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POTENTIOMETRIC STUDIES, SYNTHESIS AND CHARACTERIZATION OF MIXED-LIGAND COMPLEXES OF COPPER(II), NICKEL(II), COBALT(II) AND MANGANESE(II) WITH N-(2-ACETAMIDOIMINODIACETIC) ACID AS THE PRIMARY LIGAND AND HISTIDINE AS THE SECONDARY ONE

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ABSTRACT

The formation equilibria of new ternary mixed-ligand complexes of copper(II), nickel(II), cobalt(II), and manganese(II) with N-(2-acetamidoiminodiacetic) acid (H₂ADA) as the primary ligand and histidine (His) as the secondary one were investigated. The formation constants of these complexes have been determined at 25.0 °C in 0.3 M aqueous Na₂SO₄ solution. They show that the ternary complexes are more stable than the corresponding binary ones. The ternary complexes have been synthesized and were characterized using elemental analyses, molar conductance, IR spectra, magnetic measurements as well as electronic and ESR spectra. The spectral results support the binding of H₂ADA and histidine with, respectively, the NOO and NO sites, to copper(II), cobalt(II), and manganese(II) providing an octahedral geometry, while nickel(II) is bonded to the same ligands in a bidentate manner by the OO and NO donor groups giving a square-pyramidal complex. The other axial sites are occupied by OH⁻ or H₂O groups. Magnetic and ESR data indicate that cobalt(II) and manganese(II) adopt a high-spin configuration in the complexes and also show that the metal ions do not undergo any change in the oxidation state.

INTRODUCTION

It is well established that ternary complexes play a decisive role in the activation of enzymes and also in the storage and transport of active substances through biological membranes^{1,2}. Ternary complexes containing an amino acid as a secondary ligand are of significance as they are not only potential models for enzyme-metal ion substrate complexes, but also are related to copper(II) mixed amino acids complexes, such as the ones containing L-histidine and L-threonine, which occur³ to a significant extent among the copper(II) mixed amino acid complexes found in human serum^{4,5}. Furthermore, the considerable biological activity of N-(2-acetamidoiminodiacetic) acid provided a reasonable inducement for studying ternary complexes of this ligand with numerous other ligands.

In the present paper we report the determination of the formation constants of some copper(II), nickel(II), cobalt(II), and manganese(II) complexes with two biologically active ligands, N-(2-acetamidoiminodiacetic) acid and histidine (Fig. 1), in addition to the synthesis and characterization of the same complexes.

EXPERIMENTAL

All chemical reagents and solvents used were Fluka products and were used without purification.

Physical Measurements

Potentiometric titrations were performed in the pH (concentration) mode, using a Tacussel PHN 81 pH meter calibrated with standard buffer solutions. The conductivity values were determined at 25 °C using a Tacussel CD 810 conductivitymeter. Elemental analyses were carried out at the Central Service of Analysis, CNRS, Vernaison (France). Decomposition points were measured using a IA 9000 digital melting point apparatus. IR spectra were recorded from 4000-400 cm^{-1} on a FTS-7 Biorad Fourier transform spectrometer and KBr pellets were employed throughout. The electronic spectra of the complexes were obtained by mounting Nujol mulls on filter paper, while the solution spectra were run in freshly doubly distilled water; a Perkin Elmer lambda 9 spectrophotometer was used for these measurements. The electron spin resonance spectra were recorded with an E.9 X-band Varian spectrometer using DPPH as a field marker. Magnetic susceptibilities were measured on a B-SU 10 Bruker magnetic balance calibrated with $\text{Hg}[\text{Co}(\text{SCN})_4]$ and correcting the experimental values for diamagnetism⁶.

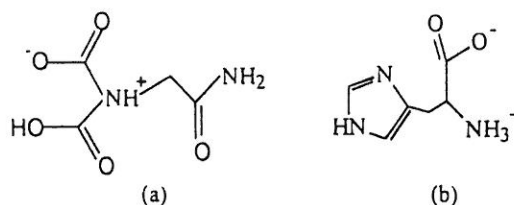


Fig. 1. Structure of the Ligands (a) H₂ADA and (b) Histidine

Potentiometric Titrations

Potentiometric titrations of different M^{2+} -H₂ADA and/or histidine mixtures in 1:1, 1:1:1 or 1:1:2 molar ratios (10^{-3} M for each) were performed at 25.0 ± 0.1 °C and 0.3 M (Na₂SO₄) ionic strength. Standardised carbonate-free NaOH solutions were used. In all cases, the total volume was kept constant at 50 mL. The solutions titrated were as follows: (a): H₂ADA + Na₂SO₄, (b): histidine + Na₂SO₄, (c): metal ion + H₂ADA + Na₂SO₄, (d): metal ion + histidine + Na₂SO₄, and (e): metal ion + H₂ADA + histidine + Na₂SO₄.

Determination of the Formation Constants

The protonation constants of the ligands were determined under the same experimental conditions as for the determination of the stability constants of the binary and ternary complexes. The calculations were performed using the computer program SIRKO⁷. The model selected was that which gave the best statistical fit and proved chemically consistent with the titration data.

General Method of the Preparation of Complexes

An EtOH solution (10 mL) containing 10 mmol each of the metal salt [CuCl₂·2H₂O (1.7048 g), NiCl₂·6H₂O (2.73 g), CoCl₂·6H₂O (2.37 g) and MnCl₂·4H₂O (1.97g)] was added to 50 mL of an EtOH-H₂O solution (50% by volume) containing 10 mmol (1.9016 g) of the ligand H₂ADA. To this mixture was added slowly with stirring an EtOH-H₂O solution (50 mL) containing 20 mmol (3.1032 g) of histidine. Since the solubility of the free acid H₂ADA and the amino acid histidine in EtOH-H₂O mixture is very low, a few drops of 0.2 M NaOH solution were added until the pH of the H₂ADA and histidine solutions attained the values 6 and 9, respectively. After stirring the mixture for four hours, the precipitates formed were filtered, washed several times with ethanol and dried *in vacuo* over P₄O₁₀. All the complexes isolated are soluble in water except for the manganese(II) complex which is fairly soluble in DMF and DMSO and insoluble in all other usual solvents.

RESULTS AND DISCUSSION

Formation Constants

Representative titration curves obtained for the different ternary systems according to the sequence described in the experimental section are displayed in Figure 2. It is noted that the binary M(II)-H₂ADA and M(II)-His curves shift to lower pH as compared to the corresponding ligand curves. This is due to a release of protons on coordination. The titration curves of 1:1:1 and 1:1:2 metal to H₂ADA to histidine molar ratios show that two species are formed; the first one begins to form at the pH range 3-6, and the second one around pH 7. Taking into account that the stability constants of the binary complexes of H₂ADA are close to those of the histidine ones, we can deduce that the two ligands coordinate simultaneously to a metal ion. They form the mixed ligand complex [M(ADA)(His)] at the lower pH values. At higher pH values an OH group is bonded to the latter ternary complex resulting in [M(ADA)(His)(OH)].

It is worth to indicate that the binary and the ternary complex solutions of manganese(II) show precipitation at pH \approx 9, so in this case further study was not possible beyond this pH value. Furthermore, and contrary to the binary metal complexes of H₂ADA with copper(II) and with cobalt(II), the ternary system curves do not show any buffer zone at high pH. This indicates that the ternary complexes formed have no tendency to undergo deprotonation of the amide group⁸ of the primary H₂ADA ligand.

The potentiometric studies showed that the ligands H₂ADA and histidine with copper(II), nickel(II), cobalt(II) and manganese(II) form ternary complexes which are more stable than the corresponding binary ones^{9,10} (Table I). Moreover, the Irving and Williams order is respected¹¹.

Characterisation of the Solid Ternary Complexes

The analyses of the ternary complexes isolated in the present study are consistent with the stoichiometry proposed, and are given in Table II. The copper(II), nickel(II) and cobalt(II) complexes display molar conductances in water (Table II) in accordance with 1:2 electrolytic behaviour¹².

IR Spectral Studies

Some important IR absorption frequencies of H₂ADA, histidine and their complexes along with their assignments are listed in Table III. Both ligands exhibit in their spectra several absorption bands in the region 3500-3000 cm⁻¹ which may be attributed to N-H stretching modes of the free amide group and the charged quaternary nitrogen of H₂ADA, the imidazole ring and the NH₃⁺ group of histidine. The asymmetric and symmetric COO⁻ stretching bands of both ligands appear in the ranges 1620-1550 cm⁻¹ and 1350-1300 cm⁻¹, respectively.

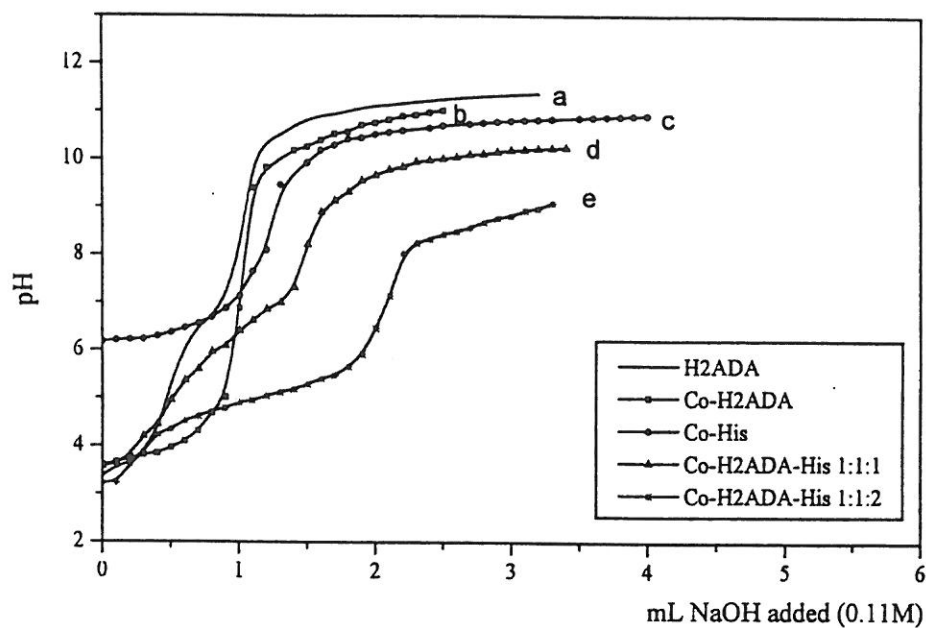


Fig. 2. Titration Curves of Co(II)-H₂ADA-His at 25.0 °C and $\mu = 0.3 \text{ mol. L}^{-1} \text{ Na}_2\text{SO}_4$ (a) H₂ADA + Na₂SO₄; (b) Co(II)+ H₂ADA + Na₂SO₄; (c) Co(II) + His + Na₂SO₄; (d) Co(II)+ H₂ADA + His + Na₂SO₄ (1:1:1); (e) Co(II)+ H₂ADA + His + Na₂SO₄ (1:1:2).

Table I. Formation Constant Values for the Different 1:1:2 Ternary Complexes at $25.0 \pm 0.1 \text{ }^\circ\text{C}$ and $\mu = 0.3 \text{ M (Na}_2\text{SO}_4)$

Log K	$\frac{M(\text{ADA})}{M(\text{ADA})(\text{His})}$	Cu(II)	Ni(II)	Co(II)
		10.2	8.7	8.5

All the complexes exhibit some common important IR frequencies. In the high frequency region, $3600\text{-}3000 \text{ cm}^{-1}$, the bands attributed in the H₂ADA IR spectrum to $\nu(\text{N-H})$ of the amide group and $\nu(\text{N-H})$ of the imidazole ring moiety are not shifted from their initial positions when complexation occurs. The $\nu(\text{OH})$ band in the spectra of the complexes around 3300 cm^{-1} indicates the presence of a bonded water molecule or an OH⁻ group¹³. The $\nu_s(\text{COO}^-)$ bands of H₂ADA and histidine show a shift towards lower wave number in the complexes, while $\nu(\text{N-H})$ of NH₃⁺ disappears on coordination, providing evidence that histidine is bonded to the metal ions through these groups^{14,15}. The band appearing in the

Table II. Physical Properties and Analytical Data of the Ternary Copper(II), Nickel(II), Cobalt(II) and Manganese(II) Complexes

Complex Formula	Formula Weight	Colour	Decomp. Temp. (°C)	Yield (%)	C	H	N	Na	M	Λ_m^a ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
					Found (calculated) (%)	Found (calculated) (%)	Found (calculated) (%)	Found (calculated) (%)		
$\text{Na}_2[\text{Cu}(\text{ADA})(\text{His})(\text{OH})] \cdot 5/2\text{H}_2\text{O}$ $\text{C}_{12}\text{H}_{22}\text{N}_5\text{O}_{10.5}\text{Na}_2\text{Cu}$	513.5	Dark Green	348	90	27.9 (28.0)	3.8 (3.7)	13.3 (13.6)	9.0 (8.9)	12.0 (12.3)	312
$\text{Na}_2[\text{Ni}(\text{ADA})(\text{His})(\text{OH})] \cdot 1/2\text{H}_2\text{O}$ $\text{C}_{12}\text{H}_{18}\text{N}_5\text{O}_{8.5}\text{Na}_2\text{Ni}$	473.6	Violet	354	68	30.3 (30.4)	3.8 (3.8)	15.0 (14.7)	9.8 (9.7)	12.1 (12.6)	190
$\text{Na}_2[\text{Co}(\text{ADA})(\text{His})(\text{OH})] \cdot 3/4\text{H}_2\text{O}$ $\text{C}_{12}\text{H}_{18.5}\text{N}_5\text{O}_{8.75}\text{Na}_2\text{Co}$	477.4	Reddish brown	>400	90	30.2 (30.1)	4.0 (3.9)	15.0 (14.6)	9.5 (9.6)	11.9 (12.3)	218
$\text{Na}[\text{Mn}(\text{ADA})(\text{His})(\text{H}_2\text{O})]$ $\text{C}_{12}\text{H}_{18}\text{N}_5\text{O}_8\text{NaMn}$	437.9	Greenish yellow	>400	90	32.3 (32.8)	4.3 (4.1)	16.0 (15.9)	5.2 (5.2)	12.1 (12.5)	-

^a in H_2O

1690-1680 cm^{-1} range in the IR spectra of all complexes is assigned to the stretching vibration of the free C=O group of the H_2ADA moiety¹⁶. It may be noted that, in addition to the shift of ν_{as} (COO^-) of the H_2ADA moiety towards higher wave numbers¹⁷⁻¹⁹, the absence of any band in the region 1750-1700 cm^{-1} in the IR spectra of all isolated ternary complexes is in accordance with the conclusion that both carboxylate groups of H_2ADA contribute to the coordination to the central metal ions *via* their oxygen atoms²⁰. The sharp and intense band which appears in the H_2ADA spectrum at 3206 cm^{-1} and is assigned to $\nu(\text{N-H})$ of the quaternary nitrogen¹⁸ is absent in the spectra of the complexes. In the spectrum of the chelate of nickel(II) a new doublet band in the 1180-1190 cm^{-1} range is observed, which is characteristic of $\nu(\text{C-N})$ of a free tertiary nitrogen. The presence of the hydrate water molecule in the copper(II), nickel(II), and cobalt(II) complexes is indicated by the appearance of a shoulder in the region 3600-3550 cm^{-1} in their IR spectra²¹. However, some new bands are observed in the regions 600-500 cm^{-1} and 500-400 cm^{-1} and indicate the formation of M-O and M-N bonds, respectively^{22,23} and support the coordination mode of the ligands.

The magnitude of the symmetric and asymmetric carboxylate stretching vibrations, *viz.* ν_{s} and ν_{as} , in a series of the coordinated amino acids has been demonstrated by Nakamoto, Morimota, and Martell¹⁹ to give a measure of the carboxylate-metal interactions. These authors further showed that for a given ligand, the difference ($\nu_{\text{as}}-\nu_{\text{s}}$) would increase as the M-O bond becomes more covalent, since the carboxylate stretching becomes correspondingly more asymmetrical. In the present investigation, if we consider the bond between a metal ion and the carboxylate of the ligand H_2ADA , we note that the difference ($\nu_{\text{as}}-\nu_{\text{s}}$) decreases from the copper(II) and manganese(II) complexes (320 cm^{-1}) to the cobalt(II) and nickel(II) ones (310 cm^{-1}). This difference being greater than 225 cm^{-1} indicates that the bond M-O is purely covalent¹⁸.

Magnetic and Electronic Spectral Studies

The room temperature magnetic moment of the copper(II) complex was found equal to 1.79 B.M. This value is due to the spin-only moment and is characteristic of a tetragonally distorted octahedral symmetry around copper(II)²⁴ and indicates that the complex is mononuclear. This was further confirmed by the electronic spectrum of the complex in which only a ligand field band in the range 16,000-14,000 cm^{-1} , probably due to the ${}^2\text{E}_g \rightarrow {}^3\text{T}_{2g}$ transition, was observed²⁵ (Table IV).

The cobalt(II) complex adopts a high-spin configuration in the reddish brown complex. Its electronic spectrum is composed of three absorption bands: the first band (ν_1) appeared

Table III. Important IR Spectral Bands (cm^{-1}) and their Assignments of the Ligands and the Ternary Copper(II), Nickel(II), Cobalt(II) and Manganese(II) Complexes

Compound	$\nu(\text{O-H})$ hyd	$\nu(\text{O-H})$ coord	$\nu(\text{N-H})^{\text{a,b}}$	$\nu_2(\text{N-H})^{\text{c}}$	$\nu_{\text{as}}(\text{COO})^{\text{a}}$	$\nu_s(\text{COO})^{\text{a}}$	$\nu_{\text{as}}(\text{COO})^{\text{b}}$	$\nu(\text{C-NH}_2^{\text{+}})$	$\nu(\text{C=N})$	$\nu(\text{M-O})$	$\gamma(\text{M-N})$
H ₂ ADA	-	-	3206 s	3400 s	1610 m	1320 s	-	-	-	-	-
Histidine	-	-	3100m	-	-	-	1578 m	1261 m	1495 s	-	-
Na ₂ [Cu(ADA)(His)(OH)]5/2H ₂ O	3550 sh	3350 sh	-	3400 sh	1635 m	1315 m	1620 sh	1261 sh	1495 w	520 ^a w 538 ^b m 570 ^a w	410 ^a w 430 ^b m
Na ₂ [Ni(ADA)(His)(OH)]1/2H ₂ O	3600 sh	3450 w	-	3400 sh	1620 w	1310 m	1630 w	1261 m	1495 w	500 ^a w 515 ^b m 530 ^d w	410 ^a m
Na ₂ [Co(ADA)(His)(OH)]3/4H ₂ O	3550 sh	3300 w	-	3400 sh	1620 w	1310 m	1640 w	1261 w	1495 w	500 ^a w 520 ^b m 540 ^d m	430 ^a w 420 ^b w
Na[Mn(ADA)(His)(H ₂ O)]	-	3300 m	-	3400 sh	1630 w	1310 w	1635 m	1261 m	1495 w	540 ^a m 570 ^b w 620 ^c m	410 ^a sh 425 ^b m

a = ADA, b = Histidine, c = Imidazole ring + Amide group, d = OH⁻, e = H₂O, m = medium, s = strong, sh = shoulder, w = weak.

Table IV. Electronic Spectral and Ligand Field Parameter Data of the Ternary Copper(II), Nickel(II), Cobalt(II) and Manganese(II) Complexes

Complex	Electronic transitions $\nu(\text{cm}^{-1})^a$	ϵ^b	Assignments	10Dq (cm^{-1})	B (cm^{-1})	β
$\text{Na}_2[\text{Cu}(\text{ADA})(\text{His})(\text{OH})]5/2\text{H}_2\text{O}$	16393	74	${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$	-	-	-
$\text{Na}_2[\text{Ni}(\text{ADA})(\text{His})(\text{OH})]1/2\text{H}_2\text{O}$	10204	7	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$	10204	753	0.72
	17543	12	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$			
	25641	81	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g} ({}^3\text{P})$			
	12820*	-	${}^3\text{B}_1 \rightarrow {}^3\text{E}$	-	-	-
	19230*	-	${}^3\text{B}_1 \rightarrow {}^3\text{A}_2$			
$\text{Na}_2[\text{Co}(\text{ADA})(\text{His})(\text{OH})]3/4\text{H}_2\text{O}$	9600	0.8	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g} ({}^4\text{F})$	10835	827	0.85
	12600	13	${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g} ({}^4\text{F})$			
	20800	140	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g} ({}^4\text{P})$			
$\text{Na}[\text{Mn}(\text{ADA})(\text{His})(\text{H}_2\text{O})]$	20000*	-	MLCT	-	-	-
	26315*	-	$\pi \rightarrow \pi^*$			

* Nujol mull spectra.

^a Wave numbers in cm^{-1} ^b Absorption molar coefficient in $\text{mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$

around $9,600 \text{ cm}^{-1}$ and is assigned to the ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g} ({}^4\text{F})$ transition; the second one (ν_2) observed at $12,600 \text{ cm}^{-1}$ is attributed to the ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g} ({}^4\text{F})$ transition and the third one is located at $20,800 \text{ cm}^{-1}$ and is due to the ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g} ({}^4\text{P})$ transition²⁶⁻²⁸.

The electronic spectrum of the pale green aqueous solution of the nickel(II) complex displays three bands located around $10,200$, $17,500$, and $25,600 \text{ cm}^{-1}$ which are probably due to the spin-allowed transitions ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g} ({}^3\text{F})$ (ν_1), ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (ν_2), and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g} ({}^3\text{P})$ (ν_3), respectively, in an octahedral environment.

The ligand field parameters (10Dq, B, and β) are calculated for these complexes²⁹ (Table IV). The Racah interelectronic repulsion parameter B is less than the free ion value²⁹. The calculated value of the ν_2/ν_1 ratio (1.71) is within the range expected for an octahedral symmetry.

The Nujol mull spectrum of the violet solid complex of nickel(II) exhibits two bands in the ranges $18,000$ - $12,000 \text{ cm}^{-1}$ and $25,000$ - $17,000 \text{ cm}^{-1}$ attributed to ${}^3\text{B}_1 \rightarrow {}^3\text{E}$ and ${}^3\text{B}_1 \rightarrow {}^3\text{A}_2$ transitions. They are reported to be characteristic of a square-pyramidal geometry for the nickel(II) complex which is confirmed by the magnetic moment (2.92 B.M.)³⁰.

Table V. ESR Spectral Data of the Copper(II), Cobalt(II) and Manganese(II) Ternary Complexes

	Solid state			Solution (H ₂ O)				
	77°K	298°K	298°K	77°K	298°K	298°K		
Na ₂ [Cu (ADA) (His) (OH)] 5/2 H ₂ O	g _{iso} 2.106	A _{iso} -	g _{iso} 2.113	A _{iso} -	g _{iso} 2.106	A _{iso} 2.118	A _{iso} 80 ^a	A _{iso} 10 ^a
Na ₂ [Co (ADA) (His) (OH)] 3/4 H ₂ O	g _{iso} 4.007 1.990	-	-	-	-	-	-	-
Na[Mn(ADA) (His) (H ₂ O)]	2.017	-	3.494	-	-	-	-	-
			2.017					

^a in Gauss

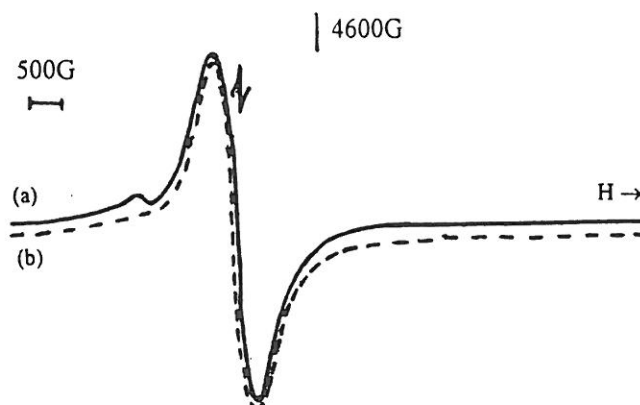


Fig. 3. ESR Spectra of Na[Mn(ADA)(His)(H₂O)] in the Solid State, (a) at 298K; (b) at 77K.

The magnetic moment of the manganese(II) complex at room temperature is characteristic of a high-spin octahedral complex of manganese(II)³¹ but it is found at a lower value than the spin-only value. This may be due to antiferromagnetic interaction in the complex in the solid state and/or a slight contamination by a Mn(III) impurity³².

The Nujol mull spectrum of the manganese(II) complex was obtained. It consists of a large shoulder around 26,300 cm⁻¹ which may be assigned to the $\pi \rightarrow \pi^*$ intraligand transition³⁰ and another shoulder at around 20,000 cm⁻¹ which is of medium intensity, probably due to a metal-ligand charge transfer transition³³.

Electron Spin Resonance

The electron spin resonance spectrum of the copper(II) complex, either in the solid state or in frozen solution, exhibits a simple isotropic line of which the g_0 value for each case is given in Table V. The spectrum in H₂O solution at room temperature consists of four equally spaced hyperfine lines ($I = 3/2$, $S = 1/2$). These lines, of different intensities, are more clearly resolved on the high field side of the spectrum³⁴. With the decrease in field the copper hyperfine lines become broader and the resolution of the superhyperfine splitting resolution becomes poorer. Each hyperfine line is split into five superhyperfine lines of equal spacing. This indicates that the lines are due to two equivalent atomic nuclei of nuclear spin $I = 1$, obviously due to ¹⁴N in the present case.

For the cobalt(II) complex, only the solid state spectra and the spectrum at liquid nitrogen temperature were obtained. An intense and anisotropic line around $g \approx 4$ and another weak

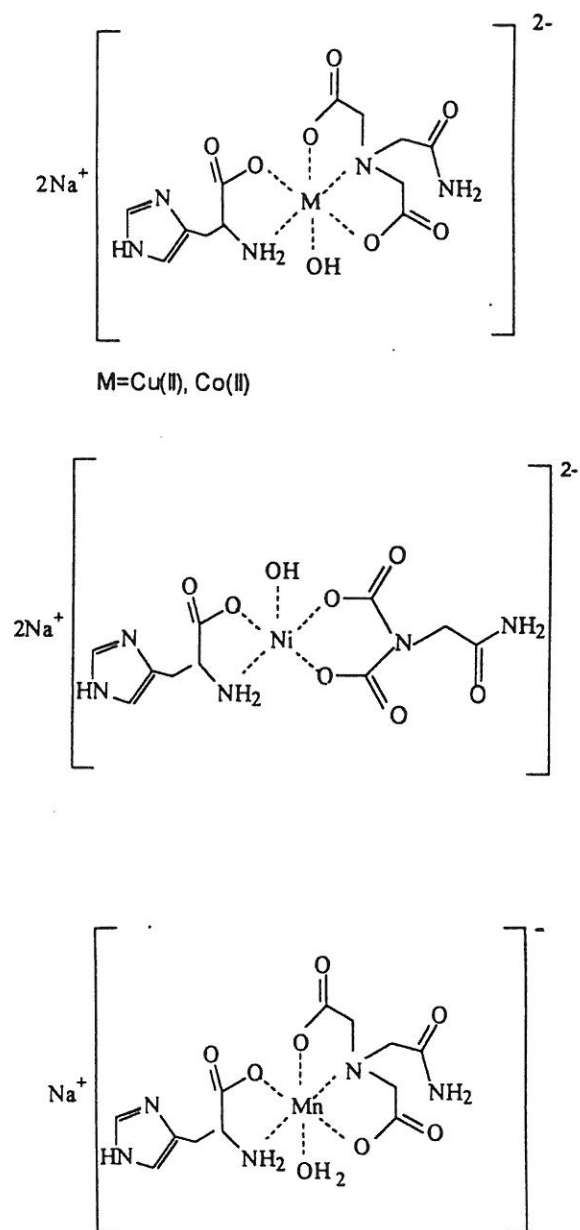


Fig. 4. Structural Scheme for the Isolated Ternary Complexes.

line around $g \approx 2$ are observed. They are characteristic of a high-spin complex of cobalt(II) with rhombic symmetry^{35, 36}.

Since nickel(II) is not a Kramer ion, the zero-field splitting can be large enough to lift all the three-fold spin degeneracy of the ground state and give no observable ESR signal³⁰.

ESR spectra of the powdered sample of the manganese(II) complex at room temperature and liquid nitrogen temperature were obtained (Fig. 3). In both cases, the $g = 2$ region consists of a strong broad signal; at room temperature the spectrum contains an additional weak component centered around $g \approx 4$. In this case the $g \approx 4$ resonance may be assigned as the $m_s = +1/2 \leftrightarrow -1/2$ fine structure transition³⁶⁻³⁸. The calculated g values from the spectra are collected in Table V. These results indicate an axially distorted-octahedral stereochemistry around manganese(II) and confirm its high-spin state in the complex studied.

On the basis of these results, the structural schemes in Fig. 4 may be proposed for the complexes.

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