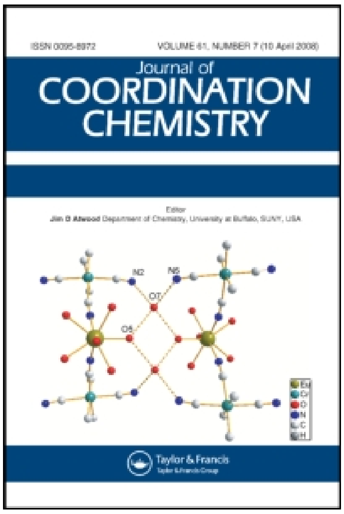

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Syntheses, Spectral, Thermal and Electrochemical Studies of 3-Carboxylacetonehydroxamic Acid and its Iron(Ii), Cobalt(Ii), Nickel(Ii), Copper(Ii) and Zinc(Ii) Complexes

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SYNTHESES, SPECTRAL, THERMAL AND ELECTROCHEMICAL STUDIES OF 3-CARBOXYLACETONEHYDROXAMIC ACID AND ITS IRON(II), COBALT(II), NICKEL(II), COPPER(II) AND ZINC(II) COMPLEXES

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3-Carboxylacetonehydroxamic acid (CAHA) and its iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes were synthesized and characterized by elemental analysis, UV-Vis and IR spectra and magnetic susceptibility. The pK_{a1} and pK_{a2} values of the ligand in aqueous solution were found to be 6.5 ± 0.1 and 8.6 ± 0.1, which correspond to dissociation of carboxyl and hydroxamic protons, respectively. The dianion CAH acts as a tetradentate ligand through the hydroxamate and carboxylate groups and coordinates to the divalent metal ions, forming coordination polymers with a metal-to-ligand ratio of 1 : 1 in the solid state. FTIR spectra and thermal decomposition of the ligand and its metal complexes were recorded and briefly discussed. The electrochemical behavior of the complexes was investigated by square wave voltammetry and cyclic voltammetry at neutral pH. In contrast to the solid state, the iron(II) and copper(II) cations form stable complex species with a metal-to-ligand ratio of 1 : 2 in solution. The iron(II), cobalt(II) and nickel(II) complexes show two-electron irreversible reduction behavior, while the copper(II) and zinc(II) complexes undergo quasi-reversible and reversible electrode reactions, respectively. The stability constants of the complexes were determined by square wave voltammetry.

Keywords: 3-Carboxylacetonehydroxamic acid; Metal complexes; Square wave voltammetry; Cyclic voltammetry

INTRODUCTION

Hydroxamic acids are both weak acids and bases [1] and during deprotonation they can behave either as O- or N-acids yielding the respective hydroxamate anion. Hydroxamate species are of biochemical interest owing to their specific role as Fe-chelating functional groups in siderophores [2]. Hydroxamic acids also have important functions

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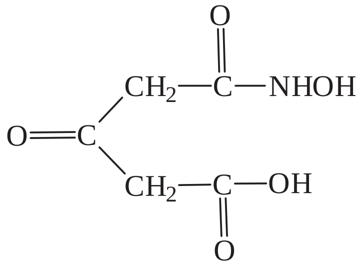

FIGURE 1 Molecular structure of CAHA.

as inhibitors of enzymatic activity by coordinating the metal center of enzymes [3]. Complexation behavior of simple hydroxamic acids has been studied both in solution and in the solid state [4–19]. It was concluded that hydroxamic acids usually act as bidentate (O,O′) chelates through the carbonyl and deprotonated hydroxyl oxygen atoms, whereas coordination of the nitrogen atom of the hydroxamate moiety has not been reported so far. Metal complexes of hydroxamic acids are also used as models for understanding the reactivity of the hydroxamate group in biological systems.

As part of our interest in the synthesis, spectral and thermal characterization of new hydroxamic acids and their metal complexes [20–22], in this paper we report the synthesis, spectral and electrochemical behavior of 3-carboxylacetonehydroxamic acid (CAHA) (Fig. 1) and its iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes.

EXPERIMENTAL

Materials and Methods

Starting materials were purchased from commercial suppliers and used without further purification. Electronic spectra were measured on a Unicam UV2 spectrophotometer in NMF solutions of the complexes in the 200–900 nm range. IR spectra were recorded on a Mattson FTIR spectrophotometer as KBr pellets in the frequency range 4000–300 cm^{-1}. Magnetic susceptibility measurements were carried out using a Sherwood Scientific MXI model Gouy magnetic balance at room temperature. The C, H and N contents were determined at TUBITAK Marmara Research Center (Gebze). Thermal analysis curves (TG, DTA and DTG) were obtained using a Rigaku TG8110 thermal analyzer in a flowing nitrogen atmosphere. A sample size of 5–10 mg and a heating rate of 10°C min^{-1} were used.

The fully protonated form of CAHA was obtained by acidifying an aqueous solution of K_2CAH and dissociation constants (pK_a) of CAHA were determined by alkalimetric titration of three samples (1×10^{-3} M) at 25.0 ± 0.1°C using a Jenway 3040 model ion analyzer.

Electrochemical measurements were performed with a Metrohm 757 VA Computrace model voltammetric analyzer. A cell with a three-electrode setup was used: a hanging mercury drop electrode (working electrode), Pt wire (auxiliary) and Ag/AgCl (reference). SWV voltammograms were taken with voltage step 0.004 V, amplitude 50 mV, scan rate 200 mVs^{-1} and frequency 50 Hz, while CV voltammograms were recorded from 0.15 to–1.40 V employing scan rates between 0.01 and 1 $V s^{-1}$. In DCP polarograms, the potential step and drop time were chosen as 0.004 V and 1 s, respectively. A 0.10 M KNO_3 solution was used as supporting electrolyte. All solutions were purged with pure and water-saturated nitrogen for 5 min prior to each voltammetric run.

Synthesis of the Potassium Salt of CAHA

$NH_2OH \cdot HCl$ (8.34 g, 120 mmol) dissolved in 30 mL methanol was neutralized with an equimolar amount of KOH dissolved in 30 mL methanol and the solution was filtered to remove the precipitated KCl. Dimethyl-1,3-acetonedicarboxylate (10.45 g, 60 mmol) dissolved in methanol was mixed with this NH_2OH solution and stirred for 15 min. A solution of KOH (6.7 g, 120 mmol) dissolved in 30 mL methanol was added to the reaction mixture dropwise and the solution was stirred until a pale-yellow precipitate formed. The potassium salt (K_2CAH) was filtered, washed with acetone and dried at 50°C.

Synthesis of the Metal Complexes

The complexes were prepared by addition of 20 mL of an aqueous solution of K_2CAH (0.5 g, 2 mmol) to 20 mL of aqueous solutions of metal salts ($FeSO_4 \cdot 7H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$) (2 mmol). After stirring for a short time, the solutions yielded the solid metal complexes, which were filtered, washed with water several times and dried in air.

RESULTS AND DISCUSSION

Synthesis and Properties

The ligand was prepared as its potassium salt (potassium 3–carboxylateacetonehydroxamate, K_2CAH) by direct reaction of dimethyl-1,3-acetonedicarboxylate with hydroxylamine and potassium hydroxide. $K_2CAH \cdot 0.5H_2O$ was found to be somewhat hygroscopic and its color changed from yellow-brown to dark brown when exposed to air for a long time. All complexes of the CAH ligand were obtained in good yields (over 75%) and the elemental analyses confirmed the proposed formula (Table I). The molar ratio of M:ligand in the complexes is 1 : 1. The complexes contain ligand and lattice water molecules as estimated by TG and DTA. As well as K_2CAH, the metal complexes are stable in air and decompose at temperatures given in Table I. The complexes do not dissolve in any common solvent, except NMF (*N*-methylformamide). Therefore, preparation of crystals of the complexes failed. Zinc(II) and copper(II) complexes readily dissolve in NMF, while the iron(II), cobalt(II) and nickel(II) complexes are slightly soluble in NMF. The insolubility of the complexes in common solvents suggests a polymeric structure through carboxylate and hydroxamate groups.

TABLE I Analytical data for K_2CAH and its metal complexes

Compound	*Color*	*Decomp. P.* (°C)	*F.Wt.*	*Anal. (Found (calcd.)* (%)			*Yield* (%)
				C	*H*	*N*	
$K_2C_5H_5NO_5 \cdot 0.5H_2O$ K_2CAH	Yellow-brown	140	246.3	24.6 (24.4)	2.0 (2.4)	5.4 (5.7)	75
$[Fe(CAH)(H_2O)_2]$	Red-brown	170	251.0	22.2 (22.5)	2.9 (3.3)	5.5 (5.6)	82
$[Co(CAH)(H_2O)_2] \cdot 0.5H_2O$	Pink-brown	185	263.1	22.9 (22.8)	3.8 (3.8)	5.7 (5.3)	76
$[Ni(CAH)(H_2O)_2] \cdot 0.5H_2O$	Pale brown	182	262.8	22.8 (22.8)	3.4 (3.8)	5.7 (5.3)	78
$[Cu(CAH)(H_2O)] \cdot 0.5H_2O$	Green-brown	180	240.7	24.2 (24.1)	2.8 (3.2)	6.0 (5.6)	87
$[Zn(CAH)(H_2O)_2] \cdot 0.5H_2O$	Pale orange	190	269.5	23.1 (22.3)	3.1 (3.7)	5.9 (5.2)	91

Spectral and Magnetic Characterization

Table II summarizes selected IR data of the free ligand and the title complexes. The ligand shows weak absorption bands at 3420 and 3155 cm^{-1} due to the $\nu(OH)$ absorption of the NH group, the lattice and ligand water molecules, respectively. The strong absorption bands at 1643 and 1600 cm^{-1} are characteristic for the ketonic and hydroxamic carbonyl groups, respectively, while the absorption bands of the $\nu_{asym}(COO)$ and $\nu_{sym}(COO)$ stretching vibrations occur at 1554 and 1393 cm^{-1}, respectively. In the metal complexes, the broad bands in the range 3350–3420 cm^{-1} are attributed to the $\nu(OH)$ absorption vibration of the water molecules with the hydrogen bond. The NH absorption bands shifted to higher frequency, while the hydroxamate absorption bands display a significant shift to lower frequency with respect to the free ligand, indicating coordination of the hydroxamate carbonyl oxygen in addition to the negatively charged oxygen of the same group [23]. The strong bands at 1520 and 1390 cm^{-1} are attributed to the $\nu_{asym}(COO)$ and $\nu_{sym}(COO)$ of the carboxylate group of CAH, respectively. The $\Delta\nu$ ($\nu_{asym} - \nu_{sym}$) values observed for metal complexes are used to determine the mode of coordination of carboxylate groups, comparing them with the $\Delta\nu$ values of parent ligands [24,25]. The complexes exhibit $\Delta\nu$ values significantly less than the parent ligands [24]. The $\Delta\nu$ values indicate bidentate coordination of the carboxylate group of CAH (Table II). These observations clearly indicate that the ligand behaves as a tetratendate ligand through the hydroxamate (O,O′) and carboxylate (O,O′) groups.

Electronic spectral data are also listed in Table II. K_2CAH displays an intense and complex band in the UV region which exhibits three principal maxima centered at 250, 309 and 354 nm due to $\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. In addition to the intraligand transitions in the range 240–360 nm, the metal complexes exhibit broad bands with low intensity in the 400–800 nm range, which are assigned to d–d transitions of octahedral coordination. The Zn(II) complex displays only transitions of CAH in the UV region. The metal complexes are high spin and the room temperature magnetic moments are in good agreement with octahedral coordination (Table II).

Thermal Analysis

The thermal decomposition behavior of $K_2CAH \cdot 0.5H_2O$ and its metal complexes under nitrogen was followed up to 1000°C by DTA, TG and DTG. Thermoanalytical data including decomposition ranges, DTA_{max} and mass loss values are summarized in Table III. $K_2CAH \cdot 0.5H_2O$ dehydrates at 85°C and decomposes between 150

TABLE II Spectral[a] and magnetic data for K_2CAH and its metal complexes

Compound	*ν(OH)*	*ν(NH)*	*ν(CO) ketonic*	*ν(CO) hydroxamic*	$\nu_{asym}(CO)$ *carboxyl*	$\nu_{sym}(CO)$ *carboxyl*	$\Delta\nu^b$	*ν(CN)*	λ_{max} *(nm)*				$\mu_{eff.}^c$ *(BM)*
									L			*d–d*	
$K_2C_5H_5NO_5 \cdot 0.5H_2O$	3420 (b)	3155 (sh)	1643 (vs)	1610 (s)	1554 (vs)	1393 (s)	161	1310 (m)	250	309	354	–	–
$[Fe(CAH)(H_2O)_2]$	3417 (b)	3230 (sh)	1632 (vs)	1575 (s)	1518 (vs)	1415 (s)	103	1260 (m)	253	306	357	481	4.72 (4.90)
$[Co(CAH)(H_2O)_2] \cdot 0.5H_2O$	3360 (b)	3235 (sh)	1633 (vs)	1591 (s)	1520 (vs)	1389 (s)	131	1257 (m)	244	303	357	470	3.55 (3.87)
$[Ni(CAH)(H_2O)_2] \cdot 0.5H_2O$	3357 (b)	3200 (sh)	1626 (vs)	1591 (s)	1516 (vs)	1389 (s)	127	1256 (m)	251	308	359	620	2.59 (2.83)
$[Cu(CAH)(H_2O)] \cdot 0.5H_2O$	3420 (b)	3215 (sh)	1634 (vs)	1573 (s)	1531 (vs)	1394 (s)	137	1263 (m)	256	313	364	697	1.61 (1.73)
$[Zn(CAH)(H_2O)_2] \cdot 0.5H_2O$	3415 (b)	3256 (sh)	1628 (vs)	1589 (s)	1518 (vs)	1383 (s)	135	1254 (m)	255	307	352	–	Diamagnetic

[a] IR frequencies in cm^{-1}. vs: very strong; s: strong; m: medium; sh: shoulder; b: broad; [b] $\Delta\nu$ ($\nu_{asym} - \nu_{sym}$); [c] spin-only values in parentheses.

TABLE III Thermoanalytical data for K_2CAH and its metal complexes

Compound	*Temp. range* (°C)	DTA_{max} (°C)[a]	*Mass loss* (%)		*Total mass loss* (%)		*Solid residue*
			Found	*Calcd.*	*Found*	*Calcd.*	
$K_2C_5H_5NO_5 \cdot 0.5H_2O$	35–125	85(+)	3.5	3.6			
	150–500	275(+)	58.0	58.2	61.5	61.8	K_2O
$[Fe(CAH)(H_2O)_2]$	40–131	92(+)	14.3	14.4			
	135–715	174(−), 598(+)	57.3	57.0	71.6	71.4	FeO
$[Co(CAH)(H_2O)_2] \cdot 0.5H_2O$	43–140	85(+), 127(+)	17.5	17.1			
	145–650	272(−), 536(+)	53.4	54.4	70.9	71.5	CoO
$[Ni(CAH)(H_2O)_2] \cdot 0.5H_2O$	35–151	97(+), 137(+)	17.4	17.1			
	155–660	303(−), 462(+)	54.9	54.5	72.3	71.6	NiO
$[Cu(CAH)(H_2O)] \cdot 0.5H_2O$	35–108	80(+)	11.2	10.8			
	110–885	237(−), 483(+)	56.1	57.3	67.3	68.1	CuO
$[Zn(CAH)(H_2O)_2] \cdot 0.5H_2O$	40–160	74(+), 115(+)	16.5	16.7			
	165–800	337(+), 600(+)	48.9	53.1	65.4	69.8	ZnO

[a] (+): Endothermic, (−): exothermic.

and 500°C. The DTA, TG and DTG curves clearly indicate that the metal complexes exhibit similar thermal decomposition behavior. The first stage of decomposition corresponds to the dehydration of the complexes. The iron(II) and copper(II) complexes give only one DTA peak at 92 and 80°C, respectively, due to the endothermic removal of two ligand water molecules, whereas the DTA curves of the other metal complexes containing both lattice and ligand water molecules show two endothermic peaks. From these findings, it is evident that the lattice and ligand water molecules are lost at different temperatures. The mass loss values for the dehydration stages are consistent with the calculated values (Table III). In contrast to the acetylsalicylhydroxamic acid complexes [21], the anhydrous CAH complexes are not stable and continue to decompose at higher temperatures and the second stage shows the overall decomposition of the complexes. Degradation of the CAH moiety of the metal complexes seems to be a complicated process with a continuous mass loss, resulting in the formation of the corresponding metal oxides as the end products at around 600 to 800°C. The total mass losses agree well with the calculated values, indicating the formation of the metal oxides as the final residue. However, the significant difference between the experimental and calculated mass loss values of the zinc complex may be due to the formation of an oxygen-deficient zinc oxide.

Dissociation Constants

In the acid form, CAHA is a diprotic acid owing to the presence of hydroxamic and carboxyl protons and the dissociation constants of CAHA can be estimated from the titration data within the pH range 3–11. Two readily detectable proton dissociations were observed and the pK_{a1} and pK_{a2} values were found to be 6.5 ± 0.1 and 8.6 ± 0.1, which correspond to dissociation of the carboxyl and hydroxamic protons, respectively. The hydroxamic acid dissociation constant ($pK_{a2} = 8.6$) falls in the normal range ($pK_a = 7–11$) for hydroxamic acids [23].

Electrochemical Behavior

Electrochemical studies were performed in aqueous solutions for the M(II)/CAH system using square wave voltammetry (SWV) and cyclic voltammetry (CV). Preliminary experiments demonstrated that pH $\cong 7$ is necessary for obtaining clear voltammograms and well-defined E_p values for the ligand and all of the metal complexes investigated. The iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of CAH were generated in situ by a stepwise addition of 100 µL ligand (1×10^{-3} M) to a 5.40×10^{-5} M solution of metals in a 0.10 M KNO_3 solution. The representative SWV voltammograms of the CAH ligand and the copper(II) ion with and without CAH are shown in Fig. 2. The addition of the ligand results in a decrease in the peak currents of the metals, but an increase in the peak currents of the ligand and the metal complexes. The observations show that the metal-to-ligand mole ratio is 1 : 1 in the cobalt(II), nickel(II) and zinc(II) complexes, but 1 : 2 in the iron(II) and copper(II) complexes. The results indicate that the iron(II) and copper(II) ions are coordinated by two CAH ligands forming the stable $[ML_2]^{2-}$ complex species in solution, although they are isolated as the solid complexes with a metal-to-ligand mole ratio of 1 : 1.

Typical CV voltammograms of the M(II)/CAH system are presented in Fig. 3. In the CV, one well-defined cathodic peak was observed for the iron(II), cobalt(II) and nickel(II) complexes. At higher scan rates, any anodic peak does not appear and therefore reduction of these complexes proceeds in an irreversible two-electron single step. Because of the small difference between the anodic and cathodic peak potentials, it was suggested that the electrode reaction of the zinc(II) complex is reversible. The CV

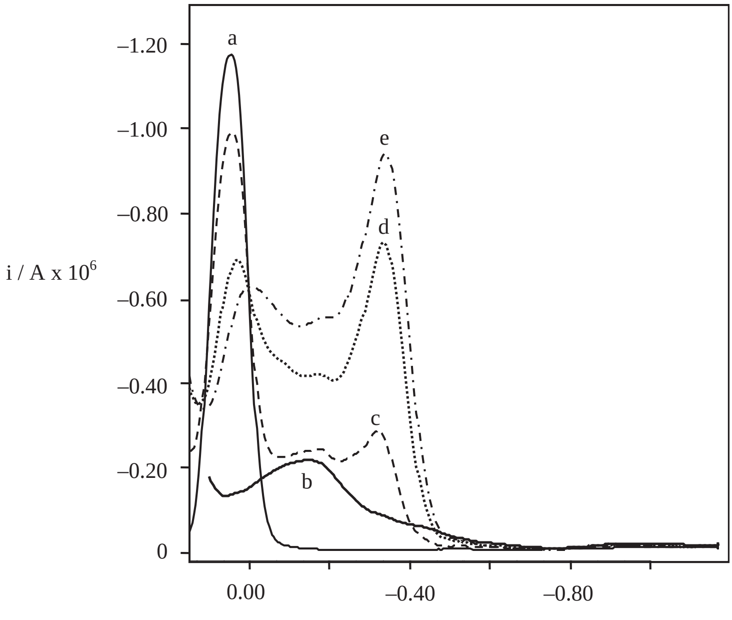

FIGURE 2 SWV voltammograms at neutral pH: (a) 5.40×10^{-5} M Cu^{2+}; (b) K_2CAH (5×10^{-5} M); (c) a + b (2×10^{-5} M); (d) a + b (4×10^{-5} M); (e) a + b (7×10^{-5} M).

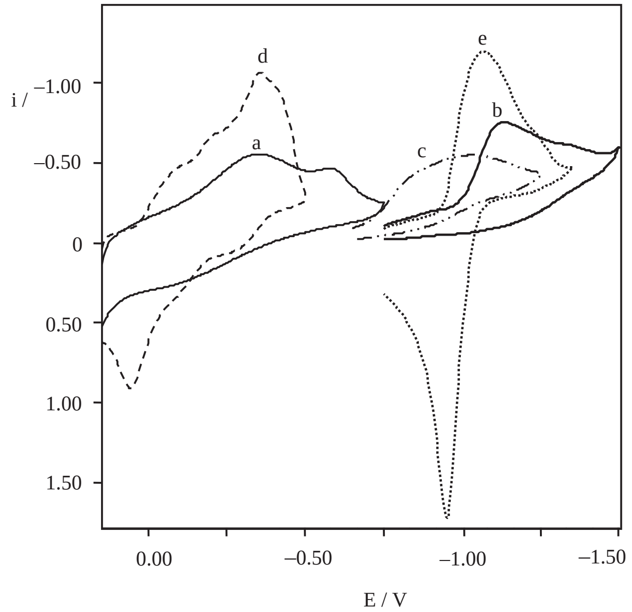

FIGURE 3 CV voltammograms of the metal–CAH complexes with (a) iron(II); (b) cobalt(II); (c) nickel(II); (d) copper(II) and (e) zinc(II) at the ten-fold excess of the ligand relative to metal ions and neutral pH (scan rate = 100 mV s − 1).

TABLE IV Voltammetric data and stability constants for the metal complexes

Complex	*M : L mole ratio*	*E_p–M(II) (mV)*	*E_p–complex (mV)*	*αn*	*logβ*
$[Fe(CAH)(H_2O)_2]$	1 : 2	−1290	−376	0.43	9.11
$[Co(CAH)(H_2O)_2] \cdot 0.5H_2O$	1 : 1	−1210	−1070	0.61	4.90
$[Ni(CAH)(H_2O)_2] \cdot 0.5H_2O$	1 : 1	−989	−810	0.62	15.23
$[Cu(CAH)(H_2O)] \cdot 0.5H_2O$	1 : 2	44	−346	0.50	5.64
$[Zn(CAH)(H_2O)_2] \cdot 0.5H_2O$	1 : 1	−967	−1020	1.51	5.01

of the copper complex shows three redox couples due to the free metal, the free ligand and the complex. The most negative potential with a small anodic peak corresponds to the copper(II) complex. The CV experiments at different scan rates produced the same results, indicating that the copper(II)–CAH complex gives a quasi-reversible electrode reaction due to a slow electrochemical reaction or a slow chemical reaction such as complex dissociation following a reversible electron transfer [26].

The stability constants were determined with DeFord and Hume expressions [27] and the Lingane method [28]. *αn* values of the metal complexes were estimated using the Heyrovski–Ilkoviç equation from direct current polarograms (DCP) [29]. The voltammetric data together with the stability constants are summarized in Table IV. The *αn* values in Table IV are in good agreement with the observations obtained from the CV voltammograms.

On the basis of the experimental data the structure of the metal complexes in solid state are suggested to be polymeric as illustrated in Fig. 4. The CAH acts as tetradentate ligand through the hydroxamate and carboxylate groups and coordinates to the

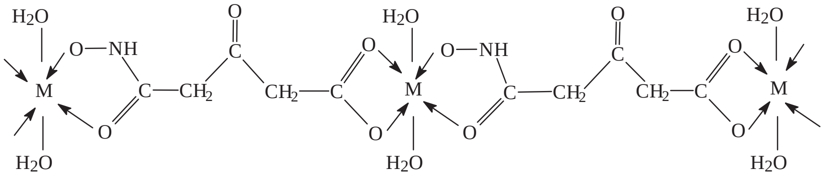

FIGURE 4 The proposed structure of the polymeric metal complexes.

divalent metal ions, forming the equatorial plane of an octahedron with water molecules occupying the axial positions. The copper(II) complex has only one aqua ligand and its coordination geometry may be suggested as a trigonal bipyramid. Of course, the structure of the metal complexes could be determined by single crystal X-ray diffraction, but the complexes do not dissolve in common solvents and attempts to prepare crystals of the complexes have therefore failed.

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References

[1] L. Bauer and O. Exner, *Angew. Chem. Int. Ed. Engl.* **13**, 376 (1974).
[2] A.M. Albrecht-Gary and A.L. Crumblis, In: A. Sigel and H. Sigel (Eds.), Iron Transport and Storage in Microorganisms, Plants and Animals (M. Dekker, New York, 1998), Vol. 35, p. 239.
[3] D.A. Brown, H. Bogge, R. Coogan, D. Doocey, T.J. Kemp, A. Muller and B. Neumann, *Inorg. Chem.* **36**, 1674 (1996).
[4] D.A. Brown, D. Mckeith and W.K. Glass, *Inorg. Chim. Acta* **35**, 5 (1979).
[5] C.P. Brink and A.L. Crumblis, *Inorg. Chem.* **24**, 4708 (1984).
[6] M.T. Caudle and A.L. Crumblis, *Inorg. Chem.* **33**, 4077 (1994).
[7] A. Evers, R.D. Hancock, A.E. Martell and R.J. Motekaitis, *Inorg. Chem.* **28**, 2189 (1989).
[8] P.C. Parekh, S.K. Manon and Y.K. Agrawal, *J. Chem. Soc., Perkin Trans.* **II**, 1117 (1989).
[9] B. Kurzak, H. Kozlowski and E. Farkas, *Coord. Chem. Rev.* **114**, 169 (1992).
[10] E.M. Khairy, M.M. Shoukry, M.M. Khalil and M.M.A. Mohamed. *Transition Met. Chem.* **21**, 176 (1996).
[11] E.C. O'Brien, S.L. Roy, J. Levaillain, D. Fitzgerald and K.B. Nolan, *Inorg. Chim. Acta* **266**, 117 (1997).
[12] J.N. Nwabueze, *Transition Met. Chem.* **22**, 123 (1997).
[13] E. Farkas, E. Kozma, M. Pethö, K.M. Herlihy and G. Micera, *Polyhedron* **17**, 3331 (1998).
[14] A. Dessi, G. Micera, D. Sanna and L. Strinna-Erre, *J. Inorg. Biochem.* **48**, 27 (1992).
[15] B. Kurzak, D. Kroczewska and J. Jezierska, *Polyhedron* **17**, 1831 (1998).
[16] S. Liu and S. Gao, *Inorg. Chim. Acta* **282**, 149 (1998).
[17] E. Farkas, E.A. Enyedy and H. Csoka, *Polyhedron* **18**, 2391 (1999).
[18] E. Farkas, E.A. Enyedy, G. Micera and E. Garribba, *Polyhedron* **19**, 1727 (2000).
[19] F. Dallavalle, G. Folesani, A. Sabatini, M. Tegoni and A. Vacca, *Polyhedron* **20**, 103 (2001).
[20] V.T. Yilmaz and F. Yilmaz, *Transition Met. Chem.* **24**, 726 (1999).
[21] V.T. Yilmaz and F. Yilmaz, *Thermochim. Acta* **348**, 139 (2000).
[22] F. Yilmaz and V.T. Yilmaz, *Synth. React. Inorg. Met-Org. Chem.* **31**, 1421 (2001).
[23] B. Chatterjee, *Coord. Chem. Rev.* **26**, 281 (1978).
[24] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th Edn. (John Wiley & Sons, New York, 1997), Part B, p. 60.
[25] G.B. Deacon and R.J. Phillips, *Coord. Chem. Rev.* **33**, 227 (1980).
[26] M.A. Santos, M. Gaspar and M.L. Goncalves, *Electroanalysis* **12**, 66 (2000).
[27] D. Deford and D.H. Hume, *J. Am. Chem. Soc.* **73**, 532 (1951).
[28] D.R. Crown, Polarography of Metal Complexes (Academic Press, London, 1969), p. 56.
[29] A.J. Bard and L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications (John Wiley & Sons, New York, 1980), pp. 163–172.