

**SYNTHESIS OF TRANSITION METAL COMPLEXES CONTAINING A SCHIFF BASE
LIGAND DERIVED FROM 1, 10-PHENANTHROLINE-2, 9-DICARBOXALDEHYDE AND
 β -MERCAPTO ETHYL AMINE HYDRO CHLORIDE**

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ABSTRACT: The synthesis of Schiff base containing, 10-phenanthroline-2, 9-dicarboxaldehyde and β -mercapto ethyl amine hydrogen chloride is described. The reaction of 1,10-phenanthroline 2,9-dicarboxaldehyde with β -mercapto ethyl amine hydrochloride leads to the isolation of 2,9-bis(2-(2-mercapto ethyl)-2-aza ethane)-1,10-phenanthroline (Ligand). The $[\text{Cu}(\text{C}_{18}\text{H}_{18}\text{N}_4\text{S}_2)\text{ClO}_4](\text{ClO}_4)$ and $[\text{M}(\text{C}_{18}\text{H}_{18}\text{N}_4\text{S}_2)\text{X}_2]$ complexes (where M = Co(II), Ni(II) and Zn(II) and X = Br) were characterized by physical and spectroscopic measurements which indicated that the ligand is acting as Tetradentate N_4 . Chelating agent.

The cobalt(II) complex has a magnetic moment of 4.78 B.M. which is a typical value of a d^7 -system with three unpaired electrons indicating a quartet state in a high spin octahedral configuration. The room temperature magnetic moment of the nickel(II) complex in the solid state is 3.28 B.M. which is typical of compounds with two unpaired electrons in a high spin octahedral d^8 -configuration. The room temperature magnetic moment of the $[\text{Cu}(\text{C}_{18}\text{H}_{18}\text{N}_4\text{S}_2)\text{ClO}_4](\text{ClO}_4)$ complex in the solid state is 1.87 B.M. as expected for monomeric ion interacting copper ions corresponding to compounds with one unpaired electron.

INTRODUCTION

Condensation reactions between dicarbonyl compounds and α, α' -primary amines have played an important role in the development of synthetic Schiff base ligands.¹⁻⁶ Usually such syntheses are carried out in the presence of a suitable metal ion which serves to direct the steric course of reaction preferentially towards cyclic rather than oligomeric/polymeric products (the kinetic template effect), and/or to stabilize the Schiff base macrocycle, once formed (the thermodynamic template effect). As a typical reaction of this type we have the condensation of an aldehyde or a ketone with β -mercaptoethylamine, which does not normally lead to the isolation of the corresponding Schiff base, but rather the main product is usually a thiazoline. Nevertheless, in solution, the thiazolidine 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 and continuing with previous studies⁷⁻¹¹, we report here the isolation and characterization of metal(II) complexes containing the Schiff base ligand L. A study of the physical properties of the bromide and perchlorate derivatives of these species will permit more extensive comparisons between complexes of cyclic planar tetradentate ligands and those of related non-cyclic ligands, and also between those containing aliphatic mercapto groups and their aliphatic analogues.

MATERIALS AND METHODS

All necessary precautions were observed to exclude oxygen and moisture during the synthesis and handling of the compounds. Analytical grade chemicals were used as received for all experiments. Fourier transforms infrared (FTIR) spectra of the ligand and its metal complexes as KBr pellets were recorded in the spectral range $4,000-400 \text{ cm}^{-1}$ with a Perkin-Elmer Series 2000 apparatus. FTIR spectra as polyethylene pellets were recorded between 450 and 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. Measurements of d-d transitions in the visible and near infrared region were taken with a Cary Recording

Spectrophotometer Model 17D, while a Perkin–Elmer spectrophotometer was used for recording the visible and u.v. regions. The contents of C, H, N and S were analysed on a LECO CHNS 932 model microanalytical instrument. The complexes were analysed for their metal content with a Perkin–Elmer atomic absorption analyzer, after decomposition with a mixture of HNO₃ and HCl followed by H₂SO₄. Magnetic susceptibilities were measured on a Johnson Matthey Magnetic Susceptibility balance at room temperature using HgCo(NCS)₄ as calibrant. Mass spectra were obtained from A.E.I. MS30 spectrometer at 70 eV. ¹H NMR spectra were run at 80 MHz on a Varian spectrometer.

SYNTHESIS OF 2, 9–BIS(2–ETHANETHIAZOLINYL)–1, 10–PHENANTHROLINE (1)

To 1 mmol of 1,10–phenanthroline–2,9–dicarboxaldehyde, prepared from 2,9–dimethyl–1,10–phenanthroline following the procedure described previously¹², in 250 mL of hot ethanol were added 2 mmol of β–mercapto ethyl amine hydrogen chloride. The solution was refluxed under nitrogen atmosphere at 50°C for 20 min to give a dark yellow precipitate. This material was filtered off and washed with ethanol and ether, and dried under reduced pressure. The product was purified by recrystallization from the same solvent (yield 72%), m.p. = 165°C.

SYNTHESIS OF METAL(II) COMPLEXES

Cobalt(II), nickel(II), copper(II) and zinc(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) (C₁₈H₁₈N₄S₂) in 10 mL of methanol. The bromide and perchlorate metal(II) complexes of L(C₁₈H₁₈N₄S₂) 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 (yield 30–45%), m.p. = 300°C.

RESULTS AND DISCUSSION

The elemental analyses agree well with a 1:1 metal–to–ligand stoichiometry for all the complexes (table 7.1). The nickel(II) and copper(II) complexes are green. The cobalt(II) complex is light brown, 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. Molar conductance values in nitromethane vary from 20.0 to 35.0 S cm² mol⁻¹, revealing the non–electrolytic nature of the bromo complexes, albeit they are uni–univalent electrolytes in DMSO and DMF¹³. The copper(II) perchlorate complex is a uni–univalent electrolyte in DMSO and nitromethane suggesting that only one perchlorate group is bonded to the central atom. The [M(L)Br₂] complexes described here were prepared according to Scheme 1. The characterizational data support the formulation of the complexes as tetradentate with respect to the ligand and including two bromide anions in the axial positions in MeNO₂ solution, but not in DMF or DMSO. The copper(II) complex has one ClO₄ anion in the axial position in MeNO₂ or DMSO solutions.

Table 7.1: Analytical data of (C₁₈H₁₈N₄S₂) and the [M(L)Br₂] and [Cu(L)ClO₄][ClO₄] complexes

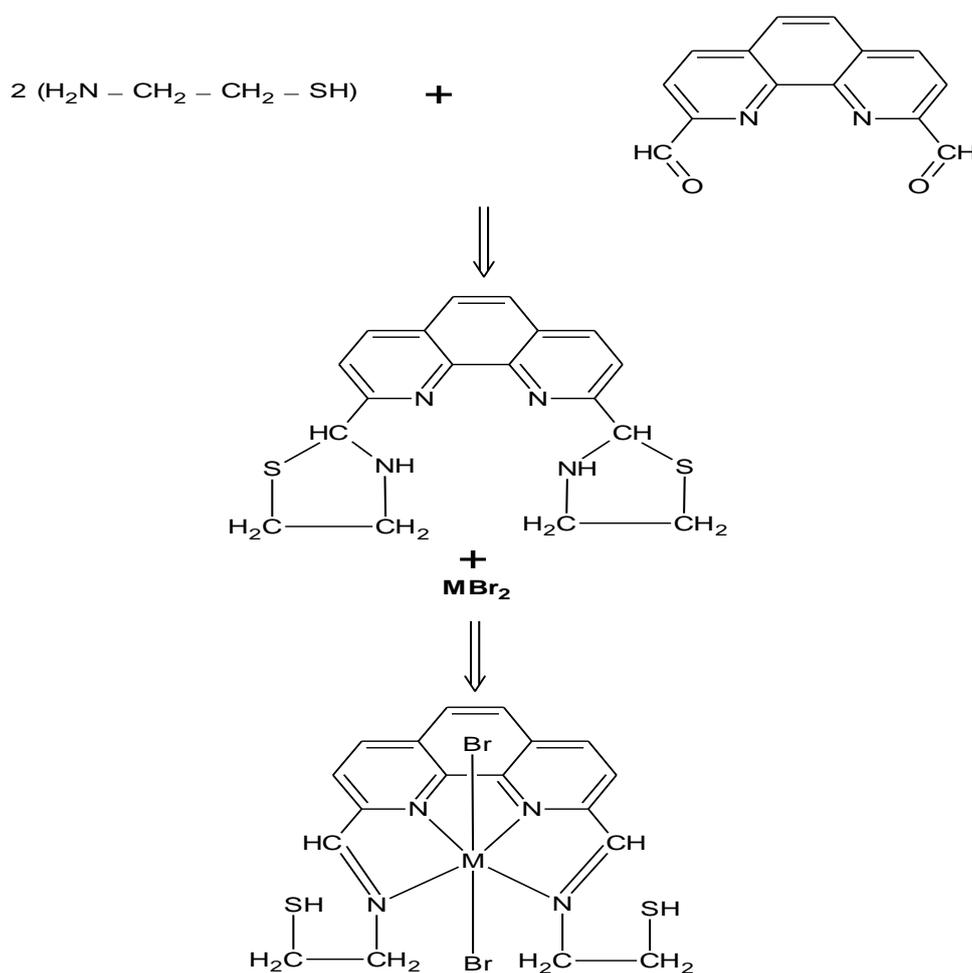
Compound	Found (Calculated)%				
	C	H	N	S	Metal
(C ₁₈ H ₁₈ N ₄ S ₂)(L)	60.90 (61.01)	4.91 (5.08)	15.70 (15.81)	17.91 (18.07)	
[Co(L)Br ₂]	37.6 (37.70)	3.0 (3.14)	9.61 (9.77)	11.0 (11.17)	10.15 (10.28)
[Ni(L)Br ₂]	37.61 (37.71)	3.0 (3.14)	9.60 (9.77)	11.0 (16.17)	10.10 (10.28)
[Cu(L)ClO ₄][ClO ₄]	34.87 (35.03)	2.80 (2.91)	8.87 (9.08)	10.20 (10.38)	10.20 (10.30)
[Zn(L)Br ₂]	32.10 (37.25)	3.0 (3.10)	8.1 (8.4)	10.84 (11.03)	11.20 (11.35)

The mass spectrum of the ligand shows an $m/z = 354$ based on $N=14$, $S=32$ which is consistent with the molecular weight. The metal(II) complexes were also identified by mass spectra (peaks at m/z 350 nickel(II), 351 cobalt(II) 352 copper(II) and 352 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(III), mercury(II) and tin(II) ions were unsuccessful.

The ^1H NMR spectrum of the ligand shows a multiplet in the region 7.1–9.0 ppm which is assigned to aromatic ring protons. However, no band could be assigned to aldehyde or amine protons, suggesting that the proposed complexes are formed by the condensation reaction. A singlet at 8.2–8.5 ppm could be assigned to the two equivalent carboximine protons ($\text{CH}=\text{N}$, 2H).

IR Spectral Studies:

The IR spectroscopy can provide valuable information as to whether or not reaction has occurred. The IR spectrum of the bis thiazolanyl product shows no absorption bands which can be assigned to $\nu(\text{S}-\text{H})$ or $\nu(\text{C}=\text{O})$ vibrational modes coming from β -mercaptoethylamine and 1,10-phenanthroline-2,9-dicarboxaldehyde moieties, respectively. The absence of such absorptions together with the presence of a single amine stretching mode of medium intensity at $3,350\text{ cm}^{-1}$ is consistent with the product being the expected 2,9-bis(thiazolanyl-1, 10-phenanthroline (I)^{14,15}. This potential tetradentate ligand undergoes rearrangement induced by cobalt(II), nickel(II), copper(II) and zinc(II) ions. The appearance of new bands in the $440\text{--}475$ and $1,600\text{--}1,630\text{ cm}^{-1}$ ranges attributed to $\nu(\text{M}-\text{N})$ and $\nu(\text{C}=\text{N})$ vibrations, respectively¹⁶, and the absence of $\nu(\text{N}-\text{H})$ vibrations observed in the spectra of the complexes suggest that the Schiff base product $\text{L}(\text{C}_{18}\text{H}_{18}\text{N}_4\text{S}_2)$ have been formed. The $[\text{M}(\text{L})\text{X}_2]$ complexes also show bands at $1,420\text{--}1,460$, $1,070\text{--}1,100$ and $720\text{--}740\text{ cm}^{-1}$ which can be assigned to phenyl ring vibrations¹⁷. The IR spectra of the complexes show $\nu(\text{M}-\text{Br})$ bands at 220, 223 and 230 cm^{-1} for bromide bonded to the cobalt, nickel and zinc atoms, respectively. The copper(II) complex shows characteristic bands at $1,100\text{ cm}^{-1}$ for the perchlorate bonded to the copper atom and one at $1,080\text{ cm}^{-1}$ corresponding to the free perchlorate ion. Medium intensity band appearing in the $2,830\text{--}2,950\text{ cm}^{-1}$ region corresponds to aliphatic $\nu(\text{C}-\text{H})$, while aromatic $\nu(\text{C}-\text{H})$ stretches appear in the $3,000\text{--}3,100\text{ cm}^{-1}$ region.^{18,19}



Scheme 1. The preparation of $[\text{M}(\text{L})\text{Br}_2]$ complexes

MAGNETIC MEASUREMENT STUDIES

Notwithstanding that the reaction were carried out under nitrogen atmosphere, presumably air oxidations could have occurred and the ligand $\text{L}(\text{C}_{18}\text{H}_{18}\text{N}_4\text{S}_2)$ having delocalized π -orbital system would be able to coordinate to the zinc(II) ion under the form of semithioquinone, allowing to obtain a paramagnetic complex. To test for the formation of radical species, corrected magnetic moments have been calculated from the molar magnetic susceptibilities using Pascal's constants¹⁸. The values for (I) ($\text{C}_{18}\text{H}_{18}\text{N}_4\text{S}_2$) and the $[\text{Zn}(\text{L})\text{Br}_2]$ complex are only 0.10–0.20 B.M. suggesting that no oxidation occurs. These values clearly indicate that these compounds have no unpaired electrons and they show no EPR signals at room temperature.

The magnitudes of the magnetic moments for the paramagnetic complexes fall within the ranges associated with high spin ions in octahedral fields and they are unlikely to be of value in discriminating between the metal ions in five and six coordinate geometries. The cobalt(II) complex has a magnetic moment of 4.78B.M. which is a typical value of a d^7 system with three unpaired electrons indicating a quartet state in a high spin octahedral configuration? The EPR spectrum recorded at the X-band frequency at room temperature shows a single line with no hyperfine splitting due to ⁵⁹Co (100% natural abundance, nuclear spin $I = 7/2$). Our $g = 2.01$ agrees quite well with other high spin cobalt(II) complexes. The room temperature magnetic moment of the nickel(II) complex in the solid state is 3.28 B.M. which is typical of compounds with two unpaired electrons in a high spin octahedral d^8 configuration.^{20,21} The room temperature magnetic moment of the $[\text{Cu}(\text{C}_{18}\text{H}_{18}\text{N}_4\text{S}_2)\text{ClO}_4][\text{ClO}_4]$ complex in the solid state is 1.87 B.M. as expected for monomeric non-interacting copper ions, corresponding to

compounds with one unpaired electron. The EPR spectrum of the solution as a DMSO glass at 77 K is illustrated in Fig. 1 and shows g value ($g_{\parallel} = 2.31$ and $g_{\perp} = 2.08$) resembling those of copper(II) in other five coordinate geometries. Four lines of equal area were observed due to splitting by copper(II) ion ($I = 3/2$ for ^{63}Cu and ^{65}Cu). The trend $g_{\parallel} > g_{\perp} > g_e$ (free ion value, 2.0023) and the axial symmetry value, $G = 3.9$, which falls in the 2.9–5.2 range, indicate that the unpaired electron is present in the $d_{x^2-y^2}$ orbital and there is no exchange interaction between the copper centres¹⁹.

ELECTRONIC SPECTRAL STUDIES

The electronic spectrum of the Schiff base ($\text{C}_{18}\text{H}_{18}\text{N}_4\text{S}_2$) shows a band of the phenyl ring at 230 nm. This band of high intensity shifts slightly towards lower wavelength at 215–220 nm range on complex formation. The spectra of the ligand ($\text{C}_{18}\text{H}_{18}\text{N}_4\text{S}_2$) as well as the complexes in DMSO solutions show the broad bands in the regions 275–320 and 320–380 nm range due to the $\pi-\pi^*$ ($>\text{C}=\text{N}-$) transition of the chromophore and the secondary band of the benzene ring, respectively.²²

The electronic spectrum of $[\text{Co}(\text{L})\text{Br}_2]$ $\text{L}-(\text{C}_{18}\text{H}_{18}\text{N}_4\text{S}_2)$ is characteristic of a cobalt(II) complex with octahedral symmetry. The lower energy bands observed in the regions of 370 and 760 nm are normally assigned to the ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$ transitions, respectively. The third spin allowed transition ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ appears as a shoulder at 340 nm. The origin of the broad area of absorptions below 1,100 nm is unknown, although, as in the case of the nickel(II) spectrum, of which it is reminiscent, it may be due to a species of lower symmetry which could be formed by dissociation in solution.^{23,24}

The $[\text{Ni}(\text{C}_{18}\text{H}_{18}\text{N}_4\text{S}_2)\text{Br}_2]$ electronic spectrum is also characteristic of a nickel(II) complex with octahedral geometry. The lower energy bands, observed in the regions 780 and 1,180 nm are assigned to the transitions ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\nu_1)$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})(\nu_2)$, respectively. The third spin allowed transition ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ is obscured in the spectrum by a charge transfer band. An additional band is assigned to the spin-forbidden transition ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g$ at 950 nm.

The electronic spectrum of the copper(II) complexes shows two bands at 270 and 350 nm which may be attributed to transitions within the organic molecule. The band at 350 nm is too high to be assigned as a d–d transition. The copper(II) ion has a d^9 electronic configuration and originates only one spectral term in electronic spectra, ${}^2\text{D}$. The d–d electronic transition in an octahedral field is ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ with a possible unfolding of this band because of Jahn–Teller distortion. Five coordinated complexes of copper(II) usually present the d–d band at 500–660 nm range. In fact, the spectrum of the copper(II) complex presents only one d–d transition band centred at 590 nm suggesting lower symmetries than O_h .^{25,26}

In the spectrum of the zinc(II) complex, a smooth band was observed at 560nm which could be assigned as a charge transfer band. It has been reported²⁰ that a metal is capable of forming $d\pi-p\pi$ bands 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 nitrogen donor atom of the ligand $\text{L}(\text{C}_{18}\text{H}_{18}\text{N}_4\text{S}_2)$.

STRUCTURE OF COMPLEXES

The ligand ($\text{C}_{18}\text{H}_{18}\text{N}_4\text{S}_2$) has several potential donor atoms, but due to steric constraints, it can provide a maximum of four donor atoms at any one time for coordinating to a metal. On the assumption that four nitrogen atoms of the ligand are coordinated to the metal, as seems likely from an inspection of molecular models, it follows that the complexes would be four coordinate with respect to the ligand.²⁷

From the models it appears that both planar or approximately planar configurations of the ligand are possible. However, without a full structural analysis one cannot make a distinction between these possibilities. Despite the crystalline nature of the products none proved suitable for X–ray structure determination. The nature of the data suggests that the bromo complexes in the solid state are octahedral with the ligand functioning as a tetradentate donor, hold in an approximate square–planar array of

nitrogen atoms and two bromo atoms in axial position. A rectangular pyramidal or square pyramidal structure is proposed for the copper(II) perchlorate complex.²⁸⁻³²

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