COPPER(II), NICKEL(II) AND COBALT(II) COMPLEXES OF N-AMINOALKYLAMINOMETHANEPHOSPHONIC ACIDS, (N-AMPA).

*L. M. Durosinmi, I.A.O. Oje and Jide Ige, Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria.

ABSTRACT

The chelating properties of N-aminoalkylaminomethane-phosphonic acids, N-AMPA of general formula, $NH_2(CH_2)_nNHCH_2PO_3H_2$ *(n=2,3,4,6), were investigated and compared with those of α, ω, diaminocarboxylic acids as well as the α-aminoalkylphosphonic acids,* $NH_2(CH_2)_nPO_3H_2$, *N-APA. Elucidation of the possible coordination sites with metals, composition of the metal complexes as well as possible structures of the complexes were investigated. Copper (II), nickel (II) and cobalt (II) ions form complexes with the ligands in the ratios 1:1, 1:2 and 1:3. Some of the complexes were isolated and characterized both by chemical methods and spectroscopically. N-AMPA (n=2,3), behave as bidentate ligands and form complexes with the metals in which the central atoms are coordinated via the two nitrogen atoms, that is the terminal amino and the imino groups. The coordination becomes monodentate when n equals or is greater than four. The phosphonate group is found not to be involved in the coordination. The behaviour of this group of zwitterionic compounds shows a significant deviation from that involving the α- aminophosphonic acids.*

INTRODUCTION

Metal complexes play many important roles in biological systems. Metal complexation reactions are also utilised in several important hydrometallurgical operations like in the recovery of very expensive metals that are industrially useful[1]. Similarly, metal toxicity can be overcome by chelation therapy.

The copper complexes of the diamino monocarboxylic acids in which the α-amino and the α-carboxylic groups participate in the formation of the complex and the ω-amino group stays free have been used in peptide synthesis for the preparation of ω-modified derivatives. Aminophosphonic acids too have been used as structural units of phosphonopeptides.

α-Aminoalkylphosphonic acids have been found to be effective in the extraction of gold from its salt solutions, as rust removers and in the prevention of scale deposits[2,3]. The chelating property of aminophosphonic acids therefore is not only of theoretical importance but of practical significance. Further to earlier reports on the novel synthesis of a series of α, ω, aminophosphonic acids and the bioactivity studies of their guanidino derivatives[4,5], we present in this work studies on the chelating properties of these new sets of aminophosphonic acids, the α-,ω, amino-alkylaminomethanephosphonic acids, N-AMPA which contain both α - and ω -amino groups and a P-CH_2-N- linkage. Previously studied aminophosphonic acids contain one amino group either in the α- or in the ω -position

It is hoped that this study will throw some light on the coordination chemistry of these ligands.

EXPERIMENTAL

Preparation of the ligands

The N-AMPA were synthesised by condensing chloromethyl phosphonic acid with the corresponding α,ω-diaminoalkane compound as previously described[4].

Determination of the stoichiometry of the metal-ion complexes

Absorbance measurements of different mixtures of solutions of the metal ions and the aminophosphonic acids were taken using the mole ratio, slope ratio and continuous variation methods[6-8].

Preparation of the complexes

Different mixtures of metal and ligand in the mole ratio of 1:1, 1:2 and 1:3 were prepared. Metal (II) acetate crystals were added to a hot aqueous solution of the amino acid.

The hot mixture was stirred for about 5min and filtered. The filtrate was then concentrated by heating in a water bath and left to cool. The resulting crystals

---

**Author for correspondence.*

were recrystallised from an ethanol/water mixture and then dried in a vacuum oven at 70°C for one hour.

All the complexes were stored in a dessicator over calcium chloride. The results of the chemical analysis are summarised in Table 1.

Table 1: Analytical data for some of the metal complexes

Complex	Colour	*D-temp. (°C)	¹Condty (Ω cm⁻¹) *10⁻⁴	Analysis found (²calcd) (%) C	H	N	P	Metal
Cu-N-2-AMPA								
1 · 1.2H_2O	Deep blue	230	3.50	14.31 (14.20)	5.68 (5.91)	10.76 (10.94)	12.07 (12.23)	25.56 (25.19)
1 : 2	V. Deep blue	245	3.00	19.60 (19.40)	5.87 (6.00)	15.00 (15.10)	16.87 (16.67)	16.92 (17.20)
1 : 3	Deep blue	260	-	17.82 (20.55)	5.64 (6.28)	13.97 (15.98)	18.12 (17.69)	14.08 (12.17)
Co-N-3-AMPA								
1 : 2	Violet	260	-	-	-	-	16.87 (16.89)	15.74 (16.08)
Ni-N-3-AMPA								
1 : 1	Light green	226-228	1.25	-	-	-	10.65 (11.78)	22.59 (22.06)
1 : 2	Deep green	230	1.8	-	-	-	16.28 (15.70)	15.56 (15.48)
1 : 3	Deep green	> 260	2.2	-	-	-	16.98 (16.52)	11.12 (10.48)

* = decomposition temperature, 1 = conductivity * 10^{-4}, 2 = calculated

Table 2: Some relevant infrared frequencies (cm^{-1}) for the ligands and the copper (II) complexes.

Ligand	1 : 1 complex	1 : 2 complex	1 : 3 complex	TA
3200 (m)	3100-3400 (v.br, s)	3000-3500 (v.br, s)	3100-3400 (v.br, s)	√ (N-H), NH_2.
3000 (b, s)				√ (N-H), NH_2
2800-2900 (br, s)	2800-2900 (br, s)	2800-2900 (br, s)	2900 (br, s)	√ (C-H)
1550-1620 (m)	1550-1600 (br, s)	1550-1620 (s)	1550-1620 (m, br)	δ (N-H)
1280 (m)	1270 (s)	1270 (s)	1270 (s)	δ (P-O)
1050 (w)	1030-1040 (br)	1040-1050 (m, br)	1040 (m, br)	δ (C-H)

TA = Tentative Assignment
s = strong, m = medium, w = weak, v.br = very broad, br = broad.

Chemical and spectroscopic measurements

The aminophosphonic acids were characterised as described for glycine using phenylisocyanate[10]. Their melting points as well as those of the complexes were determined with a Gallenkamp melting point apparatus.

The infrared spectra of the ligands and complexes were recorded on an SP-300 Pye-Unicam infrared spectrometer in the wavelength range 4000-200cm^{-1} using KBr pellets.

Potentiometric titrations were carried out using a Radiometer RTS 822 recording titration system. The visible electronic spectra of the complexes in water were obtained on a Pye-Unicam SP8-400 UV/visible spectrophotometer.

Conductivity measurements were carried out in water using the YSI model 31 conductivity bridge.

The CHN analysis was done by the microanalytical laboratory of the North London Polytechnic (now University of North London) while the metal ions and phosphorus content were determined with a Link Analytical XR300 energy dispersive X-ray fluorescence spectrometer at the Obafemi Awolowo University.

Table 3: Some relevant infrared frequencies for N-3-AMPA and its Nickel (II) complexes.

N-3-AMPA	1 : 2 Complex	1 : 3	Assignment
-	3400-3500	-	ν-(HOH)
	2700-3400 (s, v.br)	2700-3400 (s, v.br)	ν (N-H) NH_2 ν (C-H)
2800-2900 (v. s, br)			ν (N-H) NH_2 ν (C-H)
2800-2900 (v.s, br)	2700-3400 (s, v.br)	2700-3400 (s.v.br)	ν (N-H), NH_2; ν (O-H), P-OH ν (C-H), NH_2
1620	1600	1600	δ (N-H)
1550	1550	1550	
1450	1400 (sh, m)	1400 (sh, m)	δ (C-H)
1350 (sh, m)	1350, (w)	1350 (w)	δ (C-H)
1280 (sh, m)	1280 (sh, m)	1280 (sh, m)	ν (P-O)
1050-1100 (s, br)	1050-1100 (s, br)	1050-1100 (s, br)	ν (P-O)
980, 850	970	970	δ (O-H)
	500 (s, br)	500 (s, br)	ν (Ni-N)
	420 (m)	420 (m)	
	370 (m)	370 (m)	
	320 (m)	320 (m)	δ (Ni-N)

s = strong, v.br = very broad, m = medium, sh = sharp, w = weak.

Table 4: Relevant infrared frequencies for N-1-APA and its copper (II) complex

N-1-APA	Copper (II) complex	Assignment
	3300, 3450 (s, br)	ν-(HOH) ν-(N-H), NH_2
3300 (sh, m)		
3000 (m)	-	ν-(N-H), NH_2
2700-2800 (m, br)		ν-(O+H), P-OH
1600 (w)	1600 (s)	δ (N-H)
1430 (m, br)		
1400 (m)	1400 (s, br)	δ (C-H)
1300 (s, m)	1250	ν-(P=O)
1050-1150 (m, br)	900-1000 (w, br)	ν-(P-O)
950 (w)	-	δ (O-H)
400, 300 (sh, m)	-	ν (M-O)

s = strong, v. br = very broad, m = medium, sh = sharp, w = weak.

RESULTS AND DISCUSSION.

The pronounced colour change (a result of excitation of electrons from lower to higher energy levels) in the metal complexes when compared to the aquo metal ion alone and the shift of the electronic spectral bands of N-AMPA could be attributed to chelation. Changes in the vibrational frequency observed in the infrared spectra of the complexes when compared with those of ligands suggest coordination of the metal ion to the ligands. These vibrational changes are due to the stretching and bending vibrations of N-AMPA which are perturbed by coordination. The infrared band assignments (Tables 2-4) and other analytical data on the metal complexes (Table 1) indicate that the terminal amino group (NH_2) is one of the coordinating sites. The lower frequency of symmetric and asymmetric N-H vibrations can be attributed to the involvement of the amino group (-NH_2) in coordination.

The strong and very broad bands between 3100and 3400cm^{-1} in the infrared spectra of the complexes as against the medium, strong band in the ligands could be attributed to both the stretching N-H frequency of the amino group upon complexation as well as to hydrogen-bonded 0-H of coordinated water molecules.

Involvement of the terminal amino group in the coordination to the metal ion centre is also confirmed by the non-formation of any product when the metal complexes are reacted with phenylisocyanate due to the non-availability of a primary amino group to derivatize with phenylisocyanate.

These findings are not very surprising because terminal amino groups are among the most common metal-binding loci despite their high pk$_a$ and amino nitrogen donors make much larger contributions to the enthalpy of complexation. Also there is the strong ligand field effect of nitrogen.

The non-involvement of phosphonate group in the coordination in the N-AMPA series is demonstrated by the relatively small shift of about 10cm^{-1} in the position of the phosphoryl (P=0) frequency band in the complex relative to the N-AMPA. In some complexes, the band is unaffected. Furthermore, there is no appreciable change in the conductance measurements of the aqueous solutions of the copper(II) complexes in the ratios 1:1 and 1:2, (conductance values are 3.50 and 3.00 x 10^{-4} n^{-1} respectively) since formation of a complex via the phosphonate group should increase the hydrogen ion concentration of the solution. Similarly, for the nickel(II) complexes, conductance values for the 1;1, 1:2 and 1:3 complexes are 1.25, 1.8 and 2.2 x 10^{-4} n^{-1} respectively.

Non-coordination of the phosphonate group has also been observed in a multidendate ligand, N, N- Bis (2-hydroxybenzyl)-ethylenediamine-N,N-bis(methylenephosphonic)-acid, where donor groups such as the phenolate, imino and phosphonate groups are present[11].

However, for the N-APA series, that is the α-aminophosphonic acids, $NH_2(CH_2)_nPO_3H_2$, there is a large shift of 50cm^{-1} in the ν(P=0), (Table 4), and this can be attributed to the participation of the phosphonate group. This further confirms the previous assertion that nitrogen of amino groups is preferentially coordinated where there is a choice between nitrogen and oxygen.

Copper(II) complexes

All the complexes gave rise to one absorption band in the visible region (Figure 1). The weakness of the band is because the electrons are moving from one orbital that is centrosymmetric to another that is also centrosymmetric and this type of transition is normally forbidden.

The absorption spectra of copper(II) complexes of N-AMPA in the visible region are similar to those of copper(II) -amine complexes[12] This is an evidence that supports the binding of nitrogen atom to copper(II) ion.

Figure 1 shows that the absorption maximum of a mixture of copper(II) and N-2-AMPA in the stoichiometric ratio of 1:1 is about 690nm while that of the metal complexes in the metal: ligand mole ratio 1:2 and 1:3 is 670nm. This is to say that the absorption peak of copper(II) ion in the complexes shifts toward shorter wavelengths as coordination number is increased. This agrees with results for other systems[6-9,12] and is indicative of favourable thermodynamic binding (via coordination) between the metal ion and the ligands.

The great disparity between the expected (?) metal composition and that observed experimentally for the 1:3 complex of copper(II) ion suggests that the solid metal complex isolated from the aqueous 1:3 metal: ligand mixture is not in the stoichiometric ratio of 1:3. This can be linked to the fact that axial nitrogens (from the same ligand molecule) are less stable, due to steric effect, compared to when these positions are occupied by water molecules.

There is also the possibility that the complex isolated might be in a 2:3 (metal-ligand) mole ratio since the calculated values for CHN of copper:2-AMPA in the mole ratio 2:3 seem closer to the experimental values, (Table 1).

Cobalt(II) complexes

Absorption bands of cobalt(II) in different mole ratios are of the same shape and at about the same wavelength (Figure 2). The band is at about 530nm wavelength and can be assigned to the highest energy transition $4T_{1g}(F) - - 4T_{1g}(P)$ for octahedral complexes.

The broadness of the band is due to the fact that in octahedral systems, the $4A_{2g}$ level derived from a $t_{2g}^{3}e^{4}$ electronic configuration is usually close to the $4T_{1g}(P)$ level (derived from a $t_{2g}^{5}e^{2}$ configuration) and the transitions to these two levels are close together. Hence the $4T_{1g}(F) - - 4A_{2g}$ transition, being essentially a two-electron excitation, is believed to be so weak that it is completely obscured by the $4T_{1g}(F - - 4T_{1g}(P)$ band occurring at the same frequency.

The similarity in the visible spectra of the 1:1, 1:2 and 1:3 complexes suggests that a single compound is probably formed in solution under the conditions used. The existence of other complexes is not

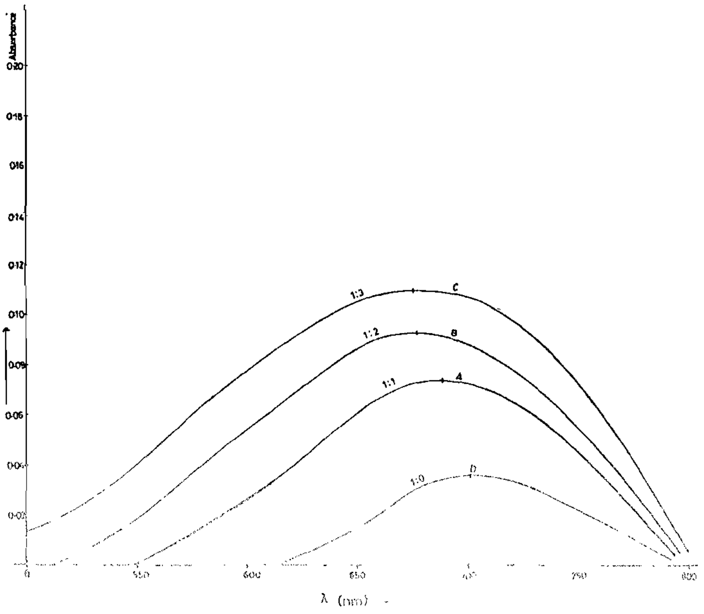


Fig 1: Absorption spectra of solutions containing Copper (II) and N-2-AMPA ions in the ratios 1:1 1:2 and 1:3. The 1:0 curve is due to Copper (II) ion alone

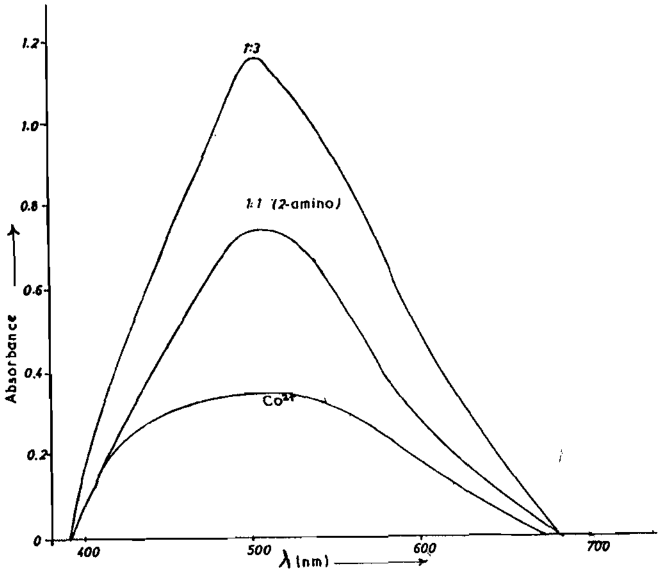


Fig. 2 Absorption spectra of 2 x 10^{-2} mol dm^{-3} cobalt(II) and 2 x 10^{-2} mol dm^{-3} 2-aminomethanephosphonate solutions in the ratios 1:0, 1:1 and 1:3 (path length =4cm).

excluded since the determination of the coordination number and formulae of metal complexes of some systems show that a single method does not reveal the existence of all possible complexes.

Nickel(II) complexes

The hexa-aquonickel(II) complex has its maximum at 720nm with a splitting at about 770nm due to spin-orbit coupling which mixes the $^3T_{1g}$ (F) and ^1E_g states which are very close in energy at the n° value given by six water molecules.

For the nickel(II)-AMPA complexes, the visible spectrum showed bands with maxima at 650nm and 630nm for the nickel(II)-3-AMPA complexes in the ratios 1:2 and 1:3 respectively (Figure 3).

Possible structure of the complexes

Potentiometric studies[13] showed that N-AMPA exist as zwitterions(1) with pk_a ranging from 3.2 to 11.8. However, the acetate ions, $2CH_3COO^-$ (from the metal salt), being a strong conjugate base, mop up the protons on the nitrogens of the amino groups and make them available for coordination.

$$^+NH_3(CH_2)_n{}^+NH_2CH_2PO_3^- \qquad 1$$

Thus there are three potential donor sites. N-AMPA were thus thought to be tridentate ligands with the amino, imino and the phosphonate ends. Coordination through these three sites results in structure (II) which consists of two chelate rings:- two five membered rings for aminoethylaminomethanephosphonic, N-2-AMPA while for n > 2, the ring involving the two nitrogen atoms increases in size.

Although ligands with more chelate rings give more stable complexes, this assumes that the geometry of the ligands and the metal ions allows the coordination of all the donor atoms. The α, ω -

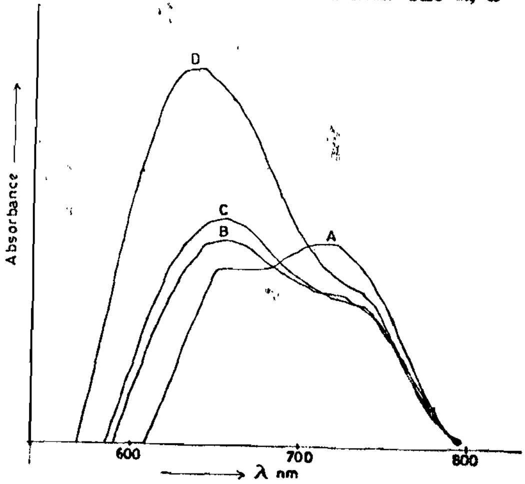
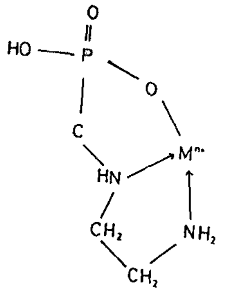


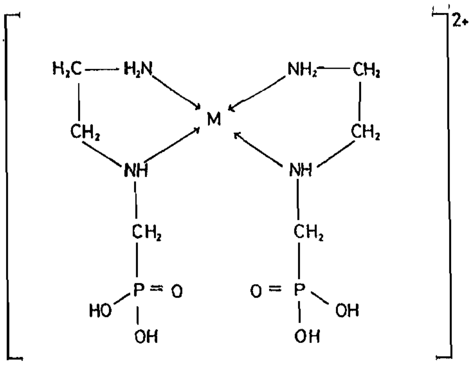
FIG. 3. Absorption spectra of 0.2M Nickel acetate solution(A) and solutions containing nickel and N-3-AMPA ions in ratios of 1:1 (B), 1:2 (C) and 1:3 (D)

amino-alkylaminomethane phosphonic acids used in this work are most likely to have a non-planar zigzag chain just like the α -aminoalkylphosphonic acids found in the literature[14,15]. Hence the coordination of both α and ω-amino groups as well as the phosphonate group in the N-AMPA appears to be sterically impossible. Thus metal complexes of N-AMPA should have the structure IIIa or IIIb. Our findings have shown that the phosphonate group does not participate in the bonding for the reason already given above. Hence structure IIIa is adopted by the metal complex.

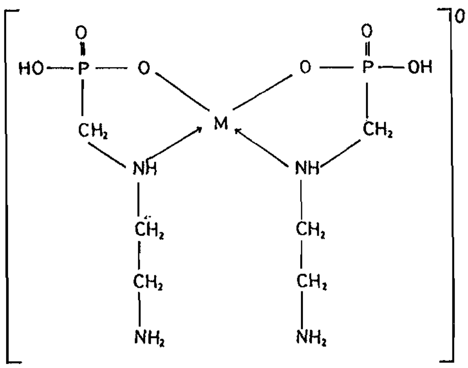
Furthermore, the existence of the copper:2-AMPA in the stoichiometric ratio of 1:3 in solution suggested that these ligands act as bidentate ligands while, for the N-4- and N-6-AMPA, (n=4,6), the mole ratio method gave a 1:4 ratio (Figures 4 and 5) suggesting a unidentate coordination.



II



IIIa



IIIb

The coordination of N-4 and N-6-AMPA with a high mole-ratio of metal-ligand complex of 1:4 agrees with steric consideration. Polydentate coordination of these ligands would result in the formation of 7-membered and 9-membered rings that would be thermodynamically unstable due to steric destabilisation.

With the diaminocarboxylic acids, binding of α- and ω-amino groups was favoured for lower members, n=1,2, while higher members used the carboxyl and α-amino groups[16]. The reason for this is that the higher members yield larger ring sizes when α- and ω-amino groups are used for coordination and this leads to a decrease in stability.

Furthermore, the use of α- and ω-amino groups by the lower members is not surprising because comparison of the values of log k for glycine and

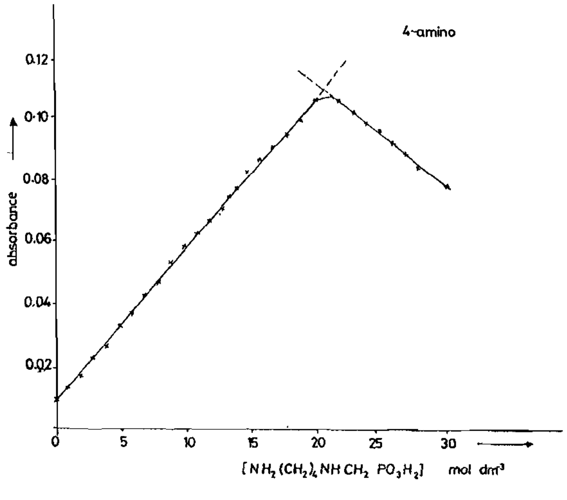


Fig 4. Mole-Ratio Method applied to Copper(II) and N-4-aminomethenephophonate ions, (λ_{max}: 650nm)

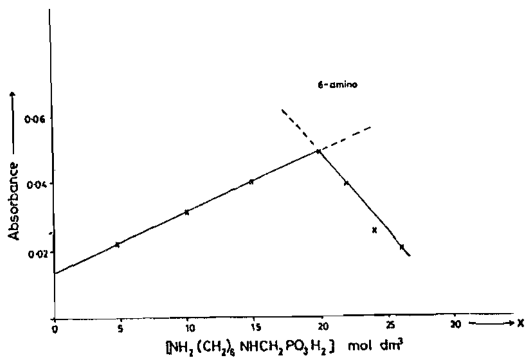


Fig 5 Mole-Ratio Method applied to Copper(II) and N-6-aminomethenephosphonate ions. (λ_{max} 630nm)

ethylenediamine (8.22 and 10.55 respectively) reveals the greater binding power of two amino groups over one amino and one carboxyl group, both possessing five membered rings.

The agreement between the expected and experimental results of elemental analysis for 1:1 and 1:2 complexes of copper (II)-N-2-AMPA suggests that the formulae for the 1:1 and 1:2 complexes are $Cu(H_2O)_2(NH_2CH_2NHCH_2PO_3H_2O)^{2+}$ and $Cu(NH_2CH_2CH_2NH_2CH_2PO_3H_2)^{2+}$ respectively in the solid state. However, in aqueous solution there is the strong possibility of two additional water molecules being coordinated to the metal. The aqueous complexes can thus be formulated as $Cu(H_2O)_4NH_2CH_2CH_2NHCH_2PO_3H_2)^{2+}$ and $Cu(H_2O)_2$-$(NH_2CH_2CH_2NHCH_2PO_3H_2)_2$ respectively.

The 1:2 complex of copper(II)-N-2-AMPA probably has a square planar configuration in the solid state while the octahedrally distorted (tetragonal) configuration will be favoured in aqueous solution.

This is not surprising because the ground state of copper(II) ion in an octahedral field is ^2E_g in six coordinate complexes and this is subject to considerable Jahn-Teller distortion.

This observation is similar to what has been reported for copper (II)-bis ethylenediamine and copper (II)-tetraamine complexes. The two complexes were found to have the square planar configuration in the solid state with the structural formulae $Cu(en)_2$ and $Cu(NH_3)_4^{2+}$ respectively but they are found to have the distorted tetragonal configuration in aqueous solution with the formulae $Cu(H_2O)_2(en)^{2+}$ and $Cu(H_2O)_2(NH_3)_4^{2+}$ respectively.

For the 1:1 complex, the inherent shape of the water molecules present will render the planarity of the molecule sterically impossible, hence a tetrahedral (distorted) geometry is expected.

Therefore, in the absence of suitable crystals for X-ray analysis, Figures 6 and 7 are proposed for the 1:2 copper(II)-N-aminopropane aminomethane-phos-phonate complex in the solid state and in aqueous solution respectively.

CONCLUSION

N-AMPA form complexes with metal ions in solution. The mode of chelation depends on the number of methylene groups. Thus when n=2 or 3, N-AMPA act as bidentate ligands via the two nitrogen atoms of the amino groups.

The coordination becomes monodentate involving only the terminal amino group when n=4 or 6. The phosphonate group was found not to be involved in the coordination.

N-APA, however, coordinates through the phosphonate group and the terminal amino group. The implication of these results is that N-AMPA are potential chelating agents which can be used to detect and estimate metal ions in solution.

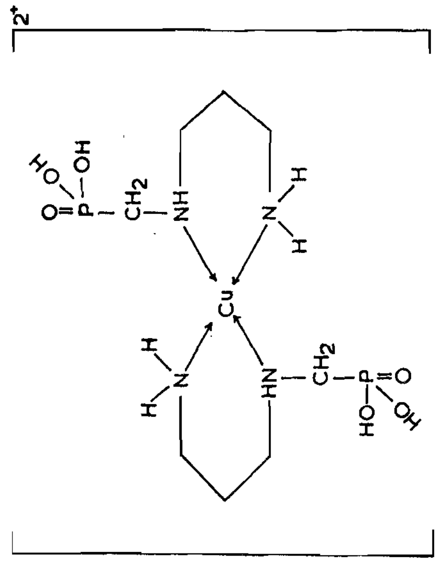


Figure 6 Proposed structure for copper (II)-3-AMPA in the ratio 1:2 in the solid state

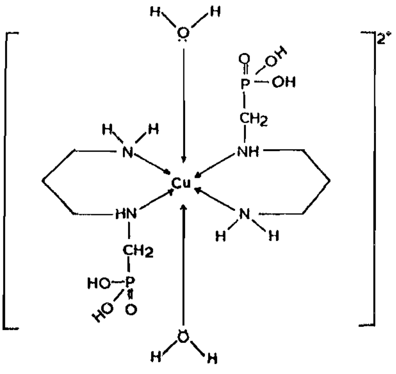


Figure 7 Proposed structure for copper (II)-3-AMPA in the ratio 1:2 in the aqueous solution

REFERENCES

1. Bell, C.F. Principles and Application of Metal Chelation, Clarendon Press, Oxford, 1977.

2. Jagodic, V. and Herak, M.J., J. Inorg. Nucl. Chem., 1970, 32, 1323.

3. Jagodic, V., Herak, M.J., Sipalo, B. and Radosevic, J., J. Inorg. Nucl. Chem., 1971, 33, 365.

4. Cameron, D.G., Hudson, H.R., Ojo, I.A.O. and Pianka, M., Phosphorus and Sulfur, 1988, 39, 139.

5. Cameron, D.G., Hudson, H.R., Ojo, I.A.O. and Pianka, M., Phosphorus and Sulfur, 1988, 40, 183.

6. Gould, R.K. and Vousburgh, W.C., J. Am. Chem. Soc., 1942, 64, 437.

7. Vousburgh, W.C. and Copper, G.R., J. Am. Chem. Soc., 1941, 65, 437.

8. Norman, C. and Doody, E., J. Am. Chem. Soc., 1954, 76, 221.

9. Potts, L.W., Quantitative Analysis-Theory and Practice, p. 442, Harper and Row, New York, 1987.

10. Wild, F., Characterization of organic compounds, 2nd ed., p. 171, Cambridge University Press, 1960.

11. Macmillan, D.T., Murase, I. and Martell, A.E., Inorg. Chem., 1975, 14, 468.

12. Borsook, H. and Thimann, K.V., J. Biol. Chem., 1932, 98, 671.

13. Durosinmi, L.M., Synthesis, characterisation and some properties of aminophosphonic acids, Ph.D. Thesis, Obafemi Awolowo University, Ile-Ife, 1992.

14. Okaya, Y., Acta Crysta., 1966, 20, 712.

15. Glowiak, T. and Sawka-Dobrowoska, W., Acta. Crysta., 1960, 36, k 961.

16. Greenstein, J.P. and Wintz, M., Chemistry of the amino acids, p. 618, John Wiley & Sons, New York, 1961.

accepted 1/8/96
received 26/4/96