Synthesis and spectral studies on copper(II) and cobalt(II) complexes of macrocyclic ligand containing thiosemicarbazone moiety

Sulekh Chandra* & Sangeetika
Department of Chemistry, Zakir Husain College (University of Delhi) New Delhi 110 002, India
E-Mail : amit1984@mantranline

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New copper(II) and cobalt(II) complexes of macrocyclic Schiff base ligand containing thiosemicarbazone moiety have been prepared with a general composition [M(H2L2)X2] where M = Cu(II) or Co(II); H2L2 = 3,4,9,10-tetraphenyl-1,2,5,6,8,11-hexaazacycldodeca-7,12-dithione-2,4,8,10-tetraene; X = Cl?, NO3?, 1/2 SO4?, and ML2 where salt used is copper acetate and cobalt thiocyanate. When the mesocycle 6-ethoxy-1,6-diphenyl-4-thio-2,3,5-triazine (H2L1) in ethanol react with metal salt (chromium chloride) acting as template using high dilution technique, the macrocyclic ligand H2L2 was formed. The complexes have been characterized on the basis of elemental analysis, molar conductance, magnetic susceptibility, IR, electronic 1H NMR, Mass and EPR spectral studies. The complexes from H2L2 show different characteristics stoichiometry ratio with a variable grade of deprotonation in the ligand, depending upon the salt used [Cl?, NO3?, 1/2 SO4?, CH3COO? or SCN?] and working conditions.

Schiff base macrocyclic ligands derived from thiosemicarbazone are of significant interest not only for their pharmacological properties as antibacterial, anticancer, antiviral and antifungal agents but also for their capacity for chemical recognition of anions and metals of biochemical, medical and environmental importance. They can yield mono- or polynuclear complexes, some of which are biologically relevant. In particular, first row of transition metal complexes with such ligands containing thiosemicarbazone moieties have a wide range of biological properties. The number and relative proportion of donor atoms and the cavity size in the macrocyclic compounds gave special reactivity to these molecules. The most important factors in the condensation reactions [1+1], [1+2] or [2+2] are nature of relative proportions of reactants; chain length and presence of heteroatoms in the precursor molecules, type of condensation; experimental conditions such as solvent, pH and temperature.

In the present paper we report the synthesis and characterization of a series of copper(II) and cobalt(II) complexes obtained from 3,4,9,10-tetraphenyl-1,2,5,6,8,11-hexaazacycldodeca-7,12-dithione-2,4,8,10-tetraene(H2L2) structure I.

Experimental
All the chemicals used were of AnalAr grade. Solvents were purified according to standard procedures before use.

Preparation of ligand

Synthesis of ligand H2L1
An ethanolic (50 mL) solution of thiosemicarbazide (0.01 mol, 0.92 gm) was added to an ethanolic (50 mL) solution of benzil (0.01 mol, 2.1 gm) in the presence of 25 mL of 2M HCl. All the reagents were added alternatively dropwise with stirring. After addition of all the reagents, the mixture was heated with stirring for 7-8 h. On keeping it overnight, a yellow coloured crystalline solid was formed, which was filtered, washed with ethanol and dried in vacuo over P2O5 (yield 70 %, m.pt. 190°C). Structure I.

PhKPh

NH-N H-N

N

S:C- )-(-C:S

Synthesis of macrocyclic ligand H2L2
An ethanolic (50 mL) solution of chromium(III) chloride hydrated (0.001 mol, 0.26 gm) was added to an ethanolic (50 mL) solution of H2L1 (0.001 mol, 0.31 gm). The mixture was stirred at room temperature until the cream solid H2L2 formed, which was filtered, washed with ethanol and dried in vacuo over P2O5 (yield 68 %, m.pt. 170°C). Structure I.

Structure I.
Preparation of complexes

A warm ethanolic (10 mL) solution of corresponding metal salt (0.001 mol) was added to a warm ethanolic (10 mL) suspension of H₂L₂ (0.001 mol, 0.539 gm). The mixture was heated under reflux with stirring for 2 h. On cooling a coloured complex precipitated out, which was filtered, washed with ethanol and dried in vacuo over P₂O₅ (yield 60-70%, m.pt. – 200°C).

Microanalysis (C, H and N) of these complexes were carried out on a Carlo-Erba 1106 elemental analyzer. IR spectra were recorded on a Perkin Elmer 137 instrument as nujol mulls/KBr pellets. Electronic spectra were recorded in DMSO solution on a Shimadzu UV mini-1240 spectrophotometer. Molar conductance is measured on an ELICO Conductivity Bridge (Type C M 82 T). Magnetic susceptibility measurements were made on Gouy Balance at room temperature using CuSO₄.5H₂O as calibrant. Electron Impact Mass spectra were recorded on a JEOL, JMS, DX-303 mass spectrometer. ¹H NMR spectra were recorded on Hitachi FT-NMR, Model R-600 spectrometer using CDCI₃ as solvent. Chemical shifts are given in ppm relative to tetramethylsilane. EPR spectra of the complexes were recorded as powder samples at room temperature on an E-4 EPR spectrometer using DPPH as the g-marker. Molecular weight of the complexes were determined in benzene (freezing point).

Results and discussion

The reaction of a H₂L¹ with chromium chloride in ethanol at room temperature yield a cream solid H₂L² i.e a macrocyclic ligand. The analytical data confirms the [1+1] and [2+2] condensation of benzil and thiosemicarbazide (Table 1).

The reaction of mesocycle H₂L¹ with chromium chloride under the described conditions, is the first direct procedure to isolate a free macrocycle H₂L² containing thiosemicarbazone moieties. The complexes are stable in air and moisture. The analytical data of the complexes are consistent with the proposed stoichiometries which are summarized in Table 1.

The mass spectrum of H₂L¹ confirms the proposed formula showing a peak at 311 amu corresponding to the molecular ion [C₁₇H₁₇N₃OS⁺]. It also shows series of peaks corresponding to loss of ethanol i.e at 266 amu (M-OC₂H₅) and various fragments. These data suggests the 1+1 cyclization of benzil and thiosemicarbazide.

<table>
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<tr>
<th>Compound/Molecular Formula</th>
<th>Found (Calc.) %</th>
<th>( \mu_{eff} ) (BM)</th>
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<tr>
<td>H₂L¹</td>
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<tr>
<td>C₁₂H₁₇N₃OS</td>
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<tr>
<td>H₂L²</td>
<td>M 67.65, C 3.99</td>
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<td>10.03, 61.23, 3.43</td>
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Table 1 — Characterization data of ligands and their complexes
The mass spectrum of H₂L² show a peak at 530 amu corresponding to macrocyclic species \([\text{C}_{30}\text{H}_{22}\text{N}_6\text{S}_2]^-\). It also shows series of peaks corresponding to various fragments. Their intensity gives the idea of stability of fragments.

As reference\(^\text{12}\), \(^1\text{H}\) NMR spectral data of H₂L¹ in CDCl₃ confirms the absence of terminal amine group and presence of ethanol inserted, as well as two signals assigned to the NH group. It exhibit signals in ppm as: 10.1s(NH), 10.9s(NH), 7.2-7.37m(Ph), 3.6q(CH₃) and 1.5tt(CH₃).

The NMR spectrum of H₂L² confirms the absence of ethanol inserted or as a crystallization molecule. It exhibit signals in ppm as: 10.5s(NH), 8.0-7.1m(Ph). The \(^1\text{H}\) NMR spectra of aceto complex of copper and thiocynate complex of cobalt indicates the deprotonation of the ligands.

The infrared spectra of the ligands and their complexes give important information regarding the coordination to the metal ion. The absence of bands in the region 2600-2800 cm\(^{-1}\) and its metal complexes suggest the absence of any thiourea tautomer in the solid state\(^\text{13-14}\).

The IR spectrum of H₂L² shows several bands between 3398 and 3098 cm\(^{-1}\) corresponding to N-H stretching vibrations, which indicates that ligand is present in neutral form according to the analytical data. The most significant bands of H₂L² in KBr are: 3325, 3149 cm\(^{-1}\) (NH), 1609 cm\(^{-1}\) (CN), 1464 cm\(^{-1}\) (thioamide 1) and 767 cm\(^{-1}\) (thioamide 2).

The spectra of copper(II) and cobalt(II) complexes show that the C=N band slightly shifting to higher frequency indicates that the ligand is bonded to the metal ion through four imine nitrogen atoms. The band assigned to thioamide 1 remains at the same position as in the free ligand which indicates that this group is not involved in coordination\(^\text{15}\). The IR spectra of nitrito complexes of Cu(II) and Co(II) display multiple bands in the region 1475-1002 cm\(^{-1}\). So it is difficult to assign the coordination behaviour of nitrito group\(^\text{15}\). However, there is no broad absorption band at 1390 cm\(^{-1}\) which corresponds to uncoordinated nitrito group. The IR spectra of sulphato complexes of Cu(II) and Co(II) show two bands at 1170 and 1104 cm\(^{-1}\) (v₁) and 765 and 695 cm\(^{-1}\) (v₄) corresponding to unidentate sulphate group.

The sulphato complex possesses C₄v symmetry showing penta-coordination. The IR spectra of complexes obtained by using copper(II) acetate and cobalt(II) thiocynate confirm the deprotonation of ligands.

**Copper (II) complexes**

The magnetic moment of all the Cu(II) complexes at room temperature lie in the range 1.90-2.04 B.M. (Table 1) corresponding to one unpaired electron which are higher than spin-only value of 1.73 BM for one unpaired electron. This reveals that these complexes are monomeric in nature and also shows the absence of metal-metal interaction along the axial positions.

Electronic spectra of six-coordinate Cu(II) complexes have either D₂h or C₄v symmetry, and e₂g and t₂g level of 5D free ion term will split into B₁g, A₁g, B₂g and E₁g level respectively. Thus the three spin allowed transitions are expected in the visible and near IR region. But only few complexes are known\(^\text{16}\) in which such bands are resolved, either by Gaussian Analysis or single crystal polarisation studies. These bands may be assigned to following transitions, \(^2\text{B}_1g \rightarrow ^2\text{A}_1g\) (dₓ²−ᵧ²→dₓz), \(^2\text{B}_2g \rightarrow ^2\text{B}_2g\) (dₓ²−ᵧ²→dₓz), \(^2\text{E}_g\) (dₓ²−ᵧ²→dₓz, dₓz, dₓ²−y²) in order of increasing energy.

The electronic spectra of the complexes [Cu(H₂L²)X₂] (X = Cl, NO₃) display two characteristics bands in the region 20080-22471 cm\(^{-1}\) and 10319-10330 cm\(^{-1}\). These may be assigned to \(^2\text{B}_1g \rightarrow ^2\text{E}_g\) and \(^2\text{B}_2g \rightarrow ^2\text{A}_1g\) transitions respectively. The third band assigned to \(^2\text{B}_1g \rightarrow ^2\text{B}_2g\) transition band is usually not observed as a separate band in the tetragonal field. Sulphato complex of copper display two d-d transition bands at 21276 and 16300 cm\(^{-1}\) corresponding to transitions \(^2\text{B}_1g \rightarrow ^2\text{A}_1g\) and \(^2\text{B}_1g \rightarrow ^2\text{E}_g\). The complex CuL² displays broad band at 17482 cm\(^{-1}\) and 22471 cm\(^{-1}\) corresponding to transitions \(^2\text{B}_1g \rightarrow ^2\text{A}_1g\) and \(^2\text{B}_1g \rightarrow ^2\text{E}_g\) which suggests the square planar geometry\(^\text{16}\).

The EPR spectra recorded as polycrystalline sample possesses a characteristic spectrum having one asymmetric band with two g values. The g₁ and g₄ values were computed from the spectrum using DPPH free radical as ‘g’ marker. The ‘g’ values and spin Hamiltonian parameters are summarized in Table 2. Kivelson and Neiman\(^\text{17}\) have reported the g₁ value < 2.3 for covalent character of the metal-ligand bond and > 2.3 for ionic character. Applying this criteria, the covalent character of the metal-ligand bond in the complexes under study can be predicted. The trend g₁ > g₄ > g₀(2.0023) observed for these complexes shows that the unpaired electron is localized in dₓ²−y² orbital of the Cu(II) ions and the spectral features are...
characteristic of axial symmetry. The complex under study may have six-coordinate tetragonal geometry.

In addition, there is exchange coupling interaction between two copper centres explained by Hathaway expression $G = (g_1 - 2g_2) / (g_1 - 2)$. According to Hathaway, if the value of $G$ is greater than four, the exchange interaction is negligible, whereas when the value of $G$ is less than four, a considerable interaction is indicated in solid complex. The calculated $G$ values are given in Table 2.

The fraction $\alpha^2$ which is taken as a measure of covalent nature, is evaluated by the expression. $\alpha^2 = \frac{A_\parallel}{P} + \frac{(g_\perp - 2.0023)}{3}(g_\perp - 2.0023) + 0.04$

where $A_\parallel$ is the parallel coupling constant expressed in cm$^{-1}$ value of $P=0.036$. The $\alpha^2$ values for the present copper complexes lie in the range 0.286-0.567 supporting the covalent nature of these complexes (Table 2).

For the EPR spectra of sulphato complex $g_3 > g_2 > g_1$ the ratio$^{21}$ of $(g_2 - g_1) / (g_3 - g_2)$ called the parameter $R$ is very useful. If the ground state is predominantly $d_{xy}^{2} - e_{z}^{2}$, the value of $R$ is less than one. On the other hand if the ground state predominantly $d_{xy}^{2}$, the value of $R$ is greater than one. The complex under study shows the value of $R$ less than one, thus indicating $d_{xy}^{2} - e_{z}^{2}$ ground state and may have five coordinate square pyramidal geometry.

**Cobalt(II) complexes**

The magnetic moment of cobalt(II) complexes lie in the range of 4.95-5.08 BM corresponding to three unpaired electrons due to contribution of orbital angular momentum. Whereas, the complex [CoL$^2$] prepared using thiocyanate salt show magnetic moment 1.94 BM indicates the low-spin square planar geometry for cobalt(II) complex (Table 1).

The electronic spectra of [Co(H$_2$L$_2$)X$_2$] (X = Cl, NO$_3$) show spin-allowed bands at 10131-11261 cm$^{-1}$, 22471-23419 cm$^{-1}$ along with shoulder at 14475-14800 cm$^{-1}$ which is not observed in all the complexes. These transitions may be assigned to $^4T_1g$ $\rightarrow$ $^4T_2g(F)$, $^4T_1g$ $\rightarrow$ $^4A_2g(F)$ and $^4T_1g$ $\rightarrow$ $^4T_1d(P)$ respectively. The position of bands indicates that these complexes have distorted octahedral geometry and might possesses $D_{4h}$ symmetry. The electronic spectrum of sulphato complex of cobalt displays three bands at 10131(v$_1$), 11261(v$_2$) and 21000(v$_3$) cm$^{-1}$ corresponding to five-coordinate distorted square pyramidal geometry and might possess $C_{4v}$ symmetry. Cobalt(II) complex, CoL$_2$ displays narrow band near 10132 cm$^{-1}$ and broader band near 22400 cm$^{-1}$ which suggests that the complex has low spin Co(II) complex possessing square planar geometry.

The various ligand field parameters were calculated for the cobalt(II) complexes. The value of $Dq$ has been calculated from transition energy diagrams using the $v_3/v_1$ ratio. The value of $Dq$ lies in the range 1144 -1375 cm$^{-1}$. Our results corresponds to respective positions of anions in the spectrochemical series. The nephelauxetic parameters $\beta$ is readily obtained using the relation;

$$\beta = \frac{B(\text{complex})}{B(\text{free ion})}$$

where $B(\text{free ion})$ is 1120 cm$^{-1}$. The value of $\beta$ lies in the range 0.464 - 0.682. The value of $\beta$ indicates that the covalent character of metal ligand $\sigma$ bond is low. Ligand field stabilization energy calculated for chloro and nitrate complexes are 109.34, 131.40 respectively.

The EPR spectra of Co(II) complexes were recorded as polycrystalline samples. No EPR signal
was observed at room temperature because the rapid spin lattice relaxation of Co(II) broadens the lines at higher temperature. All the complexes show a very broad signal at liquid nitrogen temperature. The ‘g’ values are given in Table 2. The deviation of ‘g’ values from the free electron value (2.0023) may be due to angular momentum contribution in the complexes.

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References