



**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.**

H. Hamrit, S. Djebbar-Sid, O. Benali-Baitich, Mustayeen A. Khan, G. Bouet.

► **To cite this version:**

H. Hamrit, S. Djebbar-Sid, O. Benali-Baitich, Mustayeen A. Khan, G. Bouet.. 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.. Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 2000, 30 (10), pp.1835-1848. 10.1080/00945710009351872 . hal-03208783

**HAL Id: hal-03208783**

**<https://univ-angers.hal.science/hal-03208783>**

Submitted on 30 Apr 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

H. Hamrit <sup>a</sup>, S. Djebbar-Sid <sup>a</sup>, O. Benali-Baitich<sup>a\*</sup>, M. A. Khan<sup>b</sup> and G. Bouet<sup>b</sup>

<sup>a</sup>Laboratoire de Chimie de Coordination, Institut de Chimie,  
USTHB, BP32, El Alia, Alger, Algeria

<sup>b</sup>Laboratoire de Chimie de Coordination, Faculté de Pharmacie,  
16 Boulevard Daviers, F-49100 Angers, France

**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 (H<sub>2</sub>ADA) 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 Na<sub>2</sub>SO<sub>4</sub> 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 H<sub>2</sub>ADA 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<sup>-</sup> or H<sub>2</sub>O 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<sup>1,2</sup>. 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 occur<sup>3</sup> to a significant extent among the copper(II) mixed amino acid complexes found in human serum<sup>4,5</sup>. 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<sup>-1</sup> 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 E9 X-band Varian spectrometer using DPPH as a field marker. Magnetic susceptibilities were measured on a B-SU 10 Bruker magnetic balance calibrated with Hg[Co(SCN)<sub>4</sub>] and correcting the experimental values for diamagnetism<sup>6</sup>.

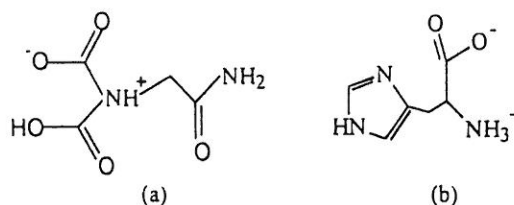


Fig. 1. Structure of the Ligands (a) H<sub>2</sub>ADA and (b) Histidine

#### Potentiometric Titrations

Potentiometric titrations of different  $M^{2+}$ -H<sub>2</sub>ADA and/or histidine mixtures in 1:1, 1:1:1 or 1:1:2 molar ratios ( $10^{-3}$  M for each) were performed at  $25.0 \pm 0.1$  °C and 0.3 M (Na<sub>2</sub>SO<sub>4</sub>) 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): H<sub>2</sub>ADA + Na<sub>2</sub>SO<sub>4</sub>, (b): histidine + Na<sub>2</sub>SO<sub>4</sub>, (c): metal ion + H<sub>2</sub>ADA + Na<sub>2</sub>SO<sub>4</sub>, (d): metal ion + histidine + Na<sub>2</sub>SO<sub>4</sub>, and (e): metal ion + H<sub>2</sub>ADA + histidine + Na<sub>2</sub>SO<sub>4</sub>.

#### 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 SIRKO<sup>7</sup>. 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 [CuCl<sub>2</sub>·2H<sub>2</sub>O (1.7048 g), NiCl<sub>2</sub>·6H<sub>2</sub>O (2.73 g), CoCl<sub>2</sub>·6H<sub>2</sub>O (2.37 g) and MnCl<sub>2</sub>·4H<sub>2</sub>O (1.97g)] was added to 50 mL of an EtOH-H<sub>2</sub>O solution (50% by volume) containing 10 mmol (1.9016 g) of the ligand H<sub>2</sub>ADA. To this mixture was added slowly with stirring an EtOH-H<sub>2</sub>O solution (50 mL) containing 20 mmol (3.1032 g) of histidine. Since the solubility of the free acid H<sub>2</sub>ADA and the amino acid histidine in EtOH-H<sub>2</sub>O mixture is very low, a few drops of 0.2 M NaOH solution were added until the pH of the H<sub>2</sub>ADA 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 P<sub>4</sub>O<sub>10</sub>. 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)-H<sub>2</sub>ADA 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 H<sub>2</sub>ADA 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 H<sub>2</sub>ADA 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 H<sub>2</sub>ADA 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 group<sup>8</sup> of the primary H<sub>2</sub>ADA ligand.

The potentiometric studies showed that the ligands H<sub>2</sub>ADA and histidine with copper(II), nickel(II), cobalt(II) and manganese(II) form ternary complexes which are more stable than the corresponding binary ones<sup>9,10</sup> (Table I). Moreover, the Irving and Williams order is respected<sup>11</sup>.

### **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 behaviour<sup>12</sup>.

### **IR Spectral Studies**

Some important IR absorption frequencies of H<sub>2</sub>ADA, 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<sup>-1</sup> which may be attributed to N-H stretching modes of the free amide group and the charged quaternary nitrogen of H<sub>2</sub>ADA, the imidazole ring and the NH<sub>3</sub><sup>+</sup> group of histidine. The asymmetric and symmetric COO<sup>-</sup> stretching bands of both ligands appear in the ranges 1620-1550 cm<sup>-1</sup> and 1350-1300 cm<sup>-1</sup>, respectively.

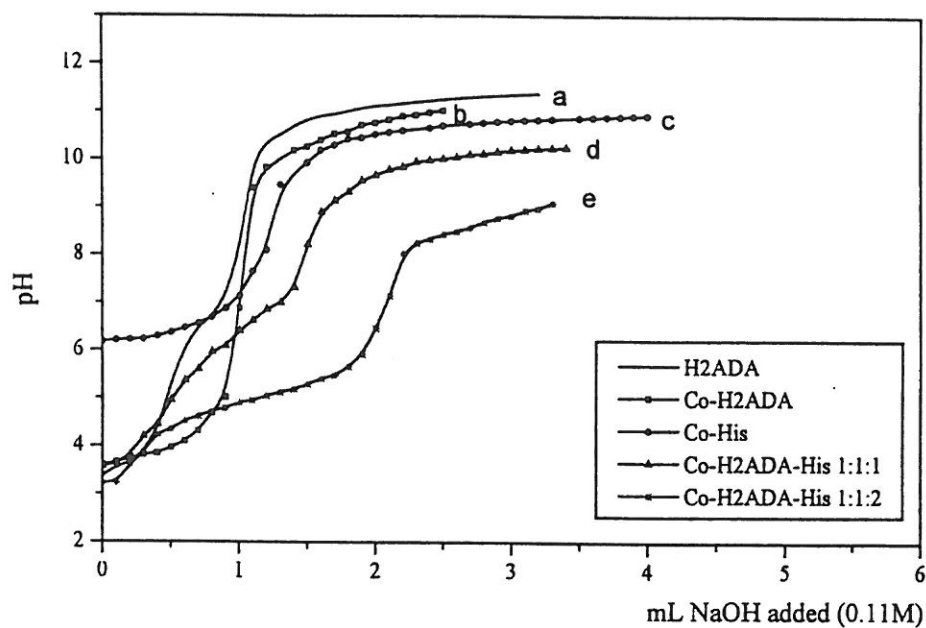


Fig. 2. Titration Curves of Co(II)-H<sub>2</sub>ADA-His at 25.0 °C and  $\mu = 0.3 \text{ mol. L}^{-1} \text{ Na}_2\text{SO}_4$  (a) H<sub>2</sub>ADA + Na<sub>2</sub>SO<sub>4</sub>; (b) Co(II) + H<sub>2</sub>ADA + Na<sub>2</sub>SO<sub>4</sub>; (c) Co(II) + His + Na<sub>2</sub>SO<sub>4</sub>; (d) Co(II) + H<sub>2</sub>ADA + His + Na<sub>2</sub>SO<sub>4</sub> (1:1:1); (e) Co(II) + H<sub>2</sub>ADA + His + Na<sub>2</sub>SO<sub>4</sub> (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  $\mu = 0.3 \text{ M (Na}_2\text{SO}_4\text{)}$

	Cu(II)	Ni(II)	Co(II)
$\text{Log } K_{\frac{M(\text{ADA})}{M(\text{ADA})(\text{His})}}$	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 H<sub>2</sub>ADA 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  $3300 \text{ cm}^{-1}$  indicates the presence of a bonded water molecule or an OH<sup>-</sup> group<sup>13</sup>. The  $\nu_s(\text{COO}^-)$  bands of H<sub>2</sub>ADA and histidine show a shift towards lower wave number in the complexes, while  $\nu(\text{N-H})$  of NH<sub>3</sub><sup>+</sup> disappears on coordination, providing evidence that histidine is bonded to the metal ions through these groups<sup>14,15</sup>. 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	$\Lambda_m^a$ ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ )
$\text{Na}_2[\text{Cu}(\text{ADA})(\text{His})(\text{OH})] \cdot 5/2\text{H}_2\text{O}$ $\text{C}_{12}\text{H}_{22}\text{N}_5\text{O}_{10.5}\text{Na}_2\text{Cu}$	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)	-

<sup>a</sup> in  $\text{H}_2\text{O}$

1690-1680  $\text{cm}^{-1}$  range in the IR spectra of all complexes is assigned to the stretching vibration of the free C=O group of the  $\text{H}_2\text{ADA}$  moiety<sup>16</sup>. It may be noted that, in addition to the shift of  $\nu_{\text{as}}$  ( $\text{COO}^-$ ) of the  $\text{H}_2\text{ADA}$  moiety towards higher wave numbers<sup>17-19</sup>, the absence of any band in the region 1750-1700  $\text{cm}^{-1}$  in the IR spectra of all isolated ternary complexes is in accordance with the conclusion that both carboxylate groups of  $\text{H}_2\text{ADA}$  contribute to the coordination to the central metal ions *via* their oxygen atoms<sup>20</sup>. The sharp and intense band which appears in the  $\text{H}_2\text{ADA}$  spectrum at 3206  $\text{cm}^{-1}$  and is assigned to  $\nu(\text{N-H})$  of the quaternary nitrogen<sup>18</sup> 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  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  in their IR spectra<sup>21</sup>. However, some new bands are observed in the regions 600-500  $\text{cm}^{-1}$  and 500-400  $\text{cm}^{-1}$  and indicate the formation of M-O and M-N bonds, respectively<sup>22,23</sup> and support the coordination mode of the ligands.

The magnitude of the symmetric and asymmetric carboxylate stretching vibrations, *viz.*  $\nu_{\text{s}}$  and  $\nu_{\text{as}}$ , in a series of the coordinated amino acids has been demonstrated by Nakamoto, Morimota, and Martell<sup>19</sup> 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  $\text{H}_2\text{ADA}$ , we note that the difference ( $\nu_{\text{as}} - \nu_{\text{s}}$ ) decreases from the copper(II) and manganese(II) complexes (320  $\text{cm}^{-1}$ ) to the cobalt(II) and nickel(II) ones (310  $\text{cm}^{-1}$ ). This difference being greater than 225  $\text{cm}^{-1}$  indicates that the bond M-O is purely covalent<sup>18</sup>.

#### 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)<sup>24</sup> 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  $\text{cm}^{-1}$ , probably due to the  ${}^2\text{E}_g \rightarrow {}^3\text{T}_{2g}$  transition, was observed<sup>25</sup> (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 ( $\nu_1$ ) appeared



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

a = ADA, b = Histidine, c = Imidazole ring + Amide group, d =  $\text{OH}^-$ , e =  $\text{H}_2\text{O}$ , 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 $\nu(\text{cm}^{-1})^a$	$\epsilon^b$	Assignments	10Dq ( $\text{cm}^{-1}$ )	B ( $\text{cm}^{-1}$ )	$\beta$
$\text{Na}_2[\text{Cu}(\text{ADA})(\text{His})(\text{OH})]5/2\text{H}_2\text{O}$	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.

<sup>a</sup> Wave numbers in  $\text{cm}^{-1}$ <sup>b</sup> 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 ( $\nu_2$ ) 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  ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g} ({}^4\text{P})$  transition<sup>26-28</sup>.

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  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g} ({}^3\text{F})$  ( $\nu_1$ ),  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$  ( $\nu_2$ ), and  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g} ({}^3\text{P})$  ( $\nu_3$ ), respectively, in an octahedral environment.

The ligand field parameters (10Dq, B, and  $\beta$ ) are calculated for these complexes<sup>29</sup> (Table IV). The Racah interelectronic repulsion parameter B is less than the free ion value<sup>29</sup>. The calculated value of the  $\nu_2/\nu_1$  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 ( $2.92 \text{ B.M.}$ )<sup>30</sup>.

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

	Solid state				Solution (H <sub>2</sub> O)			
	77°K		298°K		77°K		298°K	
	$g_{iso}$	$A_{iso}$	$g_{iso}$	$A_{iso}$	$g_{iso}$	$A_{iso}$	$g_{iso}$	$A_{iso}$
Na <sub>2</sub> [Cu (ADA) (His) (OH)] 5/2 H <sub>2</sub> O	2.106	-	2.113	-	2.106	-	2.118	80 <sup>a</sup>
Na <sub>2</sub> [Co (ADA) (His) (OH)] 3/4 H <sub>2</sub> O	4.007 1.990	-	-	-	-	-	-	-
Na[Mn(ADA) (His) (H <sub>2</sub> O)]	2.017	-	3.494 2.017	-	-	-	-	-

<sup>a</sup> in Gauss

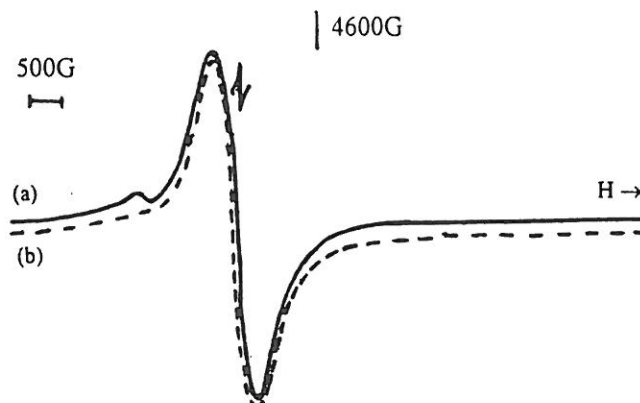


Fig. 3. ESR Spectra of  $\text{Na}[\text{Mn}(\text{ADA})(\text{His})(\text{H}_2\text{O})]$  in the Solid State,  
(a) at 298K; (b) at 77K.

The magnetic moment of the manganese(II) complex at room temperature is characteristic of a high-spin octahedral complex of manganese(II)<sup>31</sup> 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) impurity<sup>32</sup>.

The Nujol mull spectrum of the manganese(II) complex was obtained. It consists of a large shoulder around  $26,300\text{ cm}^{-1}$  which may be assigned to the  $\pi \rightarrow \pi^*$  intraligand transition<sup>30</sup> and another shoulder at around  $20,000\text{ cm}^{-1}$  which is of medium intensity, probably due to a metal-ligand charge transfer transition<sup>33</sup>.

#### 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  $\text{H}_2\text{O}$  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 spectrum<sup>34</sup>. 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  $^{14}\text{N}$  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

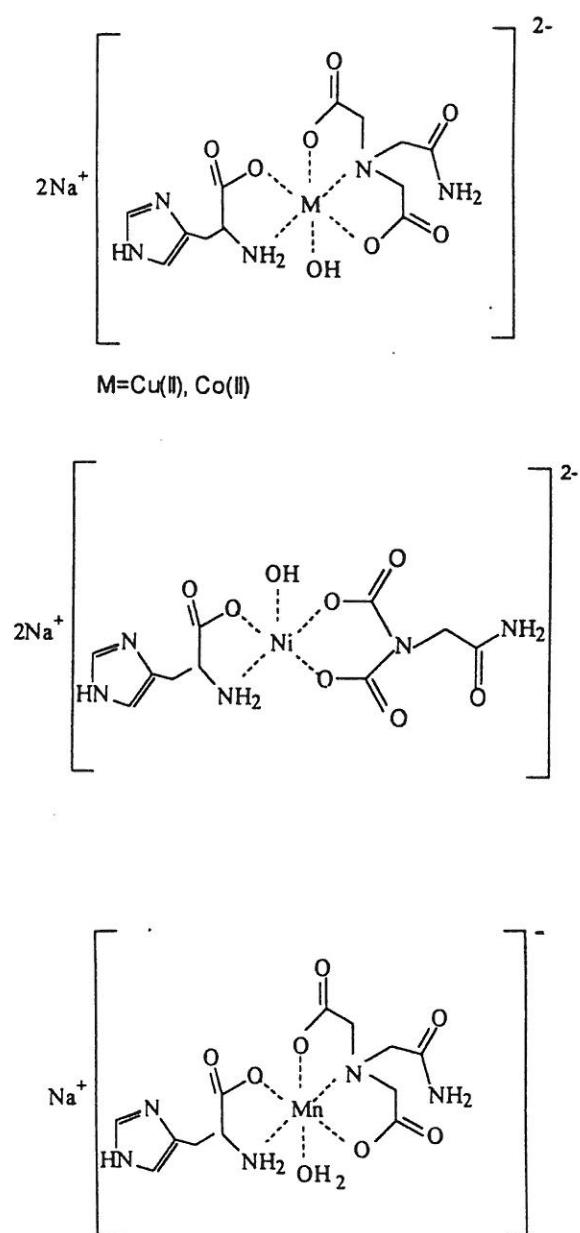


Fig. 4. Structural Scheme for the Isolated Ternary Complexes.

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

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 signal<sup>30</sup>.

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 transition<sup>36-38</sup>. 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.

#### REFERENCES

1. H. Sigel, "Metal ion in Biological Systems", Marcel Dekker, New York (1979).
2. G. L. Eichorn, "Inorganic Biochemistry", Elsevier, Amsterdam (1973).
3. B. Sarkar, M. Bersohn, Y. Wigfield, and T.C. Chiang, *Can. J. Biochem.*, **46**, 595 (1968).
4. B. Sarkar and T. P. A. Kruck, "The Biochemistry of Copper", Eds., J. Peisah, P. Aisendud and W. E. Blumberg, p. 183, Academic Press, New York (1966).
5. M. Petit- Ramel and M. R. Paris, *Bull. Soc. Chim. Fr.*, 2791 (1967).
6. A. Earnshaw, "Introduction to Magnetic Chemistry", Academic Press, London (1969).
7. V. I. Vetrogon, N. G. Slukyanenko, M-J. Schwing-Weill, and F. Arnaud-Neu, *Talanta*, **1**, 2105 (1994).
8. S. A. Ibrahim, M. R. Mahmoud, M. B. Saleh and I. T. Ahmed, *Transition Met. Chem.*, **19**, 494 (1994).
9. E. D. Lance, C. W. Rhodes and R. Nakon, *Anal. Biochem.*, **133**, 492 (1983).
10. R. J. Sundberg and R. B. Martin, *Chem. Rev.*, **74**, 472 (1974).
11. H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953).
12. W. J. Geary, *Coord. Chem. Rev.*, **7**, 81, (1971).
13. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", Wiley Interscience, New York (1986).
14. L. Larson, *Acta. Chem. Scand.*, **4**, 27, (1950).
15. W. U. Malik and R. Bembi, *Ind. J. Chem.*, **14 A**, 211 (1976).
16. I. T. Ahmed and A. A. A. Borai, *Synth. React. Inorg. Met.-Org. Chem.*, **27**, 169 (1997).

17. W. L. Kwick and K. P. Ang, *J. Inorg. Nucl. Chem.*, **42**, 303 (1978).
18. N. Israely, P. Gouzerh and P. Souchay, *Rev. Chim. Min.*, **3**, 897 (1966).
19. K. Nakamoto, Y. Morimota and A. E. Martell, *J. Amer. Chem. Soc.*, **83**, 4528 (1961).
20. D. H. Bush and J. C. Bailar, *J. Amer. Chem. Soc.*, **75**, 457 (1953) and **78**, 716 (1956).
21. S. N. Chaubey, J. P. Srivastava and L. K. Mighra, *Inorg. Chim. Acta.*, **23**, 1 (1977).
22. Z. Karwecka and L. Pajdowski, *Polish. J. Chem.*, **52**, 2053 (1978); *Chem. Abstr.*, **90**, 80157c (1979).
23. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Wiley Eastern, Ltd (1970).
24. C. A. Agamber and K. G. Orell, *J. Chem. Soc.*, 897 (1969).
25. A. B. P. Lever, J. Levis and R. S. N. Nyholm, *J. Chem. Soc.*, 1253 (1962).
26. K. H. Reddy, G. K. Krishnaiah and Y. Srenivasulu, *Polyhedron.*, **10**, 2787 (1991).
27. K. K. Narang, M. K. Singh, K. B. Singh and R. A. Lal, *Synth. React. Inorg. Met.-Org. Chem.*, **26**, 528 (1996).
28. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, London (1984).
29. E. Konig, "Structure and Bonding", Berlin, **9**, 182, (1971).
30. G. Wilkinson, "Comprehensive Coordination Chemistry", Pergamon Press, Oxford (1987).
31. A. K. Usha and S. Chauda, *Synth. React. Inorg. Met.-Org. Chem.*, **22**, 971, (1992).
32. N. Tidjani- Rahmouni, S. Djebbar- Sid, N. Chenah and O. Benali-Baitich, *Synth. React. Inorg. Met.-Org. Chem.*, **29**, 979, (1999).
33. K. K. Narang and M. K. Singh, *Inorg. Chim. Acta*, **131**, 245 (1987).
34. I. Rani, K.B. Pandeya and R. P. Singh, *J. Inorg. Nucl. Chem.*, **43**, 2743 (1981).
35. F. E. Mabbs and D. Collison, "EPR of Transition Metal Compounds", Elsevier, Amsterdam (1992).
36. W. Weltner. "Magnetic Atoms and Molecules", Dover Publications, Inc., New York (1989).
37. M. Mc Cann, R. M. T. Casey, M. Denevieux, M. Curran and V. Cekee, *Polyhedron*, **15**, 2323 (1996).
38. G. Batra and P. Mathur, *Transition Met. Chem.*, **19**, 161 (1994).

Received: 25 August 1999  
Accepted: 22 July 2000

Referee I: D. Dollimore  
Referee II: M. H. Dickman