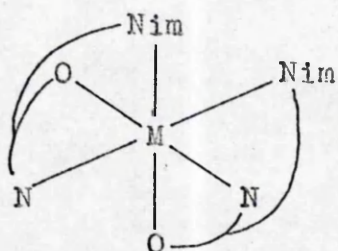
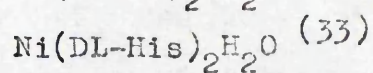
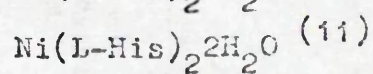
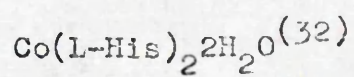
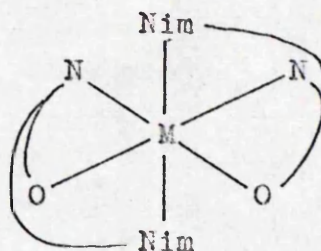
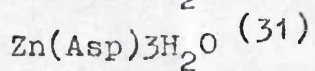
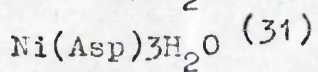
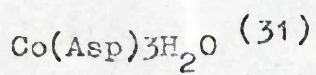
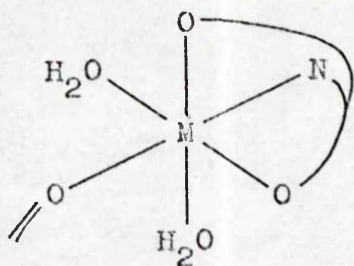
Figure I. Crystal Structures of Metal-Amino Acid Complexes

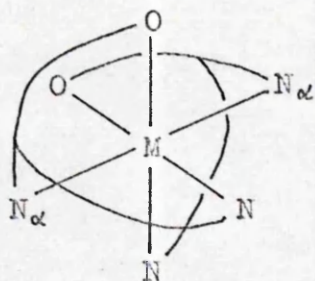



 Cu(Pen)_2 (23)

 $\text{Ni}(\alpha\text{-NH}_2\text{-iBut})_2 4\text{H}_2\text{O}$ (24)

 Zn(L-Ser)_2 (25)

 Cu(D-Ala)_2 (26)

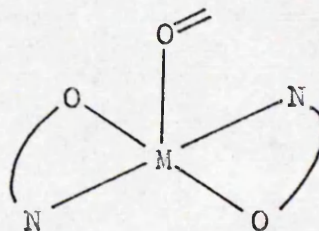
 Cu(L-Ser)_2 (27)

 $\text{Co(L-Ala)}_3 \text{H}_2\text{O}$ (28)

 $\text{Cu(Glu)} 2\text{H}_2\text{O}$ (29)

 $\text{Zn(Glu)} 2\text{H}_2\text{O}$ (30)

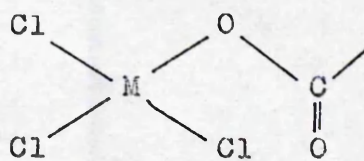




$\text{Co}(\text{L-Dap})_2\text{Br}$ (39)



$\text{Cu}(\text{L-Tyr})_2$ (40)



$\text{Hg}(\text{L-HisH}_2)\text{Cl}_3$ (41)

chelated amino acids are represented as "N-O", oxygen atoms of the adjacent complexes are indicated as "O=" and the imidazole nitrogen atoms as "Nim". Since the primary interest was in the metal binding sites of the amino acid, functional groups not involved in metal binding are omitted and other details such as the conformations of the ligands, configurations at asymmetric centres, and nonplanarity of the chelate rings are ignored.

Freeman⁽¹¹⁾ has tabulated the metal-ligand bond lengths of many complexes and calculated the average lengths of the different metal-to-ligand bond types for each metal. Some of the results are shown in Table 1.

Despite the large variety of structures described, the number of different metal-ligand interactions is surprisingly small. The nitrogen atom of the amino group is almost always involved in the chelate ring. Although the coordination of the carboxyl group is more complicated, it acts, fundamentally, either as a monodentate or a bridging bidentate ligand. In all cases, the nitrogen (α - or β -amino) and oxygen (α - or β -carboxyl) atoms of each amino acid molecule occupy adjacent corners of the coordination sphere forming a 5- or 6-membered ring. The well known instability of 7-membered ring is best exemplified by the two glutamic acid complexes in which the γ -carboxyl group binds to an adjacent metal atom. It is interesting to note that the γ -carboxyl group of glutamic acid binds both oxygen atoms to the same metal atom forming a rare example of 4-membered ring.

It is not surprising to note that of all the metals described, only copper(II) (and zinc(II) to some extent) shows significant changes in coordination geometry. This is,

Table 1 Average Metal-Ligand Bond Lengths in Complexes of Amino Acids

| Bond type M-L | Bond length (in Å) to metal M | | | | |
|---|-------------------------------|---------|--------|---------------------|---------------------|
| | Co(II) | Co(III) | Ni(II) | Cu(II) ^a | Zn(II) ^b |
| M-N (amino) | 2.15 | 2.00 | 2.11 | 2.00 | 2.09 |
| M-N (imidazole) | 2.18 | - | 2.09 | - | 2.20 |
| M-O (carboxyl), in chelate ring | 2.12 | 1.85 | 2.13 | 1.98 | 2.15 |
| M-O (carboxyl), second oxygen in chelated group | - | - | - | 2.25 | 2.05 |
| M-O (carboxyl), not in chelate ring | - | - | - | 1.97 | 2.06 |

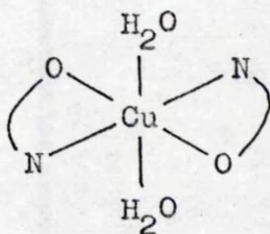
a) Octahedral, square-pyramidal or square-planar Cu(II).

b) Octahedral Zn(II).

c) Tetrahedral Zn(II).

in fact, not unexpected and may be due to the d^9 electronic state of copper(II) which is subject to the Jahn-Teller effect.⁽⁴²⁾ To illustrate this observation, the electronic absorption spectra of bis-(amino acidato)copper(II) in both solution and solid are tabulated, together with the bond lengths of the axial ligands, in Table 2.

The solution spectra show clearly that all bis-(amino acidato)copper(II) complexes in aqueous solution are surrounded by an almost identical environment, that is, they exist in solution as dihydrated complexes in which the two amino acid molecules occupy the square plane with two water molecules in more distant axial positions to give a distorted octahedral configuration (iv).



(iv)

Also, the differences of the axial bond lengths suggest that the difference in coordination of the copper atom in the crystalline complexes may occur in the axial directions and may be dominated by lattice packing requirements.^(45,46)

Even so, the cis-trans isomerism of bis-(amino acidato)copper(II) in solution should not be neglected.⁽²⁶⁾

In almost every case, crystal structure analysis show that the structures of metal-amino acid complexes are in good agreement with those predicted by spectroscopic measurements in the solid state. Consequently, in cases where single

Table 2 Electronic Spectra and Axial Bond Lengths of Bis-(amino acidato)copper(II) Complexes

| Complexes | Solution | | λ_{\max} (cm ⁻¹) | ϵ_{\max} | Solid | | Reference |
|--|--------------------------------------|--------------------------------------|--------------------------------------|-------------------|------------------------|------------------|-----------|
| | λ_{\max} (cm ⁻¹) | λ_{\max} (cm ⁻¹) | | | Axial Ligands | Bond Lengths (Å) | |
| Cu(DL-Pro) ₂ | 16,400 | 16,210 | 65 | | 2 H ₂ O | 2.5 | 43 |
| Cu(Gly) ₂ | 15,820 | 15,700 | 43 | | O=, H ₂ O | 2.3; 2.6 | 43 |
| Cu(L- α -Ala) ₂ | 15,820 | 16,200; 17,210 | - | | 2 O= | 2.8 | 44 |
| | | | | | (polarized components) | | |
| Cu(DL- α -NH ₂ But) ₂ | 16,100 | 16,950 | 60 | | 2 O= | 2.8 | 43 |
| | 16,100 | 16,200; 17,214 | - | | | | 44 |
| | | | | | (polarized components) | | |
| Cu(Pen) ₂ | 16,400 | 16,950; 19,600 | 66 | | 2 O= | 3.2 | 43 |
| | | | | | (overlapping) | | |
| Cu(L-tyr) ₂ | 16,100 | 16,500 | - | | O= | 2.4 | 45 |

crystals are difficult to grow, the structures of the compound in the solid state may be assigned with some degree of confidence using general spectroscopic techniques.

(iii) Infrared Spectroscopy

The state of a n -atom molecule at any instant can be completely described by specifying the Cartesian coordinates of each of the n atoms, all relative to some fixed origin. Without changing the mass of the molecule and the angular momentum involved, the combination of translational and rotational motions of the molecule as a whole and the vibrational motions of the constituent atoms will produce a number of normal vibrations given by

$3n - 6$ for non-linear molecule, or

$3n - 5$ for linear molecule.

The transitions between two vibrational levels of the molecule in the electronic ground state occur in the infrared region of the spectrum. In order that a vibration is active in the infrared region, the dipole moment of the molecule must change during the vibration. The spectrum of a molecule is then determined by its symmetry which can be rigorously assigned with the aid of the group theory.⁽⁴⁷⁾

The application of infrared spectroscopy in investigating the structures of coordination compounds lies mainly in correlating the changes in the spectrum with the changes in geometry. Since the spectra themselves are determined by the relative spacial arrangement of the atoms - bond lengths and angles, mass of the molecule and force constants between the atoms - any changes within the molecule will cause changes of

vibrational motions. On coordination, at least one additional atom is introduced into the ligand, thus the vibrational motions of the donor atom(s) concerned will alter; this, in effect, will cause significant changes in the spectrum. Hence, by comparison of the infrared spectrum of the free ligand with that of the coordinated ligand, together with those in which the structures are known, the structure of the compound under investigation can be inferred.

However, interpretation of infrared spectra of a complicated molecule requires certain assumptions. The principal assumptions are:⁽⁴⁸⁾

a) The vibrational frequency (or, more fundamentally, the force constant) in the ligand will not be greatly altered when the ligand becomes coordinated to the metal ion.

b) The vibrations of a bound ligand will not be strongly coupled to the vibrations of other ligands, similar or different, nor to the other vibrations of the coordination compound (skeletal vibrations). Thus, the frequencies of the vibrations will not be greatly altered by coupling.

c) The slight coupling of the vibrations in the ligand to other vibrations in the compound will not seriously disturb or split up the degeneracy inherent in the free ligand.

It must be admitted that these assumptions are not completely valid and are subject to some limitations, such as solid state effects.

The most obvious changes in the spectrum are the changes of absorption band position and intensity, the appearance of new absorption bands, and splitting of absorption bands.

When a ligand is coordinated to a metal ion, the

vibrational bands associated with the stretching of the bonds involving the coordinated atom(s) usually moves to lower frequency. Consider the N-H stretching frequency of amine: when the nitrogen atom is coordinated to a metal ion, the lone pair electrons of the nitrogen atom are displaced towards the metal ion. This, in turn, will cause the nitrogen to bind less firmly to the hydrogen atoms and decreases the force constant in the N-H bond; consequently, the absorption frequency of the N-H stretching mode will move to lower frequency in the spectrum.⁽⁴⁹⁾ Similarly, the coordination of the oxygen atom of the carbonyl group will decrease the C-O bond force constant by draining π -electron density out of the carbonyl group.⁽⁵⁰⁾

It is well known that carbon monoxide can coordinate to a transition metal in one of the two ways, namely terminal and bridging. The relative intensities of the carbonyl stretching frequencies corresponding to the terminal and bridging carbonyls are often useful in predicting the structure of metal-carbonyl complexes.⁽⁵¹⁾

If hydrogen bonding is more important within the complex than in the free ligand, absorption bands involving the hydrogen atoms often show considerable intensification.⁽⁵²⁾

The appearance of new absorption bands in the spectrum may originate in several ways. The most important are new chemical bonds formed as a result of coordination such as metal-ligand bonds. Also, coordination may reduce the effective symmetry of the free ligand and cause some of the infrared inactive vibrations to become active in the coordinated ligand.

Just as a lowering in symmetry upon coordination may cause the appearance of new absorption bands, it may also split the absorption bands which are degenerate in the free ligand. The nitrate ion could well serve to illustrate these points.

The nitrate ion can function as an ionic, monodentate or bidentate ligand.^(53,54) Figure II shows some possible coordination modes of the nitrate ion.

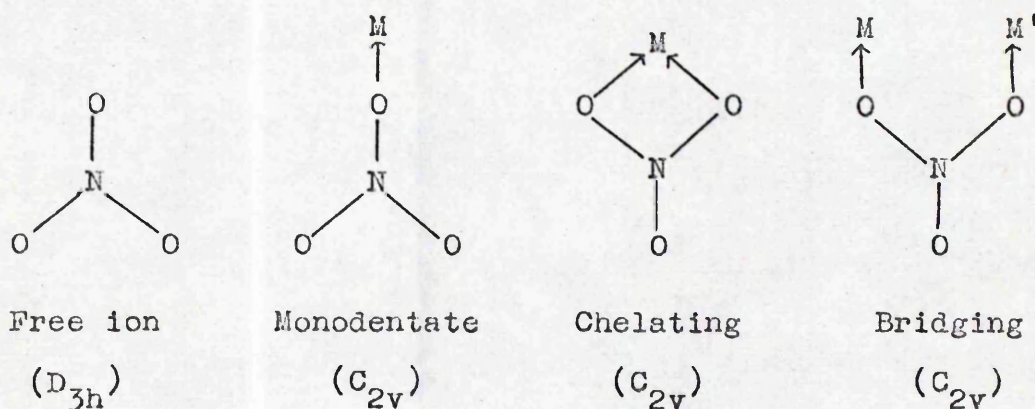


Figure II The Coordination Modes of Nitrate Ion

In the free ion, nitrate has D_{3h} symmetry. The infrared spectrum shows three bands, ν_2 (out-of-plane deformation), ν_3 (doubly degenerate stretch), and ν_4 (doubly degenerate in-plane bending). The ν_1 (symmetric stretching) is normally inactive, but sometimes becomes weakly active through crystal interactions.

When the nitrate ion acts as a monodentate ligand, its symmetry reduces to C_{2v} if the metal ion is ignored. In the C_{2v} symmetry, all bands become active, shifts in band positions occur, and the degeneracy of ν_3 and ν_4 is lifted. Although the bidentate (either chelating or bridging) nitrate ion remains with C_{2v} symmetry, the splitting of the degenerate

vibrations is much larger in the bidentate than in the monodentate complex. Table 3 lists the N-O vibrational absorption frequencies of some nitrate complexes to illustrate these points.

Since the stretching frequency involving the donor atom of the ligand shows considerable alteration in the infrared spectrum upon coordination, it is then possible to distinguish the coordination site within a multidentate ligand. Quagliano and co-workers⁽⁵⁵⁾ have measured the infrared spectrum of a series of metal-urea complexes, and found that the carbonyl stretching absorbs at ca. 1725 cm^{-1} in the Pt(II) and Pd(II) complexes but shifts to ca. 1610 cm^{-1} in the Cr(III), Fe(II), Zn(II) and Cu(II) complexes. The shift to lower frequency obviously indicating oxygen-to-metal bond formation in these complexes, and a nitrogen-to-metal bond is presumably formed in the Pt(II) and Pd(II) complexes.

Changes in the relative intensities of the absorption frequencies of the coordinated and uncoordinated groups also enable one to speculate upon the number of coordinated groups of a multidentate ligand having more than one similar donating groups. Busch and Bailar⁽⁵⁶⁾ showed that the presence of a weak absorption peak at 1730 cm^{-1} in addition to a strong absorption peak at 1630 cm^{-1} in the infrared spectrum of an EDTA complex of cobalt(III) indicated that one of the four carboxyl groups of the ligand is not coordinated. However, in another EDTA complex of cobalt(III), only one strong peak at 1638 cm^{-1} was observed showing that all four of the carboxyl groups are coordinated.

The infrared data can provide significant evidence in differentiating between the cis- and trans-isomers of some

Table 3 Infrared Spectral Data of Nitrate Ion, cm^{-1} . (54)

| Compound | Type | ν_2 | ν_3 | ν_4 |
|---|-------------|-----------|----------------|----------------------|
| $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$ | ionic | 823 m, sp | 1368 vs, br | 704 w, sp |
| $[\text{Ni}(\text{en})_2(\text{NO}_3)_2]$ | monodentate | 818 m, sp | 1305 s; 1480 s | 708 w, sp; 788 w, sp |
| $[\text{Ni}(\text{en})_2(\text{NO}_3)]\text{ClO}_4$ | bidentate | 809 m, sp | 1290 s; 1476 s | 695 vw, 746 w, sp |

square-planar or pseudo-square-planar complexes. Herlinger and co-workers⁽⁵⁷⁾ correlated the infrared absorption frequencies of complexes whose geometries have been elucidated by X-ray crystallography in order to develop a vibrational criterion that allows discrimination between cis- and trans-configurations of the copper(II) complexes of α -amino acids. Sometimes, careful interpretation of infrared spectra may even suggest the conformation of the ligand.⁽⁵⁸⁾

The first spectroscopic evidence of the zwitterion structure of α -amino acid was given by Edsall's studies on the Raman spectra of these compounds.^(59,60) Later, infrared studies of α -amino acids also strongly suggested that α -amino acids in the solid state or at their isoelectric points in aqueous solutions exist almost exclusively as zwitterions.⁽⁶¹⁾ The absorption frequencies of primary interest are in the N-H stretching and the carboxyl stretching regions. The free α -amino acids do not show any absorption bands in the normal N-H stretching range of $3500\text{--}3300\text{ cm}^{-1}$. Most of them exhibit a weak absorption near 3070 cm^{-1} due to the NH_3^+ group. With salt formation the NH_2 group reappears without a charge and normal N-H stretching bands also appear.

In the 1600 cm^{-1} region, a strong absorption corresponding to the ionized carboxyl group appears in amino acids of all types, and in their salts. In the corresponding hydrochlorides, this band disappears and is replaced by a typical carbonyl absorption near 1700 cm^{-1} . In addition, a weaker absorption near 1400 cm^{-1} has been related to the symmetric stretching vibration of the ionized carboxyl group.

Upon coordination with transition metals, both the N-H and COO^- stretching frequencies are expected to undergo certain

changes. The nitrogen atom will be attached by four atoms in the complex. To a first approximation, a sp^3 hybridization about the nitrogen atom will give rise to a sp linear covalent bond between the metal ion and the nitrogen atom. As a consequence, the N-H stretching absorption will shift to a lower frequency, and this is what has been observed.⁽⁶²⁾

In the free α -aminoacid, the ionized carboxyl group has equivalent carbon-to-oxygen bond character as shown in Figure IIIa. Upon coordination, there are two possibilities

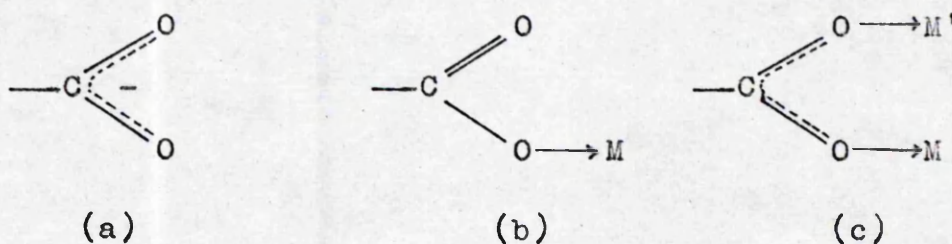


Figure III. Resonance Structures of Carboxyl Group.

to consider. If the metal-to-oxygen bond is essentially electrostatic, the resonance of the ionized carboxyl group will not be considerably altered. Thus the corresponding stretching frequencies of the carboxyl group will not be significantly changed.⁽⁶²⁾

If the metal-to-oxygen bond has partial covalent character, the resonance of the ionized carboxyl group will undergo some change. The obvious is one in which one of the carbon-to-oxygen bonds gains more double bond character while the other gains more single bond character as shown in Figure IIIb. The result of this change will be probably that the asymmetric stretching absorption of the carboxyl group will shift to higher frequency whereas the symmetric stretching

absorption will shift to lower frequency.⁽⁶³⁾ Consequently, if the infrared spectra of metal-amino acid complexes were measured at the same physical state, the difference between the asymmetric and symmetric stretching frequencies of the carboxyl group may be used as a measure of relative covalent strength of the metal-to-oxygen bond.⁽⁶⁴⁾

However, if the carboxyl group becomes bidentate, the resonance of the free carboxyl group will be restored as shown in Figure IIIc. Again, no significant alteration of the carboxyl stretching frequencies would be observed.⁽⁶⁵⁾ Since crystal structure analyses⁽¹¹⁾ have already shown that the bidentate function of the carboxyl group is not uncommon, one must be careful in interpreting the infrared absorptions of the carboxyl group.

Using different models for normal-coordinate analyses Lane and co-workers⁽⁶⁶⁾ and Condrate and Nakamoto⁽⁶³⁾ assigned metal-nitrogen and metal-oxygen stretching modes differently. Table 4 shows the assignments for the trans- and cis-[Pt(glycinato)₂]. Lane and co-workers⁽⁶⁷⁾ have also performed a normal-coordinate analysis for the metal-valine complexes and an approximate description of the vibrational modes has been described.

Recently, Herlinger et al.⁽⁵⁵⁾ reported the infrared spectra of a large number of copper(II)-amino acid complexes with known crystal structures and suggested an empirical criterion to differentiate the cis- and trans-isomers of the complexes. From the symmetry consideration of the complexes formed from optically active and racemic amino acids within a square-planar molecular model that ignores axial coordinations and chelate ring non-planarity, the trans-isomer

Table 4. Infrared Data of Metal-Ligand Stretching
Frequencies (cm^{-1}) for Bis-(glycinato)platinum(II)

| Observed Frequency | | Assignment | |
|--------------------|------------|---|--|
| <u>Trans</u> | <u>Cis</u> | Lane and co-workers (66) | Condrate and Nakamoto (63) |
| 552 m | 549 w | } COO^- wagging and rock + $\delta(\text{CCN})$ | $\nu_{\text{M-N}}$ |
| 502 s | 509 s | | Ring deformation + $\delta_{\text{C=O}}$ |
| 418 s | 406 sh | $\nu_{\text{M-N}}$ asym. | } $\nu_{\text{M-O}} + \nu_{\text{M-N}}$ |
| | 389 s | $\nu_{\text{M-N}}$ sym | |
| 339 s | 329 s | Ring deformation | Ring deformation, out-of-plane |

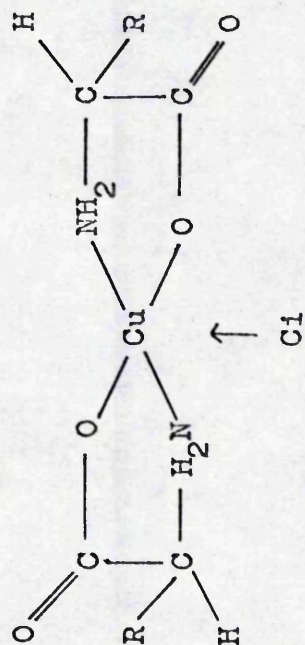
of the racemic complex (Figure IVa) belongs to the C_i point group for which only the asymmetric copper-ligand stretching vibrations are infrared active, whereas the cis-isomer of the racemic complex (Figure IVb) belongs to the non-centrosymmetric C_s molecular point group for which both asymmetric and symmetric metal-ligand stretching vibrations are infrared active. Although both the trans- and cis-isomers of optically active α -amino acid complexes (Figure IVc and d) belong to C_2 molecular point group, the local centrosymmetry of the binding groups about copper atom of the trans-isomer may dictate the activity of the copper-ligand stretching vibrations. Thus, only the asymmetric copper-ligand stretching vibrations are infrared active in the trans-isomers, whereas both the asymmetric and symmetric copper-ligand stretching vibration are infrared active in the cis-isomers.

The validity of this empirical criterion may be demonstrated by the measurements and assignments of the copper-oxygen and copper-nitrogen stretching absorptions of metal- α -amino acid complexes of known geometries as listed in Table 5.

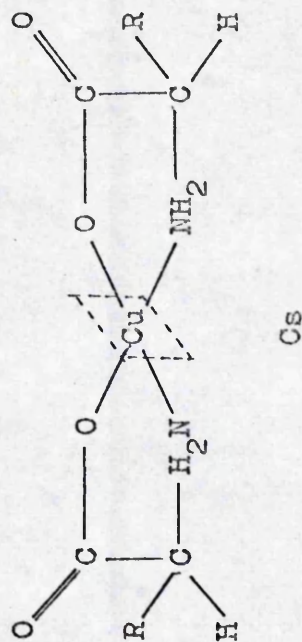
The notion that the infrared spectra of cis-isomers are more complex than those of corresponding trans-isomers has been applied to distinguish the geometric isomers of glycine complexes of Pt(II) and Cu(II)^(68,69) and the tyrosine complexes of Cu(II).⁽⁴⁵⁾

Graddon and Munday⁽⁴³⁾ have shown that the carboxyl absorption spectra of the copper(II)-amino acid complexes in the 1600 cm^{-1} region fall into two distinct groups as a result of different kinds of hydrogen bondings associated with the oxygen atoms. The first group consists of the anhydrous

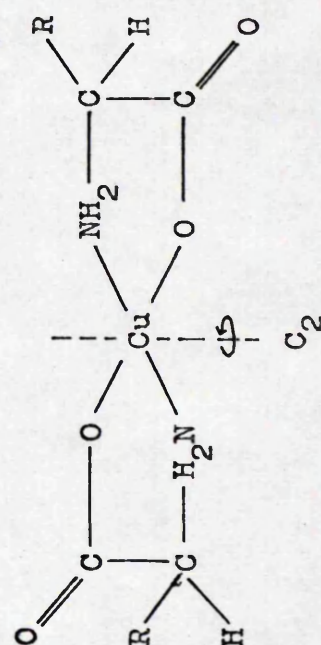
Figure IV. Geometries of Square-Planar Complexes Formed from Racemic and Optically Active α -Amino Acids (after Laurie⁽⁴⁵⁾).



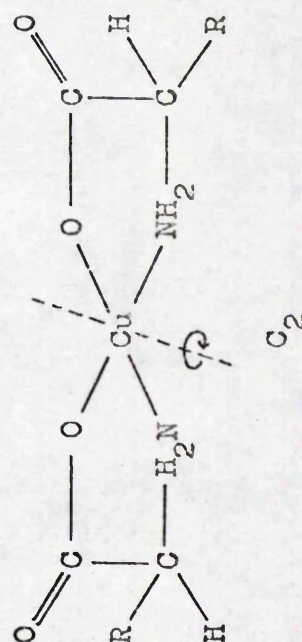
(a) trans



(b) cis



(c) trans

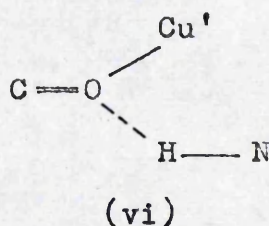
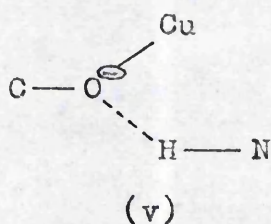


(d) cis

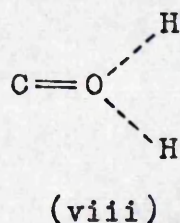
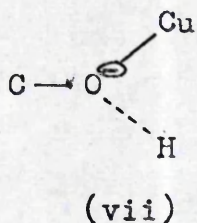
Table 5. Copper-Ligand Stretching Frequencies (cm^{-1}) of Copper(II)- α -Amino Acid Complexes whose structures have been determined by X-ray diffraction. (55)

| Complex | $\nu_{\text{Cu-N}}$ | | $\nu_{\text{Cu-O}}$ | |
|--|---------------------|------|---------------------|------|
| | Asym. | Sym. | Asym. | Sym. |
| <u>Trans-isomer</u> | | | | |
| Bis-(glycinato)copper(II) dihydrate | 477 | | 334 | |
| Bis-(L-alaninato)copper(II) | 484 | | 332 | |
| Bis-(DL- α -amino-n-butyrate)copper(II) | 498 | | 341 | |
| Bis-(DL-prolinato)copper(II) dihydrate | 498 | | 349 | |
| <u>Cis-isomers</u> | | | | |
| Bis-(glycinato)copper(II) monohydrate | 471 | 454 | 330 | 277 |
| Bis-(D-alaninato)copper(II) | 483 | 441 | 325 | 276 |
| Bis-(L-isoleucinato)copper(II) monohydrate | 471 | 407 | 342 | 298 |

compounds, characterized by a strong peak at $1610-1620\text{ cm}^{-1}$ with a weaker peak on the low frequency side near 1570 cm^{-1} , was related to almost identical environments about the two carboxyl oxygen atoms. That is, each oxygen atom being hydrogen-bonded to one amino hydrogen atom and inter- or intramolecularly coordinated to one copper atom as shown in (v) and (vi).



The second group which consists of hydrated compounds, characterized by a broad, strong absorption near 1600 cm^{-1} with a weaker peak on the high frequency side near 1670 cm^{-1} , was related to the formation of two hydrogen bonds by the $\text{C}=\text{O}$ oxygen atom to either two water molecules or one water molecule and one amino group as shown in (vii) and (viii). Thus, the three main absorption peaks in the 1600 cm^{-1} region



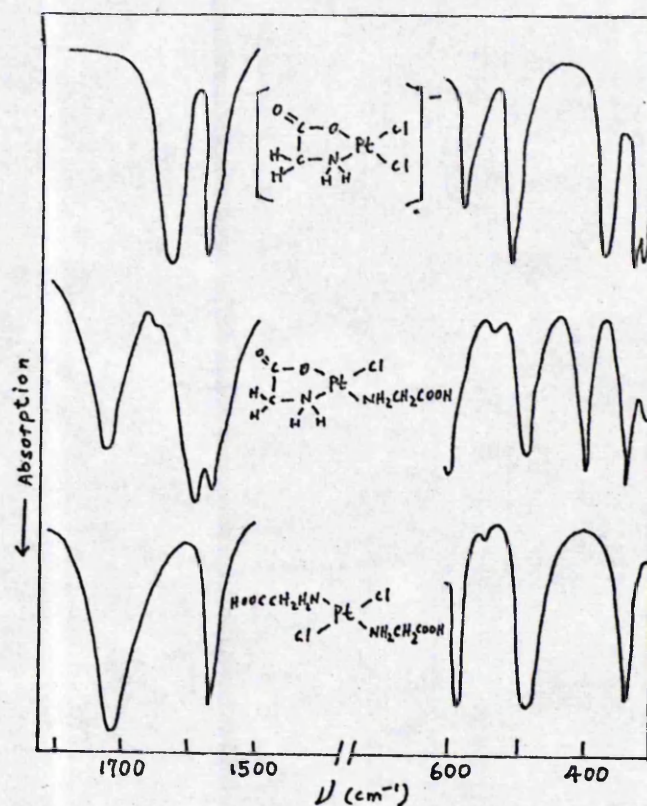
may be related to three different environments about the carboxyl group in the copper(II)-amino acid complexes in the following ways:

| | |
|----------------------------|---------------------|
| near 1570 cm^{-1} | as in (vi) |
| near 1600 cm^{-1} | as in (v) and (vii) |
| near 1670 cm^{-1} | as in (viii) |

Table 6. The COO Stretching Frequencies (cm^{-1}) of Pt-Glycine Complexes.

| Complex | $\nu_{\text{C=O}}$ asym. | ν_{COO} asym. |
|---|------------------------------|--------------------------|
| $[\text{Pt}(\text{NH}_2\text{CH}_2\text{CH}_2\text{COOH})_2\text{Cl}_2]$ | monodentate 1708 | |
| $[\text{Pt}(\text{NH}_3)_2(\text{NH}_2\text{CH}_2\text{COO})_2]$ | monodentate | 1610 |
| $\text{K}[\text{PtCl}_2(\text{NH}_2\text{CH}_2\text{COO})]$ | bidentate | 1645 |
| $[\text{Pt}(\text{NH}_2\text{CH}_2\text{COO})_2]$ | bidentate | 1643 |
| $[\text{Pt}(\text{NH}_2\text{CH}_2\text{COOH})\text{Cl}(\text{NH}_2\text{CH}_2\text{COO})]$ | monodentate and bidentate | 1730 1655, 1600 |

Figure V. Infrared Spectra of $K[Pt(gly)Cl_2]$, $[Pt(gly)(glyH)Cl]$, and trans- $[Pt(glyH)_2Cl_2]$



In the presence of another ligand, glycine may act as a monodentate ligand, a bidentate ligand or as both in the mixed platinum(II) complexes.⁽⁷⁰⁾ The distinction of mono- and bidentate glycinato complexes of Pt(II) is readily apparent from their infrared spectra in the COO stretching and Pt-O stretching regions. As shown in Table 6, the bidentate glycinato complex absorbs at 1645 cm^{-1} , which is different from either the ionized monodentate complex at 1610 cm^{-1} or the unionized monodentate complex at 1710 cm^{-1} . Furthermore, the bidentate glycinato complex exhibits a Pt-O stretching band at 388 cm^{-1} , whereas the monodentate complexes have no absorption between 470 and 350 cm^{-1} .

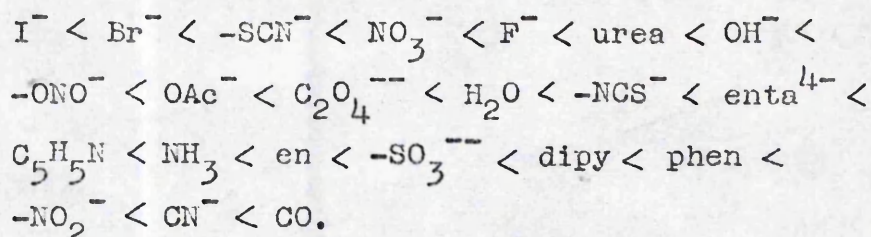
It is interesting to note that the infrared spectrum of the platinum(II) complex which contains both mono- and bidentate glycine may be approximated roughly by adding the spectra of mono- and bidentate glycine complexes as shown in Table 6 and Figure V.⁽⁷⁰⁾

(iv) Electronic Spectroscopy

In order to correlate the physical properties of the coordination compounds with the nature and position of the ligand atoms which surround the central transition-metal ion, Bethe⁽⁷¹⁾ first introduced the so-called crystal field theory to study the effect of the ligand atoms on the electronic properties within the central atom. It is now well-known⁽⁷²⁾ that the essence of the theory lies in the correlation of the splitting of the degenerate d- or f-orbitals of the transition-metal ion with respect to the interactions caused by the ligand atoms.

For octahedral and tetrahedral complexes, the splitting

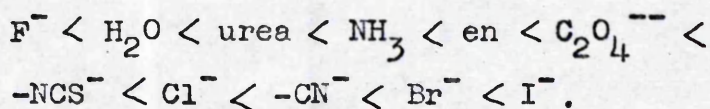
parameter, Δ (or $10 Dq$), provides significant information about the metal-ligand interactions. For a given metal and stereochemistry, Dq increases with ligands in the following manner, known as the spectrochemical series:



For a mixed ligand complex, the rule of average environment⁽⁷³⁾ states that the Δ value is given by the weighed average of the Δ values for each of the individual ligands. For example, for the complex MA_nB_{6-n} we have

$$\Delta = \frac{1}{6} \{ n\Delta^A + (6-n)\Delta^B \}$$

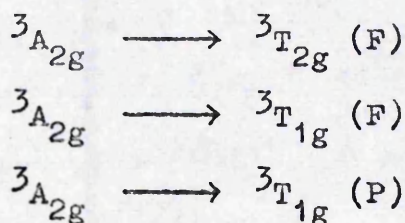
It has also been demonstrated that the extent of overlapping (or degree of covalency) of the metal-ligand interactions for a fixed metal increases with ligands in the following order, known as the nephelauxetic series:



The electronic absorptions of transition metal complexes corresponding to the electronic excitations of a molecule from the electronic ground state to the next higher energy electronic state occur in the near infrared, visible, and ultraviolet region of the spectrum. Here we will only consider the visible absorption which is largely localized on the metal ion.

The observed visible absorption bands are usually weak and broad because these absorptions originating within the d-orbitals of the transition metal ion are forbidden by Laporte's rule but occur due to spin-orbit coupling, Jahn-Teller effects, or vibronic coupling.⁽⁷²⁾

For a d^8 electronic configuration, such as nickel(II), in an octahedral environment, the Orgel diagram⁽⁷⁴⁾ (Figure VI) shows that three transitions could occur as governed by the selection rules:



According to crystal field theory calculation⁽⁷⁵⁾ the following energies are expected:

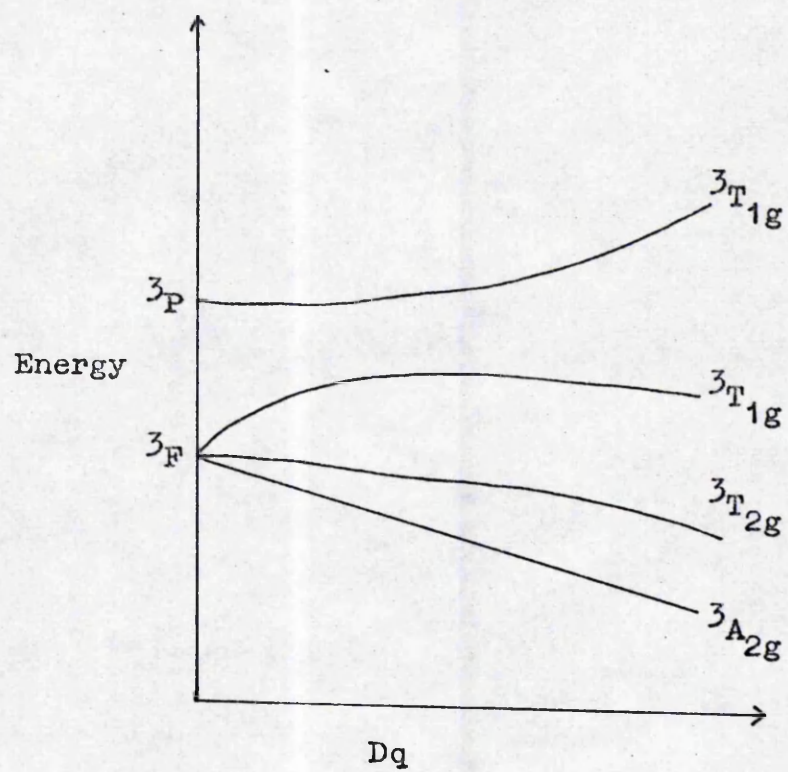
$$\begin{aligned} E\{ {}^3A_{2g} \longrightarrow {}^3T_{2g} \text{ (F)} \} &= 10 Dq \\ E\{ {}^3A_{2g} \longrightarrow {}^3T_{1g} \text{ (F)} \} &= \left(\frac{15}{2}\right)B + 15 Dq - \frac{1}{2}\{(15B - 6 Dq)^2 + 64(Dq)^2\}^{\frac{1}{2}} \\ E\{ {}^3A_{2g} \longrightarrow {}^3T_{1g} \text{ (P)} \} &= \left(\frac{15}{2}\right)B + 15 Dq + \frac{1}{2}\{(15B - 6 Dq)^2 + 64(Dq)^2\}^{\frac{1}{2}} \end{aligned}$$

where B is a Racah parameter.

The electronic structure and stereochemistry of nickel(II) complexes have been reviewed by Sacconi⁽⁷⁶⁾ who has discussed the topic in depth with considerable interests.

So far only octahedral structures have been found for bis-(amino acidato)nickel(II) complexes in a high spin state.^(77,78) The electronic spectra of these compounds resemble typical nickel(II) complexes with an octahedral coordination^(76,79,80) which is characterized by three absorption bands in the visible region. The first band is

Figure VI. Orgel Diagram for d^8 Configuration in Octahedral Complexes.



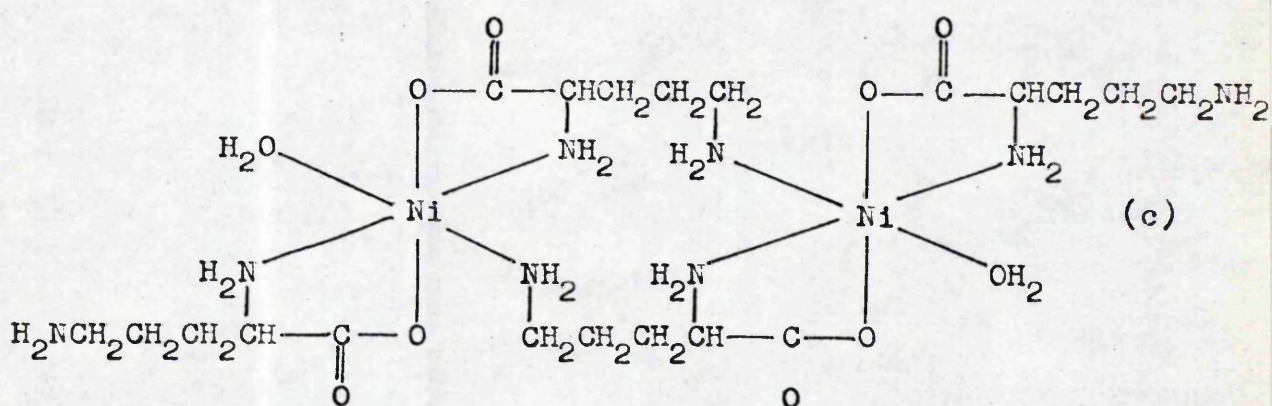
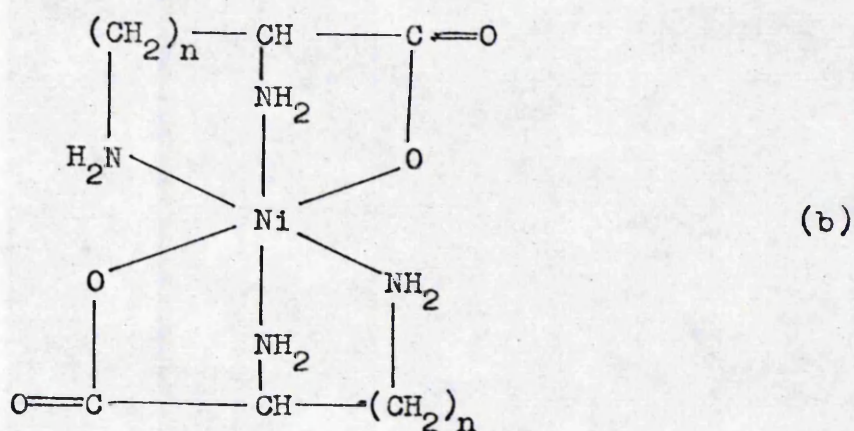
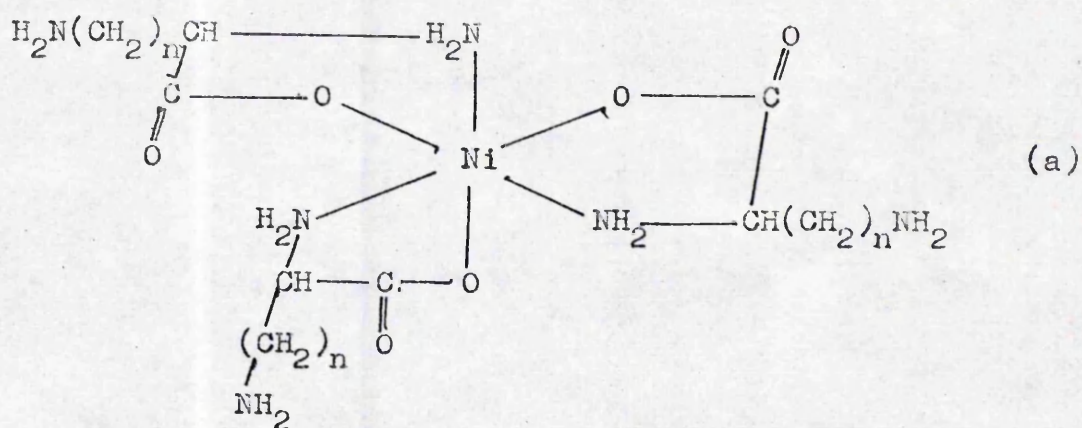
usually found in the region 9,000-11,000 cm^{-1} , assigned to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ (F); the second band, assigned to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (F) is found in the region 13,000-19,000 cm^{-1} , and the third band in the region 21,000-30,000 cm^{-1} is assigned to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (P).

As has been noted elsewhere,⁽⁷⁶⁾ the first absorption band corresponds to the ligand field splitting energy, and its value can therefore reveal the kind of donor atoms which coordinate to the nickel(II) atom in a mixed ligands complex. Thus Brubaker and Busch⁽⁸¹⁾ were able to deduce the functional groups used in chelation by α, ω -diaminocarboxylic acids in their nickel(II) complexes. From the position of the first absorption band in these complexes (Table 7) and other chemical evidence, they assigned the following structures for tris(α, ω

Table 7. Electronic Absorption Spectra of Solutions Containing Nickel(II) Complexes.

| Compound | Ni ⁺⁺ environment | ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ (F) cm^{-1} | ϵ_{max} |
|---|------------------------------|--|-------------------------|
| $\text{Ni}(\text{H}_2\text{O})^{++}$ | 6 O, | 8,500 | - |
| $\text{Ni}(\text{gly})(\text{H}_2\text{O})_4^+$ | 5 O, 1 N | 9,200 | 6.0 |
| $\text{Ni}(\text{gly})_2(\text{H}_2\text{O})_2$ | 4 O, 2 N | 9,900 | 9.2 |
| $\text{Ni}(\text{gly})_3^-$ | 3 O, 3 N | 10,000 | 10.2 |
| $\text{Ni}(\text{en})(\text{gly})_2$ | 2 O, 4 N | 10,500 | 12.8 |
| $\text{Ni}(\text{en})_2(\text{gly})^+$ | 1 O, 5 N | 10,800 | 9.2 |
| $\text{Ni}(\text{en})_3^{++}$ | 6 N | 11,200 | 4.7 |
| $\text{Ni}(\text{DabaHCl})_3^-$ | 3 O, 3 N | 9,700 | - |
| $\text{Ni}(\text{Daba})_2$ | 2 O, 4 N | 10,700 | 7.8 |
| $\text{Ni}(\text{OrHCl})_3^-$ | 3 O, 3 N | 10,000 | 8.8 |
| $\text{Ni}(\text{Or})_2$ | 2 O, 4 N | 10,800 | 9.2 |
| $\text{Ni}(\text{LyHCl})_2$ | 3 O, 3 N | 10,000 | 10.5 |

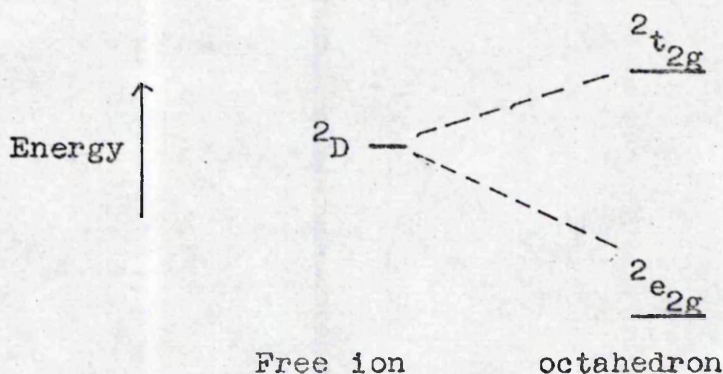
Figure VII. Structures of Nickel(II) Complexes with α, ω -diaminocarboxylic acids



-diaminocarboxylic acid monohydrochloride)nickel(II) ion (Figure VIIa), bis(α, ω -diaminocarboxylato)nickel(II) (Figure VIIb) and bis(lysine monohydrochloride)nickel(II) (Figure VIIc).

The d^9 configuration of copper(II) may be considered simply as a hole-equivalent of d^1 . In octahedral d^9 complexes, the 2D ground state of the free ion is splitted⁽⁷⁴⁾ (Figure VIII), and only one transition from the $^2e_{2g}$ to the $^2t_{2g}$ state is possible. However, as a result of Jahn-Teller distortion, further splitting in crystal fields of different symmetries

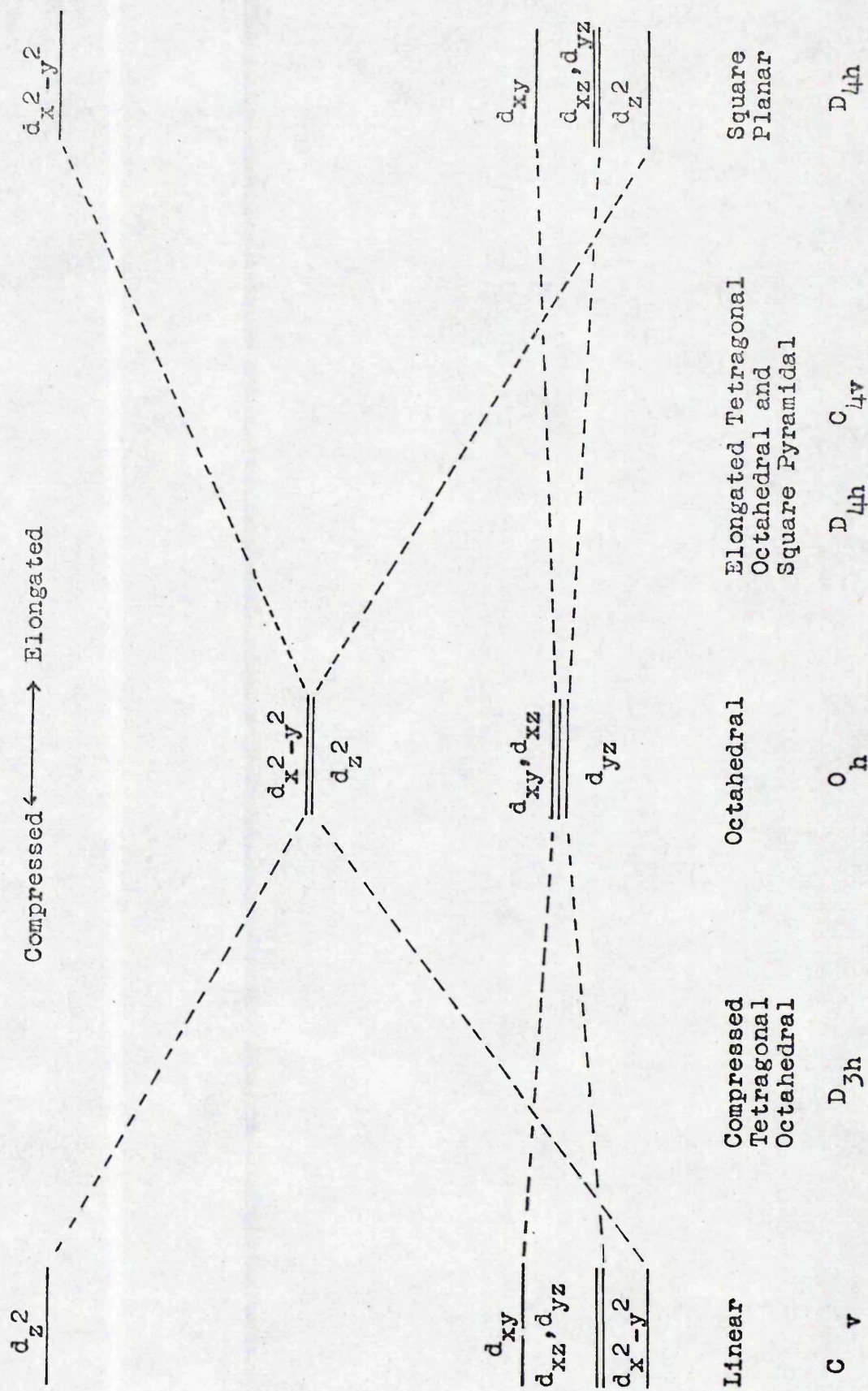
Figure VIII. Energy Level Diagram for d^9 Configuration.



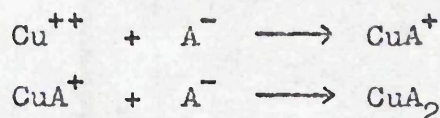
are observed⁽⁸²⁾ (Figure IX). Although crystal field calculation cannot give precise energies or even detailed orderings, it can, fortunately, specify which of the five d-orbitals has the highest energy and which will, therefore, contain the odd electron of the d^9 configuration. The vast majority of copper(II) complexes give rise to orbitally nondegenerate ground state, ($d_{x^2-y^2}^2$), involving a static form of distortion (i.e. elongated tetragonal-octahedral).⁽⁸²⁾

The electronic spectra of complexes of copper(II) and nickel(II) with amino acids have been extensively studied, and spectroscopic data for other metal ions (possibly except

Figure IX. The Splitting of the One Electron Energy Levels of the Copper(II) Ion in Crystal Fields of Axial Symmetry.



Co^{3+}) are still lacking. Hare and co-workers⁽⁸³⁾ have shown that in aqueous solution, addition of amino acid anion (A^-) to Cu^{++} follows the formation sequences



in which water hydration is replaced by the bidentate amino acids. The electronic absorption spectra of this sequence have well-defined isosbestic points which are indicative of the isolated equilibria. The species CuA^+ all have maximum extinction coefficients of about 20 at $13,800\text{ cm}^{-1}$ whilst the species CuA_2 have maximum extinction coefficients between 60 and 75 at $16,100\text{ cm}^{-1}$, the wavelengths of maximum absorption.

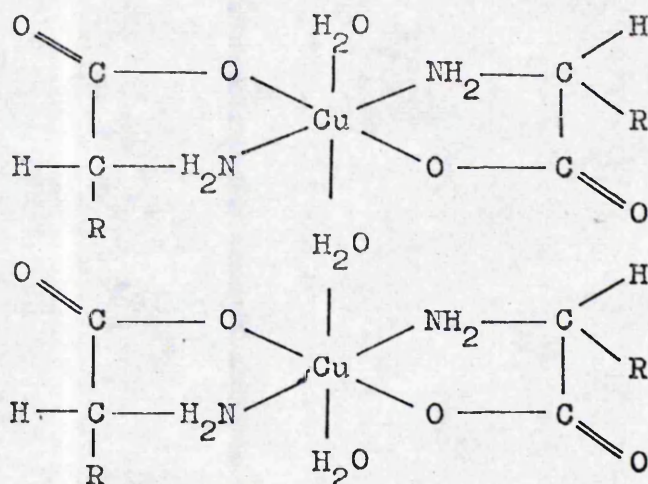
Graddon and Munday⁽⁴³⁾ have obtained similar results and concluded that this must be due to the fact that in aqueous solution, the copper atom has the same environment for all amino acids. That is, each copper atom is coordinated to two nitrogen and two carboxyl oxygen atoms in the molecular plane and two water molecules in the axis normal to this plane. Gillard and co-workers⁽²⁶⁾ agreed with this conclusion but suggested the possibility of cis-trans geometrical isomerism.

The electronic spectra of the metal-amino acid complexes in the solid state is more intriguing.

Graddon and Munday⁽⁴³⁾ divided the complexes into three groups based on different coordination environments. The first group consists of hydrated copper(II) amino acid complexes which are characterized by a well-defined absorption maximum at ca. $16,100\text{ cm}^{-1}$; similar to that observed in the aqueous solution. These are assigned a structure in which the copper atom achieves elongated-octahedral symmetry by

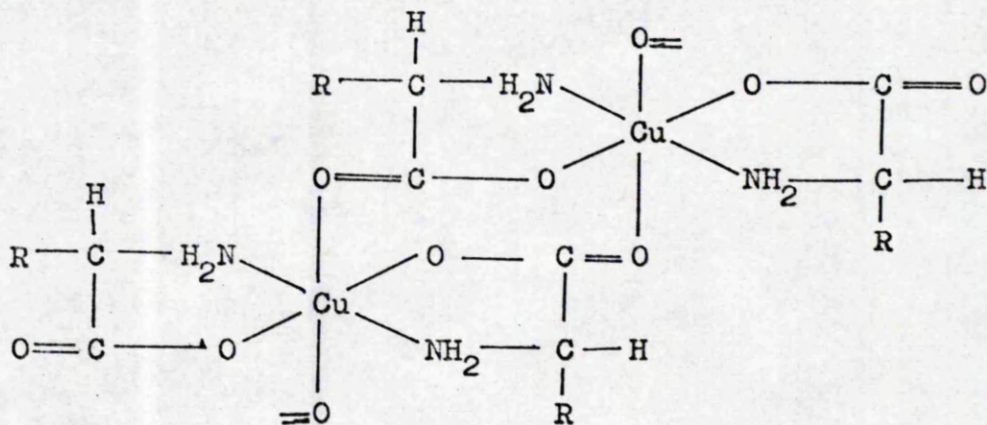
coordination of water molecules along the axis normal to the molecular plane Figure X or (iv) .

Figure X. Polymeric Structure of Monohydrated Bis(Amino Acidato)Copper(II).



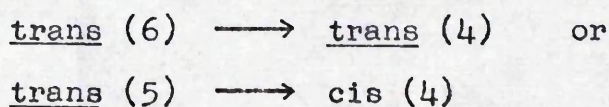
The second group consists of anhydrous complexes which are characterized by a single, rather broad band near $17,100\text{ cm}^{-1}$, and are assigned a structure in which the copper atom achieves elongated-octahedral symmetry by coordination of the C=O oxygen atoms of neighbouring molecules in the fifth and sixth positions (Figure XI).

Figure XI. Polymeric Structure of Anhydrous Bis(Amino Acidato)Copper(II).

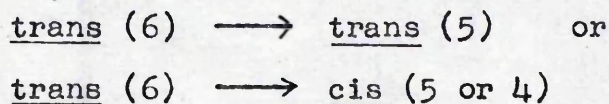


The third group is represented by anhydrous complexes having a rather low intensity absorption band resolvable into components with maxima at 19,600 and 16,950 cm^{-1} . These were predicted⁽⁴⁶⁾ to be truly square-planar copper(II) complexes, and this has been proved by X-ray analysis.⁽²³⁾

Yasui and Shimura⁽⁸⁴⁾ have pointed out that a more intense absorption band at the longer wavelength ($< 16,100 \text{ cm}^{-1}$) in the diffuse reflectance spectra of copper(II)-amino acid complexes may be correlated with a cis-coordination of the two amino acid residues about the copper atom. Laurie⁽⁴⁵⁾ argued from the symmetry point of view that increase in intensity for λ_{max} is consistent with the lowering of symmetry and shift of λ_{max} to a lower wavelength may be the result of a lowering of the coordination number. Thus, in cases where there are no increase in intensity as λ_{max} shifts to lower wavelength, the configuration transformation may be



where the numbers in parentheses are the coordination numbers. However, if there is an increase in intensity, then the possible transformation could be



These reflect the six possible configurations of the copper(II) chromophore, namely - a trans configuration with 6-, 5- or 4-coordination (D_{2h} , C_{2v} and D_{2h} microsymmetry point groups respectively), or a cis configuration (C_{2v} , C_1 and C_{2v} microsymmetry point groups respectively).

Sarkar and Wigfield⁽⁸⁵⁾ have measured the absorption

Table 8. Absorption Maxima and Extinction Coefficients of Copper(II) Complexes.

| pH | Cu(II)-imidazole | | Cu(II)-alanine | | Cu(II)-histamine | | Cu(II)-histidine | |
|------|-------------------|---|-------------------|---|-------------------|---|-------------------|---|
| | ϵ_{\max} | $\lambda_{\max} \text{ (cm}^{-1}\text{)}$ | ϵ_{\max} | $\lambda_{\max} \text{ (cm}^{-1}\text{)}$ | ϵ_{\max} | $\lambda_{\max} \text{ (cm}^{-1}\text{)}$ | ϵ_{\max} | $\lambda_{\max} \text{ (cm}^{-1}\text{)}$ |
| 5.5 | 24.5 | 14,650 | 38.0 | 15,400 | 37.0 | 15,300 | 66.0 | 16,100 |
| 6.5 | 34.0 | 15,750 | 44.5 | 15,810 | 63.5 | 16,400 | 84.2 | 15,850 |
| 8.0 | 40.0 | 16,100 | 51.5 | 16,000 | 80.0 | 16,620 | 92.0 | 15,750 |
| 10.0 | | | 48.6 | 16,100 | 80.5 | 16,620 | 90.5 | 15,700 |

maxima of bis(L-histidinato)copper(II) at several pH values and found that the absorption maximum shifts to longer wavelength as the pH is increased. This contrasts with other copper(II) complexes in which the λ_{max} shifts to lower wavelengths as pH increases (Table 8).

In order to assign the transitions in the solid bis(amino acidato)copper(II) complexes, Dijkgraab^(44,86) measured the polarized single crystal electronic spectra of bis(L- α -alaninato)copper(II) and bis(DL- α -aminobutyrate)-copper(II), and showed that the transitions arise from a 2A ground state.

(v) Magnetic Susceptibility

Magnetic susceptibility measurements play an important role in the characterization and investigation of transition metal complexes, since it concerns the effects arising from incomplete shells of electrons which are, to a first approximation, isolated from each other.⁽⁸⁷⁻⁸⁹⁾

When a substance is placed in a magnetic field, the total field, B , within the substance is due to the coupling of the internal field with the applied external field, of strength H_0 , and is defined as

$$B = H_0 + 4 \pi I \quad (1)$$

where I is the so-called intensity of magnetization, corresponding to the induced magnetic moment per unit volume. If expression (1) is divided through by H_0 , one obtains

$$B/H_0 = 1 + 4 \pi k \quad (2)$$

where k is the volume susceptibility, a measure of how easy it

is to magnetically polarize the substance. For chemists, the quantity of susceptibility per mole of a substance is more interesting, and the gram molecular susceptibility is given by

$$\chi_M = k \times V = \frac{k}{d} M \quad (3)$$

where V is the molecular volume, M is the molecular weight and d is the density of the substance.

On the basis of their magnetic susceptibilities, substances may be divided into three categories: diamagnetic, paramagnetic and ferro- or antiferromagnetic, as shown in Table 9.

Diamagnetic susceptibility which results from the motion of electrons within the substance, is often used to determine the structure of organic molecules⁽⁸⁷⁾ and has little practical value in coordination chemistry except for the correction of paramagnetic susceptibility.⁽⁸⁸⁾

The spin and orbital angular momenta of electrons give rise to the phenomenon of paramagnetism and its extensions - ferromagnetism and antiferromagnetism.⁽⁸⁷⁻⁸⁹⁾ The possession of these forms of angular momentum can be regarded as converting an atomic system into a micromagnetic dipole of moment, $\vec{\mu}$

$$\vec{\mu} = \vec{L} + 2\vec{S} \quad (4)$$

where \vec{L} is the total orbital angular momentum and \vec{S} is the total spin angular momentum (in units of $\frac{h}{2\pi}$) of a set of electrons in the atom. For a filled shell of electrons, the spin and orbital angular moments sums each vanish, so that the magnetic dipole associated with a filled shell is zero. Paramagnetism, is then, characteristic of partially filled electron shells.

If a substance with a permanent magnetic moment μ is

Table 9. Types of Magnetic Susceptibility Behaviour.

| Types of Magnetic Susceptibility | Sign | Magnitude c.g.s. | Dependence on H_0 | Origin |
|----------------------------------|----------|------------------------|----------------------------------|-----------------------------|
| Diamagnetic | Negative | 1×10^{-6} | Independent | Electron charge |
| Paramagnetic | Positive | $0-100 \times 10^{-6}$ | Independent | Electron spin |
| Ferromagnetic | Positive | $10^{-2} - 12^4$ | Dependent May be Dependent | Electron spin } exchange |
| Antiferromagnetic | Positive | $0-100 \times 10^{-6}$ | | |

placed in a magnetic field with the molecular magnets free to orient themselves, they will be subjected to two opposing effects: i) the magnetic field of strength H_0 which tends to align all molecular magnets in the same direction, and ii) the thermal effect of vibration, rotation and translation which tends to make the direction of the molecular magnets entirely random. It can be shown that the effective magnetic moment, μ_{eff} (substitute diamagnetically corrected χ_M , for χ_M) can be expressed as

$$\mu_{\text{eff}} = \left(\frac{3k}{N\beta^2} \right)^{\frac{1}{2}} (\chi_M T)^{\frac{1}{2}} \quad (5)$$

where k is Boltzmann's constant, β the Bohr magnetron, N Avogadro's number, and T the absolute temperature. If the Curie law is obeyed, μ_{eff} is independent of temperature. More generally, the Curie-Weiss law is employed, and the effective magnetic moment can be calculated from

$$\mu_{\text{eff}} = 2.828 \left\{ \chi_M (T + \theta) \right\}^{\frac{1}{2}} \quad (6)$$

where θ is the Weiss constant.

For many coordination compounds, particularly of the first transitional series, it is possible to assume that only the spin angular momentum of the electrons is effective in forming the elementary magnetic dipole due to the quenching of orbital momenta;⁽⁸⁹⁾ and so a very simple expression can be given for μ_{eff} , i.e.

$$\mu_{\text{eff}} = \{n(n+2)\}^{\frac{1}{2}} \text{B.M.} \quad (7)$$

where n is the number of unpaired electrons in the unfilled shell. Hence the number of unpaired electrons can be deduced

from the magnetic moment. From this it is then possible to infer the valency of, stereochemistry of, and types of bond to the metal atom.

Although the interpretation of magnetic moment is still a subject of much controversy,⁽⁸⁷⁾ it has a definite usefulness in establishing the stereochemistry of those compounds to which valency bond theory is applicable. The relationship between the valency, stereochemistry and magnetic behaviour of nickel in its complexes has been reviewed.⁽⁹⁰⁾ The stereochemistry and magnetic moments of nickel and copper complexes, are summarized in Table 10. It is possible then to distinguish the bond type and stereochemistry in 4-coordinated or 6-coordinated nickel(II) complexes, as well as to discriminate the different valency of the nickel ion in the complexes.

Usually, magnetic moments observed are higher than those spin-only value because of the orbital contribution. Thus for nickel(II) complexes in a regular octahedral environment, the spin-orbit coupling arising from the ground state ${}^3A_{2g}$ and the first excited state ${}^3T_{2g}$ (F) leads to an increase in the spin-only value of 2.83 B.M. Usually, the values of the magnetic moment are found in between 2.9 and 3.3 B.M.^(76,91)

Tetrahedral nickel(II) has an orbitally degenerate ground state, 3T_1 , and relatively large contribution from orbital angular momentum to the observed magnetic moment is expected. In fact, for regular tetrahedral complexes μ_{eff} occur within the range 3.5-4.0 B.M.^(76,91)

Five coordinate nickel(II) may be either high spin with two unpaired electrons and moments in the range 3.0-3.4 B.M. or low spin with no unpaired electrons and moments close to zero.^(76,91)

Table 10. Stereochemistry and Magnetic Moments of Nickel(II) and Copper(II) Complexes.

| Metal ion | Number of Unpaired Electrons | Stereochemistry | Magnetic Moment (B.M.) | |
|------------|---------------------------------|--------------------------------|------------------------|--------------|
| | | | Expected | Experimental |
| Nickel(II) | 2 | Octahedral | 2.83 | 2.9 - 3.3 |
| Nickel(II) | 2 | Tetrahedral | 2.83 | 3.5 - 4.0 |
| Nickel(II) | 2 | Square pyramidal | 2.83 | 3.0 - 3.4 |
| Nickel(II) | 0 | or trigonal bipyramidal | 0 | ~ 0 |
| Nickel(II) | 0 | Square planar | 0 | ~ 0 |
| Copper(II) | 1 | Octahedral or square planar | 1.73 | 1.9 - 2.2 |

It has now become increasingly evident that many transition metal complexes show anomalous magnetic behaviour.^(92,93) A great number of copper(II) complexes have moments less than the spin-only value for one unpaired electron, 1.73 B.M., and this has been generally considered due to the copper-copper interaction.⁽⁹²⁾

In the case of nickel(II) complexes, moments which fall in the range 0-2.8 B.M. are classified as anomalous, and several mechanisms have been postulated to account for this behaviour.⁽⁹³⁾

So far, all metal-amino acid complexes were found to have normal magnetic moments.⁽⁷⁷⁾

METAL COMPLEXES OF L-ARGININE

(1) Introduction

The fundamental importance of metal chelation in medical applications has been recognized.⁽⁹⁴⁾ The treatment of lead poisoning with ethylenediaminetetraacetic acid was a remarkable discovery, so is the treatment of Wilson's disease with L-penicillamine.⁽³⁾ In fact, it has been suggested that metal chelation apparently plays a definite role in the cause and treatment of cancer.⁽⁹⁵⁾

Arginine, being an essential amino acid, is required for urea synthesis, transamination and to increase insulin secretion.⁽⁹⁶⁾ An arginine deficiency in man results in the reduction of the number of spermatozoa.⁽⁹⁷⁾ In protein, the guanido group of arginine remains free and protonated. The inherent resonance stabilization makes it chemically distinct from other basic groups.⁽⁹⁸⁾ It has been assumed⁽⁹⁹⁾ that in trypsin hydrolysis with toluenesulphonylargininemethylester, there is the formation of a tetracoordinated copper(II) complex with the enzyme imidazole, the carboxyl group oxygen and nitrogens of guanido group of the substrate. These well known biological functions coupled with the lack of solid complexes of arginine in the literature has prompted the present investigation.

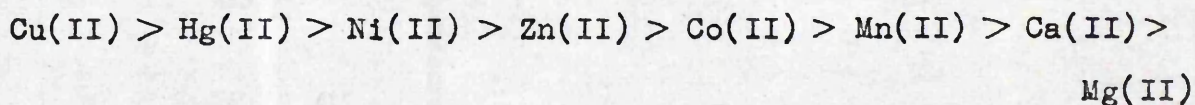
From potentiometric measurements Albert⁽¹⁰⁰⁾ has proposed that arginine functions predominantly as a bidentate ligand, binding bivalent metal ions through the α -amino and carboxyl groups. Li and Doody⁽¹⁰¹⁾ have confirmed this observation, and suggested that the large dissociation constant of the copper(II) arginine complex is due to the electrostatic

repulsion on the copper(II) cation by the positively charged guanido group bending towards the α -amino group resulting in a somewhat lesser degree of complex formation. Tanford and Shore⁽¹⁰²⁾ have also shown that the smaller association constants of cobalt(II) arginine complex compared to that of cobalt(II) α -alanine can be successfully explained due to the electrostatic influence of the positively charged guanido group of arginine. Arginine complexes of ferric⁽¹⁰³⁾ and ferrous⁽¹⁰⁴⁾ ions have been studied by means of potentiometric titrations, and results show that the guanido group of arginine is not involved in coordination.

Peffetier⁽¹⁰⁵⁾ used Bjerrum's method to determine the formation constants of arginine complexes with a series of metal ions, and discussed the thermodynamic quantities in terms of complex formation. The significance of thermodynamic quantities associated with formation of arginine and glycine silver complexes have also been discussed separately.⁽¹⁰⁶⁾

Arginine complexes of nickel(II) and cobalt(II) have been a subject of a kinetic study.⁽¹⁰⁷⁾ These results show that the reactivity of arginine in complex formation is less reactive than most chelating agents, in agreement with other studies.⁽¹⁰⁰⁻¹⁰⁶⁾

Recently, Clark and Martell⁽¹⁰⁸⁾ considered the complex formation of arginine in both its monoprotonated and unprotonated form with a series of bivalent transition metal ions. Stability constants followed the Irving and Williams' order of stability:⁽¹⁰⁹⁾



In the protonated form, arginine forms 1:1 and 1:2 chelates and function as simple bidentate α -amino acids with the guanido group protonated and free. In the unprotonated form, tridentate arginine involving the guanido group was suggested.

Qualitative and quantitative applications of arginine complexes in separation and determination of basic amino acids in protein have been reported.^(110,111) In addition to this, arginine complexes have been mentioned in other complex studies.⁽¹¹²⁻¹¹⁶⁾

A structural study of the chelates formed between copper(II) and amino acids is important in order to understand physiological copper transport,⁽¹¹⁷⁾ and this, in turn, may yield some knowledge of the role of copper in the catalysis of amino acid ester hydrolysis,⁽¹¹⁸⁾ and copper coordination in metalloenzymes such as ceruplasmin.⁽¹¹⁹⁾

(ii) Results and Discussion

Before any discussion, it is worthwhile to examine and assign the infrared absorptions of L-arginine in the regions of interests. In the solid state, X-ray technique shows⁽¹²⁰⁾ that L-arginine dihydrate takes the form of a zwitterion in which the proton residues on the guanido group leaving the α -amino group free. Knowing precisely the crystal structure of L-arginine, the next step is to correlate the infrared absorptions with the aid of known assignments of other amino acids.^(61,66,67,77,121-126)

The infrared spectrum of L-arginine has been discussed,^(122,123) as has that of L-arginine monohydrochloride.⁽¹²¹⁾ In table 11, some important infrared frequencies of L-arginine and related compounds have been

Table 11. Some Infrared Frequencies (cm⁻¹) of L-Arginine and Related Compounds.

| L-Arginine (a) | L-Arginine (122) | Arginine (123) | L-Arginine.HCl (121) | Guanidinium (125) | Assignment |
|----------------|------------------|----------------|----------------------|-------------------|------------------------------------|
| 3358 s,sp | 3356 | 3380 | 3250 s,sp | 3410 s | ✓NH |
| 3295 s,b | | 3220 | | 3275 s | |
| 3055 s,b | 3155 | 3030 | 3050 s,sp | 3150 s | ✓NH ₃ ⁺ |
| | 3030 | | | | |
| 2940 s,sp | 2857 | 2940 | 2855 s,b | | ✓CH |
| 2858 m,sp | 2755 | | | | |
| | 2597 | | 2090 w,b | | ✓NH ₃ ⁺ ? |
| 1720 m,sh | 1739 | | | | |
| 1670 s,sp | 1684 | | 1680 s,sp | 1670 s | ✓C=N |
| 1610 s,b | 1550 | | 1565 s,b | | ✓COO asym |
| 1550 s,sp | 1613 | | 1645 s,sp | 1640 s | δNH ₂ |
| | 1511 | | 1540 s,sp | 1538 m | |
| 1470 m,sp | | | 1460 m,sp | | δCH |
| 1446 w,sp | | | | | |
| 1435 w,sp | | | | | |
| 1417 m,sp | 1420 | | 1415 s,sp | | ✓COO sym |

(a) The present work.

tabulated with tentative assignments.

In the regions of interest, that is, the NH and COO stretching regions, the NH stretching frequencies were assigned without much difficulty.⁽⁶¹⁾ The only confusing assignment is the antisymmetric carboxyl stretching and the NH bending absorptions. While Larsson⁽¹²²⁾ assigned the antisymmetric COO stretching to a band at 1550 cm^{-1} , and the NH bending to a band at 1613 cm^{-1} ; the reverse assignment is more appropriate as the guanido group in arginine is planar⁽¹²⁰⁾ and assumes a D_{3h} symmetry⁽¹²⁵⁾ in which the NH bending vibration will absorb near 1640 cm^{-1} . The fact that this band, overlapped by the stronger C=N stretching, shifts to 1560 cm^{-1} upon deuteration supports this assignment. Also, as crystallography result shows⁽¹²⁰⁾ that the α -amino group is hydrogen bonded to the guanido group, a lower NH_2 deformation (at 1550 cm^{-1}) would be expected.⁽⁶¹⁾ The most telling piece of evidence is, however, that the band at 1610 cm^{-1} was present in the deuteriated compound, further supports the assignment as the COO antisymmetric stretching.

Copper(II) Complexes of L-Arginine Several copper(II) complexes of L-arginine have been isolated. The most interesting is the anhydrous and hydrated perchlorate complexes. The monohydrated complex, $[\text{Cu}(\text{L-ArgH})_2\text{H}_2\text{O}](\text{ClO}_4)_2$, was prepared by recrystallization of the anhydrous compound, $[\text{Cu}(\text{L-ArgH})_2(\text{ClO}_4)_2]$, from water. The Nujol mull infrared spectra of these complexes are distinctively different, especially those absorption frequencies associated with the perchlorate ion (Table 12, and Figure XII), but the KBr disc spectra are practically similar.

Table 12. Some Significant Infrared Frequencies (cm^{-1}) of Copper(II)-L-Arginine Perchlorate Complexes

| Compound | ν_{OH} | ν_{NH} | $\nu_{\text{C=N}}$ | $\nu_{\text{COO asym}}$ | $\nu_{\text{COO sym}}$ | δ_{NH_2} | ClO_4^- |
|--|-------------------|-------------------|--------------------|-------------------------|------------------------|------------------------|------------------|
| $[\text{Cu}(\text{L-ArgH})_2(\text{ClO}_4)_2]^{(a)}$ | | | | | | | |
| | | 3480 s, sp | 1656 s, b | 1614 m, sp | 1395 m, sp | 1575 m, sp | 1125 s, s |
| | | 3460 s, sp | | | | | 1090 s, s |
| | | 3395 s, sp | | | | | 1065 s, s |
| | | 3370 s, sp | | | | | 931 w, s |
| | | 3340 s, sp | | | | | 636 w, sh |
| | | 3330 w, sp | | | | | 625 w, sh |
| | | 3255 s, sp | | | | | 620 m, s |
| | | 3180 s, sp | | | | | |
| | | 3040 w, sh | | | | | |
| $[\text{Cu}(\text{L-ArgH})_2(\text{ClO}_4)_2]^{(b)}$ | | | | | | | |
| | | 3450 s, sp | 1658 s, sp | 1624 s, sp | 1390 m, wp | 1594 s, sp | 1140 s, s |
| | | 3360 s, b | | | | | 1115 s, s |
| | | 3270 s, sp | | | | | 1085 s, s |
| | | 3235 s, sp | | | | | 940 w, s |
| | | 3170 s, sp | | | | | 635 m, s |
| | | 3040 w, sh | | | | | 630 m, s |
| | | | | | | | 625 m, s |
| $[\text{Cu}(\text{L-ArgH})_2\text{H}_2\text{O}](\text{ClO}_4)_2^{(a)}$ | 3590 m, b | 3455 s, b | 1655 s, sp | 1615 s, b | 1398 m, sp | 1600 s, b | 1095 s, b |
| | | 3370 s, sp | | | | | 620 m, b |
| | | 3330 s, sh | | | | | |
| | | 3240 s, sp | | | | | |
| | | 3180 s, b | | | | | |

continued....

Table 12 continued.

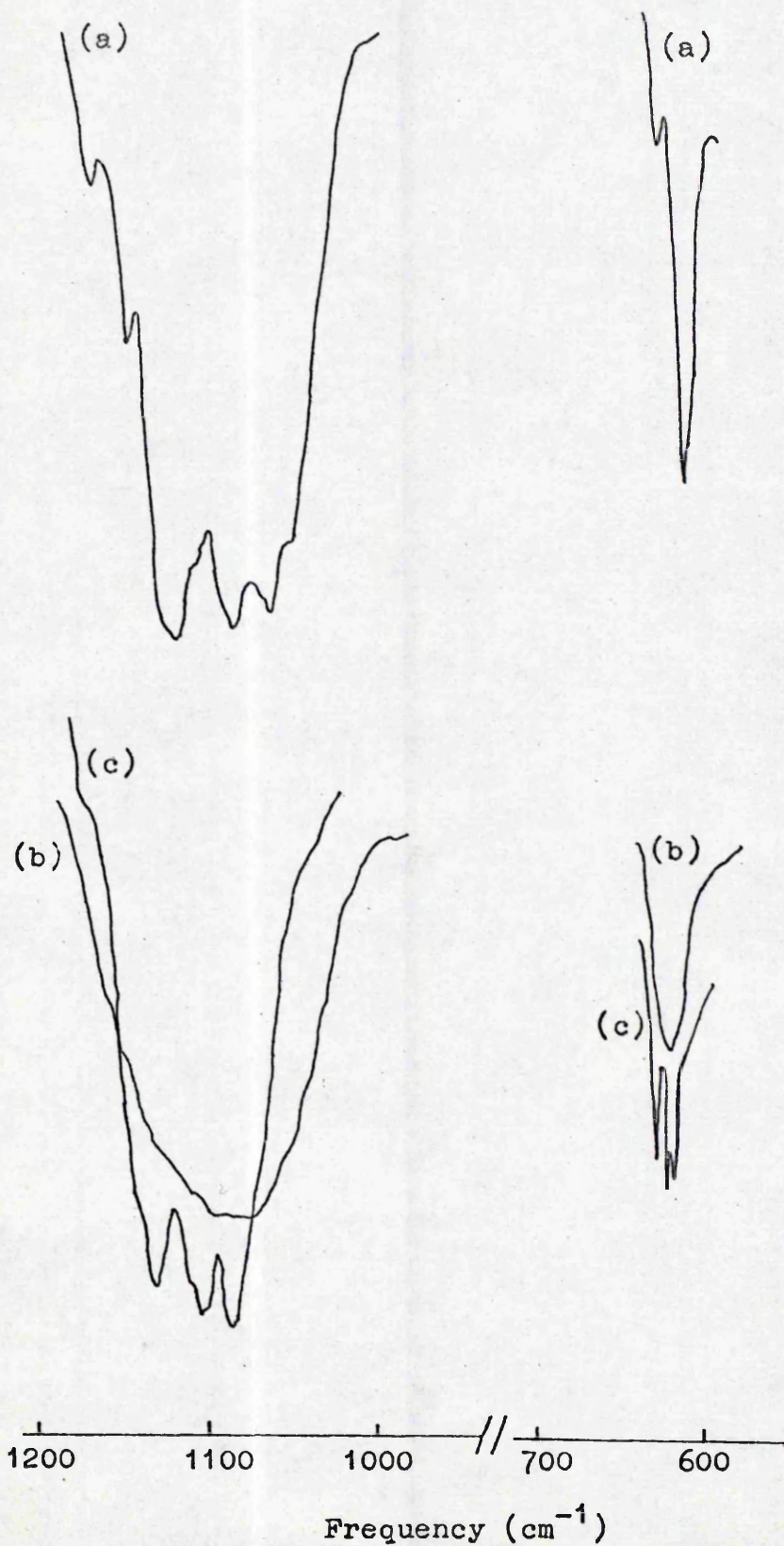
| Compound | ν_{OH} | ν_{NH} | $\nu_{C=N}$ | $\nu_{COO \text{ asym}}$ | $\nu_{COO \text{ sym}}$ | δ_{NH_2} | ClO_4^- |
|--|------------|------------|-------------|--------------------------|-------------------------|-----------------|-----------|
| $[Cu(L-ArgH)_2(ClO_4)_2] \cdot H_2O^{(b)}$ | | | | | | | |
| | | 3350 s,b | 1650 s,sp | 1615 s,b | 1396 m,sp | 1598 s,b | 1137 s,s |
| | | 3300 s,b | | | | | 1110 s,s |
| | | 3220 s,sp | | | | | 1083 s,s |
| | | 3165 s,sp | | | | | 936 w,s |
| | | | | | | | 632 m,s |
| | | | | | | | 625 m,s |
| | | | | | | | 621 m,s |

(a) Nujol mull spectrum

(b) KBr disk spectrum

Figure XII. Infrared Spectra of Perchlorate Group to
Copper(II)-L-Arginine Complexes

- (a) $[\text{Cu}(\text{L-ArgH})_2(\text{ClO}_4)_2]$ (Nujol mull)
 (b) $[\text{Cu}(\text{L-ArgH})_2\text{H}_2\text{O}](\text{ClO}_4)_2$ (Nujol mull)
 (c) $[\text{Cu}(\text{L-ArgH})_2\text{H}_2\text{O}](\text{ClO}_4)_2$ (KBr disk)



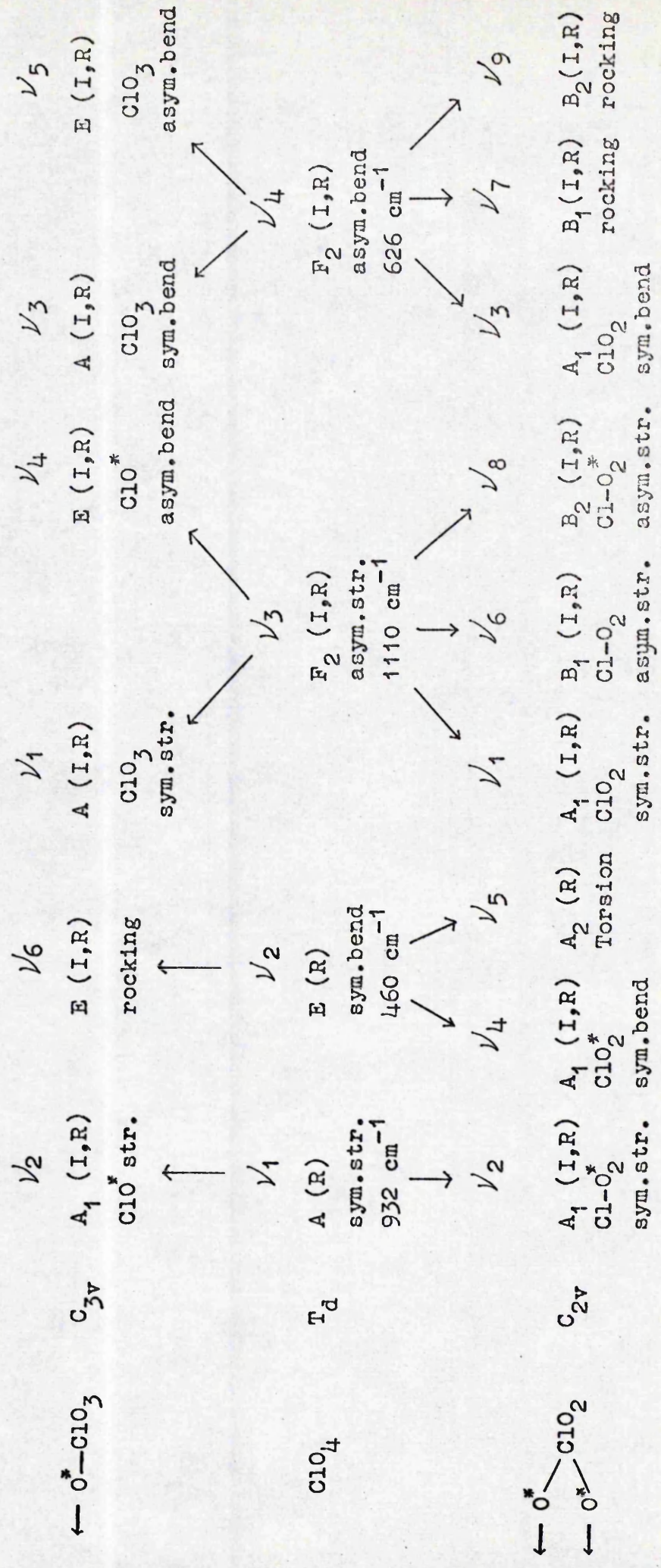
It is well known that the infrared absorptions of perchlorate ion depend very much on the stereochemical structures of the ion.⁽¹²⁷⁻¹²⁹⁾ Hathaway and Underhill⁽¹²⁷⁾ have shown that the free perchlorate ion has symmetry T_d , but lowered to C_{3v} or C_{2v} depending upon whether it acts as monodentate or bidentate ligand through the oxygen atoms. Table 13 illustrates the correlation between the absorption frequencies and the symmetries of the perchlorate group. Each of the two infrared active bands in T_d symmetry, ν_3 and ν_4 , are split into two components in C_{3v} symmetry, and into three components in C_{2v} symmetry. Thus, the state of the perchlorate ion can be deduced from infrared absorption spectra.

The infrared spectra of anhydrous bis(L-arginine)copper(II) perchlorate consist of three well defined bands at ca. 1125, 1090 and 1062 cm^{-1} ; and 636, 675 and 620 cm^{-1} together with a weak band at 931 cm^{-1} are characteristic of a bidentate perchlorate ion. However, the Nujol mull spectrum of bis(L-arginine)copper(II) perchlorate monohydrate has only one broad band at ca. 1095 cm^{-1} and a weak band at ca. 620 cm^{-1} indicative of ionic perchlorate group. Surprisingly, the KBr disk spectrum of the hydrated complex again shows the presence of bidentate perchlorate group. Since it has previously been noted that bromide ion will replace the coordinated perchlorate ion in KBr discs,⁽¹³⁰⁾ and since rearrangement only takes place under extreme pressure, this probably indicates that this is not a common KBr effect.

The infrared spectra of metal-amino acid complexes have been well investigated,^(47,77,131) and a good deal of information about bonding sites may be thus obtained. While both the carboxyl and amine stretching vibrations are

Table 13. Vibrations of the Perchlorate Group as a Function of Symmetry

State of ClO_4 Symmetry



A and B, non-degenerate. E, doubly degenerate. F, triply degenerate. I, infrared active.
 R, Raman active. O^* , coordinated oxygen atom.

susceptible to hydrogen-bonding effects, it is significant that the COO stretching frequencies in the complexes and free ligand are very similar, whereas the NH stretchings are more complicated and shift to lower frequencies in the complexes than in the free ligand (Table 12), which is indicative of copper-nitrogen bonding.⁽⁷⁷⁾

Moreover, diffuse reflectance spectra (Table 14 and Figure XIII) indicate a CuN_2O_4 coordination moiety.^(43,45,83) Graddon and Munday⁽⁴³⁾ have discussed the electronic spectra of copper(II)-amino acid complexes and the band near $16,100\text{ cm}^{-1}$ in these complexes is indicative of an N_2O_4 coordination. In particular, the position of the band is at much too high energy for it to result from a CuO_6 moiety (resulting from the ligand coordinating via the carboxylate groups) which absorbs at $12,500\text{ cm}^{-1}$. The resemblance of the electronic spectra of the anhydrous copper(II) complex and the hydrated analogue in the KBr disk indicates almost identical coordination environment in accord with the observed infrared evidence.

The effective magnetic moments of these complexes (Table 15) are in the normal range of mononuclear copper(II) complexes.⁽¹³²⁾ As in all known copper(II) complexes, the 'effective' electronic ground state is orbitally non-degenerate, there is no inherent orbital contribution to the magnetic moment of the ground state, and hence no stereochemical information is forthcoming from this source.

Nevertheless, available spectroscopic informations suggest that the anhydrous complex bis(L-arginine)copper(II) perchlorate is likely to adopt the following structure, (ix); while the monohydrated bis(L-arginine)copper(II) perchlorate

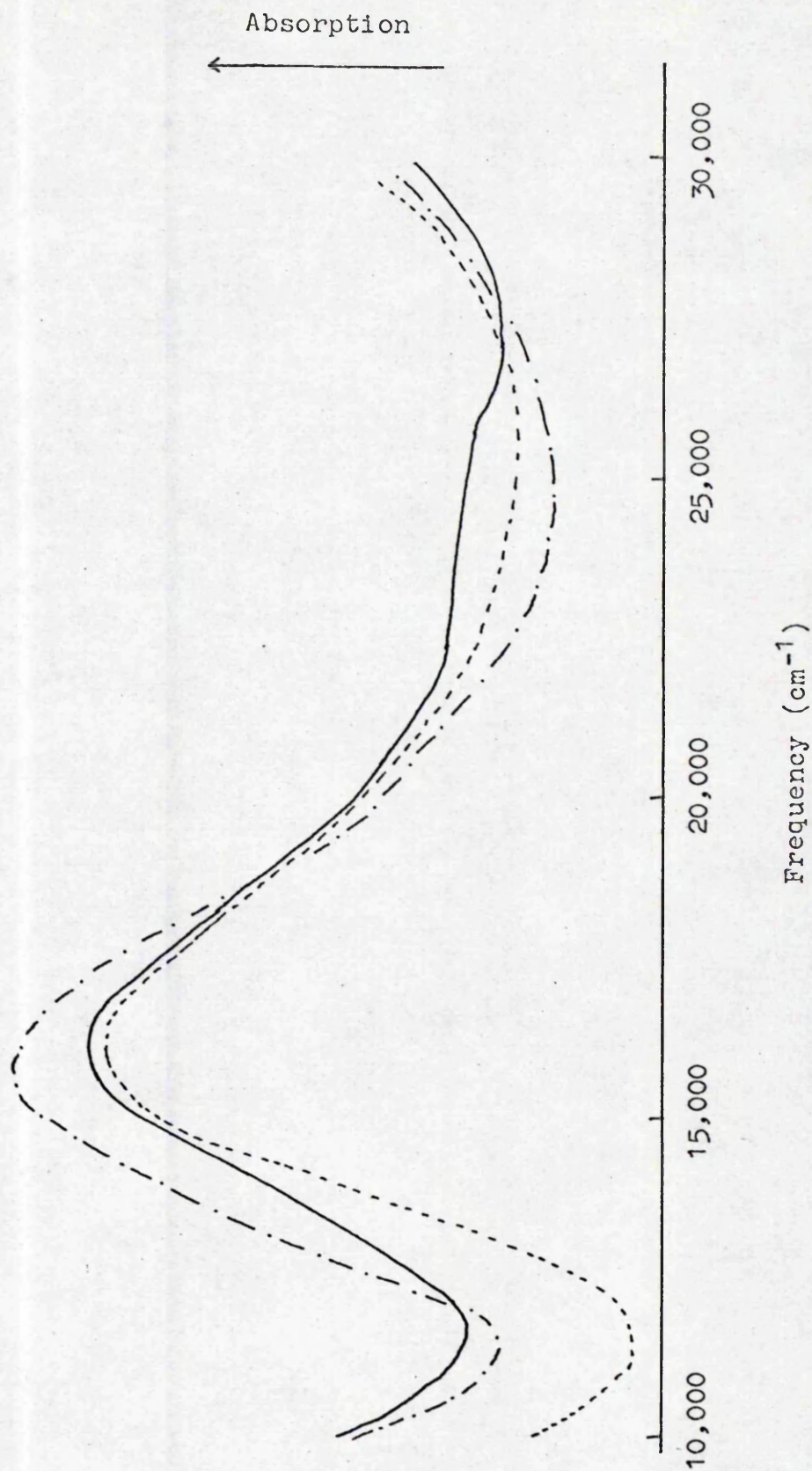
Table 14. Reflectance Absorption Maxima (cm^{-1}) of Copper(II)-L-Arginine Complexes

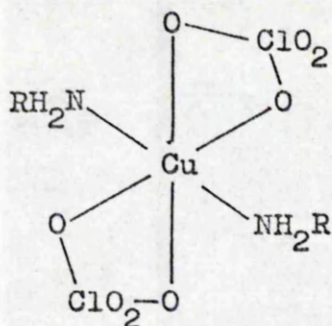
| Compound | λ_{max} |
|---|------------------------|
| $[\text{Cu}(\text{L-ArgH})_2(\text{ClO}_4)_2]$ | 16,100 |
| $[\text{Cu}(\text{L-ArgH})_2\text{H}_2\text{O}](\text{ClO}_4)_2$ | 15,750 |
| $[\text{Cu}(\text{L-ArgH})_2(\text{ClO}_4)_2]\text{H}_2\text{O}$ KBr disk | 16,100 |
| $[\text{Cu}(\text{L-ArgH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ | 16,400 |
| $[\text{Cu}(\text{L-ArgH})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ | 15,900 |
| $[\text{Cu}(\text{L-ArgH})_2(\text{H}_2\text{O})_2](\text{OH})_2$ | 16,500 |
| $[\text{Cu}(\text{L-Arg})\text{ClO}_4\cdot 3\text{H}_2\text{O}]$ | 15,300; 13,150 (sh) |

Table 15. The Effective Magnetic Moment, μ_{eff} (B.M.) of Copper(II)-L-Arginine Complexes

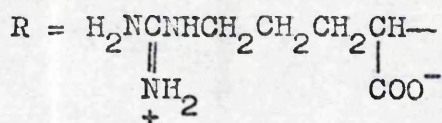
| Compound | μ_{eff} |
|---|--------------------|
| $[\text{Cu}(\text{L-ArgH})_2(\text{ClO}_4)_2]$ | 2.07 |
| $[\text{Cu}(\text{L-ArgH})_2\text{H}_2\text{O}](\text{ClO}_4)_2$ | 2.18 |
| $[\text{Cu}(\text{L-ArgH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ | 1.92 |
| $[\text{Cu}(\text{L-ArgH})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ | 2.01 |
| $[\text{Cu}(\text{L-ArgH})_2(\text{H}_2\text{O})_2](\text{OH})_2$ | 1.82 |
| $[\text{Cu}(\text{L-Arg})(\text{ClO}_4)\cdot 3\text{H}_2\text{O}]$ | 1.95 |

Figure XIII. Solid Electronic Spectra of $[\text{Cu}(\text{L-ArgH})_2(\text{ClO}_4)_2] (\text{---})$,
 $[\text{Cu}(\text{L-ArgH})_2(\text{H}_2\text{O})](\text{ClO}_4)_2 (\text{-- -- --})$, and $[\text{Cu}(\text{L-ArgH})_2(\text{H}_2\text{O})](\text{ClO}_4)_2$ (KBr disk)
 (.....).

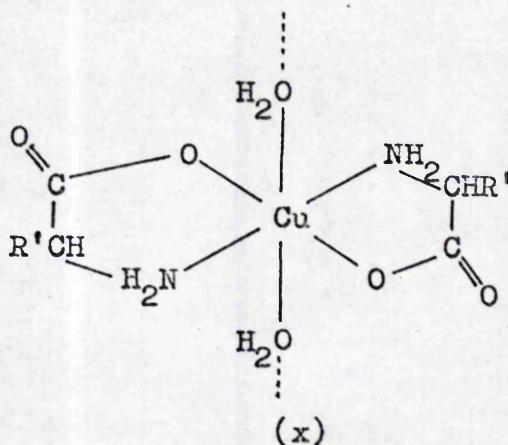




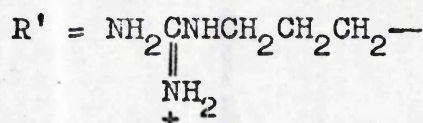
(ix)



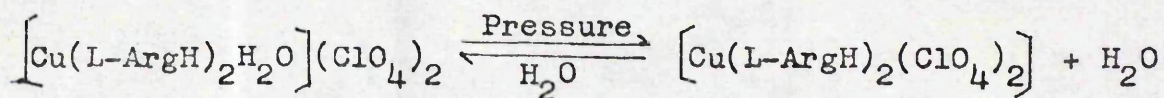
probably has structure (x).



(x)



When (x) is pressed in a KBr die, the resulting infrared spectrum indicates that the water molecules and carboxyl groups have been replaced by bidentate perchlorate groups, and the reflectance spectrum of the KBr disk is similar to the authentic sample of (ix). Thus the following process may be envisaged:



This pressure rearrangement has been investigated thoroughly, and it is concluded that the rearrangement does not occur until the complex (x) - KBr mixture is put under extreme pressure. Thus, merely mixing (x) with KBr or hand-grinding does not bring this rearrangement about, because the electronic spectrum is still identical to that of the unmixed (x). As far as can be ascertained the use of pressure in effecting a rearrangement of groups within the same molecule is unique.

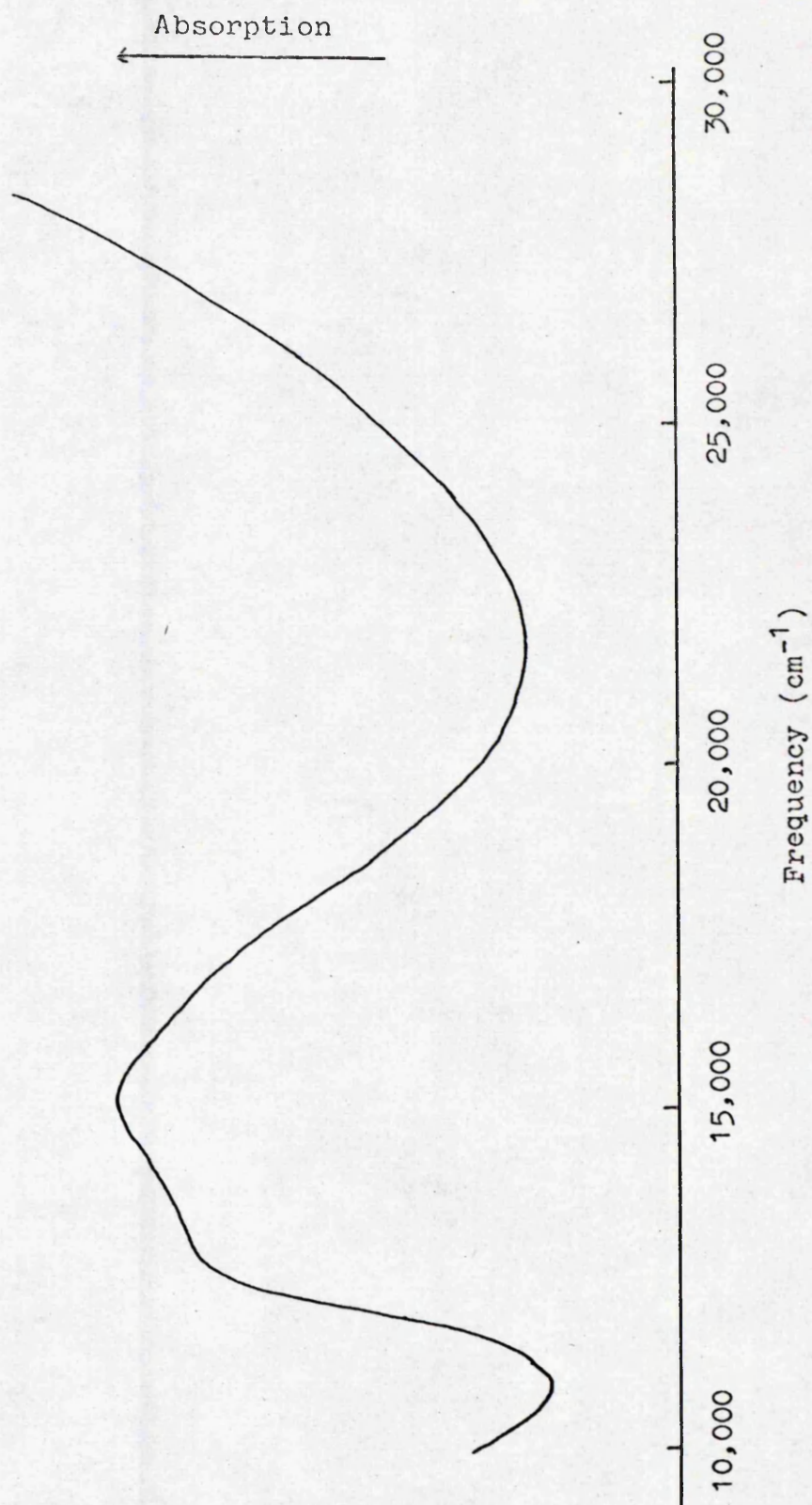
The infrared spectrum of L-argininatocopper(II) perchlorate trihydrate is essentially similar to that of bis(L-arginine)copper(II) perchlorate (Table 16). This implies that the functions of L-arginine and perchlorate ion are similar in the two complexes. Although the magnetic moment of $\left[\text{Cu}(\text{L-Arg})\text{ClO}_4 \cdot 3\text{H}_2\text{O} \right]$ (Table 15) lies within normal range, the electronic absorption (Table 14 and Figure XIV) is too low for N_2O_4 moiety. Laurie⁽⁴⁵⁾ has correlated the reflectance spectra of copper(II)-amino acid complexes with stereochemistry of copper(II). However, in this case, the shift of λ_{max} to lower frequency is neither associated with a change of coordination number nor a change in geometry, but more closely related to a NO_5 moiety. Apparently, the broad absorption may be resolved into two absorptions centred near 15,300 and 13,150 cm^{-1} . This may be due to a strong Jahn-Teller distortion giving rise to a very distorted octahedron.^(133,134) Hence, a possible structure for $\left[\text{Cu}(\text{L-Arg})\text{ClO}_4 \cdot 3\text{H}_2\text{O} \right]$ is one similar to (xi).

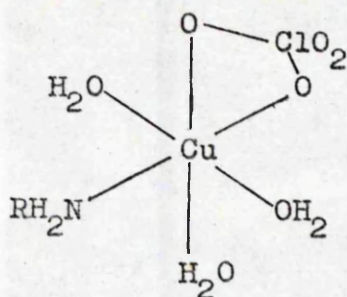
Table 16. Significant Infrared Absorption Frequencies (cm^{-1}) of Copper(II)-L-Arginine Complexes.

| Compound | ν_{OH} | ν_{NH} | $\nu_{\text{C=N}}$ | $\nu_{\text{COO asym}}$ | $\nu_{\text{COO sym}}$ | δ_{NH_2} | Anion |
|--|-------------------|--|--------------------|-------------------------|--------------------------|------------------------|---|
| $[\text{Cu}(\text{L-Arg})(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}]$ | 3570 w, sh | 3480 s, sp 3460 s, sp 3400 s, sp 3380 s, sp 3340 s, sp 3310 m, sp 3250 s, sp 3178 s, sp | 1660 s, b | 1615 s, b | 1395 m, sp | 1575 s, sp | 1130 s, sp 1080 s, b 1060 s, sh 532 w, sp 638 w, sh 622 s, sp 620 w, sh |
| $[\text{Cu}(\text{L-ArgH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ | 3500 s, b | 3370 s, b 3278 s, sp 3190 s, b 3040 w, sh | 1690 s, sp | 1630 s, sp | 1390 s, b ^(a) | 1592 s, b | 814 m, s |
| $[\text{Cu}(\text{L-ArgH})_2(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$ | 3450 m, b | 3342 s, b 3282 s, sp 3240 s, sp 3175 m, sh 3050 w, sh | 1666 s, sh | 1630 s, b | 1405 m, sp | 1560 w, sh | |
| $[\text{Cu}(\text{L-ArgH})_2(\text{H}_2\text{O})_2](\text{OH})_2$ | | 3340 s, sp 3230 s, b 3125 s, sp | 1665 s, b | 1635 s, sp | 1392 m, sp | 1588 s, b | 3470 s, sp |

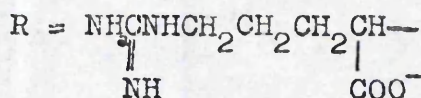
(a) overlapped with NO_3 absorption

Figure XIV. Solid Electronic Absorption Spectrum of $[\text{Cu}(\text{L-Arg})(\text{ClO}_4)(\text{H}_2\text{O})_2]$





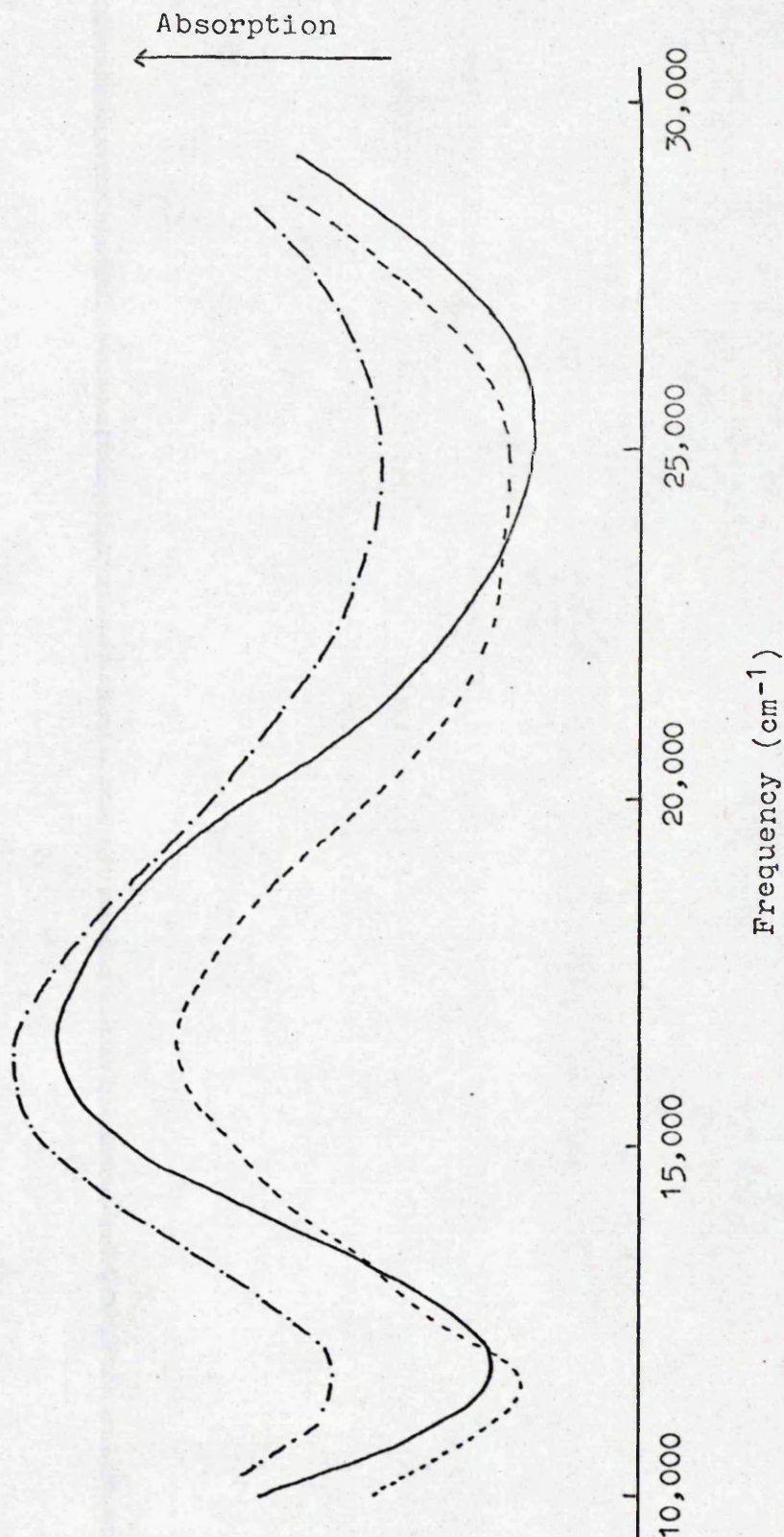
(xi)



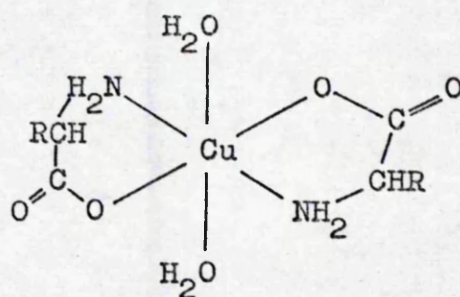
The other copper(II) complexes, namely bis(L-arginine)-copper(II) nitrate dihydrate, bis(L-arginine)copper(II) chloride dihydrate and bishydroxobis(L-arginine)copper(II) dihydrate, may be grouped together. The most significant difference in their infrared spectra compared with those mentioned earlier is the shift of the antisymmetric stretching of carboxyl group to a higher frequency, ca. 1630 cm^{-1} . Nakamoto and co-workers⁽⁶⁴⁾ have discussed the nature of the metal-carboxyl coordinate linkages with respect to the antisymmetric and symmetric carboxyl stretchings. As an increase in the covalent character of metal-oxygen bond leads to a more asymmetric structure of the carboxyl group and results in an increase in the frequency separation of the two carboxyl bands. The separation of about 240 cm^{-1} in these complexes compared to about 220 cm^{-1} in $[\text{Cu}(\text{L-ArgH})_2\text{H}_2\text{O}](\text{ClO}_4)_2$ clearly indicates a stronger metal-oxygen bond in these complexes.

While the magnetic moments (Table 15) and electronic spectra (Table 14 and Figure XV) of these complexes

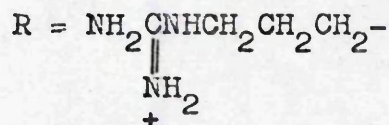
Figure XV. Solid Electronic Absorption Spectra of $[\text{Cu}(\text{L-ArgH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ (—), $[\text{Cu}(\text{L-ArgH})_2(\text{H}_2\text{O})_2](\text{OH})_2$ (.....), and $[\text{Cu}(\text{L-ArgH})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ (-.-.-.-.)



unambiguously suggest a tetragonally-distorted octahedron coordination around the central copper atom, infrared absorption frequencies do not indicate the coordination of the nitrate ion, ^(53,54) nor the hydroxyl ion although its presence is strongly evidenced by a strong, sharp absorption at 3470 cm^{-1} . ⁽⁴⁷⁾ Hence, it may be suggested that these complexes adopt a common structure similar to (xii).



(xii)



In order to establish the geometrical structure of copper(II)-L-arginine complexes, the infrared absorptions of the complexes and L-arginine in the region $300\text{--}500\text{ cm}^{-1}$ were compared to determine the copper-ligand stretching frequencies. Table 17 illustrates the assignments which are derived from Condrate and Nakamoto. ⁽⁶³⁾ Following the criterion of cis-trans isomerism laid down by Herlinger and co-workers ⁽⁵⁷⁾ that only the asymmetric copper-ligand stretchings are infrared active in the trans form whereas both the asymmetric and symmetric copper-ligand stretchings are infrared active in the cis form, data shows only one absorption frequency for each of the Cu-N and Cu-O stretchings, suggesting a trans-configuration

Table 17. Copper-Ligand Stretching Frequencies (cm^{-1}) of L-Arginine Complexes

| Complex | $\nu_{\text{Cu-N}}$ | $\nu_{\text{Cu-O}}$ |
|---|---------------------|---------------------|
| $[\text{Cu}(\text{L-ArgH})_2(\text{ClO}_4)_2]$ | 420 | - |
| $[\text{Cu}(\text{L-ArgH})_2\text{H}_2\text{O}](\text{ClO}_4)_2$ | 420 | 320 |
| $[\text{Cu}(\text{L-Arg})(\text{ClO}_4)_3\text{H}_2\text{O}]$ | 420 | - |
| $[\text{Cu}(\text{L-ArgH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ | 444 | 350 |
| $[\text{Cu}(\text{L-ArgH})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ | 425 | 340 |
| $[\text{Cu}(\text{L-ArgH})_2(\text{H}_2\text{O})_2](\text{OH})_2$ | 431 | 330 |

for all complexes. The absence of Cu-O stretching frequencies in the complexes, $[\text{Cu}(\text{L-ArgH})_2(\text{ClO}_4)_2]$ and $[\text{Cu}(\text{L-Arg})(\text{ClO}_4)_3\text{H}_2\text{O}]$, further supports monodentate function of L-arginine in these complexes.

Nickel(II) Complexes of L-Arginine. The nickel(II) complexes of L-arginine prepared can be schematically divided into two groups: the $\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_n \text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{NO}_3, \text{ClO}_4$) derivatives which contain anionic ligands, and the $\text{Ni}(\text{L-ArgH})_m \text{X}_2 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{NO}_3, \text{ClO}_4, \text{OH}$) complexes which contain zwitterionic ligands.

The reflectance spectra of these complexes (Figure XVI and XVII) are characteristic of a pseudooctahedral nickel(II) environment⁽⁷⁶⁾ with three well-defined absorptions in the visible region. Jorgensen⁽⁷³⁾ has observed that the spectra of octahedral nickel(II) complexes are similar for any given combination of n nitrogen and $6-n$ oxygen donors, a phenomenon he has named the rule of average environment. Using this rule it is possible to estimate the number of each type of donor atom. The first group complexes which contain unprotonated arginine ligands exhibit spectra (Table 18 and Figure XVI) indicative of an N_2O_4 environment around the nickel atom.^(73,81,131) Moreover, the complexes exhibit almost identical spectra irrespective of the other anion (Cl^- , Br^- , NO_3^- , ClO_4^-), which is evidence that the coordination sphere of nickel does not contain these anions.

The Nujol mull infrared spectra of all anionic arginine complexes are almost similar except for absorptions due to the inorganic anions, indicating that the function of

Table 18. Solid Electronic Absorption Maxima (cm^{-1}) of the Nickel(II) Complexes and Some Spectral Parameters (a)

| Compound | Ligating atoms | ${}^3A_{2g} \rightarrow {}^3T_{2g}$ | ${}^3A_{2g} \rightarrow {}^1E_g$ | ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ | ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ | Dq | B' | β |
|--|-------------------|-------------------------------------|----------------------------------|--|--|------|-----|---------|
| $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_2]\text{ClO}_4$ | 2 N, 4 O | 9,600 | | 15,500 | 26,900 | 960 | 975 | 0.91 |
| $[\text{Ni}(\text{L-Arg})(\text{ClO}_4)_2\text{H}_2\text{O}]\text{H}_2\text{O}^{(b)}$ | 2 N, 4 O | 9,750 | | 15,500 | 26,300 | 975 | 905 | 0.86 |
| $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_3]\text{NO}_3$ | 2 N, 4 O | 9,550 | | 15,800 | 26,400 | 955 | 886 | 0.84 |
| $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_3]\text{ClH}_2\text{O}$ | 2 N, 4 O | 9,400 | | 15,300 | 26,500 | 940 | 916 | 0.85 |
| $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_2]\text{Br}$ | 2 N, 4 O | 9,700 | | 15,900 | 26,300 | 970 | 864 | 0.80 |
| $[\text{Ni}(\text{L-ArgH})_2(\text{NO}_3)_2]\text{H}_2\text{O}$ | 2 N, 4 O | 10,500 | 13,100 | 16,600 | 27,700 | 1050 | 948 | 0.88 |
| $[\text{Ni}(\text{L-ArgH})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ | 2 N, 4 O | 9,500 | | 16,200 | 26,900 | 950 | 929 | 0.86 |
| $[\text{Ni}(\text{L-ArgH})_3\text{H}_2\text{O}](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ | 2 N, 4 O | 9,700 | | 16,600 | 26,600 | 970 | 953 | 0.88 |
| $[\text{Ni}(\text{L-ArgH})_2(\text{ClO}_4)_2](\text{L-ArgH})_4\text{H}_2\text{O}^{(b)}$ | 2 N, 4 O | 10,000 | | 16,100 ^(c) | 27,100 | 1000 | 885 | 0.84 |
| $[\text{Ni}(\text{L-ArgH})_2\text{H}_2\text{O}](\text{OH})_2$ | 2 N, 4 O | 9,500 | | 15,700 | 27,000 | 950 | 870 | 0.81 |

(a) β = Racah parameter

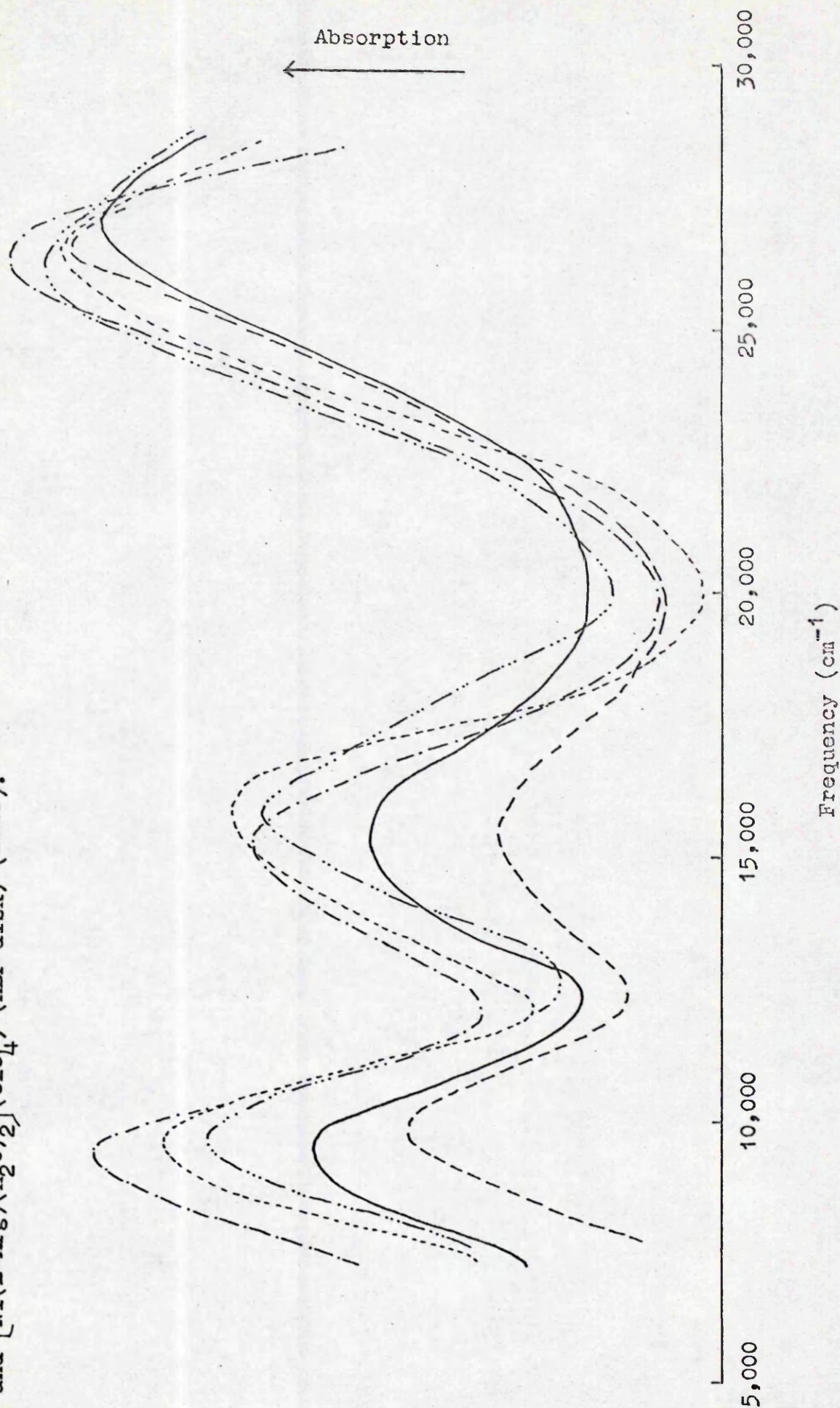
B' = the 3F_3P term separation for the Ni^{2+} complexes were calculated by an empirical method (R.S.Drago,

"Physical Methods in Inorganic Chemistry" Reinhold Publishing Corp., New York, 1965, pp.168 and 410).

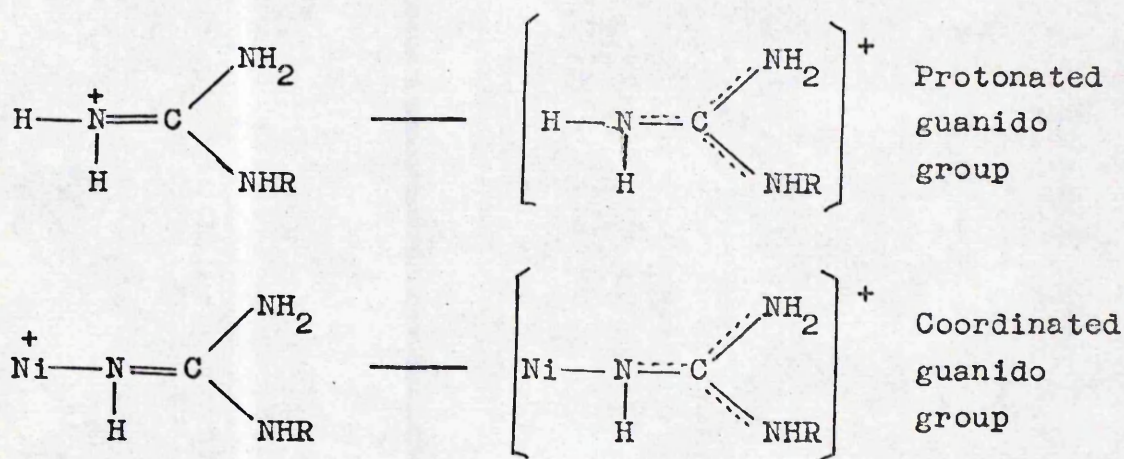
(b) Reflectance spectrum in KBr disk.

(c) A weak absorption also appears at $17,400 \text{ cm}^{-1}$.

Figure XVI. Solid Electronic Absorption Spectra of $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (—), $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_3](\text{NO}_3)_3$ (.....), $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_3]\text{Cl}\cdot\text{H}_2\text{O}$ (-.-.-), $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_2]\text{Br}$ (-.....-), and $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (KBr disk) (----).



argininate residue in these complexes is similar. All the complexes contain a broad absorption ca. 3500 cm^{-1} which can be assigned to the OH stretching mode of coordinated or lattice water. The other significant infrared frequencies are listed in Table 19. In the $3\text{ }\mu$ region, peaks observed for the ligand at 3350 and 3290 cm^{-1} are not considerably changed upon complexation, but a new peak ca. 3180 cm^{-1} was observed for all the complexes. This new peak may be assigned to the NH stretching frequency of a coordinated amino group.⁽⁷⁷⁾ The similar absorptions at 3350 and 3290 cm^{-1} for the complexes as well as the guanido group in the ligand seems to suggest that the resonance, and possibly the symmetry as well, of the guanido group is not appreciably altered, and this could be true for the deprotonated guanido group only if it is involved in coordination to the nickel:



This reasoning would also rule out any possibility of two nitrogen atoms of the guanido group being involved in coordination, and molecular models reinforce this view.

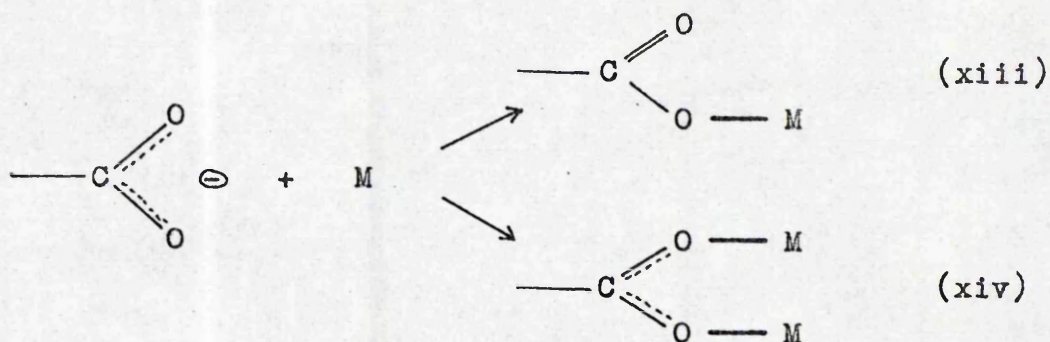
Table 19 also contains the antisymmetric and symmetric COO stretching frequencies, and Δ , the difference between them. It can be seen that Δ increases upon coordination of

Table 19. Some Significant Infrared Frequencies (cm^{-1}) of the Nickel(II) Complexes of L-Arginine (a)

| Compound | ν_{NH} | $\nu_{\text{C=N}}$ | $\nu_{\text{COO asym}}$ | $\nu_{\text{COO sym}}$ | δ_{NH_2} | Anion | Δ |
|--|----------------------------------|--------------------|-------------------------|------------------------|------------------------|--|----------|
| $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_2][\text{ClO}_4]_4$ | 3350(3330) 3290 3185(3160) | 1660(1660) | 1620(1618) | 1402(1401) | 1582(1570) | 1095(1142, 1120, 1109, 1089) | 218(217) |
| $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_3][\text{NO}_3]$ | 3340(3320) 3280 3180(3160) | 1662(1660) | 1622(1620) | 1405(1400) | 1570(1570) | 620(636,626) 1380(1380) 824(831) | 217(220) |
| $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_3][\text{ClH}_2\text{O}]$ | 3330(3325) 3160(3160) | 1655(1655) | 1616(1618) | 1403(1400) | 1580(1580) | | 213(218) |
| $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_2][\text{Br}]$ | 3320 3160 | 1660 | 1620 | 1404 | 1570 | | 216 |
| $[\text{Ni}(\text{L-ArgH})_2(\text{NO}_3)_2][\text{H}_2\text{O}]$ | 3340 3170 | 1660 | 1628 | 1402 | 1550 | 1380(b) 821 | 226 |
| $[\text{Ni}(\text{L-ArgH})_2(\text{H}_2\text{O})_2][\text{Cl}_2]$ | 3335(3330) 3160(3160) | 1660 | 1620(1620) | 1402(1402) | 1570(1575) | | 218(218) |
| $[\text{Ni}(\text{L-ArgH})_3\text{H}_2\text{O}][(\text{ClO}_4)_2\text{H}_2\text{O}]$ | 3350(3330) 3285 3165(3160) | 1670(1660) | 1634(1625) | 1405(1405) | 1575(1575) | 1090(1140, 1120, 1110, 1080) | 229(220) |
| $\text{Ni}(\text{L-ArgH})(\text{OH})_2\text{H}_2\text{O}$ | 3330 3165 | 1665 | 1633 | 1404 | 1572 | 623(638,628) 3340 | 229 |

(a) Figures in parentheses are KBr data. (b) Overlap.

the ligand, which implies a monodentate acido group as distinct from a bridging acido group.⁽⁶⁵⁾ Since Δ is a measure of the asymmetry of the C-O bonds in the acido group,^(63,65) and an increase in Δ of 20-25 cm^{-1} found in the complexes as compared with the free ligand, implies a structure of type (xiii).



Thus, the infrared spectra suggest that the arginine residue in the first group is acting as a tridentate ligand bridging two nickel atoms, as a nine-membered chelate ring would result from the guanido group coordinating to the same nickel atom as the α -amino acid groups, which is structurally very unstable.

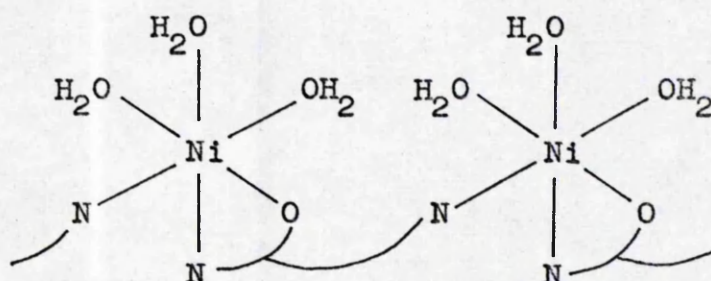
Although the visible spectra of these complexes are indicative of an octahedral configuration, the rather high effective magnetic moments (Table 20), $\mu_{\text{eff}} = 3.22 - 3.47$ B.M. suggest a tetragonal distortion.⁽¹³⁵⁾ The complex $[\text{Ni}(\text{py})_2\text{Cl}_2]$ has an effective magnetic moment of 3.37 B.M.,⁽¹³⁶⁾ but was shown to be isomorphous with violet $[\text{Co}(\text{py})_2\text{Cl}_2]$ which has been shown⁽¹³⁷⁾ to have a polymeric six-coordinate structure involving chloride bridging and trans-pyridine groups.

Thus, the infrared and visible spectral evidences

Table 20. The Effective Magnetic Moments, μ_{eff} (B.M.) of Nickel(II) Complexes

| Compounds | μ_{eff} B.M. |
|---|-------------------------|
| $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_2] \text{ClO}_4$ | 3.22 |
| $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_3] \text{NO}_3$ | 3.44 |
| $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_3] \text{ClH}_2\text{O}$ | 3.47 |
| $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_2] \text{Br}$ | 3.34 |
| $[\text{Ni}(\text{L-ArgH})_2(\text{NO}_3)_2] \text{H}_2\text{O}$ | 3.05 |
| $[\text{Ni}(\text{L-ArgH})_2(\text{H}_2\text{O})_2] \text{Cl}$ | 3.34 |
| $[\text{Ni}(\text{L-ArgH})_3(\text{H}_2\text{O})] (\text{ClO}_4)_2 3\text{H}_2\text{O}$ | 3.43 |
| $\text{Ni}(\text{L-ArgH})(\text{OH})_2 \text{H}_2\text{O}$ | 2.90 |

suggest a common structure for all the anionic arginine complexes in which the arginine is tridentate with the guanido group electrostatically coordinated to a second nickel atom, and that the inorganic anions are not involved in coordination. Bearing in mind that visible and magnetic data favour a tetragonally distorted octahedron environment around nickel atom, a structure similar to that of (xv) is suggested for the first group of nickel(II) complexes, and it should be

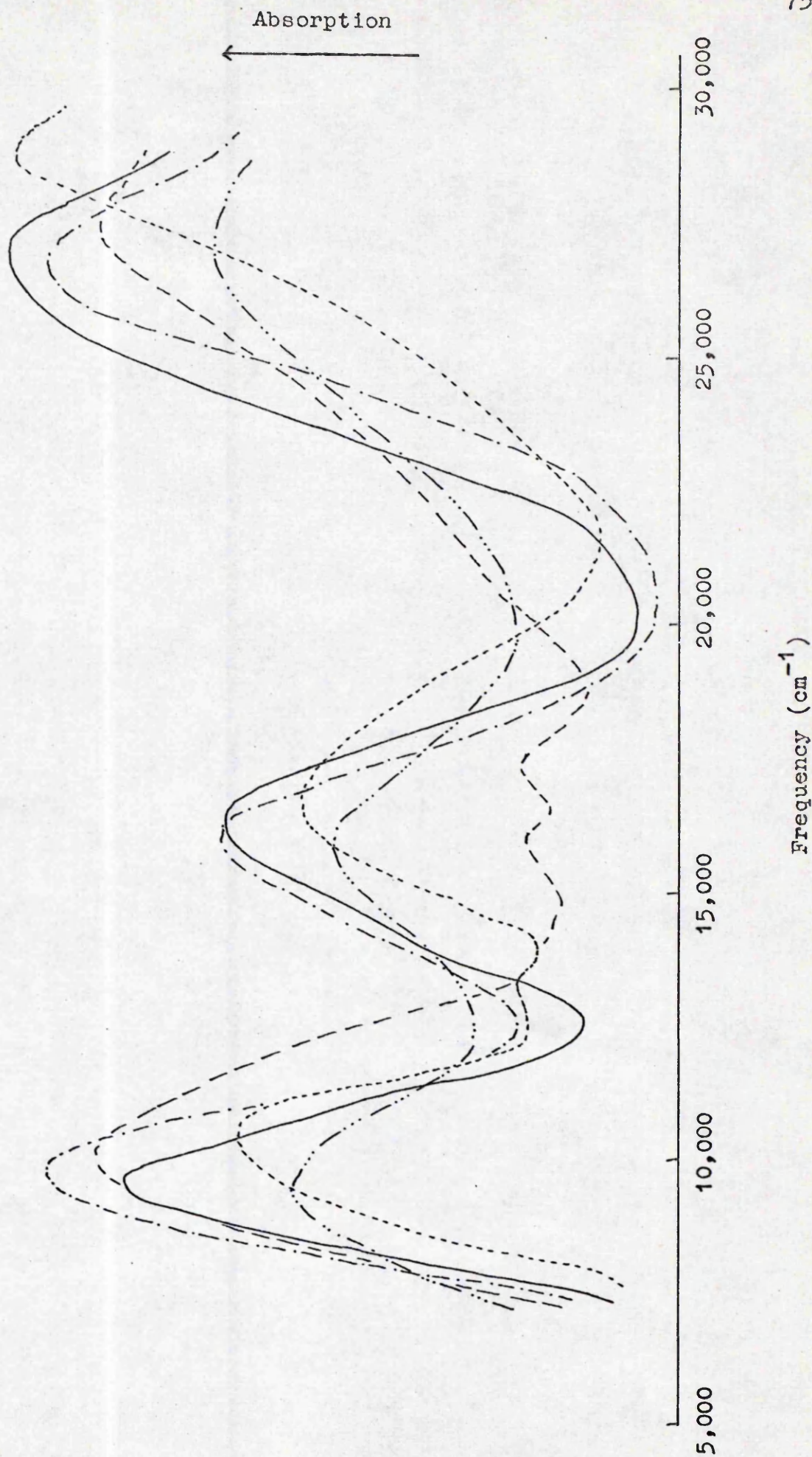


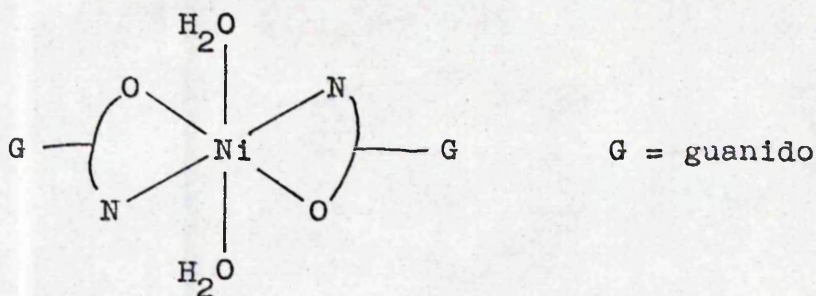
(xv)

emphasised that this structure has many possible isomers. The relative insolubility of the complexes in most solvents would also seem to verify a polymeric structural assignment.

The group of complexes containing the neutral, zwitterionic arginine are diverse inasmuch as the metal has formed bonds with one, two, or three ligands. The complex, $\left[\text{Ni}(\text{L-ArgH})_2(\text{H}_2\text{O})_2 \right] \text{Cl}_2$ has an infrared spectrum (Table 19) containing evidence for both α -amino and carboxyl coordination, and the electronic spectrum (Table 18 and Figure XVII) suggests an octahedral configuration with a N_2O_4 moiety. The magnetic moment of this complex is 3.34 B.M., which suggests considerable tetragonal distortion. Hence, the obvious structure of this complex seems to be that of (xvi).

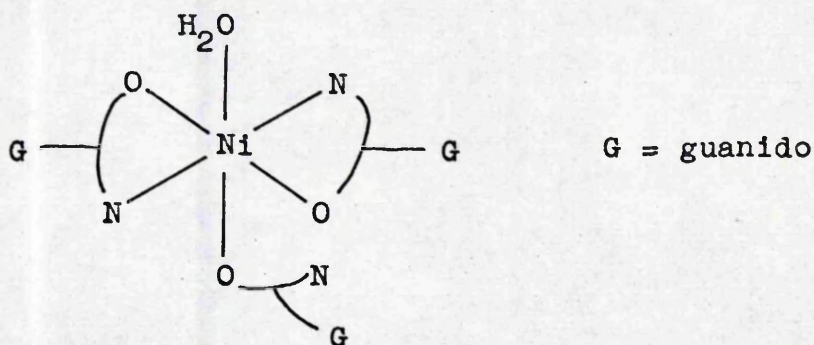
Figure XVII. Solid Electronic Absorption Spectra of $[\text{Ni}(\text{L-ArgH})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ (—), $[\text{Ni}(\text{L-ArgH})_2(\text{NO}_3)_2]\text{H}_2\text{O}$ (.....), $[\text{Ni}(\text{L-ArgH})_3(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (-.-.-), $\text{Ni}(\text{L-Arg})(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (-.-.-), and $[\text{Ni}(\text{L-ArgH})_3(\text{H}_2\text{O})](\text{ClO}_4)_2$ (KBr disk) (-----).





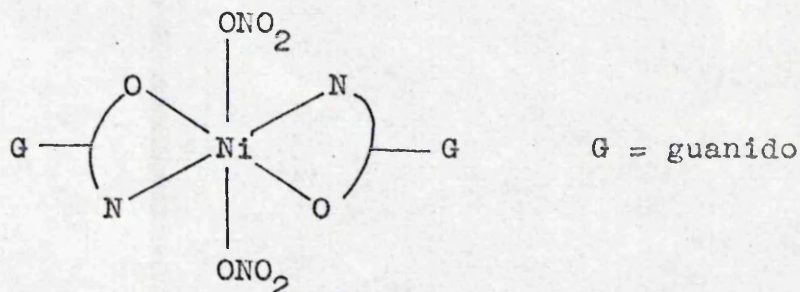
(xvi)

The most difficult structure to assign is that of $\left[\text{Ni}(\text{L-ArgH})_3(\text{H}_2\text{O}) \right] (\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$. Its electronic spectrum (Table 18 and Figure XVII) is quite typical of an octahedral N_2O_4 environment, and so a complex containing three bidentate α -amino acid is excluded. Infrared spectrum of this complex (Table 19) is extremely difficult to interpret, the only obvious information is that the perchlorate group is not involved in coordination as characterized by a strong, broad absorption band ca. 1090 cm^{-1} . Although the magnetic moment, $\mu_{\text{eff}} = 3.43 \text{ B.M.}$, again suggests a tetragonally distorted octahedral configuration, it does not provide any information about the donor atoms. In view of the recent observation that amino acid may coordinate as monodentate through the carboxyl group only,⁽⁴¹⁾ the following structure (xvii) is suggested as no other possible structures could fit the available spectral information.



(xvii)

The complex $\left[\text{Ni}(\text{L-ArgH})_2(\text{NO}_3)_2 \right] \text{H}_2\text{O}$ is extremely interesting, as the available evidence suggests that it contains coordinated nitrate group (xviii). The electronic



(xviii)

spectrum (Table 18 and Figure XVII) exhibit a much higher energy ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ transition than any other complexes studied here, and the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (F) and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (P) transitions are also at higher energy. (Also, this is the only complex in which the ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g$ band is distinguishable.) At first, this seems to suggest a N_3O_3 environment, however, molecular model does not allow this speculation as the protonated guanido group is not available for coordination. Since the position of NO_3^- in the spectrochemical series is significantly higher than H_2O ,⁽¹³⁸⁾ the coordination of NO_3^- group may account for the high energy absorptions.

Although the infrared spectra of ionic and coordinated nitrate have been well investigated,^(53,54) the infrared spectrum (Table 19) of the complex prepared here does not yield conclusive evidence for either ionic or coordinate nitrate groups due to intense ligand absorptions.

The complex $\text{Ni}(\text{L-ArgH})(\text{OH})_2\text{H}_2\text{O}$ was isolated irrespective of the nickel(II) salts (perchlorate, nitrate, halide) used.

The presence of the hydroxide ion was evident from the intense, sharp infrared absorption at 3410 cm^{-1} . No attempt is made here to postulate a structure for this complex, other than to point out that the electronic spectrum (Table 18 and Figure XVII) is once again typical of a NiN_2O_4 coordination moiety.

In order to know whether the "pressure rearrangement" of the perchlorate group in the copper(II) complexes was applicable to the nickel(II) complexes, the two perchlorate derivatives were pressed in a KBr die. The resulting infrared spectra (Table 19 and Figure XVIII) indicate that the perchlorate group has become coordinated and, moreover, is bidentate. The perchlorate bands in the original complex ca. 1095 cm^{-1} and 620 cm^{-1} are no longer present, and a series of absorptions at 1142 , 1120 , 1109 and 1089 cm^{-1} , and 636 and 626 cm^{-1} appear. However, the vibrational spectrum due to the ligand has not changed significantly when the KBr disk is prepared, and this may indicate that the ligand is attached to the nickel atom in the same way. Moreover, although the reflectance spectra (Table 18 and Figure XVI, XVII) of the KBr disk complexes are slightly changed from that of the original complexes, it is still indicative of a N_2O_4 environment around the nickel atom. Thus, for the complex $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_2]\text{ClO}_4$ the following change may be envisaged:

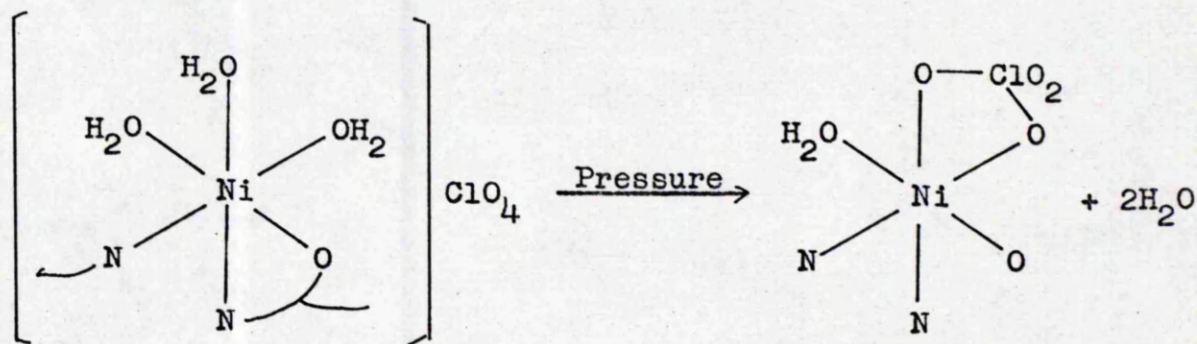
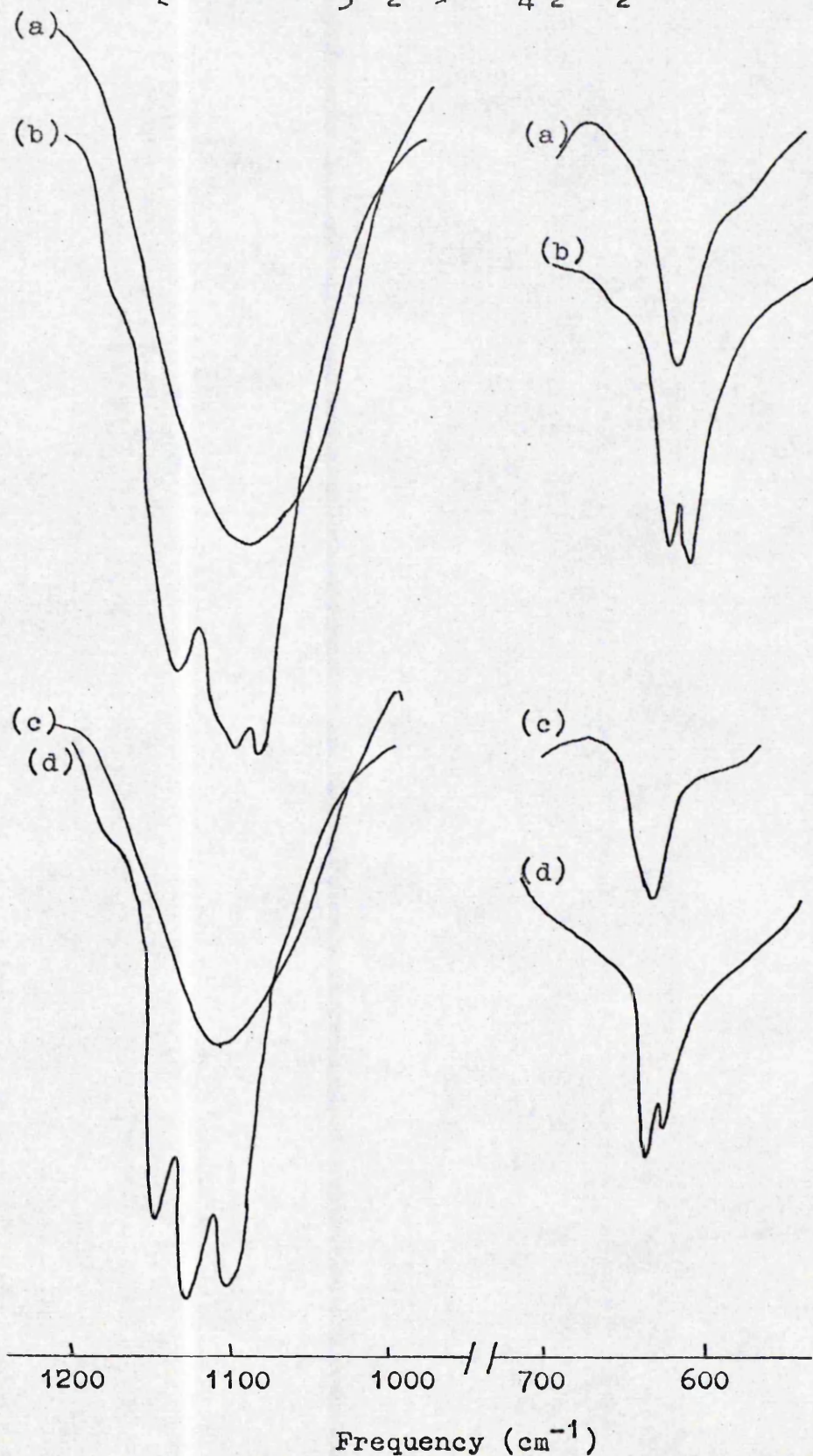
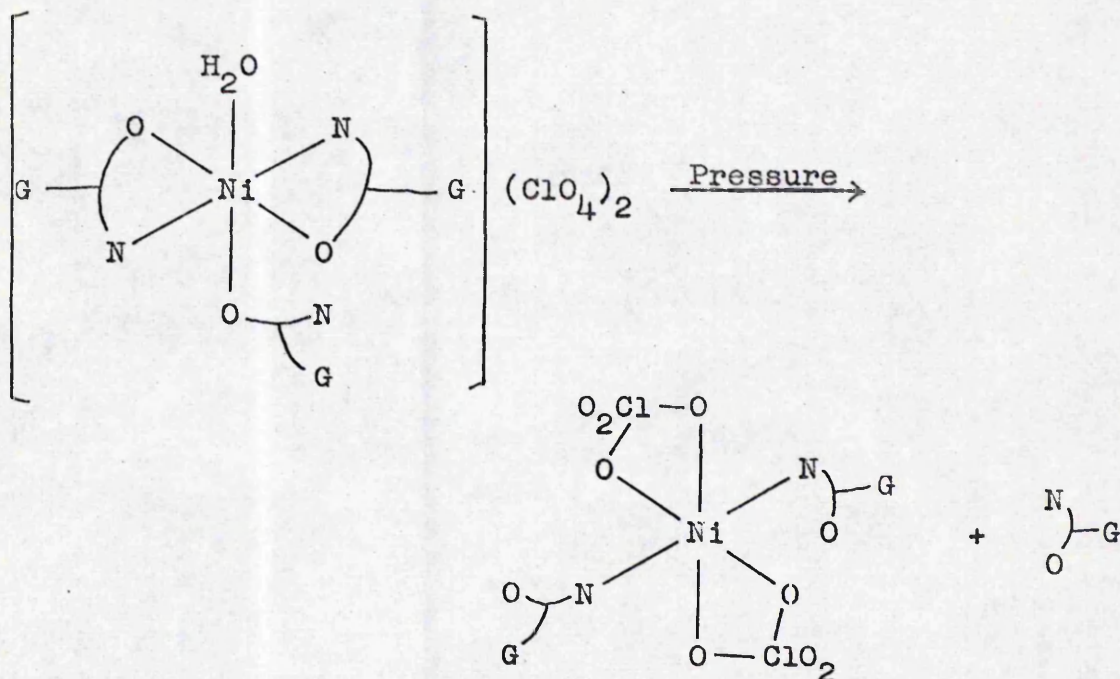


Figure XVIII. Infrared Spectra of Perchlorate Group in
Nickel(II)-L-Arginine Complexes

- (a) $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_2](\text{ClO}_4)$ (Nujol mull)
 (b) $[\text{Ni}(\text{L-Arg})(\text{H}_2\text{O})_2](\text{ClO}_4)$ (KBr disk)
 (c) $[\text{Ni}(\text{L-ArgH})_3(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (Nujol mull)
 (d) $[\text{Ni}(\text{L-ArgH})_3(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (KBr disk)



For the complex $[\text{Ni}(\text{L-ArgH})_3\text{H}_2\text{O}](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, similar change will involve the replacement of the coordinated carboxyl oxygen atoms and the monodentate arginine will not be coordinating anymore. However, this speculation is merely suggestive and has yet to be proved.



(iii) Conclusion

Although only copper(II) and nickel(II) complexes of L-arginine were discussed here, other metal complexes have also been prepared. However, no reliable results could be drawn as solid complexes isolated were not repeatable; this may be associated with the weak chelating property of L-arginine.

It can be seen from the results and discussion that L-arginine can function as monodentate (through either the α -amino nitrogen or the α -carboxyl oxygen atom), bidentate (through α -amino nitrogen and α -carboxyl oxygen atoms), or tridentate (through α -amino nitrogen, α -carboxyl oxygen and the guanido nitrogen atoms) ligand. Although flexidentate

α -amino acid is not rare,^(41,70,77,81) with the exception of histidine, the present result is by far the most complete yet, and surprisingly, flexidentate behaviour is found to occur on the same metal atom with only slight change of chemical environments (see experimental section).

The most interesting result found here is the "pressure rearrangement" of perchlorate group in the solid state.

Although there has been some considerable interest recently in the effect of pressure on chemical systems,^(139,140) these have been spectral studies of stereochemical changes of metal complexes in solution. The only relevant observations are the reverse changes, that is, KBr disks cause the originally coordinated perchlorate⁽¹³⁰⁾ or nitrate⁽¹⁴¹⁾ groups to become ionic, which is the common bromide replacement effect of KBr disks. Whether the present observation is accidental or a common phenomenon has yet to be proved.

The novel results obtained here suggest that there is still a large potential of investigations in the field concerning the metal binding with multidentate amino acids, peptides and even proteins.

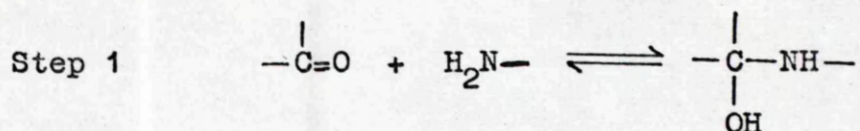
Metal Complexes of N-Salicylidenearginine

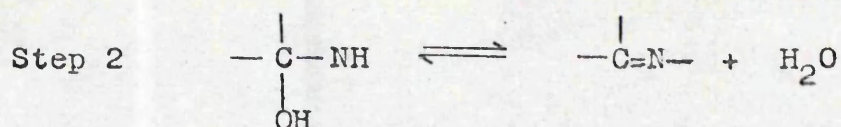
1) Introduction

Transition metal complexes of salicylaldehyde-amino acid Schiff bases are analogous to those of pyridoxal-amino acid Schiff bases which are of considerable chemical and biological interest in such reactions as the nonenzymatic catalysis of transamination.⁽¹⁴²⁻¹⁴⁴⁾ Recently interest has been focused on the activation of the α -CH position of Schiff bases of α -amino acids,⁽¹⁴⁵⁻¹⁴⁷⁾ and the synthetic applications of these Schiff base complexes.^(148,149)

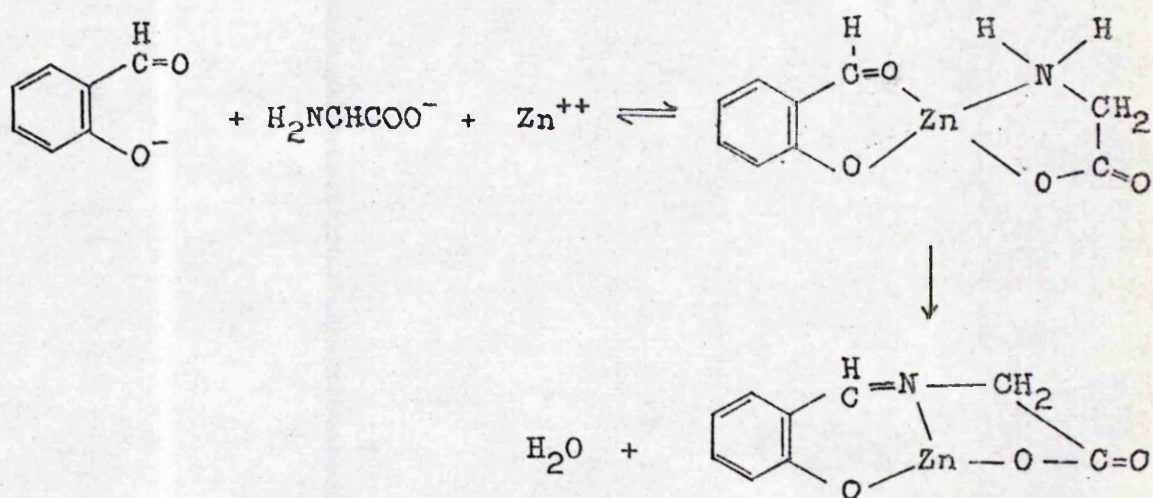
In view of the fact that the electronic spectra of the metal complexes of salicylaldehyde-amino acid Schiff bases are similar to those of pyridoxal-amino acid Schiff bases,⁽¹⁵⁰⁾ and that the former form more stable complexes,^(151,152) the results drawn from the simpler salicylaldehyde-amino acid systems may be applicable to the structurally more complicated pyridoxal-amino acid systems.⁽¹⁵³⁾

It has long been noted⁽¹⁵⁴⁾ that copper(II) stabilized the Schiff base derived from salicylaldehyde and glycine by enhancing the carbon-nitrogen double bond formation through coordination. In the absence of metal ion, Schiff base formation involved a two-step reaction between the carbonyl compound and the amino compound.⁽¹⁵⁵⁾ First, addition takes place to form a carbinolamine (step 1) which then undergoes dehydration (step 2).





In the presence of metal ions, the rate of formation of Schiff bases may be either metal-independent or metal-dependent, varying with the nature of metal ions. With copper(II) or nickel(II), an independent path was observed,^(156,157) whereas with zinc(II), a dependent path through a template mechanism was suggested.^(156,158)



However, Nunez and Eichhorn⁽¹⁵⁹⁾ showed that qualitatively formation of Schiff base complex is greatly retarded by prior reaction of either nickel(II) or copper(II) with one of the Schiff base components, and that thermodynamic stabilization of the product of a reaction by a metal ion can be accompanied by a retardation of the reaction with the metal.

Although transition metal complexes of Schiff bases have been extensively investigated,⁽¹⁶⁰⁾ those derived from salicylaldehyde and amino acids are relatively less known. Nakahara⁽¹⁶¹⁾ first isolated N-salicylideneglycinatoaquo-

copper(II) and assigned a 4-coordinate planar structure based on infrared and visible spectral data. Later, an anhydrous N-salicylidene-glycinato-copper(II) was found⁽¹⁶²⁾ to have subnormal magnetic moments, and was assigned a binuclear structure.

It is now apparent that all hydrated copper(II) complexes of N-salicylidene-amino-acidato possess normal magnetic moments,⁽¹⁶³⁻¹⁶⁵⁾ while the corresponding anhydrous complexes possess subnormal magnetic moments.^(165,166) The only exception is N-salicylidene-L-valinato-copper(II) hemihydrate⁽¹⁴⁶⁾ which has an effective magnetic moment of 1.65 B.M. at room temperature. To a first approximation, the water molecule occupies the fourth coordination site of a square planar configuration about the copper atom with the tridentate Schiff base taking up the other three coordination sites. However, in the anhydrous complexes, 4-coordination is possible only if one of the oxygen atoms acts as a bridging donor atom, thus bringing about copper(II)-copper(II) interaction which consequently lowers the observed magnetic moments. In fact, Carlisle and co-workers^(165,166) considered the effect as arising from an antiferromagnetic exchange through a tetrametallic structure as shown in Figure XIX.

However, X-ray crystallography analyses showed that the molecular structure of both N-salicylidene-glycinato-aqua-copper(II) hemihydrate⁽¹⁶⁷⁾ and N-salicylidene-glycinato-aqua-copper(II) tetrahydrate⁽¹⁶⁸⁾ are essentially square pyramids in which the top of the square pyramid is occupied by a carboxyl oxygen atom of the adjacent molecule or a water molecule, respectively.

Theriot and co-workers⁽¹⁶⁹⁾ have isolated several

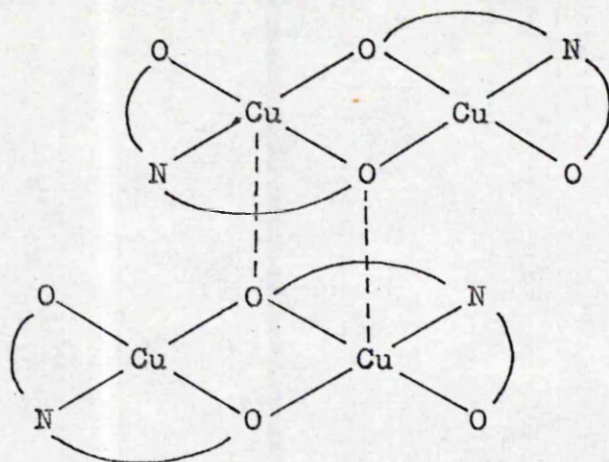
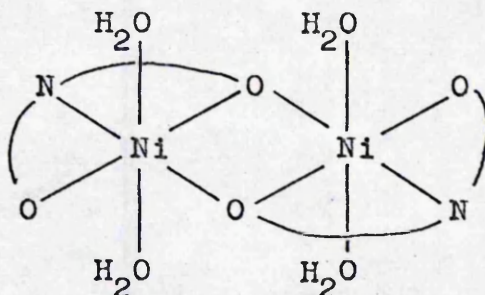


Figure XIX. A schematic representation of the tetrametallic structure of N-salicylidene-L-valinatocopper(II)

nickel(II) complexes of N-salicylideneamino acid Schiff bases, and assigned a dimeric octahedral structure (xvii) for the complexes based on spectral and magnetic properties.



(xvii)

Burrows and Bailar⁽¹⁷⁰⁾ have prepared a series of iron(III) and cobalt(III) complexes of some N-salicylidene-amino acids. The discrimination of geometrical isomers of some iron complexes was discussed.

With dibasic amino acids such as lysine and ornithine, chemical and spectrophotometric observations showed⁽¹⁷¹⁾ that condensation with aromatic aldehyde (1 mole) occurs at the

terminal amino group, but arginine behaves like a simple α -amino acid. N ^{α , ω} -disalicylidene derivative is only known^(145,172) for lysine in the copper(II) complex.

In this study metal complexes of Schiff bases derived from salicylaldehyde and L-arginine were investigated in order to elucidate the structures of the complexes, and to observe if the novel behaviour of simple metal:L-arginine systems would continue.

ii) Results and Discussion

N-Salicylidenearginine. The Schiff base was prepared by refluxing an ethanol mixture of L-arginine and salicylaldehyde till a bright yellow precipitate was formed. In order to determine which amino group of L-arginine is used to form Schiff base with salicylaldehyde, the infrared spectra of salicylaldehyde, L-arginine, and N-salicylidenearginine were compared and assigned (Table 21). Obviously, for complex molecules like this, total assignment is impossible. However, careful interpretation of the higher frequency region may yield some conclusive information.

The assignment of the infrared spectrum of salicylaldehyde was primarily derived from Bellamy,⁽⁶¹⁾ and Brooks and Morman.⁽¹⁷³⁾ The medium diffuse absorption band at 3172 cm^{-1} was assigned to strong hydrogen-bonding of the hydroxyl group. In the $1500\text{--}1700\text{ cm}^{-1}$ region, the strongest absorption band and the one at highest frequency, 1660 cm^{-1} , was attributed to carbonyl stretching. Other absorption bands in this region were assigned to aromatic C=C skeletal in-plane vibrations.⁽⁶¹⁾ The relative intensities are characteristic of conjugation

Table 21. Infrared Absorption Frequencies (cm^{-1}) of
Salicylaldehyde, L-Arginine, and N-Salicylidene-
arginine

| Salicylaldehyde | L-Arginine | N-Salicylidenearginine | Assignments |
|-----------------|------------|------------------------|-----------------------------|
| 3172 m,b | | 3408 s,sp | ν_{OH} |
| | 3350 s,sp | 3368 sh,sp | ν_{NH} |
| | 3290 s,b | 3310 s,b | |
| | 3040 s,b | 3070 s,b | $\nu_{\text{NH}_3^+}$ |
| 3059 m,sp | | 3042 ^(a) | ν_{CH} aromatic |
| 2839 m,sp | 2925 m,b | 2960 m,sp | ν_{CH} saturated |
| 2742 m,sp | 2850 m,sp | 2914 m,sp | |
| | | 2850 m,b | |
| 1660 s,sp | | | $\nu_{\text{C=O}}$ |
| 1640 s,sp | | | $\nu_{\text{C=C}}$ |
| | 1670 s,sp | 1658 s,b | $\nu_{\text{C=N}}$ |
| | 1610 s,b | 1630 s,sp | ν_{COO} asym. |
| 1615 m,sp | | 1610 ^(a) | ring |
| 1590 m,sp | | 1585 s,sp | |
| 1577 s,sp | | 1525 w,sp | |
| | | 1518 m,sp | |
| | 1550 s,sp | | δ_{NH} |
| 1485 s,sp | 1470 m,sp | 1466 m,b | CH def. |
| 1456 s,sp | 1445 m,sp | 1444 m,sp | |
| | 1435 m,sp | | |
| | 1415 m,sp | 1403 m,sp | ν_{COO} sym. |
| 1382 s,sp | 1370 m,sp | 1374 m,sp | CH def. |

(a) Overlapped.

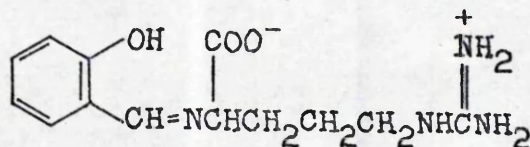
of the ring with the carbon-oxygen double bond. The assignment of L-arginine has been discussed earlier and will not be mentioned here.

The strong, sharp absorption band at 3408 cm^{-1} in the spectrum of the N-salicylidenearginine is obviously due to O-H stretching. Compared with L-arginine, absorptions at 3368 cm^{-1} , 3310 cm^{-1} , and 3070 cm^{-1} were assigned due to the N-H stretchings of the guanido group. The resemblance may indicate that the resonance of the guanido group is not significantly disturbed.

The most confused region lies between $1500\text{--}1700\text{ cm}^{-1}$ where overlapping renders precise assignments impossible. Following Burrow and Bailar's argument⁽¹⁷⁰⁾ that it is more appropriate to assign the highest frequency to the C=N stretching on a resonance consideration, the absorption band at 1658 cm^{-1} was tentatively attributed to the C=N stretch. The antisymmetric stretching of carboxyl group can then be assigned to the strongest absorption at 1630 cm^{-1} . Also the symmetric stretching of carboxyl group was assigned at 1403 cm^{-1} . The shifts of the carboxyl stretchings frequencies indicate that the resonance of the uncoordinated-ionized carboxyl group is lifted, probably due to strong hydrogen-bonding.

The most interesting observation is the disappearance of an absorption band near 1550 cm^{-1} which was assigned as the δ_{NH} mode in L-arginine. Since this band is unlikely to be due to the protonated guanido group,⁽⁶¹⁾ this absence is strongly indicative of the disappearance of the α -amino group in N-salicylidenearginine.

Although assignments were tentative, all available information suggests that condensation takes place at the α -amino group. It is noteworthy that only N^{α} -benzylidene-L-arginine has been prepared.⁽¹⁷⁴⁾ Thus, the following structure (xviii) was assumed for N-salicylidenearginine.



(xviii)

Copper Complexes of N-Salicylidenearginine. The copper(II) complexes were easily prepared either by mixing a preformed Schiff base with copper(II) salts or by dissolving L-arginine and salicylaldehyde in ethanol-water and reacting with copper(II) salts to give dark green complexes. The infrared absorption spectra of copper(II)-N-salicylidenearginine complexes are extremely difficult to interpret due to intense absorptions coupled with multi-overlapping in the regions of interest. Nonetheless, assignments were possible, and Table 22 lists some significant infrared absorption frequencies of the copper(II) complexes. In all cases, absorption due to OH stretching in the free ligand, ca. 3408 cm^{-1} , is absent in the complexes, indicative of deprotonation of the hydroxyl group and coordination of the hydroxyl oxygen. Although the stretching frequency of C=N group usually shifts to lower frequency upon coordination,⁽⁴⁷⁾ the presence of two such groups in the ligand may preclude any speculation here. The absorption frequencies associated with the carboxyl group suggest more likely a monodentate function (see the previous

Table 22. Some Significant Infrared Absorption Frequencies (cm^{-1}) of Copper(II)-N-Salicylidenearginine

Complexes.

| $[\text{Cu}(\text{Sal-ArgH})](\text{NO}_3)$ | $[\text{Cu}(\text{Sal-ArgH})(\text{NO}_3)] \cdot \text{H}_2\text{O}$ | $[\text{Cu}(\text{Sal-ArgH})] \cdot \text{Cl}_2\text{H}_2\text{O}$ | $\text{Cu}(\text{Sal-Arg}) \cdot \text{H}_2\text{O}$ | Assignment |
|---|--|--|--|--------------------------|
| 3348 s,sp | 3330 s,b | 3325 s,b | 3260 s,b | ν_{NH} |
| 3285 m,sh | 3280 m,sh | 3250 m,sh | 3215 m,sp | |
| 3186 s,b | 3190 s,b | 3160 s,b | | |
| 1667 s,sp | 1685 s,sp | 1653 s,sh | 1650 s,sp | $\nu_{\text{C=N}}$ |
| | 1666 s,sp | | | |
| 1634 s,b | 1634 s,sp | 1620 s,sp | 1625 s,sp | $\nu_{\text{COO asym.}}$ |
| 1380 s,b | 1386 s,sp | 1402 s,sp | 1400 s,sp | $\nu_{\text{COO sym.}}$ |
| 823 m,sp | 823 m,sp | | | NO_3^- |

chapter). The most positive conclusion that could be drawn here is that the nitrate ion in the complexes, $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3$ and $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3 \cdot \text{H}_2\text{O}$, is not coordinated, and the almost identical spectra of these two complexes may suggest that the water molecule is present as a lattice molecule only. Noting that the infrared technique is of little help in determination of stereochemistry of Schiff bases complexes,⁽¹⁶⁰⁾ it is better not to place too much emphasis on this technique.

The electronic reflectance spectra of $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3$, $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3 \cdot \text{H}_2\text{O}$ and $[\text{Cu}(\text{Sal-ArgH})]\text{Cl} \cdot 2\text{H}_2\text{O}$ are compiled in Table 23 and Figure XX. The spectral data are consistent

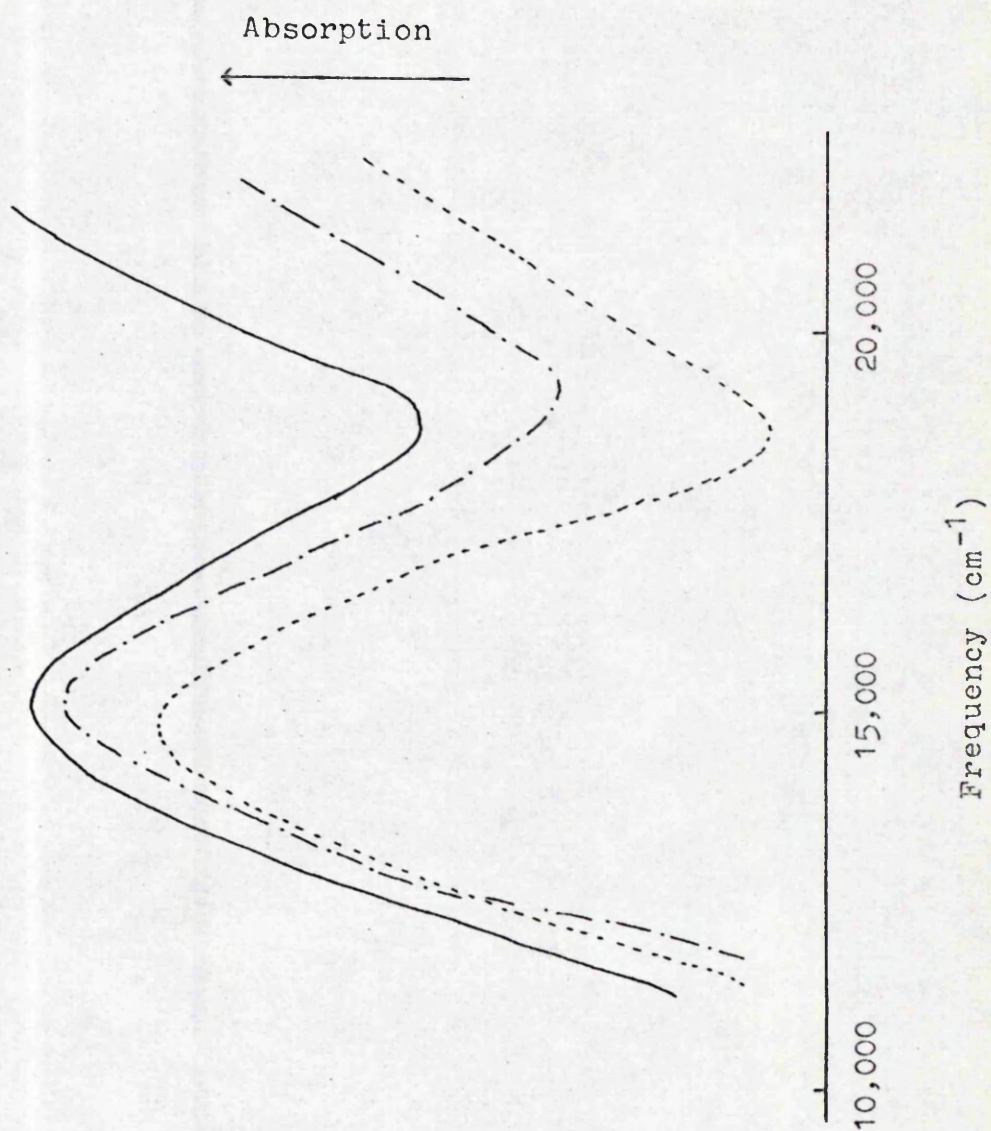
Table 23. Solid Electronic Absorption Maxima (cm^{-1}) of Copper(II)-N-Salicylidenearginine Complexes

| Compound | $\lambda_{\text{max.}}$ |
|---|-------------------------|
| $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3$ | 15,250 |
| $[\text{Cu}(\text{Sal-ArgH})](\text{NO}_3)\text{H}_2\text{O}$ | 15,250 |
| $[\text{Cu}(\text{Sal-ArgH})]\text{Cl} \cdot 2\text{H}_2\text{O}$ | 14,900 |
| $\text{Cu}(\text{Sal-Arg})\text{H}_2\text{O}$ | 17,500 |

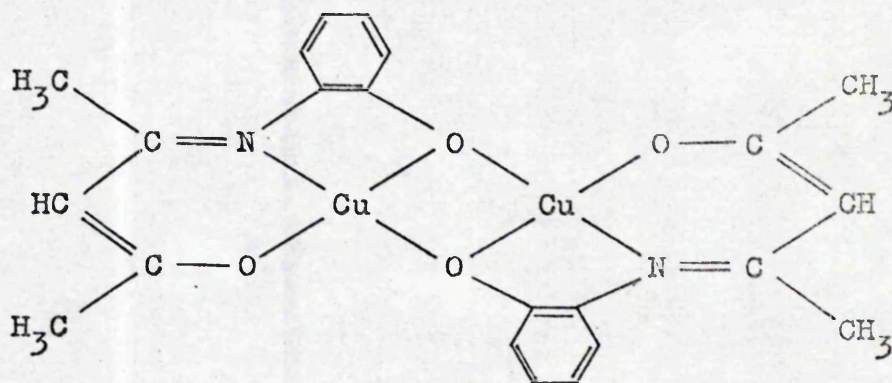
with spin-doublet species reported for copper(II)-Schiff base complexes obtained from amino acids.^(146,165,175) The absorption maxima, ca. $15,000 \text{ cm}^{-1}$, strongly suggest a common Cu(II) chromophore composed of the NO_2 donor atoms from the Schiff base and two or three additional ligands.^(167,168,176,177)

Bivalent copper complexes of Schiff bases containing oxygen and nitrogen donor atoms usually exhibit anomalous magnetic behaviour.⁽⁹²⁾ The report of low magnetic moment

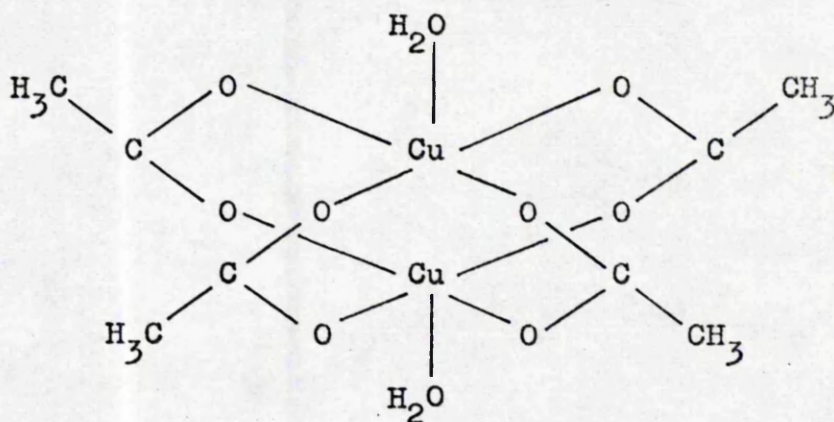
Figure XX. Solid Electronic Absorption Spectra of $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3$ (---), $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3 \cdot \text{H}_2\text{O}$ (—), and $[\text{Cu}(\text{Sal-ArgH})]\text{Cl} \cdot 2\text{H}_2\text{O}$ (.....)



for acetylacetonemono(o-hydroxyanil)copper(II)⁽¹⁷⁸⁾ with a binuclear structure (xix) which has been confirmed by X-ray crystallographic structure analysis⁽¹⁷⁹⁾ has stimulated extensive structural and magnetic investigations other than the long established copper(II) acetate monohydrate (xx) and related compounds.⁽⁹²⁾ Copper(II) complexes of Schiff bases derived from amino acids having anomalous magnetic



(xix)



(xx)

moment was first reported by Kishita and co-workers,⁽¹⁶²⁾ and

subsequently observed by others.^(146,165,166) Present observations for the copper(II)-N-salicylidenearginine system also show anomalous magnetic behaviour. The magnetic data at various temperatures for $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3$, $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3 \cdot \text{H}_2\text{O}$ and $[\text{Cu}(\text{Sal-ArgH})]\text{Cl} \cdot 2\text{H}_2\text{O}$ are compiled in Table 24 which shows low magnetic moments for the complexes at room temperature. The susceptibility was found to be independent of field strength.

In the case of $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3$ and $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3 \cdot \text{H}_2\text{O}$, the plot of magnetic susceptibility versus temperature (Figure XXI) is characteristic of antiferromagnetic interaction.^(88,91) Hatfield and Inman⁽¹⁸⁰⁾ first postulated a tetrametallic structure (similar to that in Figure XIX) to account for the super-exchange interaction that causes antiferromagnetism in the copper(II) complex with N-acetyliso-propylidene-2-hydroxyl-5-nitroaniline, and later used by Carlisle and co-workers⁽¹⁶⁶⁾ to explain the anomalous magnetic behaviour of N-salicylidene-L-valinatocopper(II). The essence of the exchange mechanism lies in a π -pathway set up by using $3d_{yz}$ or $3d_{xz}$ orbitals of the copper ion and $2p \pi$ -orbitals of the bridging oxygen atoms. Although no attempt is made here to test the validity of either the Hatfield expression⁽¹⁸⁰⁾ or Van Vleck's equation,⁽¹⁸¹⁾ it is strongly believed that the complexes, $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3$ and $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3 \cdot \text{H}_2\text{O}$, are practically identical compounds having most likely a tetrametallic structure (Figure XIX), as both complexes exhibit almost identical physical properties.

The magnetic susceptibility versus temperature plot for $[\text{Cu}(\text{Sal-ArgH})]\text{Cl} \cdot 2\text{H}_2\text{O}$ (Figure XXII) is very confusing as it

Table 24. Magnetic Data of Copper(II)-N-Salicylidenearginine Complexes at Various Temperatures

| $[\text{Cu}(\text{Sal-ArgH})\text{NO}_3]\text{H}_2\text{O}$ | | | $[\text{Cu}(\text{Sal-ArgH})\text{NO}_3]$ | | | $[\text{Cu}(\text{Sal-ArgH})]\text{Cl}_2\text{H}_2\text{O}$ | | |
|---|---------------------|-------|---|---------------------|-------|---|---------------------|-------|
| $10^6\chi_{\text{Cu}}$ | $\mu_{\text{B.M.}}$ | T°K | $10^6\chi_{\text{Cu}}$ | $\mu_{\text{B.M.}}$ | T°K | $10^6\chi_{\text{Cu}}$ | $\mu_{\text{B.M.}}$ | T°K |
| 552 | 1.13 | 291.5 | 568 | 1.15 | 293.5 | 950 | 1.49 | 291.0 |
| 568 | 1.13 | 282.5 | 606 | 1.17 | 284.5 | 1030 | 1.53 | 283.0 |
| 579 | 1.12 | 271.6 | 606 | 1.15 | 274.3 | 1050 | 1.52 | 272.8 |
| 584 | 1.11 | 264.2 | 599 | 1.13 | 265.5 | 1080 | 1.52 | 268.1 |
| 584 | 1.09 | 256.0 | 591 | 1.10 | 258.2 | 1120 | 1.53 | 259.7 |
| 568 | 1.06 | 246.7 | 606 | 1.10 | 249.8 | 1180 | 1.54 | 249.6 |
| 574 | 1.04 | 236.5 | 599 | 1.07 | 238.9 | 1230 | 1.55 | 241.8 |
| 579 | 1.02 | 225.0 | 599 | 1.05 | 228.2 | 1290 | 1.54 | 231.4 |
| 568 | 0.99 | 215.5 | 583 | 1.00 | 216.4 | 1360 | 1.55 | 221.2 |
| 525 | 0.92 | 202.2 | 552 | 0.95 | 204.0 | 1450 | 1.54 | 206.3 |
| 503 | 0.87 | 190.0 | 515 | 0.89 | 190.4 | 1540 | 1.54 | 193.5 |
| 466 | 0.81 | 174.8 | 477 | 0.82 | 176.0 | 1630 | 1.54 | 181.0 |
| 395 | 0.71 | 160.0 | 446 | 0.76 | 163.8 | 1730 | 1.51 | 165.5 |
| 363 | 0.66 | 150.8 | 401 | 0.69 | 147.0 | 1820 | 1.48 | 151.0 |
| 304 | 0.57 | 135.0 | 370 | 0.63 | 133.5 | 2020 | 1.48 | 136.0 |
| 250 | 0.49 | 119.3 | 347 | 0.58 | 122.2 | 2150 | 1.47 | 125.4 |
| 217 | 0.43 | 107.0 | 279 | 0.49 | 107.3 | 2250 | 1.44 | 115.5 |
| 217 | 0.40 | 90.8 | 263 | 0.45 | 96.5 | 2630 | 1.40 | 93.5 |
| 298 | 0.45 | 86.0 | 774 | 0.71 | 82.2 | 3120 | 1.42 | 81.2 |

Figure XXI. Magnetic Susceptibility versus Temperature
Curves for (a) $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3$ (. . .) and
 $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3 \cdot \text{H}_2\text{O}$ (x x x)

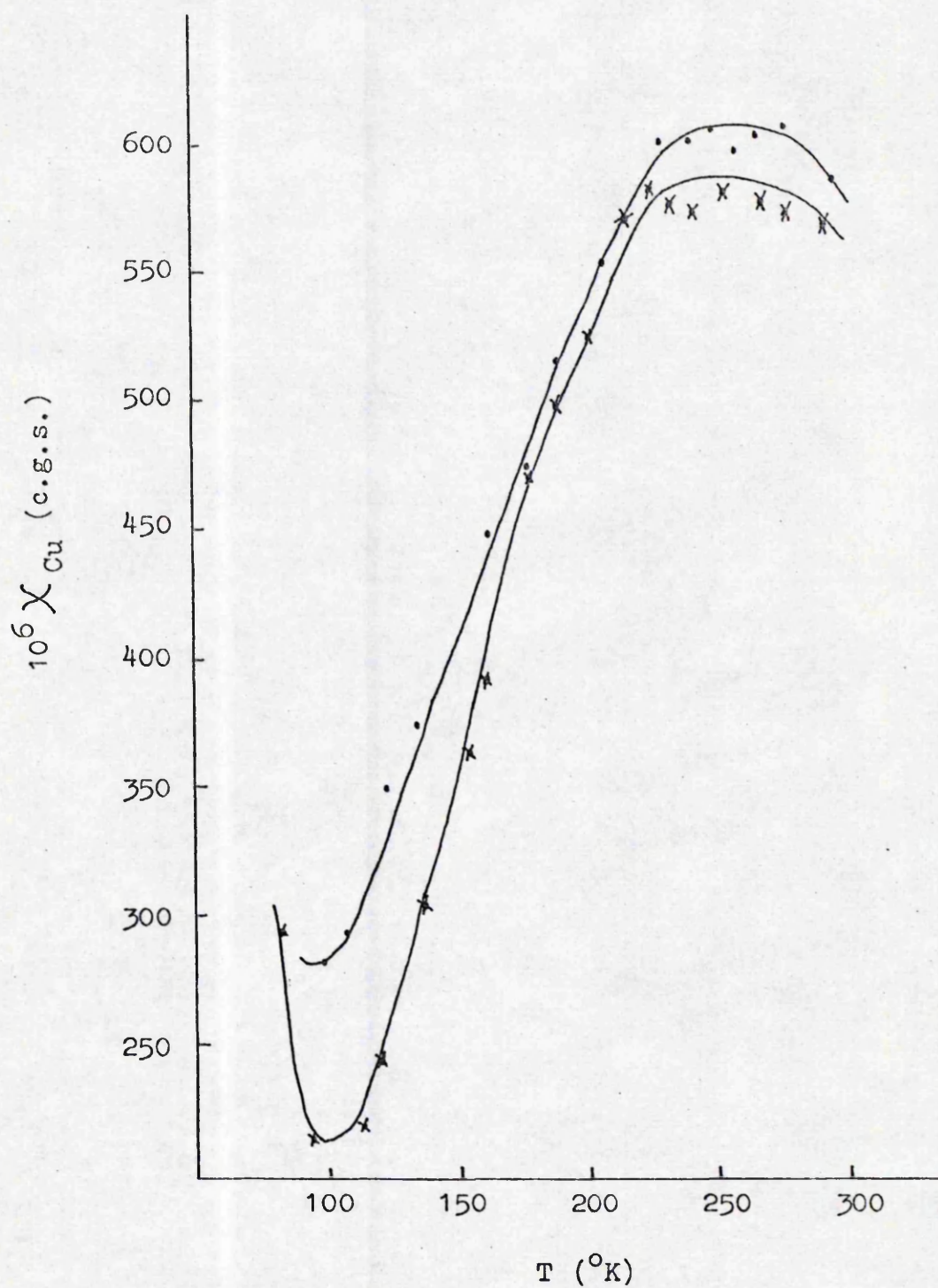
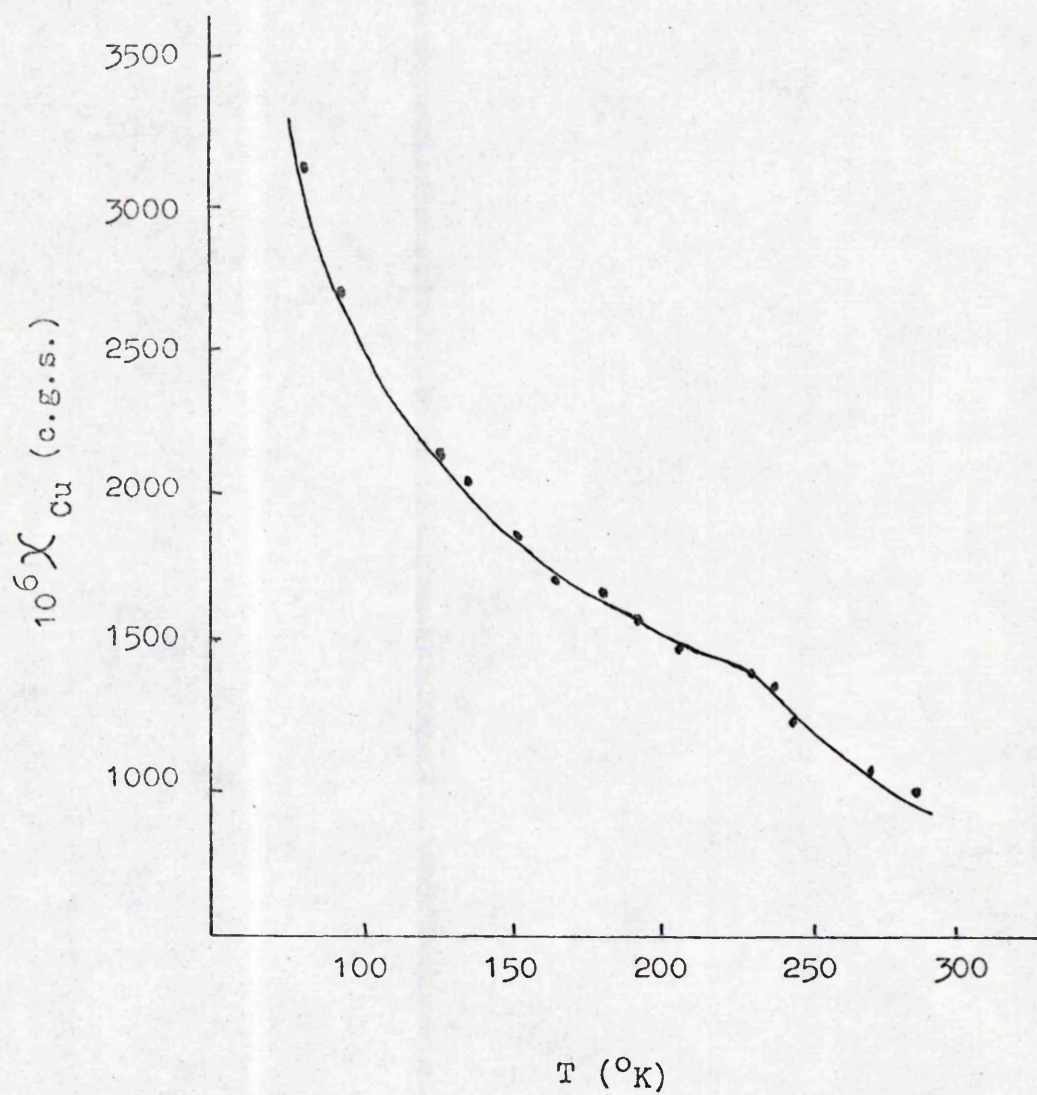


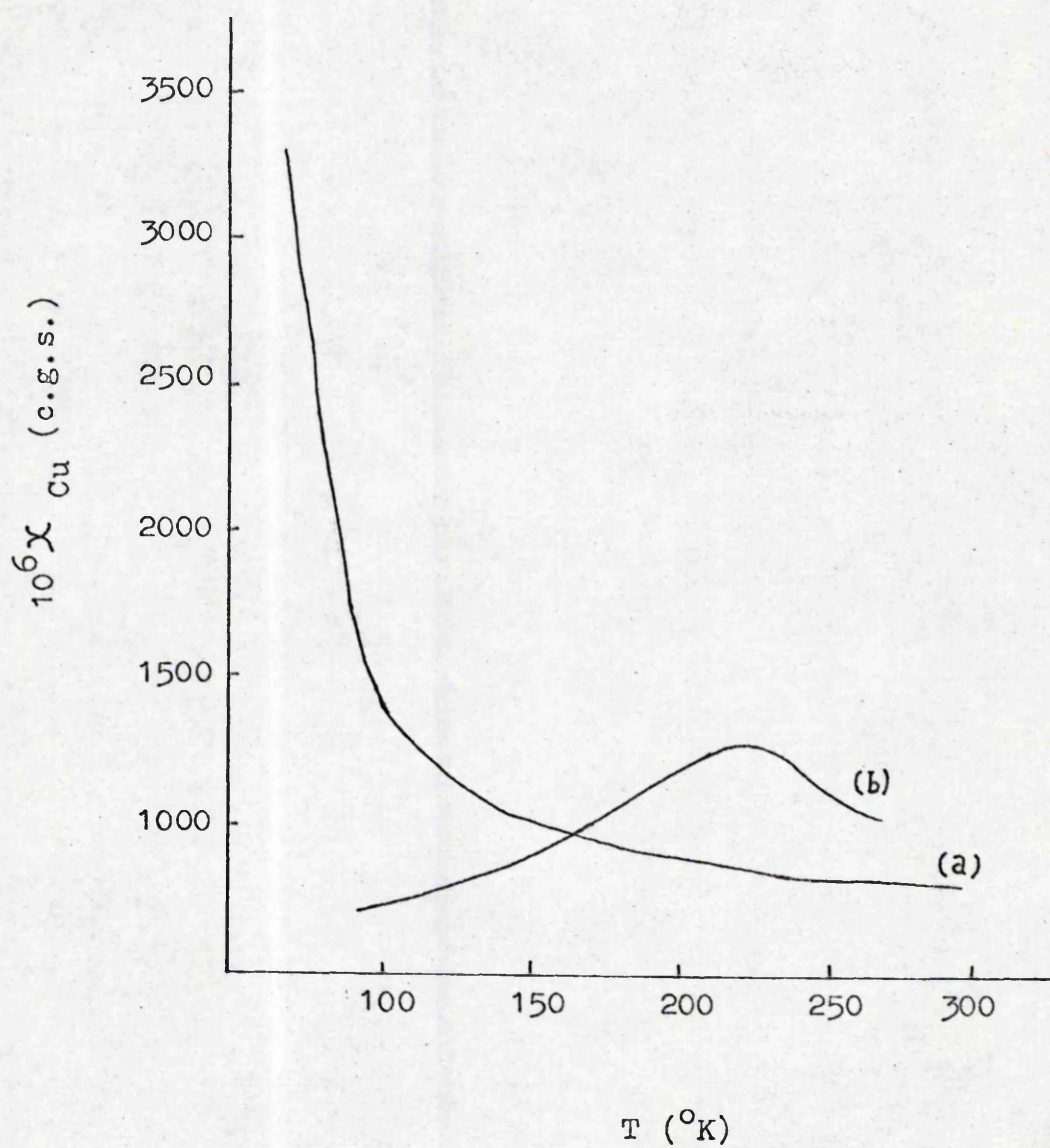
Figure XXII. Magnetic Susceptibility versus Temperature
Curve for $[\text{Cu}(\text{Sal-ArgH})]\text{Cl}\cdot 2\text{H}_2\text{O}$

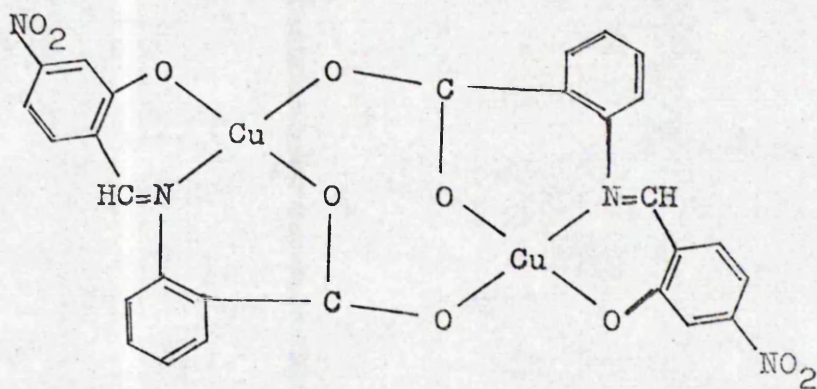


does not obey Curie-Weiss law nor characteristic of either antiferromagnetism or ferromagnetism. Kobayashi and co-workers⁽¹⁸²⁾ explained a seemingly similar χ vs T curve for 2,5-dihydroxy-p-benzoquinonatecopper(II) as a sum of an antiferromagnetic component and a Curie-Weiss component. A similar procedure was adopted by Inone and co-workers,⁽¹⁸³⁾ and Ison and Kokot⁽¹⁸⁴⁾ to elucidate the unusual magnetic behaviour of the copper(II) complexes. Thus, it seems reasonable to suggest that the magnetic susceptibilities of the complex, $[\text{Cu}(\text{Sal-ArgH})]\text{Cl}\cdot 2\text{H}_2\text{O}$, may be the sum of a Curie-Weiss law and an antiferromagnetic component as shown schematically in Figure XXIII. The fact that the maximum near 250°K of the suggested antiferromagnetic component coincides with that of $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3$ and $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3\cdot\text{H}_2\text{O}$ is evidence for the proposed scheme.

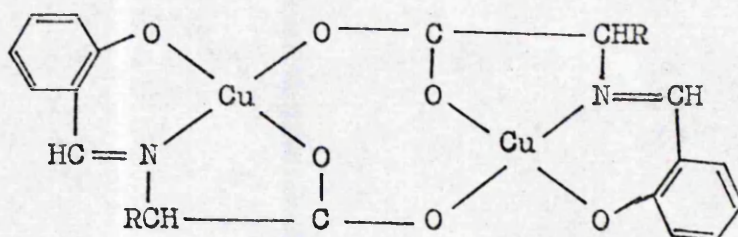
An immediate task is to visualize a possible structure which can accommodate the observed magnetic behaviour. Kishita and Kubo⁽¹⁸⁵⁾ have proposed a binuclear structure (xxi) for the copper(II) complex of 4-nitrosalicylideneanthranilic acid with a magnetic moment above the spin-only value in which the ligand possesses a carboxylic group. The relatively low absorption of the antisymmetric stretching frequency of the carboxyl group in $[\text{Cu}(\text{Sal-ArgH})]\text{Cl}\cdot 2\text{H}_2\text{O}$ compared to that of $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3$ and $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3\cdot\text{H}_2\text{O}$ (Table 22) suggest a bidentate function of the carboxyl group (see previous chapter) in $[\text{Cu}(\text{Sal-ArgH})]\text{Cl}\cdot 2\text{H}_2\text{O}$. Thus, a structure similar to (xxii) may explain the Curie-Weiss component. To account for the antiferromagnetic component, Hatfield and Inman's model⁽¹⁸⁰⁾ is applicable. Hence a structure similar to

Figure XXIII. Proposed Susceptibility versus Temperature
Curves for Paramagnetic (a) and Antiferromagnetic
(b) $[\text{Cu}(\text{Sal-ArgH})]\text{Cl}\cdot 2\text{H}_2\text{O}$

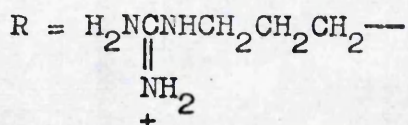




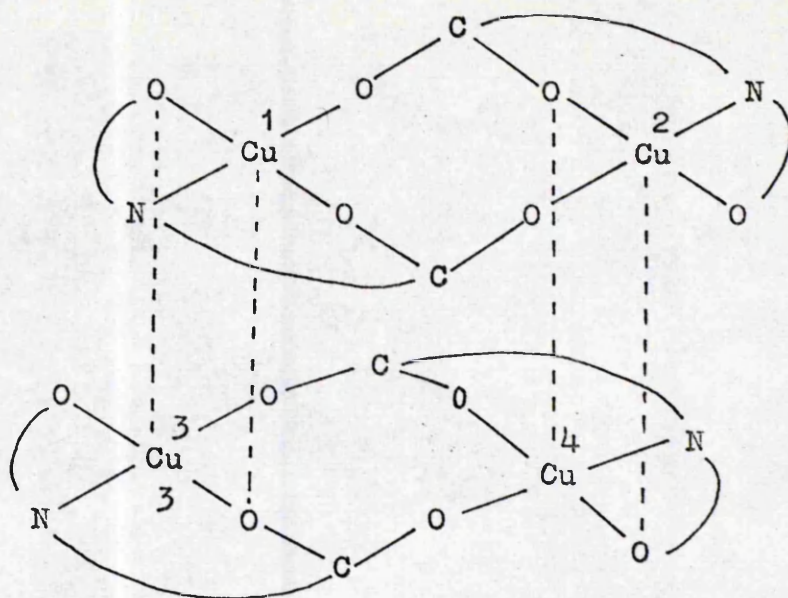
(xxi)



(xxii)



(xxiii) is suggested for $[\text{Cu}(\text{Sal-ArgH})]\text{Cl}\cdot 2\text{H}_2\text{O}$ in which the superexchange interaction occurs between the pairs of copper atoms Cu(1)-Cu(3) and Cu(2)-Cu(4). This interaction is not expected to be strong because the distance separating the two layers will preclude strong bonds between copper atoms of one layer and oxygen atoms of the other layer. The weak antiferromagnetism which would result from the proposed structure (xxiii) is in good agreement with the experimental result (Figure XXII) which shows predominately a Curie-Weiss component in the susceptibility versus temperature plot.

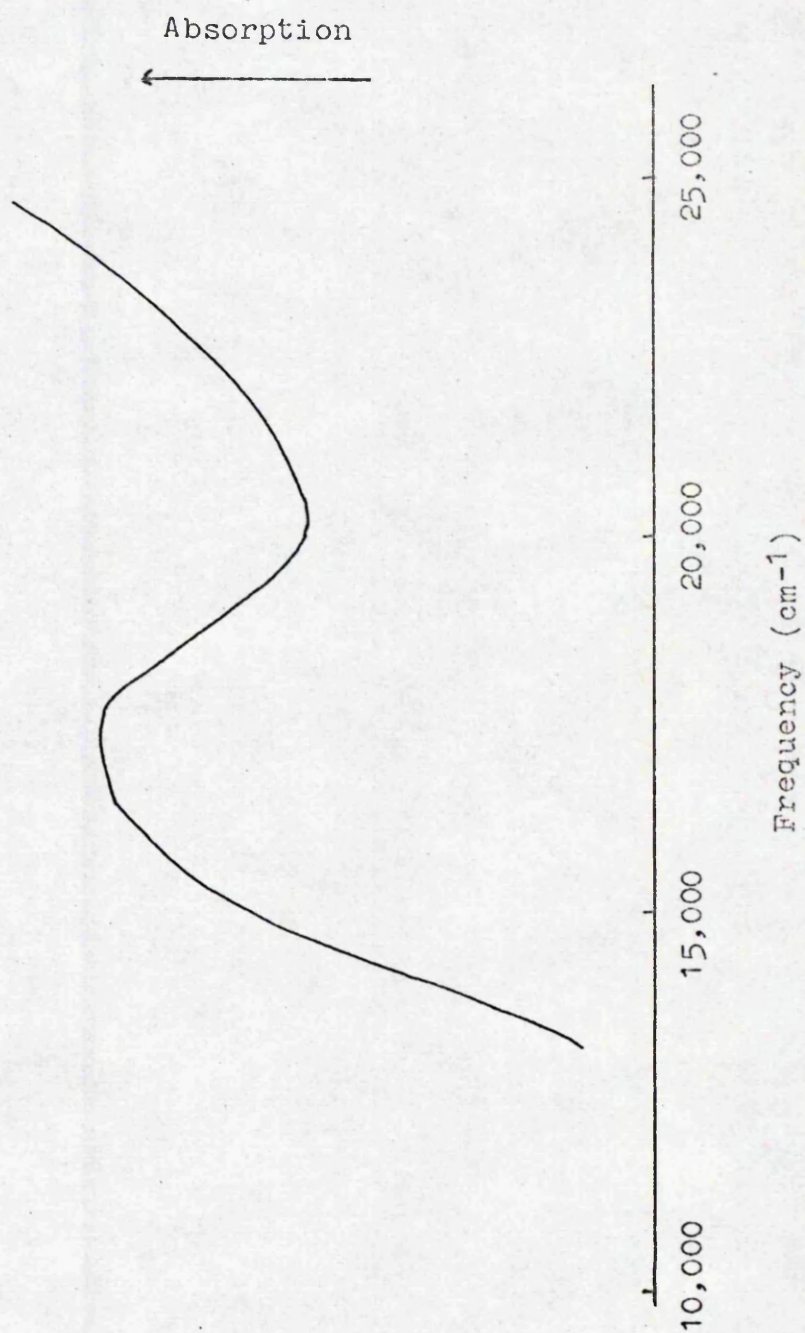


(xxiii)

Although the temperature variation of susceptibility of $[\text{Cu}(\text{Sal-Arg})]\text{H}_2\text{O}$ has not been measured, the relatively high magnetic moment of 1.58 B.M. at room temperature is comparable to 1.49 B.M. of $[\text{Cu}(\text{Sal-ArgH})]\text{Cl}\cdot 2\text{H}_2\text{O}$. Also the rather similar carboxyl stretching frequencies (Table 22) of $[\text{Cu}(\text{Sal-Arg})]\text{H}_2\text{O}$ and $[\text{Cu}(\text{Sal-ArgH})]\text{Cl}\cdot 2\text{H}_2\text{O}$ may suggest that $[\text{Cu}(\text{Sal-Arg})]\text{H}_2\text{O}$ will probably adopt a similar structure to that of $[\text{Cu}(\text{Sal-ArgH})]\text{Cl}\cdot 2\text{H}_2\text{O}$. However, the solid electronic absorption spectra (Table 23 and Figure XXIV) of $[\text{Cu}(\text{Sal-Arg})]\text{H}_2\text{O}$ seems to suggest a different Cu(II) chromophore. Until additional information is obtained, no structural speculation will be made here.

Nickel(II) Complexes of N-Salicylidenearginine. The pale blue nickel(II) complexes were prepared by either reacting the preformed Schiff base with nickel(II) salts in ethanol, or by dissolving L-arginine and salicylaldehyde in ethanol-water and treating with nickel(II) salts. In the case of the greenish-

Figure XXIV. Solid Electronic Absorption Spectrum of $\text{Cu}(\text{Sal-Arg})\text{H}_2\text{O}$



yellow $\text{Ni}(\text{Sal-Arg})\text{H}_2\text{O}$, an equivalent mole of sodium carbonate was added before treating with nickel(II) salts.

As has been noted, infrared technique plays only an informative role in elucidating the stereochemistry of Schiff base complexes, and should not be emphasised too much in structural studies. Nevertheless, some significant infrared absorption frequencies of $[\text{Ni}(\text{Sal-ArgH})]\text{NO}_3$, $[\text{Ni}(\text{Sal-ArgH})]\text{Cl}\cdot\text{H}_2\text{O}$, and $[\text{Ni}(\text{Sal-Arg})]\text{H}_2\text{O}$ are tabulated in Table 25 which shows that the ligand may coordinate to the nickel atom fundamentally as a tridentate Schiff base. The solid electronic absorption spectra (Table 26 and Figure XXV) of the nickel(II) complexes are typical of pseudooctahedral configuration.⁽⁷⁶⁾ The third band, ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g} (\text{P})$, is

Table 26. Solid Electronic Absorption Maxima (cm^{-1}) of Nickel(II)-N-Salicylidenearginine Complexes.

| Compound | ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{2g}$ | ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g} (\text{F})$ |
|--|---|--|
| $[\text{Ni}(\text{Sal-ArgH})]\text{NO}_3$ | 10,900 | 17,600 |
| $[\text{Ni}(\text{Sal-ArgH})]\text{Cl}\cdot\text{H}_2\text{O}$ | 10,800 | 17,500 |
| $[\text{Ni}(\text{Sal-Arg})]\text{H}_2\text{O}$ | 10,400 | 15,800 |

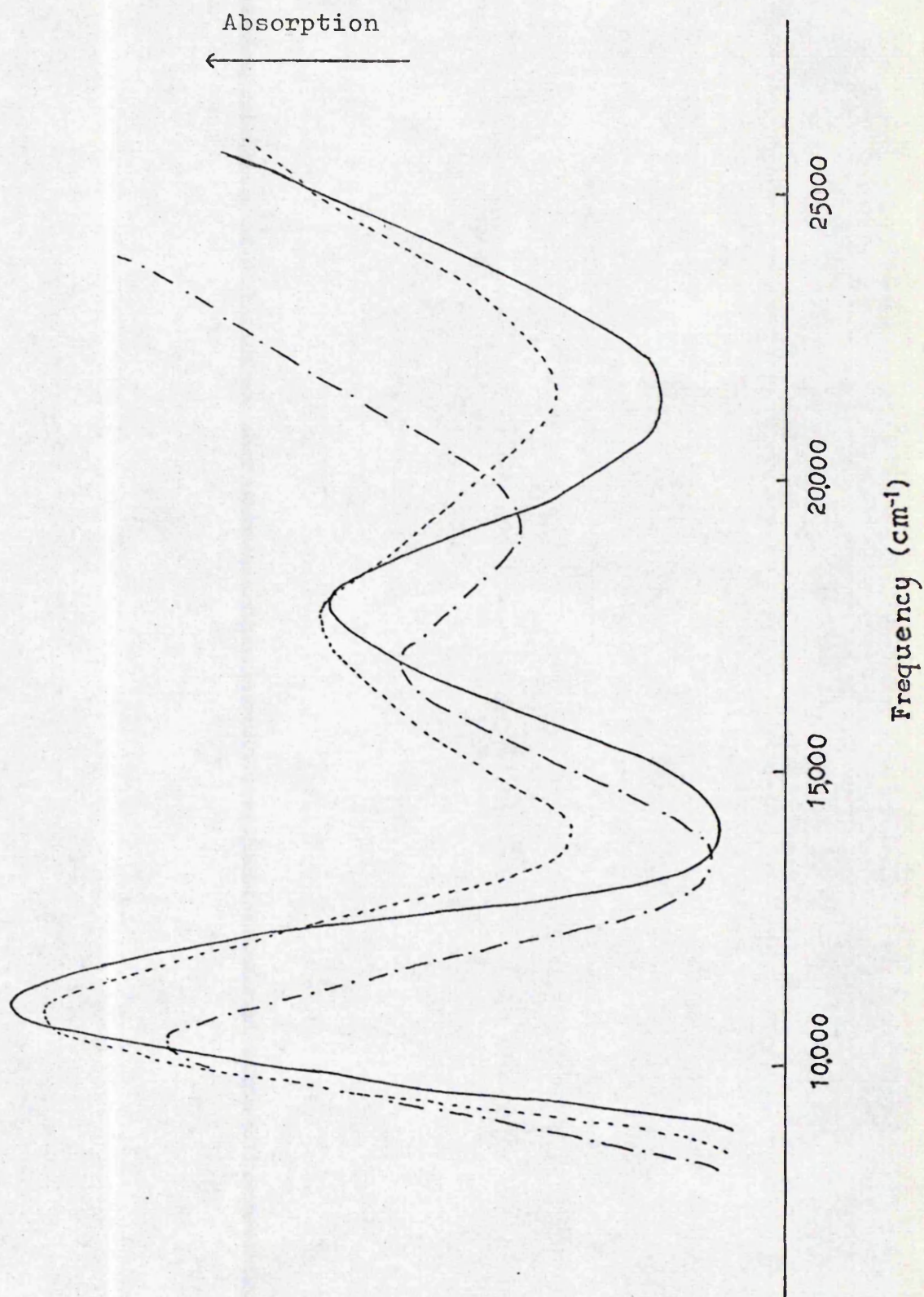
probably overlapped by the charge-transfer absorption trailing into the visible region. Thus, it seems possible that a dimeric octahedral structure (xxiv) similar to that suggested by Theriot and co-workers⁽¹⁶⁹⁾ for nickel(II) complexes of N-salicylideneamino acids may be applicable here. However, the low magnetic moments (below spin-only value of 2.8 B.M. for nickel(II) complexes) of these complexes suggest that this is not a simple system.

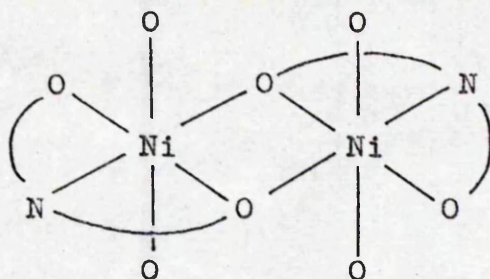
Table 25. Some Significant Infrared Absorption Frequencies (cm^{-1}) of

Nickel(II)-N-Salicylidenearginine Complexes

| $[\text{Ni}(\text{Sal-ArgH})]\text{NO}_3$ | $[\text{Ni}(\text{Sal-ArgH})]\text{ClH}_2\text{O}$ | $[\text{Ni}(\text{Sal-Arg})]\text{H}_2\text{O}$ | Assignment |
|---|--|---|---------------------------------|
| 3340 s, b | 3330 s, b | 3330 s, b | \checkmark_{NH} |
| 3270 m, sh | 3250 w, sb | 3160 s, b | |
| 3185 s, sp | 3160 s, b | | |
| 1675 s, sh | 1670 s, sh | 1666 s, sh | $\checkmark_{\text{C=N}}$ |
| 1645 s, b | 1640 s, b | 1630 s, sp | $\checkmark_{\text{COO asym.}}$ |
| 1385 m, b | 1392 m, sp | 1381 m, sp | $\checkmark_{\text{COO sym.}}$ |
| 824 m, sp | | | NO_3^- |

Figure XXV. Solid Electronic Absorption Spectra of $[\text{Ni}(\text{Sal-ArgH})\text{NO}_3]$ (—), $[\text{Ni}(\text{Sal-ArgH})\text{Cl}\cdot\text{H}_2\text{O}]$ (.....), and $[\text{Ni}(\text{Sal-Arg})\text{H}_2\text{O}]$ (-.-.-.)





(xxiv)

Many Schiff base complexes of nickel(II) are known to exhibit "anomalous magnetic behaviour"^(76,93,160) in both solution and solid states. In the solid state, low magnetic moments may result from either spin-spin equilibrium^(186,187) or configuration equilibrium.⁽¹⁸⁸⁻¹⁹⁰⁾ In the solution, additional solvent-solute, and solute-solute interactions may bring about the anomalous magnetic behaviour as well.⁽⁷⁶⁾

The magnetic susceptibilities at various temperatures for $[\text{Ni}(\text{Sal-ArgH})]\text{NO}_3$, $[\text{Ni}(\text{Sal-ArgH})]\text{Cl}\cdot\text{H}_2\text{O}$, and $[\text{Ni}(\text{Sal-Arg})]\text{H}_2\text{O}$ are recorded in Table 27 together with the calculated effective magnetic moments at various temperatures. The plots of reciprocal susceptibility versus temperature (Figure XXVI, XXVII and XXVIII) obey the Curie-Weiss law rather rigorously, and the calculated Weiss constant, θ , is surprisingly large (Table 28). The magnetic susceptibility was found to be independent of field strength indicative of absence of ferromagnetic impurities.

The fact that Curie-Weiss law is obeyed seems to preclude the possibility of spin-spin equilibrium. The ground state for octahedral nickel(II) is a spin triplet $^3\text{A}_{2g}$ state. However, axial perturbation may lower the symmetry from O_h to D_{4h} in which the ground state could be a

Table 27. Magnetic Data of Nickel(II)-N-Salicylidenearginine Complexes at

Various Temperatures

| $[\text{Ni}(\text{Sal-ArgH})]\text{NO}_3$ | | | | $[\text{Ni}(\text{Sal-ArgH})]\text{ClH}_2\text{O}$ | | | | $[\text{Ni}(\text{Sal-Arg})]2\text{H}_2\text{O}$ | | | |
|---|---------------------|-------------------|--|--|---------------------|-------------------|--|--|---------------------|-------------------|--|
| $1/\chi_{\text{Ni}}$ | $\mu_{\text{B.M.}}$ | $T^\circ\text{K}$ | | $1/\chi_{\text{Ni}}$ | $\mu_{\text{B.M.}}$ | $T^\circ\text{K}$ | | $1/\chi_{\text{Ni}}$ | $\mu_{\text{B.M.}}$ | $T^\circ\text{K}$ | |
| 553.6 | 2.04 | 292.2 | | 545.8 | 2.07 | 292.3 | | 489.5 | 2.19 | 292.3 | |
| 518.4 | 2.08 | 281.0 | | 496.1 | 2.14 | 283.2 | | 472.6 | 2.19 | 283.2 | |
| 496.1 | 2.08 | 269.3 | | 465.1 | 2.10 | 255.8 | | 455.5 | 2.19 | 272.8 | |
| 467.5 | 2.10 | 258.2 | | 425.3 | 2.13 | 240.3 | | 446.6 | 2.17 | 263.5 | |
| 454.5 | 2.12 | 254.5 | | 416.4 | 2.09 | 226.2 | | 432.7 | 2.18 | 256.2 | |
| 421.5 | 2.12 | 236.0 | | 386.7 | 2.10 | 213.5 | | 420.8 | 2.17 | 247.3 | |
| 404.9 | 2.13 | 229.2 | | 379.6 | 2.06 | 202.0 | | 406.9 | 2.16 | 236.5 | |
| 380.2 | 2.14 | 218.5 | | 352.4 | 2.07 | 188.5 | | 386.8 | 2.15 | 223.0 | |
| 366.4 | 2.13 | 208.0 | | 330.9 | 2.03 | 170.7 | | 373.4 | 2.13 | 211.8 | |
| 325.4 | 2.15 | 187.3 | | 290.6 | 1.99 | 144.2 | | 357.9 | 2.12 | 201.0 | |
| 300.2 | 2.13 | 170.0 | | 290.6 | 1.84 | 123.4 | | 333.0 | 2.11 | 185.7 | |
| 263.3 | 2.14 | 151.0 | | 217.5 | 1.98 | 106.7 | | 314.2 | 2.09 | 172.0 | |
| 232.5 | 2.18 | 137.7 | | 197.4 | 1.96 | 94.5 | | 287.9 | 2.08 | 155.5 | |
| 199.8 | 2.02 | 102.0 | | 186.3 | 1.93 | 86.8 | | 272.2 | 2.07 | 145.1 | |
| 168.8 | 2.15 | 97.5 | | 176.4 | 1.92 | 81.7 | | 254.7 | 2.06 | 134.7 | |
| 161.5 | 2.10 | 89.0 | | | | | | 229.1 | 2.06 | 121.5 | |
| 146.5 | 2.10 | 81.0 | | | | | | 202.0 | 2.05 | 106.3 | |
| | | | | | | | | 180.4 | 2.01 | 91.5 | |
| | | | | | | | | 159.6 | 2.00 | 80.2 | |

Figure XXVI. Reciprocal Magnetic Susceptibility versus Temperature Plot for $[\text{Ni}(\text{Sal-ArgH})]\text{NO}_3$

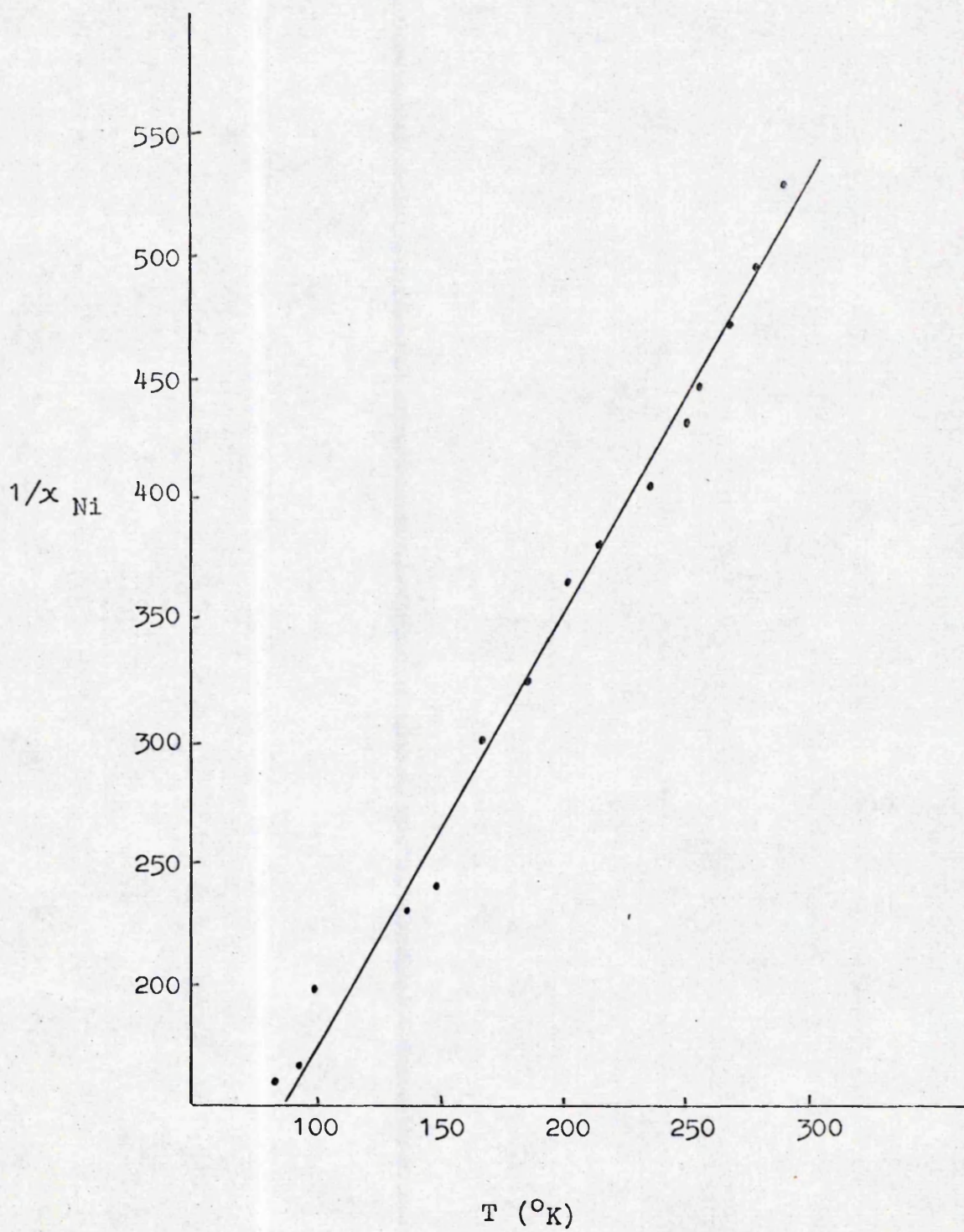


Figure XXVII. Reciprocal Magnetic Susceptibility versus Temperature Plot for $[\text{Ni}(\text{Sal-ArgH})]\text{Cl}\cdot\text{H}_2\text{O}$

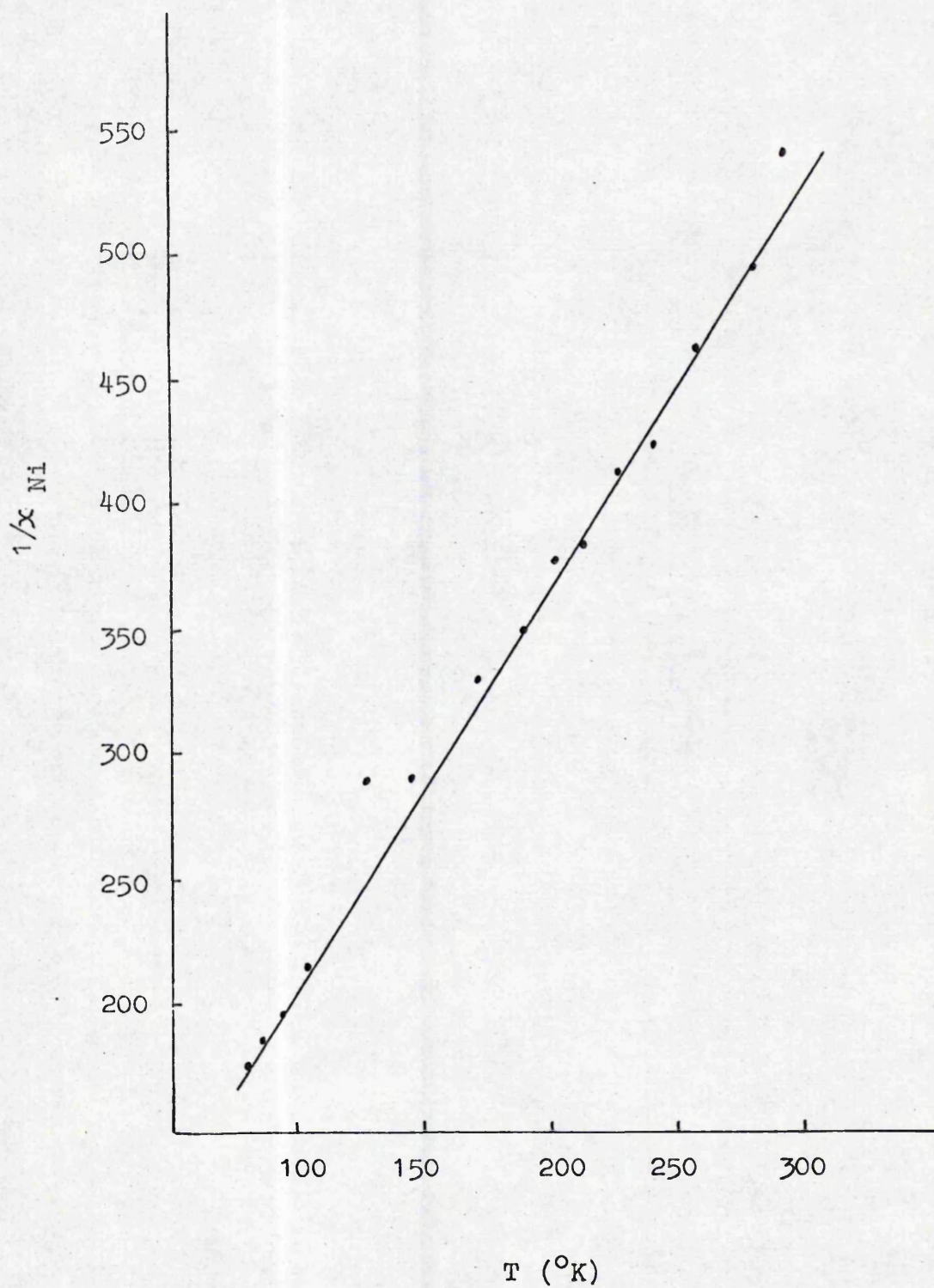


Figure XXVIII. Reciprocal Magnetic Susceptibility versus Temperature Plot for $[\text{Ni}(\text{Sal-Arg})]2\text{H}_2\text{O}$

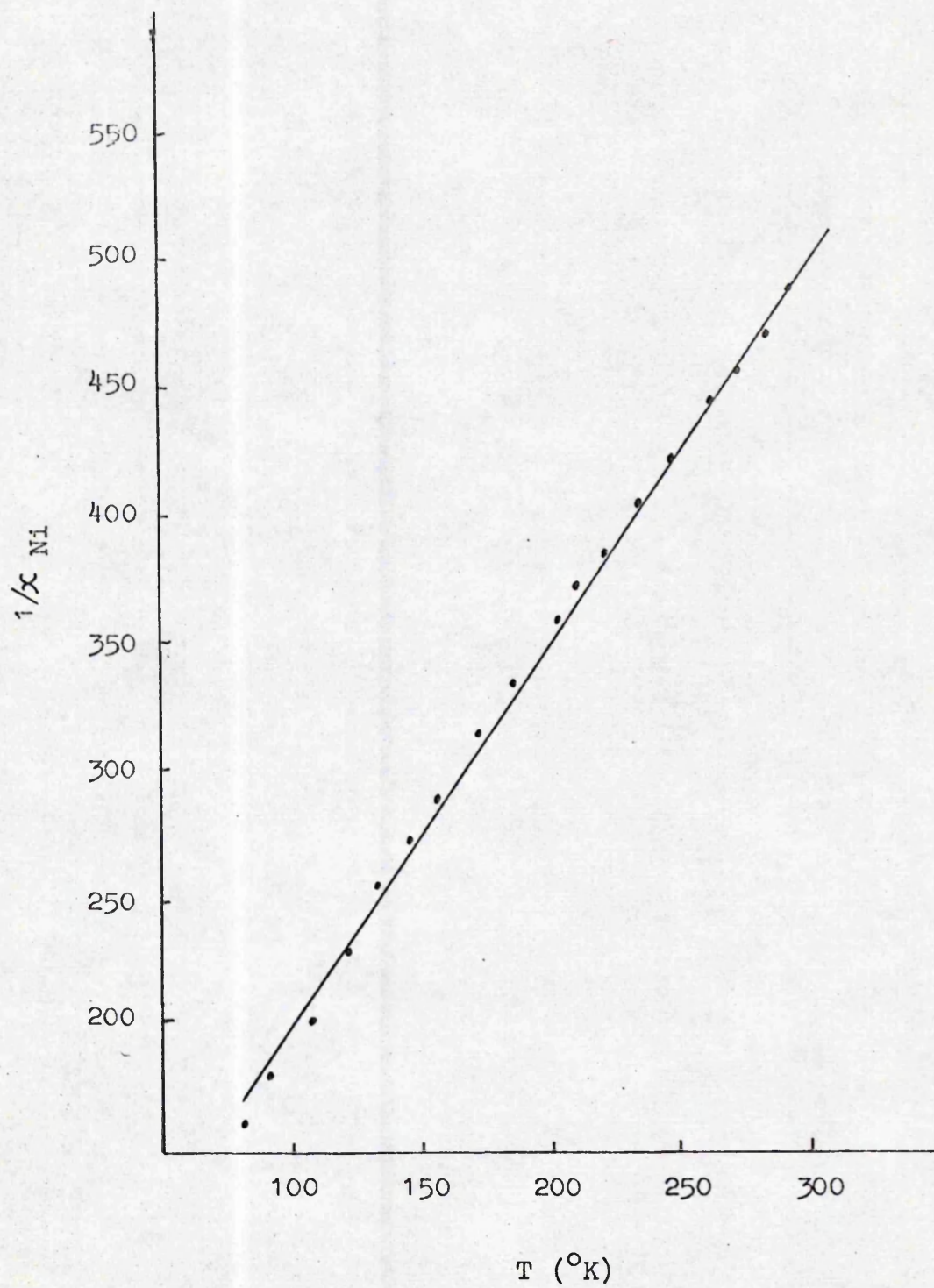


Table 28. Calculated Weiss constant, θ , for Nickel(II)-N-Salicylidenearginine Complexes.

| Compound | Weiss constant, θ °K |
|--|-----------------------------|
| $[\text{Ni}(\text{Sal-ArgH})]\text{NO}_3$ | -20 |
| $[\text{Ni}(\text{Sal-ArgH})]\text{Cl}\cdot\text{H}_2\text{O}$ | 30 |
| $[\text{Ni}(\text{Sal-Arg})]\text{H}_2\text{O}$ | 46 |

spin singlet. (191,192) When the energy difference between the singlet and triplet states is comparable to thermal energy, equilibrium between the singlet and triplet states may exist, and the distribution between the two states can be described by Maxwell-Boltzmann statistics. The magnetic susceptibility of this system may then be given by: (192)

$$\chi_M = \frac{2g^2\beta^2N}{3kT} \left\{ 1 + \frac{1}{3} \exp \frac{h\nu_1}{kT} \right\}^{-1} + N_\alpha$$

where g is the Lande splitting factor, N is Avogadro's number, β is the Bohr magneton, k is the Boltzmann constant, T is the absolute temperature, $h\nu_1$, is the energy separation between the singlet and triplet states, and N_α is the temperature independent paramagnetism. It follows from this equation that the magnetic susceptibility will increase with temperature except when $h\nu_1 \ll kT$, that is, when the singlet and triplet state are essentially degenerate.

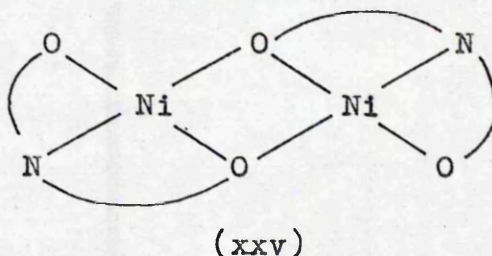
Anomalous magnetic behaviour of nickel(II) complexes may also be due to the coexistence of more than one stereochemical configuration in the crystal. The yellow form of bis(meso-stilbenediamino)nickel(II)dichloroacetate has been

shown⁽¹⁹⁰⁾ by X-ray techniques to consist of two octahedral nickel ions and one square-planar nickel ion in a crystal unit. The crystal has an electronic spectrum which is dominated by the features of the diamagnetic nickel ion, and a magnetic moment of about 2.5 B.M.⁽¹⁸⁹⁾ It has also been shown⁽¹⁸⁸⁾ that the crystal of bis(diphenylmethylphosphino)-nickel(II) bromide contains two paramagnetic tetrahedral nickel ions and one diamagnetic square-planar nickel ion. The electronic spectrum shows features of both stereochemistries, and the magnetic moment is reported to be 2.8 B.M. Brubaker and Busch⁽¹⁹³⁾ have shown that the S,S'-o-xylyl-2,3-pentanedionebis(mercaptoethylimine)nickel(II) bromide crystal unit may contain one paramagnetic and three diamagnetic nickel ions. The complex has an electronic spectrum with predominately octahedral features, and a magnetic moment of about 1.5 B.M. The magnetic susceptibilities at various temperatures follow Curie-Weiss law with a calculated Weiss constant of 1.8°K.

Although the magnetic data do not prove any particular mechanism, a configurational equilibrium between octahedral and square-planar nickel ions seems best fit to explain the observed anomalous magnetic behaviour. By assuming a paramagnetism of about 3.2 B.M. for the octahedral configuration (based on the averaged moments of nickel(II) complexes of N-salicylideneamino acids⁽¹⁶⁹⁾), it can be estimated that the ratio of paramagnetic octahedral nickel(II) complex to diamagnetic square-planar nickel complex is approximately 3 to 2 in all cases.

Thus, it may be suggested that in the nickel(II)

complexes, $[\text{Ni}(\text{Sal-ArgH})]\text{NO}_3$, $[\text{Ni}(\text{Sal-ArgH})]\text{Cl}\cdot\text{H}_2\text{O}$ and $[\text{Ni}(\text{Sal-Arg})]\text{H}_2\text{O}$, the square-planar configuration is formed by the tridentate ligand in a dimeric structure (xxv), and the octahedral configuration may be completed by adjacent carboxyl



oxygen or water molecule similar to (xxiv) in the axial positions.

(iii) Conclusion

The metal(II)-N-salicylidenearginine systems proved to be as chemically interesting as the simple metal(II)-L-arginine system. The copper(II) complexes provide two magnetically distinct but chemically similar groups. One group, exemplified by $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3$ and $[\text{Cu}(\text{Sal-ArgH})]\text{NO}_3\cdot\text{H}_2\text{O}$, consists of strong antiferromagnetism brought about mainly through direct copper-copper interaction. The other group, exemplified by $[\text{Cu}(\text{Sal-ArgH})]\text{Cl}\cdot 2\text{H}_2\text{O}$, and $\text{Cu}(\text{Sal-Arg})\text{H}_2\text{O}$, consists of very weak antiferromagnetism brought about by super-exchange through an intermolecular association. The difference lies mainly in the coordination functions of the carboxyl group. Thus, a monodentate carboxyl group affords closing up or bridging the copper atoms for interaction, while a bidentate carboxyl group rules out this possibility. The overall effect is that for copper-copper interaction, the copper atoms should be at a favourable distance or with a

favourable π -pathway.

The structures of the nickel(II) complexes are less clear, and although this may be another example of configurational equilibrium existing in the solid state, no definite conclusion can be drawn without a crystallographic study. In fact, magnetic susceptibility measurements at various temperatures have led several groups to ambiguous conclusions about the nature of the anomalous magnetic behaviour of nickel(II) complexes.⁽¹⁹⁴⁻¹⁹⁷⁾ Unfortunately, experimental conditions do not permit measurements below liquid nitrogen temperature. Thus, the $1/\chi$ vs T. curves do not show the low-temperature behaviour which may be useful in visualizing the magnetic behaviour.⁽¹⁹⁸⁾

EXPERIMENTAL

Starting Materials

L-Arginine (Koch-Light Laboratories Ltd.) cupric perchlorate hexahydrate, cupric nitrate trihydrate, cupric chloride dihydrate, nickel(II) perchlorate hexahydrate, nickel(II) nitrate hexahydrate, nickel(II) chloride hexahydrate, sodium carbonate and lithium hydroxide monohydrate (all from B.D.H. Laboratories Ltd.) and salicylaldehyde (Hopkin and William Ltd.) were used without further purification.

Preparation of Ligand

N-Salicylidenearginine,

α -HOC₆H₄CH=NCH(COO)CH₂CH₂CH₂NHC(NH₂)=NH₂, To a suspension of L-arginine (0.1 mole) in 95% ethanol (100 ml) was added salicylaldehyde (0.1 mole) with constant stirring. The resulting mixture was then refluxed for three hours to give a bright yellow precipitate. The crystalline solids were filtered, washed twice with 95% ethanol then acetone, and finally dried in vacuo over CaCl₂ overnight. The yield is over 90% based on L-arginine.

Analyses: Calculated for C₁₃H₁₈N₄O₃: C % 56.1; H % 6.5; N % 20.2. Found: C % 56.1; H % 6.6; N % 20.0. The compound melts at 196°C and is soluble in water, but insoluble in common organic solvents.

Preparations of Complexes

Bis(L-arginine)copper(II) perchlorate.

$\text{Cu}\{\text{NH}_2\text{CH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}_2\}_2(\text{ClO}_4)_2$. L-Arginine (0.50 gm, 0.0028 mole) was dissolved in water (10 ml) and treated with a solution of cupric perchlorate hexahydrate (0.51 gm,

0.0014 mole) in water (10 ml). The resulting deep blue solution was stirred vigorously for several hours until precipitates were formed. The blue scales were filtered and dried in vacuo over CaCl_2 overnight. The yield is about 90% based on L-arginine.

Analyses: Calculated for $\text{C}_{12}\text{H}_{28}\text{H}_8\text{O}_{12}\text{CuCl}_2$: C % 23.6; H % 4.6; N % 18.3. Found: C % 23.9; H % 4.8; N % 18.1. The compound decomposes at 210°C before melting and is soluble in water, dimethylsulphoxide and dimethylformamide but insoluble in organic solvents.

Bis(L-arginine)copper(II) perchlorate monohydrate.

$\text{Cu}\{\text{NH}_2\text{CH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}_2\}_2(\text{ClO}_4)_2(\text{H}_2\text{O})$. This compound was prepared by recrystallization of bis(L-arginine)-copper(II) perchlorate (0.50 gm) from minimum amount of hot water (5 ml) as a fine blue crystalline solid. The yield is quantitative.

Analyses: Calculated for $\text{C}_{12}\text{H}_{30}\text{N}_8\text{O}_{13}\text{CuCl}_2$: C % 22.9; H % 4.8; N % 17.8. Found: C % 23.2; H % 5.4; N % 17.8. The compound decomposes at 210° before melting and is soluble in water, dimethylsulphoxide and dimethylformamide, but insoluble in organic solvents.

Bis(L-arginine)copper(II) nitrate dihydrate.

$\text{Cu}\{\text{NH}_2\text{CH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}_2\}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$. L-Arginine (0.50 gm, 0.0028 mole) was dissolved in water (10 ml) and treated with a solution of cupric nitrate trihydrate (0.34 gm, 0.0014 mole) in water (10 ml) with constant stirring. The resulting deep blue solution was stirred vigorously for several hours until precipitation began. The blue precipitate was filtered, washed twice with 95% ethanol and finally dried in

vacuo over CaCl_2 overnight. Recrystallization from small amounts of hot water gave deep blue fine crystals. The yield is about 85% based on L-arginine.

Analyses: Calculated for $\text{C}_{12}\text{H}_{32}\text{N}_{10}\text{O}_{12}\text{Cu}$: C % 25.2; H % 5.6; N % 24.5. Found: C % 26.0; H % 6.1; N % 24.8. The compound decomposes at 230°C before melting and is soluble in water and sparingly in dimethylsulphoxide but insoluble in organic solvents.

Bis(L-arginine)copper chloride dihydrate.

$\text{Cu}\{\text{NH}_2\text{CH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}_2\}_2\text{Cl}_2(\text{H}_2\text{O})_2$. L-Arginine (0.50 gm, 0.0028 mole) was dissolved in water (10 ml) then treated with a solution of cupric chloride dihydrate (0.24 gm, 0.0014 mole) in water (10 ml) with constant stirring. The resulting deep blue solution was stirred vigorously for two hours then kept in the 'fridge overnight. To this chilled solution was added 95% ethanol (30 ml) and kept in the 'fridge again until crystallization began. The blue crystals were filtered, washed twice with 95% ethanol and finally dried in vacuo over CaCl_2 overnight. The yield is about 95% based on L-arginine.

Analyses: Calculated for $\text{C}_{12}\text{H}_{32}\text{N}_8\text{O}_6\text{CuCl}_2$: C % 27.8; H % 6.2; N % 21.7. Found: C % 27.7; H % 6.1; N % 21.7. The compound decomposes at 180°C before melting and is soluble in water and sparingly soluble in dimethylsulphoxide but insoluble in organic solvents.

Bishydroxobis(L-arginine)copper(II) dihydrate.

$\text{Cu}\{\text{NH}_2\text{CH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}_2\}_2(\text{OH})_2(\text{H}_2\text{O})_2$. L-Arginine (0.50 gm, 0.0018 mole) was dissolved in water (10 ml) and treated with sodium carbonate (0.15 gm, 0.0014 mole). The solution was heated to 50°C and treated with a solution of

cupric perchlorate hexahydrate (0.51 gm, 0.0014 mole) with constant stirring. The resulting deep blue solution was maintained at 50°C with stirring until precipitation began. The blue crystalline solids were filtered, washed twice with 95% ethanol and finally dried in vacuo over CaCl_2 overnight. The yield is over 80% based on L-arginine. Similar compounds were obtained when equimolar amounts of cupric nitrate trihydrate or cupric chloride dihydrate were used in place of cupric perchlorate hexahydrate.

Analyses: Calculated for $\text{C}_{12}\text{H}_{34}\text{N}_8\text{O}_8\text{Cu}$: C % 30.3; H % 7.1; N % 23.2. Found: C % 30.0; H % 6.3; N % 22.2. The compound decomposes at 186°C before melting and is only sparingly soluble in water, and insoluble in organic solvents.

(L-Argininato)copper(II) perchlorate trihydrate.

$\text{Cu}\{\text{NH}_2\text{CH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}\}(\text{ClO}_4)(\text{H}_2\text{O})_3$. L-Arginine (0.50 gm, 0.0028 mole) was dissolved in water (10 ml) and treated with sodium carbonate (0.15 gm, 0.0014 mole). This solution was then added to a solution of cupric perchlorate hexahydrate (1.02 gm, 0.0028 mole) in water (10 ml) with constant stirring. The deep blue solution was stirred vigorously for several hours until precipitation occurred. The pale blue scales were filtered and dried in vacuo over CaCl_2 overnight. The yield is over 80% based on L-arginine.

Analyses: Calculated for $\text{C}_6\text{H}_{19}\text{N}_4\text{O}_9\text{CuCl}$: C % 18.5; H % 4.9; N % 14.4. Found: C % 18.3; H % 4.9; N % 13.4. The compound decomposes at 196°C before melting and is soluble in water, dimethylsulphoxide and dimethylformamide, but insoluble in other organic solvents.

(L-Argininato)Nickel(II) perchlorate dihydrate.

$\text{Ni}\{\text{NH}_2\text{CH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}\}(\text{ClO}_4)_2(\text{H}_2\text{O})_2$. L-Arginine (0.50 gm, 0.0028 mole) and lithium hydroxide monohydrate (0.12 gm, 0.0028 mole) were dissolved in 95% ethanol (30 ml) by means of refluxing for 20 minutes, and then filtered to remove any insoluble materials. This solution was then added slowly to a solution of nickel perchlorate hexahydrate (0.76 gm, 0.0028 mole) in 95% ethanol (20 ml) with stirring. The pale green precipitate which formed immediately was filtered, washed twice with 95% ethanol, then acetone, and finally dried in vacuo over CaCl_2 overnight. The yield is about 90% based on L-arginine.

Analyses: Calculated for $\text{C}_6\text{H}_{17}\text{N}_4\text{O}_8\text{NiCl}$: C % 19.6; H % 4.6; N % 15.2. Found: C % 19.9; H % 4.8; N % 15.2. The compound decomposes at 230°C before melting and is insoluble in common solvents.

(L-Argininato)nickel(II) nitrate trihydrate.

$\text{Ni}\{\text{NH}_2\text{CH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}\}(\text{NO}_3)_3(\text{H}_2\text{O})_3$. This compound was prepared by the method similar to that employed for (L-argininato)nickel(II) perchlorate dihydrate. Pale green precipitates were obtained. The yield is about 90% based on L-arginine.

Analyses: Calculated for $\text{C}_6\text{H}_{19}\text{N}_5\text{O}_8\text{N}$: C % 20.7; H % 5.5; N % 20.1. Found: C % 21.0; H % 5.2; N % 20.2. The compound decomposes at 200°C before melting and is insoluble in common solvents.

(L-Argininato)nickel(II) chloride tetrahydrate.

$\text{Ni}\{\text{NH}_2\text{CH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}\}\text{Cl}(\text{H}_2\text{O})_4$. This compound was prepared by the method similar to that employed for (L-argininato)nickel(II) perchlorate dihydrate. Pale green

precipitates were obtained. The yield is about 90% based on L-arginine.

Analyses: Calculated for $C_6H_{21}N_4O_6NiCl$: C % 21.2; H % 6.2; N % 16.5. Found: C % 21.6; H % 5.7; N % 16.4. The compound decomposes at 210° before melting and is insoluble in common solvents.

(L-Argininato)nickel(II) bromide monohydrate.

$Ni\{NH_2CH(COO)CH_2CH_2CH_2NHC(NH_2)=NH\}Br(H_2O)$. This compound was prepared by the method similar to that employed for (L-argininato)nickel(II) perchlorate dihydrate. Pale green precipitates were obtained. The yield is about 90% based on L-arginine.

Analyses: Calculated for $C_6H_{15}N_4O_3NiBr$: C % 21.9; H % 4.6; N % 17.0. Found: C % 22.5; H % 5.4; N % 16.7. The compound decomposes at $210^\circ C$ before melting and is insoluble in common solvents.

Bis(L-arginine)nickel nitrate monohydrate.

$Ni\{NH_2CH(COO)CH_2CH_2CH_2NHC(NH_2)=NH\}_2(NO_3)_2(H_2O)$. L-arginine (0.50 gm, 0.0028 mole) and lithium hydroxide monohydrate (0.12 gm, 0.0028 mole) were dissolved in 95% ethanol (30 ml) by refluxing for 20 minutes. To the filtered solution was added slowly a solution of nickel nitrate hexahydrate (0.33 gm, 0.0014 mole) in 95% ethanol (10 ml) with constant stirring. The pale green precipitate which formed immediately was filtered, washed twice with 95% ethanol, then acetone, and finally dried in vacuo over $CaCl_2$ overnight. The yield is about 90% based on L-arginine.

Analyses: Calculated for $C_{12}H_{30}N_{10}O_{11}Ni$: C % 26.3; H % 5.5; N % 25.6. Found: C % 26.7; H % 6.4; N % 25.6. The compound decomposes at $205^\circ C$ before melting and is insoluble

in common solvents.

Bis(L-arginine)nickel chloride dihydrate.

$\text{Ni}\{\text{NH}_2\text{CH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}_2\}_2\text{Cl}_2(\text{H}_2\text{O})_2$. This compound is prepared by a method similar to that used for bis(L-arginine)-nickel(II) nitrate monohydrate. Pale green precipitates were obtained. The yield is about 90% based on L-arginine.

Analyses: Calculated for $\text{C}_{12}\text{H}_{32}\text{N}_8\text{O}_6\text{NiCl}_2$: C % 28.1; H % 6.3; N % 21.8. Found: C % 28.7; H % 6.5; N % 21.6. The compound decomposes at 195°C before melting and is insoluble in common solvents.

Tris(L-arginine)nickel perchlorate tetrahydrate.

$\text{Ni}\{\text{NH}_2\text{CH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}_2\}_3(\text{ClO}_4)_2(\text{H}_2\text{O})_4$. This compound was prepared by a method similar to that used for bis(L-arginine)nickel(II) nitrate monohydrate. Pale green precipitates were obtained. The yield is about 90% based on L-arginine.

Analyses: Calculated for $\text{C}_{18}\text{H}_{50}\text{N}_{12}\text{O}_{18}\text{NiCl}_2$: C % 25.4; H % 5.9; N % 19.7. Found: C % 25.7; H % 5.9; N % 19.4. The compound decomposes at 210°C before melting and is insoluble in common solvents.

Bishydroxo(L-arginine)nickel(II) monohydrate.

$\text{Ni}\{\text{NH}_2\text{CH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}_2\}(\text{OH})_2(\text{H}_2\text{O})$. L-Arginine (0.50 gm, 0.0028 mole) and sodium carbonate (0.15 gm, 0.0014 mole) were dissolved in water (10 ml) and heated to 50°C .

To this solution was added a solution of the hydrated nickel(II) salt (0.0014 mole) in water (5 ml) with constant stirring.

The resulting greenish solution was maintained at 50°C with stirring for two hours, then kept in a 'fridge until precipitation began. The green solids were filtered, washed

twice with 95% ethanol then acetone and finally dried in vacuo over CaCl_2 overnight. The yield is about 90% based on L-arginine.

Analyses: Calculated for $\text{C}_{13}\text{H}_{18}\text{N}_4\text{O}_5$: C % 25.3; H % 6.3; N % 19.6. Found: C % 25.4; H % 5.9; N % 19.7. The compound decomposes at 200°C before melting and is insoluble in common solvents.

N-Salicylideneargininecopper(II) nitrate.

$\text{Cu}\{\text{O}-\text{OC}_6\text{H}_4\text{CH}=\text{NCH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}_2\}(\text{NO}_3)$. A mixture of L-arginine (0.50 gm, 0.0028 mole) and salicylaldehyde (0.35 gm, 0.0028 mole) in 95% ethanol (50 ml) was refluxed for one hour to give bright yellowish crystalline solids. To the hot mixture was added a solution of cupric nitrate trihydrate (0.34 gm, 0.0028 mole) in 95% ethanol (20 ml) with stirring. The resulting deep green solution was refluxed for another two hours, then cooled to room temperature. The green crystalline solid formed was filtered, washed twice with 95% ethanol then acetone and finally dried in vacuo over CaCl_2 overnight. The yield is about 80%.

Analyses: Calculated for $\text{C}_{13}\text{H}_{17}\text{N}_5\text{O}_6\text{Cu}$: C % 38.6; H % 4.2; N % 17.3. Found: C % 38.5; H % 4.5; N % 17.1. The compound decomposes at 212°C before melting and is soluble in water, but insoluble in organic solvents.

N-Salicylideneargininecopper(II) nitrate monohydrate

$\text{Cu}\{\text{O}-\text{OC}_6\text{H}_4\text{CH}=\text{NCH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}_2\}(\text{NO}_3)(\text{H}_2\text{O})$. To a suspension of N-salicylidenearginine (0.50 gm, 0.0018 mole) in 95% ethanol (50 ml) was added a solution of cupric nitrate trihydrate (0.32 gm, 0.0018 mole) in 95% ethanol (10 ml). The resulting mixture was refluxed for two hours to give a deep green solution. Upon cooling to room temperature,

greenish crystalline solids were deposited. The green solids were filtered, washed twice with 95% ethanol, then acetone and finally dried in vacuo over CaCl_2 overnight. The yield is about 90% based on N-salicylidenearginine.

Analyses: Calculated for $\text{C}_{13}\text{H}_{19}\text{N}_5\text{O}_7\text{Cu}$: C % 37.1; H % 4.5; N % 16.6. Found: C % 36.6; H % 4.4; N % 17.1. The compound decomposes at 208°C before melting and is soluble in water but insoluble in organic solvents.

N-Salicylideneargininecopper(II) chloride dehydrate
 $\text{Cu}\{\text{O}-\text{OC}_6\text{H}_4\text{CH}=\text{NCH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}_2\}\text{Cl}(\text{H}_2\text{O})_2$. This compound was prepared by a method similar to that used either for N-salicylideneargininecopper(II) nitrate or the hydrated analogue. Green crystalline solids were obtained in the yield of 80%.

Analyses: Calculated for $\text{C}_{13}\text{H}_{21}\text{N}_4\text{O}_5\text{CuCl}$: C % 37.8; H % 5.1; N % 13.5. Found: C % 37.9; H % 5.1; N % 14.2. The compound decomposes at 164°C before melting and is soluble in water but insoluble in organic solvents.

N-Salicylideneargininatocopper(II) monohydrate
 $\text{Cu}\{\text{O}-\text{OC}_6\text{H}_4\text{CH}=\text{NCH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}\}(\text{H}_2\text{O})$. N-Salicylidenearginine (0.50 gm, 0.0018 mole) and sodium carbonate (0.08 gm, 0.0009 mole) were dissolved in the mixed solvent 95% ethanol-water (40 ml:10 ml) by means of refluxing for one hour. To the resulting yellowish solution was added a solution of hydrated cupric salts (0.0018 mole) in 95% ethanol (10 ml) with constant stirring. The resulting green solution was refluxed for two hours and filtered. Upon cooling to room temperature a dark green crystalline solid was deposited. The solid was filtered, washed twice with 95% ethanol, then acetone, and finally dried in vacuo

over CaCl_2 overnight. The yield is 70% based on N-salicylidenearginine.

Analyses: Calculated for $\text{C}_{13}\text{H}_{18}\text{N}_4\text{O}_4\text{Cu}$: C % 44.8; H % 5.1; N % 16.1. Found: C % 44.7; H % 4.7; N % 16.0. The compound decomposes at 216°C before melting and is soluble in water but insoluble in organic solvents.

N-Salicylideneargininenickel(II) nitrate.

$\text{Ni}\{\text{O}-\text{OC}_6\text{H}_4\text{CH}=\text{NCH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}_2\}(\text{NO}_3)$. L-Arginine (0.50 gm, 0.0028 mole) was dissolved in water (10 ml) and added to salicylaldehyde (0.35 gm, 0.0028 mole) in 95% ethanol (40 ml) with stirring. The resulting yellowish solution was heated to 50°C then treated with a solution of nickel nitrate hexahydrate (0.66 gm, 0.0028 mole) in 95% ethanol with constant stirring. A pale blue precipitate was immediately formed. The mixture was stirred for ten minutes, the precipitate was filtered, washed twice with 95% ethanol, then acetone, and finally dried in vacuo over CaCl_2 overnight. The yield is about 90% based on L-arginine.

Analyses: Calculated for $\text{C}_{13}\text{H}_{17}\text{N}_5\text{O}_6\text{Ni}$: C % 39.4; H % 4.2; N % 17.6. Found: C % 41.1; H % 5.0; N % 18.5. The compound decomposes at 230°C before melting and is insoluble in organic solvents.

N-Salicylideneargininenickel(II) chloride monohydrate.

$\text{Ni}\{\text{O}-\text{OC}_6\text{H}_4\text{CH}=\text{NCH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}_2\}\text{Cl}(\text{H}_2\text{O})$. This compound was prepared by the same method used for N-salicylidene-argininenickel(II) nitrate. Pale blue crystalline solids were obtained in the yield of about 90%.

Analyses: Calculated for $\text{C}_{15}\text{H}_{19}\text{N}_4\text{O}_4\text{NiCl}$: C % 40.0; H % 5.1; N % 15.6. Found: C % 40.2; H % 6.2; N % 14.9. The compound decomposes at 220°C before melting and is insoluble

in organic solvents.

N-Salicylideneargininatonickel(II) monohydrate.

$\text{Ni}\{\text{O}-\text{OC}_6\text{H}_4\text{CH}=\text{NCH}(\text{COO})\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{NH}_2)=\text{NH}_2\}\text{Cl}(\text{H}_2\text{O})$. This compound was prepared by a method similar to that used for N-salicylideneargininatocopper(II) monohydrate. A yellowish green crystalline solid was obtained in a yield of about 80% based on L-arginine.

Analyses: Calculated for $\text{C}_{13}\text{H}_{18}\text{N}_4\text{O}_4\text{Ni}$: C % 44.2; H % 5.4; N % 15.8. Found: C % 44.1; H % 6.3; N % 17.0. The compound decomposes at 205°C before melting and is insoluble in organic solvents.

Physical Measurements

Infrared spectra were recorded using a Perkin Elmer 621 double beam spectrophotometer in the range $4000\text{--}200\text{ cm}^{-1}$; samples were prepared either as KBr disks or as Nujol mulls by standard procedures.

Electronic spectra were recorded on a Beckmann DK2A spectrophotometer using MgO as dilutant over the range $5000\text{--}40,000\text{ cm}^{-1}$.

Melting or decomposition points of the compounds were determined on a Gallenkamp melting apparatus.

Magnetic measurements were performed on a Gouy balance using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as the calibrant.

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