APPENDIX
Mixed-ligand Complexes of Co(II), Cu(II) and Zn(II) with 1-Amino-2-Naphthol-4-Sulphonic Acid and Nitrogen Donor Ligands

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Nine mixed-ligand complexes of the type [ML₂B₁] where M = Co(II), Cu(II) and Zn(II), LH = 1-amino-2-naphthol-4-sulphonic acid and B is nitrogen donor ligand like quinoline, pyridine, gamma-picoline and diethylamine have been synthesised and characterised as octahedral complexes on the basis of analysis, conductance, magnetic susceptibility, IR and electronic spectral data.

In our attempt to synthesise complexes of unusual coordination number, we have been trying for the base adduct formation of some divalent metal chelates. Several such base adducts of beta-diketones and beta-ketoesters of Zn(II) and Cu(II) have been reported earlier. It was therefore thought worthwhile to extend our investigation to the synthesis of some mixed-ligand complexes using 1-amino-2-naphthol-4-sulphonic acid as the chelating ligand.

Experimental

All the chemicals used were of AnalaR grade. Metal chelates were prepared by usual manner by reacting metal chlorides (Cobalt chloride 2.36 g, Copper chloride 1.69 g and zinc chloride 1.36 g) with ethanolic solution of 1-amino-2-naphthol-4-sulphonic acid (4.7 g) followed by the dropwise addition of ammonia. The compounds thus formed were suction filtered, washed with ethanol followed by ether and dried in vacuo.

Metal chelates were suspended in ethanol, mixed with the nitrogen donor ligands in 1:2 ratio and the mixture refluxed for about 1 hr., when a clear solution was obtained. On cooling the solution, crystalline compounds separated out. These were filtered, washed with ethanol, ether and dried in vacuo.

Metal contents in the complexes were estimated by complexometric E.D.T.A. method and nitrogen by standard micro analytical method. Conductance was measured in M/1000 DMF solution of the complexes using Toshniwal’s conductivity bridge. IR spectra were recorded in KBr phase using Beckman IR-12 spectrophotometer. Electronic spectra were recorded using chloroform base solution of the complexes by Hilger-Watt UVSP2 spectrophotometer. Magnetic susceptibility measurements were carried out by Gouy method using Co[Hg(SCN₂)] as calibrant. Relevant analytical, conductance, magnetic susceptibility and IR spectral data are given in Table 1.

Results and Discussion

Complexes reported in the present investigation have the composition [ML₂B₁] where M = Co(II), Cu(II) and Zn(II), LH = 1-amino-2-naphthol-4-sulphonic acid and B is a nitrogen donor ligand like quinoline, pyridine, gamma-picoline and diethylamine. Cobalt(II) complexes are brown, copper(II) complexes are green and zinc(II) complexes are white in colour. All the nine complexes have fairly low melting points and low conductance values in DMF indicating non-electrolytic nature. Magnetic moment values show the presence of three and one unpaired electron in case of cobalt and copper complexes respectively and indicate a spin-free octahedral configuration for the cobalt and copper compounds.

The IR spectra of metal chelates and the corresponding base adducts are informative. Here 1-amino-2-naphthol-4-sulphonic acid can function as a bidentate chelating ligand using the hydroxyl oxygen and the primary amino nitrogen atom as the bonding sites, the sulphonic acid group remaining free probably due to steric reasons and spatial position. The C—O stretching vibrations in alcohols usually occur in 1260-1000 cm⁻¹ region which has appeared in the ligand at 1220 cm⁻¹ and shifted to ~ 1200 cm⁻¹ in the metal chelates indicating bonding of the oxygen atom. In the base-adducts, this band again shifts to higher frequency regions appearing at 1210 cm⁻¹ indicating the bonding of the oxygen atom to the metal ion ν(N—H) in the chelating ligand appears at 3250 cm⁻¹ as a sharp peak. In the metal chelates and base-adducts N—H stretching frequency appears either as a broad band or is split into several peaks not so sharp as in the parent compound proving indirect evidence for
bonding at the nitrogen of the primary amino group. Most of the absorption bands due to free nitrogen ligands have been modified in the complexes proving indirect evidence of their presence as coordinated ligands. This has been further substituted by the observation of \(\nu(M-O)\) and \(\nu(M-N)\) around \(\sim 430\) cm\(^{-1}\) and \(\sim 510\) cm\(^{-1}\) respectively which provide the direct evidence for the formation of metal chelates and their base adducts.

The cobalt(II) complexes in DMF solution give rise to two absorption bands with maxima at 8.6 and 19.7 K.K. region which can be assigned to \(^4T_{1g} \rightarrow ^4T_{2g}\) and \(^4T_{1g} \rightarrow ^4T_{1g}(P)\) transitions. These absorption bands, extinction coefficients and \(\mu_{\text{eff}}\) values indicate a high-spin octahedral configuration. The copper(II) complexes show one broad absorption band centered at 15.0 K.K. Though three transitions \(^2B_{1g} \rightarrow ^2A_{1g}(P_{1})\), \(^2B_{1g} \rightarrow ^2B_{2}(P_{3})\) and \(^2B_{1g} \rightarrow ^2E(P_{5})\) occur in Cu(II) complexes of D\(_{3h}\) symmetry due to Jahn-Teller distortions, they are often very close in energy and give rise to a single broad band envelop.

Zinc(II) complexes have presumably an octahedral configuration on the basis of their analysis, conductance and IR spectral data.

References

Complexes of Co(II), Ni(II), Cu(II) and Zn(II) with ethyl acetoacetate semicarbazone and thiosemicarbazone

(Received 5 January 1978; received for publication 4 August 1978)

Although a lot of work has been done on complexation by the semicarbazones and thiosemicarbazones of aldehydes[1,2] and ketones[3], there is much less about the complexing ability of the semicarbazone and thiosemicarbazone of ethyl acetoacetate, a \( \beta \) keto ester.

**EXPERIMENTAL**

All the chemicals used were of AnalyR grade. The semicarbazone and thiosemicarbazone of ethyl acetoacetate were prepared by published methods. Metal complexes were prepared by reacting an ethanolic solution of the metal chloride with the ligands dissolved in the same solvent in stoichiometric ratio, and refluxing for about 2 hr on a water bath. On keeping over night, the complexes separated. They were washed with ethanol followed by ether and dried in vacuo.

Metals were estimated by the complexometric EDTA method and nitrogen by the standard microanalytical method. Conductance was measured in M/1000 DMF solution. Magnetic moments of the complexes were found out by Gouy method using Co Hg(SCN)\(_2\) as calibrant. IR spectra were recorded in KBr discs on a Beckman IR-12 spectrophotometer. Electronic spectra were taken using a M/100 KMF solution on a Hilger-Watt UVISPECK spectrophotometer.

**RESULTS AND DISCUSSION**

The complexes found of the type \([MLCl,B]\) and \([MLCl,B]\), where \( M = \text{Co(II)}, \ Ni(II), \ Cu(II) \) and \( Zn(II) \), \( L = \text{ethyl acetoacetate semicarbazone}, \ L' = \text{ethyl acetoacetate thiosemicarbazone} \) and \( B = \text{H}_2\text{O} \). The Co(II) complexes are brown, the Ni(II) complexes are green. The Cu(II) complexes with semicarbazone are green and with thiosemicarbazone brown, and the Zn(II) complexes are white. All the complexes have low m.p. and are fairly soluble in DMF. The DMF solutions have low conductance values (\( \lambda \text{DMF} \)) in the range 5-10 \( \mu \text{cm}^2 \text{mol}^{-1} \) indicating nonelectrolytes. Magnetic moment values of the Co(II), Ni(II), and Cu(II), complexes indicate high-spin octahedral configurations.

The semicarbazone and thiosemicarbazone of ethyl acetoacetate behave as tridentate ligands.

In case of the thiosemicarbazone ligand, the thiocarbonyl sulphur, imino nitrogen atom and carbonyl oxygen are the donating atoms whereas, ethyl acetoacetate semicarbazone uses two carbonyl oxygen atoms and the imino nitrogen atom. \( v(\text{C} = \text{S}) \) in the free ligand occurs[4] at 1090 cm\(^{-1}\) and shifts in the complexes to lower frequency (\( \sim 1075 \text{ cm}^{-1} \)) indicating bonding through the thiocarbonyl sulfur. \( v(\text{C} = \text{N}) \), observed around 1580 cm\(^{-1}\) in the ligands decreases by 10-15 cm\(^{-1}\) in the complexes and this shows the coordination of the imino nitrogen atom[5,6] of the azomethine group to the metal ions. The appearance of a sharp band around 1720 cm\(^{-1}\) in the free ligands is attributable to \( \nu(\text{C} = \text{O}) \). In the complexes, this band is shifted to lower frequency.
-1700 cm\(^{-1}\), which indirectly supports bonding of the carbonyl oxygen to the metal ions. In the complexes a broad hump is observed at 3450 cm\(^{-1}\) indicating the presence of coordinated water[1, 3]. However, conclusive evidence of bonding is obtained by the occurrence[9] of bands at -260 cm\(^{-1}\), -450 cm\(^{-1}\), -370 cm\(^{-1}\) which correspond to \(v(M-S)\), \(v(M-O)\) and \(v(M-N)\) respectively.

### Table 1. Analysis, M.p., conductance, magnetic susceptibility, IR and electronic spectral data

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.p. (^{\circ})C.</th>
<th>Metal Found (Calc.)</th>
<th>%</th>
<th>Conductance (\Omega \text{cm}^2/\mu\text{A})</th>
<th>(\nu_{\text{max}}) ((\text{cm}^{-1}))</th>
<th>(\tau(C-S))</th>
<th>(\tau(C=O))</th>
<th>(\tau(M-S))</th>
<th>(\tau(M-O))</th>
<th>(\tau(M-N))</th>
<th>(\mu_{\text{max}}) ((\mu_B))</th>
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<tr>
<td>L</td>
<td>1291</td>
<td>22.25</td>
<td>1580</td>
<td>1720</td>
<td>1585</td>
<td>1724</td>
<td>450</td>
<td>370</td>
<td>9.66(6)</td>
<td>15.5(8)</td>
<td>25.6(15)</td>
</tr>
<tr>
<td>L'</td>
<td>88</td>
<td>20.21</td>
<td>1570</td>
<td>1700</td>
<td>1570</td>
<td>1705</td>
<td>440</td>
<td>360</td>
<td>8.2(14)</td>
<td>20.5(30)</td>
<td>15.5(30)</td>
</tr>
<tr>
<td>[Ni(C2L2)B]</td>
<td>2201</td>
<td>17.34</td>
<td>12.34</td>
<td>3.9</td>
<td>1570</td>
<td>1705</td>
<td>445</td>
<td>365</td>
<td>15.5(30)</td>
<td>25.6(15)</td>
<td>15.5(30)</td>
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<tr>
<td>[Co(C2L2)B]</td>
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<td>17.16</td>
<td>12.38</td>
<td>5.6</td>
<td>1570</td>
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<td>440</td>
<td>360</td>
<td>8.2(14)</td>
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<td>[Cu(C2L2)B]</td>
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<td>10.06</td>
<td>12.16</td>
<td>6.4</td>
<td>1570</td>
<td>1705</td>
<td>445</td>
<td>365</td>
<td>15.5(30)</td>
<td>25.6(15)</td>
<td>15.5(30)</td>
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<tr>
<td>[Zn(C2L2)B]</td>
<td>212</td>
<td>18.89</td>
<td>11.27</td>
<td>8.6</td>
<td>1570</td>
<td>1705</td>
<td>455</td>
<td>365</td>
<td>24.8(14)</td>
<td>15.5(30)</td>
<td>25.6(15)</td>
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<tr>
<td>[Ni(C2L2)B]</td>
<td>2251</td>
<td>16.71</td>
<td>11.58</td>
<td>7.6</td>
<td>1570</td>
<td>1705</td>
<td>440</td>
<td>365</td>
<td>9.8(6)</td>
<td>14.7(7)</td>
<td>24.8(14)</td>
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<tr>
<td>[Co(C2L2)B]</td>
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<td>16.97</td>
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<td>5.6</td>
<td>1570</td>
<td>1705</td>
<td>440</td>
<td>360</td>
<td>8.5(15)</td>
<td>20.7(22)</td>
<td>15.5(30)</td>
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<tr>
<td>[Cu(C2L2)B]</td>
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<td>17.92</td>
<td>12.07</td>
<td>6.7</td>
<td>1570</td>
<td>1705</td>
<td>450</td>
<td>370</td>
<td>15.2(28)</td>
<td>25.6(15)</td>
<td>15.5(30)</td>
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<td>[Zn(C2L2)B]</td>
<td>240</td>
<td>18.36</td>
<td>11.82</td>
<td>9.2</td>
<td>1570</td>
<td>1705</td>
<td>455</td>
<td>365</td>
<td>24.8(14)</td>
<td>15.5(30)</td>
<td>25.6(15)</td>
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</table>

L = Ethylacetoacetate semicarbazone, L' = ethylacetoacetate thiosemicarbazone, B = H\(_2\)O.

### Notes
- Decomposition.

### REFERENCES
ADDUCTS OF BIS (ETHYLACETOACETATO) COPPER (II) WITH NITROGEN LIGANDS

Bonding of additional ligands along the axis normal to the molecular plane of planar complexes like beta-diketonates and related compounds, which involve keto-enol tautomerism, have invoked a lot of interest in recent years. Since beta-keto esters are closely related to the beta-diketones, it was thought worthwhile to extend the investigation to such chelates and this communication reports some base adducts of bis-(ethyl acetoacetato) copper (II) with substituted pyridines, viz., 2-, 3-, and 4-methyl pyridines.

Ethanolic solution of cupric chloride was reacted with ethyl acetoacetate in (1:2) proportion, followed by dropwise addition of ammonia with constant stirring. The green product obtained was filtered off, washed with ethanol and ether and dried in a vacuum desiccator. Metal chelate and the nitrogen ligands (in 1:2 ratio) were taken in minimum quantity of ethanol and refluxed for thirty minutes. On cooling the solution overnight, crystalline compounds separated out.

Metal ion in the compounds was estimated by EDTA procedure. Conductance was measured in M/1000 acetone solution using a Toshniwal conductance bridge. Magnetic susceptibility was measured on the solid specimen by Gouy method. Infrared spectra were recorded in nujol mulls with Unicam SP 200 Spectrophotometer. U.V. and visible spectra were recorded using M/100 chloroform-base solution in Unicam SP 500 Spectrophotometer. The relevant analytical, conductance and magnetic susceptibility data are recorded in Table I.

Results and Discussion

The green crystalline compounds have the composition Cu(EAA)$_2$L$_2$ where 'L' is substituted pyridine. The compounds are stable in air, have low melting points. Acetone solutions of the complexes have low molar conductance values, $\Delta M$ being in the range of 2-4 mhos, indicating non-electrolytic nature.

Most of the absorption bands due to the free nitrogen ligands are shifted in the adducts indicating bonding to the metal, information being obtained by the "Finger Print" technique, $\nu$ (C=O) and $\nu$ (C=C) of the ester which occur at 1650 and 1630 cm$^{-1}$ respectively shift to lower frequency region (1600 and 1525 cm$^{-1}$) on chelation and again shift to higher frequency (1620 and 1540 cm$^{-1}$ respectively) in the nitrogen base adducts providing additional evidence for bonding of the ester and nitrogen ligand. Direct evidence could not be obtained as $\nu$ (Cu-O) and $\nu$ (Cu-N) were beyond the range of instrument used.

An intense band appeared in the U.V. region around 260 nm ($\epsilon = 15000$) in solution spectrum of the chelate and base adducts due to the more probable $\pi \rightarrow \pi^*$ transition rather than charge transfer. In the visible region, a broad absorption band was observed around 660 nm ($\epsilon = 60$) in the chelate which was found around 650 nm ($\epsilon = 85$) in the base adducts. On coordination of the nitrogen ligands there is not much shift in the position of the absorption band though the intensity increases. This is in conformity with some earlier observations. Hence the complexes are six-coordinated, presumably having a tetragonally distorted octahedral configuration. Though distorted octahedral Cu (II) complexes have three transitions ($2B_{1g} \rightarrow 2B_{2g}$, $2B_{1g} \rightarrow 2E_{1g}$, $2B_{2g} \rightarrow 2A_{1g}$), often the three bands appear in a single broad asymmetric band envelope.

The base adducts appear to be far more stable than their beta-diketonato analogues since in absence of the added base, there is no change in the position of absorption band in solution spectrum indicating "no appreciable dissociation" of the ligands.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Colour and form</th>
<th>MP (°C)</th>
<th>$\Delta M$ cm$^{-1}$</th>
<th>$\nu_{eff}$ (B.M.)</th>
<th>% Metal</th>
<th>%N Metal</th>
<th>% Metal</th>
<th>% N</th>
<th>Found</th>
<th>% Metal</th>
<th>% N</th>
<th>Found</th>
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<tbody>
<tr>
<td>Cu (EAA)$_2$ (α-pic)$_2$</td>
<td>Green crystalline</td>
<td>160</td>
<td>2.8</td>
<td>1.76</td>
<td>1.56</td>
<td>12.0</td>
<td>5.52</td>
<td>5.3</td>
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<tr>
<td>Cu (EAA)$_2$ (β-pic)$_2$</td>
<td>do.</td>
<td>180</td>
<td>3.0</td>
<td>1.74</td>
<td>12.56</td>
<td>12.1</td>
<td>5.52</td>
<td>5.25</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Cu (EAA)$_2$ (γ-pic)$_2$</td>
<td>do.</td>
<td>175</td>
<td>4.2</td>
<td>1.78</td>
<td>12.56</td>
<td>11.9</td>
<td>5.52</td>
<td>5.32</td>
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</tbody>
</table>
Department of Chemistry, Ravenshaw College, Cuttack 3 (Orissa),
February 21, 1976.

In our programme of preparing complexes of rare and higher coordination number with first transition series metal ions, we have been synthesizing number of polydentate chelating ligands, since such ligands dominate the area of higher coordination polyhedra from kinetic and thermodynamic stability point of view. Earlier, we have studied the complexation behaviour of a number of bi-, tri- and tetra-dentate schiff's bases. This communication reports complexes of Co(II), Ni(II), Cu(II), and Zn(II) ions with a bidentate schiff's base derived from salicylaldehyde and 2,4-dinitrophenyl hydrazine.

Experimental

All the chemicals used were of AnalyR grade. Salicylaldehyde-2,4-dinitrophenyl hydrazine was prepared by the conventional method.

An ethanolic solution of the Schiff's base was reacted with ethanolic solution of metal chlorides in (2 : 1) ratio followed by dropwise addition of ammonia, when the metal chelate separated. These were filtered, washed with ethanol and ether and dried in vacuo.

Metal in the complexes was estimated by EDTA titration method and nitrogen by microanalytical method. Conductance was measured in M/1000 D.M.F. or chloroform solution of the complexes. Magnetic susceptibility measurements were made over solid specimens by Gouy method. Infrared spectra were recorded in KBr phase using Perkin-Elmer model 337 and 621 spectrophotometers. Spectra were recorded in M/100 solutions using a Hilger-Watt spectrophotometer.

All the relevant analytical and spectral data are...
Complexes reported in the present investigation have the composition \([ML_2(H_2O)_2]\) where \(M=\) Co(II), Ni(II), Cu(II) and Zn(II) and \(L\) is the anion of the Schiff's bases derived from salicylaldehyde and 2,4-dinitrophenyl hydrazine. All are crystalline compounds, Cobalt complex is brown, nickel and copper are green and zinc is brownish white. These have low conductance values, indicating non-electrolytic nature of complexes. Magnetic moment values are indicative of the presence of three, two and one unpaired electrons in case of Cobalt(II), Nickel(II) and Copper(II) complexes respectively and suggest an octahedral configuration of these compounds.

Although there are three sites for coordination viz oxygen of the -OH group, nitrogen of -NH, bonding has actually taken place through the oxygen and azomethine nitrogen atoms. \(\nu(C=O)\) usually occurs \(\sim 1610 \text{ cm}^{-1}\) which has decreased to lower frequency region (on coordination) due to the reduction of electron density in the azomethine link. \(\nu(C-O)\) appears \(\sim 1200 \text{ cm}^{-1}\) region. A medium broad band appears around 3450 cm\(^{-1}\) region assignable to \(\nu(\text{OH})\) of coordinated water molecule present. The sharp band due to \(\nu(N-H)\) has probably been superimposed in this broad band envelope. Decrease in both \(\nu(C-O)\) and \(\nu(C=O)\) compared to the ligand suggests bonding at these sites. This has been further substantiated by the observation of two bands at 450 an 510 cm\(^{-1}\) assignable to \(\nu(M-O)\) and \(\nu(M-N)\) respectively in the far infrared spectra of complexes.

In the visible electronic spectra, two absorption bands appear at 18.8 (35) and \(8.5(20)\) k.k. attributable to \(^4T_g \rightarrow ^4T_g\) (P) and \(^4T_g \rightarrow ^4T_g\) (F) transitions respectively. Position of absorption bands, molar absorptivity values and magnetic moment suggest a high-spin octahedral configuration for the Cobalt(II) complex. Nickel(II) complex exhibits three absorption bands at 8.8(6), 14.7(10) and 25.0(15) k.k. assignable\(^{2,5}\) to \(^4A_2g \rightarrow ^4T_g\), \(^4A_2g \rightarrow ^4T_g\) (F) and \(^4A_2g \rightarrow ^4T_g\) (P) transitions respectively characteristic of high-spin octahedral or distorted octahedral configuration. Copper(II) complex shows one broad absorption band at 15.5 (45) k.k. indicating probably a tetragonally distorted octahedral configuration. On the basis of analysis, conductance and infrared spectral data Zinc(II) complexes presumably have an octahedral environment around the metal ion.

References

6. J. R. Ferraro, "Low frequency vibration of inorganic
Cu(II), Ni(II) & Zn(II) Complexes with Ethyl Methyl Ketone Thiosemicarbazone

THE coordination behaviour of semicarbazones and thiosemicarbazones of aldehydes has been investigated by Russian workers. A few reports are also available on the coordination behaviour of thiosemicarbazones of some ketones. In this note, preparation and characterization of the complexes of Co(II), Ni(II) and Zn(II) with ethyl methyl ketone thiosemicarbazone are reported.

All the chemicals used were of AR grade. The above thiosemicarbazone was prepared by standard method and its purity checked, m.p. 110°.

Complexes of Ni(II) chloride and nitrate were prepared by refluxing ethanolic solution of the salts with ethanolic solution of the ligand in 1:2 proportion for 3 h, while other complexes were prepared by evaporating the solution in air. Analytical data of the complexes are recorded in Table 1.

The complexes are of the type [ML₂X₂] except the perchlorate complex which is of the composition [ML₂ClO₄] where L=ligand, M=Co(II), Ni(II), Zn(II), X=Cl, NCS⁻, NO₃⁻ and Y=ClO₄⁻. Co(II) complexes are either pink or light pink crystalline whereas Zn(II) complexes are white crystalline. Acetone solution of the complexes have low molar conductance values (λ_m) in the range of 10⁻⁴ mO·cm²/mole, except the perchlorate complex, indicating their non-electrolytic nature. λ_m values for perchlorate complexes are >150 mO·cm²/mole indicating these to be 1:2 electrolytes. Molar refractivity moments of Co(II) and Ni(II) complexes (Gay method) indicate high-spin octahedral configuration for all the complexes, except the perchlorate complexes which seem to have a tetrahedral environment around the metal ions.

The IR spectra (v, cm⁻¹) exhibit two sharp bands ~2080 and ~700 which may be attributed to the groups v(C=S) and v(C=S) of N-bonded terminal thiosemicarbazone groups. The nitrato group exhibits v, and v, bands (NO₃⁻ asymmetric and symmetric stretch) appear ~1400 and ~2800 respectively. The position of v, and v, and their separation (Δν) of ~20 cm⁻¹ suggests the nitrate group to be monodentate. In the case of perchlorate complexes a broad hump appears in the region 1050 to 1150 indicative of an ionic perchlorate group which is in conformity with the conductance data which show them to be 1:2 electrolytes.

The thiosemicarbazones have the structure (II). It has four bonding sites, namely the thiosemicarbazone sulphur, nitrogen of the amino groups and the imino nitrogen. v(C=S) in the ligand occurs around 1120 and is shifted in the complexes to lower frequency, i.e. 1100, indicating bonding through thiosemicarbazone sulphur. The v(C=N) observed at 1600 in the ligand, remains unaffected in the complexes indicating non-coordination through this nitrogen. Broadening and splitting of v(N-H) which occurs ~3250 in the ligand, remains unaffected in the complexes indicating non-coordination through the amino group. However, it is difficult to ascertain whether primary or secondary amino group is bonded. Bonding through nitrogen, and sulphur has been further substantiated by the appearance of v(M-N) and v(M-S) ~360 and ~290 respectively.

In the electronic spectra of Cu(II) (chloride, nitrate, and thiocyanate) complexes three absorption bands are observed around 20.6 (12), 18.7 (30) and 8.5 (13) kK attributable to transition bands T₂→T₁(F) and T₁→T₂(F) transitions respectively indicating high spin octahedral configuration. The perchlorate complex exhibits two intense bands at 16.1 (1500) and 8.8 (2000) kK attributable to T₂→T₁(F) and T₃→T₄(F) transition respectively suggesting a tetrahedral geometry. Ni(II) chloride, nitrate and thiocyanate complexes show three bands at 9.4, 14.6 (7) and 26.6 (14) kK.
A number of complexes of the general formula $[ML_X]_n$ where $M = \text{Co(II), Ni(II), Zn(II)}$, $X = \text{Cl, NCS, NO}_3$, and L is ethyl methyl ketone thiosemicarbazone, and of the type $[ML_2]_n Y$, where Y is $\text{ClO}_4$, have been synthesized and characterized on the basis of analysis, conductance, magnetic susceptibility, IR and electronic spectral data. $[ML_X]_n$ complexes are octahedral while $[ML_2]_n Y$ complexes have presumably tetrahedral configuration involving both nitrogen and sulphur coordination.

Table 1 — Characterization Data of the Complexes

<table>
<thead>
<tr>
<th>Compd</th>
<th>Found (%) (Calc.)</th>
<th>$\delta$(BM)</th>
<th>$\Delta\mu$ (mho cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{NiL}_2(\text{NCS})_4]$</td>
<td>12-38 27-24 23-45</td>
<td>(12-63 27-34 24-40)</td>
<td>2-9 188</td>
</tr>
<tr>
<td>$[\text{CoL}_2(\text{NCS})_4]$</td>
<td>12-62 28-16 23-34</td>
<td>(12-63 27-24 24-08)</td>
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References