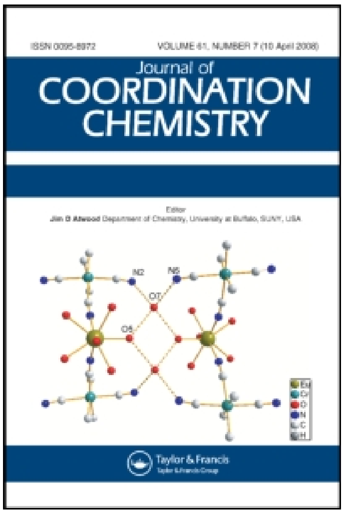

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Synthesis and characterization of manganese(II), nickel(II), copper(II) and zinc(II) Schiff-base complexes derived from 1,10-phenanthroline-2,9-dicarboxaldehyde and 2-mercaptoethylamine

J. R. Anacona[a]; V. E. Marquez[b]; Yulia Jimenez[a]
[a] Departamento de Quimica, Universidad de Oriente, Cumana, Venezuela [b] Departamento de Quimica, Instituto Universitario de Tecnología, Cumana, Venezuela

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Synthesis and characterization of manganese(II), nickel(II), copper(II) and zinc(II) Schiff-base complexes derived from 1,10-phenanthroline-2,9-dicarboxaldehyde and 2-mercaptoethylamine

J.R. ANACONA*†, V.E. MARQUEZ‡ and YULIA JIMENEZ†

†Departamento de Quimica, Universidad de Oriente, Apartado Postal 208, Cumana, Venezuela
‡Departamento de Quimica, Instituto Universitario de Tecnología, Apartado Postal 255, Cumana, Venezuela

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The synthesis of a new Schiff base containing 1,10-phenanthroline-2,9-dicarboxaldehyde and 2-mercaptoethylamine is described. The reaction of 1,10-phenanthroline-2,9-dicarboxaldehyde with 2-mercaptoethylamine leads to 2,9-*bis*(2-ethanthiazolinyl)-1,10-phenanthroline (**I**) which undergoes rearrangement when reacted with manganese, nickel, copper or zinc ions to produce complexes of the tautomeric Schiff base 2,9-*bis*[2-(2-mercaptoethyl)-2-azaethene]-1,10-phenanthroline (**L**). The $[M(L)Cl_2]$ complexes [where $M = Mn(II)$, Ni(II), Cu(II) and Zn(II) ions] were characterized by physical and spectroscopic measurements which indicated that the ligand is a tetradentate N_4 chelating agent.

Keywords: Schiff-base complexes; Transition metals; Phenanthroline derivatives

1. Introduction

Compounds containing an azomethine group (–CH=N–) are Schiff bases, formed by condensation between a carbonyl compound and a primary amine [1]. Schiff bases of aliphatic aldehydes are relatively unstable and are readily polymerizable [2], while those of aromatic aldehydes having an effective conjugation system are more stable [3]. Usually such syntheses are carried out in the presence of a suitable metal ion which directs the course of reaction preferentially towards cyclic rather than oligomeric/polymeric products (the kinetic template effect) [4–6]. As a typical reaction of this type we have the condensation of an aldehyde or a ketone with 2-aminobenzenethiol, which does not lead to isolation of the corresponding Schiff base but rather a benzothiazoline. Nevertheless, in solution, the benzothiazolidine may exist in equilibrium with its tautomeric Schiff base which is stabilized by complex formation and cannot be isolated free of its associated metal ion. As an example of this

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*Corresponding author. Email: juananacona@hotmail.com

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and continuing with previous studies [7–11], we report here the isolation and characterization of metal(II) complexes containing the Schiff base L. A study of the physical properties of the chloride derivatives of these species permits more extensive comparisons between complexes of cyclic planar tetradentate ligands and those of related noncyclic ligands, and, between those containing aromatic mercapto groups and their aliphatic analogs.

2. Experimental

2.1. *Materials and methods*

Oxygen and moisture were excluded during the synthesis and handling of the compounds. Analytical R grade chemicals were used as received for all experiments. Fourier transform infrared (FT-IR) spectra of the ligand and its metal complexes as KBr pellets were recorded from 4000–400 cm^{-1} with a Perkin–Elmer Series 2000. FT-IR spectra as polyethylene pellets were registered between 450–120 cm^{-1} using a Bruker IFS 66V spectrophotometer. EPR spectra were recorded on a Bruker ECS 106 spectrometer operating in the X-band (9.76 GHz). α-α'-Diphenyl–β-picrylhydrazide free radical was used as the g marker. UV–Vis spectra were recorded using a Perkin–Elmer spectrometer. The contents of C, H, N, and S were analyzed on a LECO CHNS 932 model microanalytical instrument. The complexes were analyzed for their metal content with a Perkin–Elmer atomic absorption analyzer, after decomposition with a mixture of HNO_3 and HCl followed by H_2SO_4. Magnetic susceptibilities were measured on a Johnson Matthey Magnetic Susceptibility balance at room temperature using $HgCo(NCS)_4$ as calibrant. Mass spectra were obtained with a A.E.I. MS30 spectrometer at 70 eV. ^{1}H-NMR spectra were run at 80 MHz on a Varian spectrometer.

2.2. *Synthesis of 2,9-*bis*(2-ethanthiazolinyl)-1,10-phenanthroline (I)*

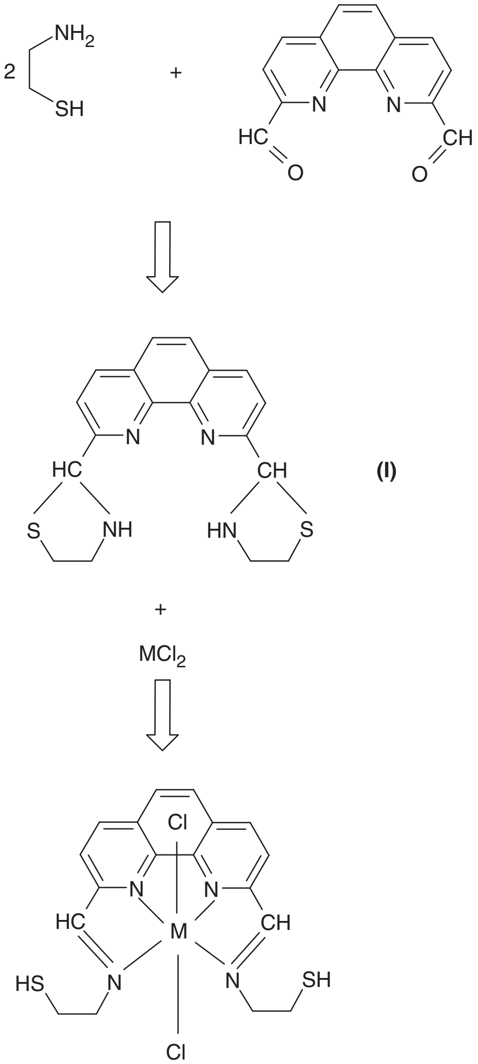
To 1 mmol of 1,10-phenanthroline-2,9-dicarboxaldehyde, prepared from 2,9-dimethyl-1,10-phenanthroline following the procedure described previously [12], dissolved in 250 mL of hot ethanol were added 2 mmol of 2-mercaptoethylamine in 10 mL ethanol. The solution was refluxed under nitrogen at 50 °C for 20 min to give a dark yellow precipitate which was filtered and washed with ethanol and ether and dried under reduced pressure. The product was purified by recrystallization from the same solvent (yield 65%).

2.3. *Synthesis of metal(II) complexes*

All metal(II) complexes were prepared by the same general method. To a hot solution of 2 mmol of the appropriate metal salt in 20 mL of methanol was slowly added with stirring a solution of 2 mmol of **I** in 10 mL of methanol. The chloride complexes were separated from the reaction mixture as crystalline solids and washed several times with methanol and ether and dried under reduced pressure at room temperature. The yields of the products are the following: Mn (45%), Ni (60%), Cu (70%), Zn (75%). There was no evidence that other complexes might be formed.

3. Results and discussion

The metal(II) complexes of the type [M(L)Cl_2] described in this report were prepared according to scheme 1. The nickel(II) complex is green and the copper(II) complex maroon. The manganese(II) complex is light orange while the zinc(II) complex is dark yellow. They are air stable solids, soluble in DMSO, acetonitrile or DMF and insoluble in water, MeOH, ethanol, chloroform and dichloromethane. The elemental analyses



Scheme 1. The preparation of [M(L)Cl_2] complexes.

Table 1. Analytical data of **I** and the metal(II) complexes.

	Found (calculated)%				
Compound	C	H	N	S	Metal
I	61.5 (61.3)	4.7 (4.5)	16.2 (15.9)	18.3 (18.2)	
[Mn(L)Cl_2]	45.7 (45.2)	3.3 (3.4)	11.4 (11.7)	13.8 (13.4)	11.2 (11.5)
[Ni(L)Cl_2]	44.8 (44.8)	3.5 (3.3)	11.7 (11.6)	13.5 (13.3)	12.5 (12.2)
[Cu(L)Cl_2]	44.1 (44.4)	2.5 (3.3)	11.6 (11.5)	13.5 (13.1)	13.1 (13.1)
[Zn(L)Cl_2]	44.5 (44.2)	3.6 (3.3)	11.1 (11.5)	19.6 (19.3)	13.7 (13.4)

agree well with a 1:1 metal-to-ligand stoichiometry for all the complexes (table 1). Molar conductance values in nitromethane vary from 20.0 to 30.0 $S\,cm^2\,mol^{-1}$, revealing the non-electrolytic nature of the chloro complexes, indicating that all the anions are held in the coordination sphere of metal(II) ions [13].

However, the observed value may be due to the strong donor capacity of nitromethane which leads to the partial displacement of coordinated chloride. Conductance measurements in DMSO, which has high solvolytic character, indicates 1:2 electrolyte behavior, suggesting that the species present in solution are almost certainly $[M(L)(dmso)_2]^{2+}$, in equilibrium with $[M(L)(H_2O)_2]^{2+}$. These results suggest that when metal salts of non-coordinating anions such as nitrate, acetate and perchlorate are used, different types of complexes could be formed, emphasizing the importance of reaction conditions and type of anion on the structure of complexes. Mercapto groups often give metal derivatives that are extremely insoluble, bridged or even polymeric. However, if other strong ligands are introduced, polymeric products can often be avoided even under conditions favoring sulfur bridging. The characterization data support formulation of the complexes as tetradentate with respect to the ligand and including two chloride anions in the axial positions in nitromethane solution, but not in DMSO.

The mass spectrum of the ligand shows an $m/z = 352$ based on $N = 14$, $S = 32$ which is consistent with the molecular weight. The metal(II) complexes were also identified by mass spectra, but did not provide direct confirmation of the presence of the compounds since no parent ions peaks were observed, only those due to ligand fragments (peaks at m/z 348 manganese(II), 349 nickel(II), 350 copper(II) and 350 zinc(II) are consistent with the molecular weight of the ligand). Attempts to form complexes of a well-defined stoichiometry, in the above mentioned conditions, with chromium(III), iron(II), cobalt(II), mercury(II) and tin(II) ions were unsuccessful.

The ^{1}H-NMR spectrum of **I** shows the following signals: phenanthroline multiplet at 7.0–8.5 δ, –CH at 4.0 δ, –NH at 4.2 δ, and $-CH_2$ at 3.1–3.5 δ (table 2). However, no signal could be assigned to HC=O, SH or NH_2 protons, suggesting that the proposed structure **I** was formed by condensation, further confirmed by the IR spectrum. The ^{1}H-NMR spectrum of the zinc(II) complex slightly changed as compared with free **I** and the signals appeared downfield, as expected, due to increased conjugation on coordination. Two peaks at 7.8–7.9 and 3.1 δ are attributable to the two equivalent carboximine protons (HC=N, 2H) and –SH groups, respectively.

Table 2. Spectral data of the ligand and complexes[a].

	IR									NMR	Mass
Compound	C=O	C=N	NH	SH	phen				M–N	δ (p.p.m)	m/z
1	1700		3190		1518	1426	845	730		HC=O (2H, s) 9.1	236
I					1516	1423	843	728		NH (2H, s) 4.2 CH_2 (4H, m) 3.1–3.5 phen (6H, m) 7.0–8.5 CH (2H, s) 4.0	352
$[Mn(L)Cl_2]$		1625		2570	1516	1423	844	728	440		348
$[Ni(L)Cl_2]$		1621		2573	1517	1422	844	729	440		349
$[Cu(L)Cl_2]$		1618		2575	1516	1423	846	729	460		350
$[Zn(L)Cl_2]$		1617		2572	1517	1422	844	728	475	HC=N (2H, s) 7.8–7.9 CH_2 (4H, m) 3.6–4.0 phen (6H, m) 7.1–9.0 SH (2H, s) 3.1	350

[a] **1** = 2,9-dicarboxaldehyde-1,10-phenanthroline, phen = phenanthroline.

3.1. *IR spectra*

Spectral data of the ligand and its complexes are listed in table 2. The IR spectrum of **I** shows no absorption bands which can be assigned to ν(S–H) or ν(C=O) coming from the 2-aminoethanethiol and carboxaldehyde moieties, respectively. The absence of such absorptions together with the presence of a single N–H stretching mode of medium intensity at 3190 cm^{-1} is in accord with the product being the expected 2,9-*bis*(2-ethanthiazolinyl)-1,10-phenanthroline **I** [14]. This potential tetradentate ligand undergoes rearrangement induced by manganese(II), nickel(II), copper(II) and zinc(II) ions. The appearance of new bands in the 440–475 cm^{-1} range attributed to ν(M–N), in the 1615–1630 cm^{-1} range attributed to ν(C=N) and in the 2550–2580 cm^{-1} range attributed to (S–H) [15], observed in the spectra of metal complexes of (**I**) suggest that $[M(L)Cl_2]$ have been formed. The IR spectra of the complexes shows (M–Cl) bands in the 310–330 cm^{-1} range attributed to chloride bonded to the metal(II) ions [16]. Medium intensity bands appearing in the 2830–2950 cm^{-1} region correspond to aliphatic ν(C–H) while aromatic ν(C–H) stretches appear in the 3000–3100 cm^{-1} region. No signals from the metal-sulfur bond were found, at 330–390 cm^{-1}, suggesting that the metal ion is only linked to nitrogen [17–20].

3.2. *Magnetic properties*

In order to test the formation of radical species, corrected magnetic moments have been calculated from the molar magnetic susceptibilities using Pascal's constants [21]. The values for the ligand and the zinc(II) complex are within the interval 0.10–0.20 B.M., suggesting that no oxidation of L occurs. These values clearly indicate that these compounds have no unpaired electrons and they show no EPR signals at room temperature.

The magnetic moments for paramagnetic complexes fall within the ranges associated with high-spin ions in octahedral fields and are unlikely to be of value in discriminating between metal ions in five- and six-coordinate geometries [22]. The manganese(II) complex has a magnetic moment of 5.72 B.M., typical of a d^5 system in a high-spin octahedral configuration [23]. The EPR spectrum recorded at the X-band frequency at room temperature (figure 1) shows a single line with no hyperfine splitting due to ^{55}Mn 100% natural abundance, $I = 5/2$. Our $g = 2.28$ agrees quite well with other high-spin octahedral manganese(II) complexes. The room temperature magnetic moment of the nickel(II) complex in the solid state is 3.75 B.M., which is higher than values for octahedral (2.90–3.30) and five-coordinate (3.20–3.40) geometries and falls in the range expected for tetrahedral (3.2–4.1) geometry [22, 23]. However, because of the planarity of the ligand, octahedral geometry is likely. Differences in locations of different metal cations in the structures would lead to different antiferromagnetic interactions, which would be reflected in wide differences of magnetic moments [24, 25]. The room temperature magnetic moment of the copper(II) complex in the solid state is 1.78 B.M., expected for monomeric non-interacting copper(II). Figure 1 presents the EPR spectrum of [Cu(L)Cl$_2$] complex in solid state at room temperature which shows an

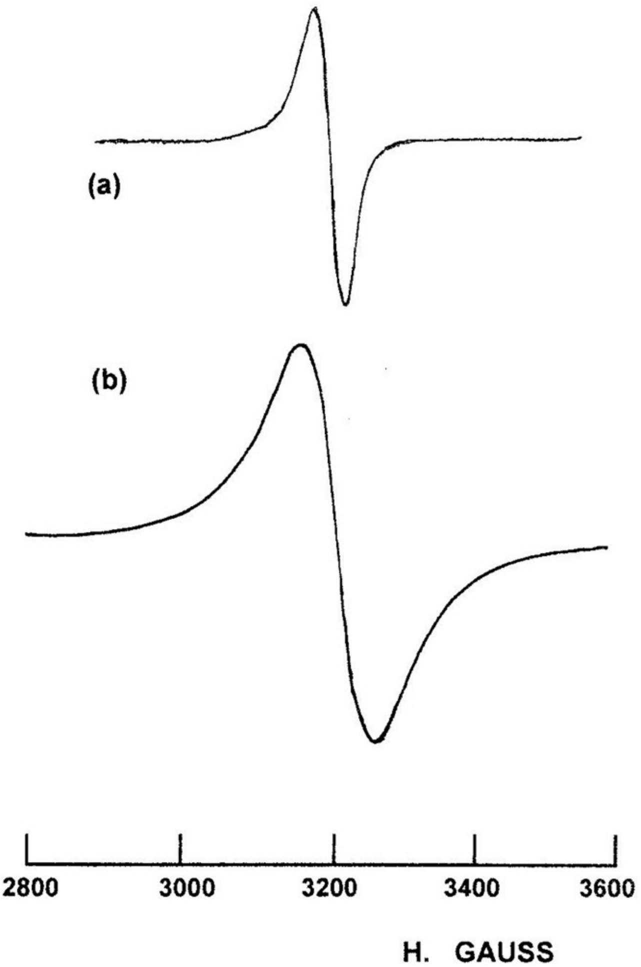


Figure 1. EPR spectra of complexes (a) [Cu(L)Cl$_2$], (b) [Mn(L)Cl$_2$].

isotropic signal centered at $g = 2.13$, which can be assigned to a slightly distorted octahedral geometry due to the Jahn–Teller effect. Similar results have also been found for $K_2PbCu(NO_2)_6$ and for other pseudo octahedral copper(II) complexes [26].

3.3. *Electronic spectra*

Spectra of the ligand and complexes in DMSO show broad bands in the regions 275–320 and 320–380 nm due to π–π^* transitions of the (>C=N–) chromophore and of the phenanthroline ring, respectively. The manganese(II) complex with octahedral geometry and high spin showed very weak absorption bands ($\varepsilon < 10$) near 570 nm, probably due to spin-forbidden transitions.

The $[Ni(L)Cl_2]$ electronic spectrum is characteristic of a nickel(II) complex with octahedral geometry. The lower energy bands at 560 and 620 nm are assigned to the transitions ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1), respectively. The third spin allowed transition ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ is obscured in the spectrum by a charge transfer band. An additional weak band is assigned to the spin-forbidden transition ${}^3A_{2g} \rightarrow {}^1E_g$ at 760 nm.

The electronic spectrum of the copper(II) complex shows bands at 270 and 350 nm attributed to transitions within the organic molecule. The electronic spectrum of the copper(II) complex presents only one band centered at 480 nm which does not discriminate between O_h and lower symmetries.

In the spectrum of the zinc(II) complex, a smooth band was observed at 580 nm, assigned as charge transfer band. It has been reported [27] that a metal is capable of forming dπ–pπ bonds with ligands containing nitrogen as the donor atoms. The zinc(II) ion has its 4d orbitals completely vacant and hence L → M bonding can take place by the acceptance of a lone pair of electrons from a nitrogen donor of the ligand.

3.4. *Structure of complexes*

The ligand has several potential donors, but due to steric constraints, can provide a maximum of four donor atoms at any one time for coordination to a metal. The amine nitrogen shows better affinity than sulfur towards bivalent 3d metal cations.

From models it appears that a planar or approximately planar configuration of the ligand is possible, however, without a full structural analysis one cannot make a distinction between these possibilities. Despite the crystalline nature of the products, we could not succeed in obtaining single crystals, even after inordinate attempts, suitable for X-ray structure determination. As the ligand is potentially tetradentate, it is quite feasible that the metal(II) ions are six coordinate with chlorides at the vertices of an octahedron.

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