CHAPTER VII

ANALYSIS AND PHYSICAL MEASUREMENTS
CHAPTER VII

ANALYSIS AND PHYSICAL MEASUREMENTS:

Different methods used for analysis and elucidation of probable structure or the complexes reported under the present investigation are described below:

(a) Estimation of elements in the complexes:

METALS

Copper: Copper was estimated\(^1\) gravimetrically as copper bis pyridine thiocyanate\([CuPy_2] (SCN)_2\) after decomposing the complex with a mixture of concentrated acids (nitric acid 5 ml, sulphuric acid 3 ml and perchloric acid 2 ml).

Nickel: Nickel was estimated\(^2\) gravimetrically as bis (dimethylglyoximato) nickel(II), \([\text{Ni(dmg)}_2]\).

Cadmium: Cadmium was estimated\(^3\) gravimetrically as cadmium ammonium phosphate monohydrate, \((\text{CdNH}_4\text{PO}_4)_\text{H}_2\text{O}\).

Zinc: Zinc was estimated\(^4\) gravimetrically as zinc ammonium phosphate, \(\text{ZnNH}_4\text{PO}_4\).

Mercury: Mercury was estimated\(^5\) gravimetrically as mercuric sulphide, \(\text{HgS}\).

NONMETALS

Halides: The halides were estimated\(^6\) gravimetrically as silverhalides in the presence of dilute nitric acid.

In the mixed halide complexes, the halides have been estimated together. The total weight of the precipitated combined silver halides was determined first and the weight due to individual halides was calculated for different ratios and the correct ratio was ultimately arrived at.
Thiocyanate: The thiocyanate was estimated\(^7\) gravimetrically as silver thiocyanate after acidifying the cold solution with dilute nitric acid.

Cyanide: The cyanide was estimated\(^8\) gravimetrically as silver cyanide.

Sulphur: Sulphur in thiourea was estimated\(^9\) as BaSO\(_4\) after digesting the complexes in nitric acid. The dithiocarbamato complexes were dissolved in CCl\(_4\) and the sulphur in these complexes was oxidised\(^9\) to sulphate by adding bromine water followed by nitric acid. The sulphate thus formed was estimated gravimetrically as BaSO\(_4\).

Nitrogen: Nitrogen was estimated microanalytically.

Carbon and Hydrogen: Carbon and hydrogen were estimated by using semi-micro combustion train.

(b) Physical measurements:

i) Melting Point: The melting points of the compounds reported in the present investigation, were taken, using a Toshniwal melting point apparatus.

ii) Conductance measurement: Under an influence of electromotive force, the conductance of a solution is the sum total of individual contributions of all the ions present in the solution. It depends upon the number of ions per unit volume of the solution and upon the velocities with which these ions move under the influence of the applied electromotive force.
The conductance measurements provide an important experimental evidence in determining the structure of coordination compounds. It is made to determine whether the complex compounds are electrolytes or non-electrolytes. It also predicts whether the negative radical is bonded to the central metal ion or not. In the present investigations, \( \sim 10^{-3} \text{M} \) solutions of compounds in acetone, acetonitrile, nitrobenzene, pyridine, methanol or dimethyl formamide have been used to determine the molar conductance values. Some of the values for 1:1 & 1:2 electrolytes in different solvents have been given in Table.3-1 (Page 30).

In the present work, conductance measurements were carried out using a Toshniwal conductivity bridge type CL 0102 and a dip type cell calibrated with an aqueous solution of potassium chloride whose cell constant was found to be 0.902. Systronics direct reading conductivity meter 303 was also used for measurement of conductivities of the complexes. Calculation was made as follows:

\[
\Lambda_M = \text{Cell constant} \times \frac{\text{(conductance of solution - conductance of solvent)}}{\text{molecular weight}} \times \frac{\text{concentration of the solution (gms. per mole)}}{\text{molecular weight}}
\]

**iii) Magnetic susceptibility measurement:**

There are various methods to determine the magnetic moment of complex compounds, such as the Faraday method, the Gouy method and the Quincke method. The author has used the Gouy method in the present investigation which is described below briefly:
Gouy method: In this method the solid specimen is taken in a small glass or perspex tube, called Gouy tube. The tube is carefully packed up to the mark by introducing powdered sample in small portions each time with several tappings of the tube till the material inside behaves as an uniform solid rod. It is then hung below one of the balance pans, its lower end lying between the poles of a powerful electromagnet. The specimen is weighed with and without the application of magnetic field.

A paramagnetic substance has an increase in weight \( w \) in the presence of magnetic field over the actual weight, \( W \) (weight in absence of field). The increase in weight is a measure of the number of unpaired electron in the complex. The magnetic susceptibility is calculated from the equation,

\[
\chi_g = \frac{\alpha + \beta w}{W}
\]

where \( \chi_g \) is the gramme susceptibility of the material, \( \alpha \) is the tube constant, allowing for the displaced air and is equal to specimen volume times 0.029. \( \beta \) is the tube calibration constant. The molar magnetic susceptibility, \( \chi_M \) and the corrected one, \( \chi'_M \) are calculated as:

\[
\chi_M = \chi_g \times \text{Mol.wt.}
\]

and

\[
\chi'_M = \chi_M + \text{diamagnetic correction.}
\]

The effective magnetic moment, \( \mu_{\text{eff}} \) in Bohr magneton is then obtained by using the equation,

\[
\mu_{\text{eff}} = 2.84 \left( \chi'_M \times T \right)^{\frac{1}{2}}
\]

where \( T \) is the temperature in absolute scale at which the measurement is made.
Calibration of Gouy tube:

The constants, \( \alpha \) and \( \beta \) of the Gouy tube used in the present work are determined by taking powdered sample of A.R. CuSO\(_4\cdot5\)H\(_2\)O as reference substance. The magnetic susceptibility of CuSO\(_4\cdot5\)H\(_2\)O is known to be \( 5.92 \times 10^{-6} \) cgs units at 20°C.

Diamagnetic correction:

In practice, most of the transition metal compounds are 'magnetically dilute', that is the atom with a permanent magnetic moment is surrounded by other atoms without any permanent moment. As the atoms with paired electrons are slightly diamagnetic, it is necessary to correct the experimentally determined susceptibility for the combined effect of the diamagnetism of all the atoms in the compounds. The diamagnetic correction is calculated by summing up the known diamagnetism of each component atom. Diamagnetic corrections for some of the elements and groups are given below:

<table>
<thead>
<tr>
<th>Element</th>
<th>Diamagnetic Correction (values in ( 10^{-6}) g·atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(^{+2})</td>
<td>11.0 N(ring) = 4.61 C-I = -4.1</td>
</tr>
<tr>
<td>Ni(^{+2})</td>
<td>12.0 N(open chain) = 5.55 N=N = -1.8</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>23.4 O(alcohol, ether) = 4.61 C=N = -8.15</td>
</tr>
<tr>
<td>Br(^-)</td>
<td>34.6 O(aldehyde, ketone) = 1.72 C≡N = -0.8</td>
</tr>
<tr>
<td>I(^-)</td>
<td>50.6 O(carboxyl) = 3.36 acac(^-) = 52</td>
</tr>
<tr>
<td>NO(_3^)</td>
<td>18.9 C=C = -5.5 oxinate = 86</td>
</tr>
<tr>
<td>ClO(_4^)</td>
<td>32.0 C≡C = -0.8 water = 13</td>
</tr>
<tr>
<td>SCN(^-)</td>
<td>31.0 -C=C-C≡C- = 10.6 bipyridyl = 105</td>
</tr>
<tr>
<td>CNO(^-)</td>
<td>21.0 C(benzene) = -0.24 phenanthro = 128</td>
</tr>
<tr>
<td>C</td>
<td>6.0 C-Cl = -3.1 line</td>
</tr>
<tr>
<td>H</td>
<td>2.93 C-Br = -4.1 picoline = 50.5</td>
</tr>
<tr>
<td>S</td>
<td>15.0</td>
</tr>
</tbody>
</table>
iv) **Infrared spectra:**

In the present investigation, the infrared absorption spectra in the range (4000 - 200) cm\(^{-1}\) were recorded on Perkin Elmer I R spectrophotometer model - 157 and 577 using KBr pellet technique, at C.D.R.I. Lucknow.

v) **Electronic spectra:**

Electronic spectrum gives information regarding the structure of the complex and the ligand influence on the crystal field of the metal ion.

In the present investigation, the visible spectra were recorded in various non-aqueous solvents using Unicam SP 500 and Elico model CL 24 spectrophotometer. The electronic spectra of few complexes were recorded at C.D.R.I. Lucknow, by Hitachi-320 spectrophotometer. In recording the absorption spectra, two cells were used, one as reference cell filled with the solvent and other as the sample cell filled with solution. Sometimes in the case of insoluble substances, Nujol mull technique was employed in which a small piece of filter paper dipped in Nujol served as the reference and a thin Nujol mull on a piece of filter paper was used as the sample. This method was adopted due to nonavailability of reflectance attachment.

The values of optical density, D, were used to calculate the extinction coefficient (molar absorbance) \(\varepsilon\).
of the solution from the following relationship:

\[ D = c \cdot c_a \cdot l \]

where 'c' is the molar concentration of the solution and 'l' is the length of the light path in solution i.e. 1 cm. In the present work optical density has been plotted against the wavelength from which the position of these bands have been determined. The bands are attributable to different electronic transitions from which the structure of the complexes has been predicted.

vi) **Thermogravimetric measurement:**

Thermogravimetric measurements of some complexes were carried out on a Simultane Thermo Analyse balance, model 429(W.Germany) at a heating rate of 10°C per minute and were studied by T G and D T A techniques (Tables 4-3 & 5-3). These gave vital evidence regarding coordination of the ligands.
References:


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Specialised Reference Books:

Magnetic, Spectral and Thermal Studies on Some Mixed Ligand Complexes of Copper(II) and Nickel(II)

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Several mixed ligand complexes of copper(II) and nickel(II) having the compositions [M(aa)(tca)] and [M(aa)(tca)L₂], where aaH is acetylacetone, tcaH is trichloroacetic acid; L is γ-picoline, imidazole, 2-picoline-N-oxide or thiourea and M is Cu(II) or Ni(II), have been isolated and characterised on the basis of their analyses, molar conductance, magnetic susceptibility, infrared, electronic spectral data and thermogravimetric measurements. The infrared spectra reveal the presence of uninegative bidentate acetylacetonate and trichloroacetate groups in all these complexes. As the temperature increases, the mixed ligand complexes start decomposing with the loss of neutral donor ligand, followed by trichloroacetate ion and acetylacetone ion in definite steps and ultimately forming MO at 600-675°. Square planar, tetrahedral, distorted octahedral and octahedral structures have been proposed for the complexes, [Cu(aa)(tca)], [Ni(aa)(tca)], [Cu(aa)(tca)(L)], and [Ni(aa)(tca)L₂], respectively.

ISOLATION and characterisation of several mixed ligand complexes of copper(II)² and nickel(II)⁴ β-diketonate with neutral hetero donor ligands have been reported in the literature. But reactions of mixed chelate complexes of these metals containing β-diketone and hetero-chelate with neutral donor ligands do not appear to have been studied extensively. The present paper relates to a systematic study of some mixed ligand complexes having the compositions [M(aa)(tca)] and [M(aa)(tca)L₂], where M is Cu(II) or Ni(II), aaH is acetylacetone, tcaH is trichloroacetic acid and L is γ-picoline (γ-pi), imidazole (iz), 2-picoline-N-oxide (2-pic-N-O) or thiourea (tu)⁻¹.

Experimental

[M(aa)(tca)]: The mixed chelate complex of copper(II) was obtained by refluxing a mixture of bis(acetylacetonato) copper(II) and trichloroacetonic acid in chloroform for 10 min. The corresponding nickel(II) complex was isolated after refluxing bis(acetylacetonato) nickel(II) and trichloroacetic acid in chloroform for 10 min. The infrared spectra of the complexes as KBr pellets were scanned on a Perkin Elmer 137 Infracord spectrophotometer. Electrical conductances of 10⁻⁹ M methanolic solutions of these complexes were measured on a Toshniwal conductivity bridge with dipping electrode cell. Magnetic susceptibility measurements were made on a Gouy magnetic balance using Hg[Co(NCS)₄] as calibrant.

Results and Discussion

Composition : On the basis of elemental analyses and low molar conductance values (4.2-9.2 mhos) (Table 1) the molecular formulae assigned to the complexes are [M(aa)(tca)] and [M(aa)(tca)L₂].

Magnetic moments : All the copper(II) complexes have magnetic moments ranging between 1.83
and 1.86 B.M. The \( \mu_{\text{eff}} \) value of 3.5 B.M. for the complex \([\text{Ni}(\text{aa})(\text{tca})]\) suggests a tetrahedral stereochemistry. The magnetic moments of other nickel(II) complexes lie in the range 3.15-3.30 B.M., which are characteristics of octahedral nickel(II) complexes.

**Infrared spectra:** Bonding sites of the ligands and probable structure of the complexes are elucidated by comparing the infrared spectra of the metal complexes with those of the ligands. In the spectra of the mixed chelate complexes, [M(aa)(tca)], the occurrence of bands due to \( v(\text{C}=-\text{C}) \) around 1525-1515 cm\(^{-1}\) and \( v(\text{C}=-\text{O}) \) around 1690-1620 and 1570-1470 cm\(^{-1}\) respectively are observed.

**Electronic spectra:** The electronic spectra of [Cu(aa)(tca)] exhibit a broad absorption band at 14080 cm\(^{-1}\) suggesting a square planar stereochemistry. This is supported by the fact that tetrahedral copper(II) complexes do not show d-d absorption bands in the region 10000-20000 cm\(^{-1}\). The room temperature magnetic moment value of 1.83 B.M. for the complex also favours the square planar structure. The complexes [Cu(aa)(tca)L3] display one broad absorption band in the region 13000-15800 cm\(^{-1}\) characteristic of distorted octahedral copper(II) complexes. Other nickel(II) complexes show bands around 11100, 16600 and 25600 cm\(^{-1}\) in the region 10000-20000 cm\(^{-1}\) characteristic of octahedral nickel(II) complexes.

**Thermogravimetric measurements:** The thermogravimetric measurements of some mixed ligand complexes of copper(II) and nickel(II) (Table 3) studied by TG and DTA techniques provide further evidence regarding coordination of the ligands. The complexes start losing weight at 110-170° with the loss of neutral donor ligand, trichloroacetate ion and acetylacetone ion in the given order, ultimately forming copper oxide or nickel oxide at 600-675° with an exothermic peak in the DTA derivatograph. The loss in weight of the complexes at different temperatures accompanied by exothermic

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**Table 1—Colour, m.p. and Analytical Data of the Mixed Ligand Complexes of Copper(II) and Nickel(II)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>m.p. °C</th>
<th>Analysis % Found/(Calcd.)</th>
<th>( \mu_{\text{eff}} ) B.M.</th>
<th>( \Delta H ) kJ/mols</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(aa)(tca)]</td>
<td>Parrot green</td>
<td>&gt;250</td>
<td>20.11 (19.54) 33.21 (32.71)</td>
<td>1.83</td>
<td>7.2</td>
</tr>
<tr>
<td>[Cu(aa)(tca)(2-pic-NO)(_2)]</td>
<td>Blue</td>
<td>189</td>
<td>12.64 (12.43) 21.33 (20.81)</td>
<td>1.85</td>
<td>8.1</td>
</tr>
<tr>
<td>[Cu(aa)(tca)(2-pic-NO)(_2)]</td>
<td>Deep blue</td>
<td>135</td>
<td>12.81 (13.27) 23.49 (23.05)</td>
<td>1.86</td>
<td>8.7</td>
</tr>
<tr>
<td>[Cu(aa)(tca)(2-pic-NO)(_2)]</td>
<td>Deep green</td>
<td>148</td>
<td>11.28 (11.70) 18.71 (19.58)</td>
<td>1.85</td>
<td>9.2</td>
</tr>
<tr>
<td>[Ni(aa)(tca)]</td>
<td>Greenish blue</td>
<td>165</td>
<td>18.73 (18.33) 32.34 (32.21)</td>
<td>3.50</td>
<td>4.2</td>
</tr>
<tr>
<td>[Ni(aa)(tca)(2-pic-NO)(_2)]</td>
<td>Blue</td>
<td>210</td>
<td>11.66 (11.59) 21.33 (21.01)</td>
<td>3.25</td>
<td>9.1</td>
</tr>
<tr>
<td>[Ni(aa)(tca)(tu)(_2)]</td>
<td>Blue</td>
<td>258</td>
<td>12.86 (12.99) 23.30 (22.79)</td>
<td>3.30</td>
<td>7.4</td>
</tr>
<tr>
<td>[Ni(aa)(tca)(7-pic)(_2)]</td>
<td>Light blue</td>
<td>237</td>
<td>11.28 (10.90) 20.24 (19.75)</td>
<td>3.15</td>
<td>6.2</td>
</tr>
<tr>
<td>[Ni(aa)(tca)(tu)(_2)]</td>
<td>Bottle green</td>
<td>205*</td>
<td>12.18 (12.42) 22.40 (22.51)</td>
<td>3.20</td>
<td>8.3</td>
</tr>
</tbody>
</table>

**Table 2—Infrared Spectral Data (cm\(^{-1}\)) of Complexes of Cu(II) and Ni(II)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( v(C=O) )</th>
<th>( v(C=C) )</th>
<th>( v_{\text{sym}}(\text{OCO}) )</th>
<th>( v_{\text{asym}}(\text{OCO}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(aa)(tcs)]</td>
<td>1640</td>
<td>1525</td>
<td>1690</td>
<td>1570</td>
</tr>
<tr>
<td>[Cu(aa)(tcs)(2-pic)]</td>
<td>1560</td>
<td>1438</td>
<td>1620</td>
<td>1508</td>
</tr>
<tr>
<td>[Cu(aa)(tcs)(tu)(_2)]</td>
<td>1610</td>
<td>1490</td>
<td>1670</td>
<td>1545</td>
</tr>
<tr>
<td>[Cu(aa)(tca)]</td>
<td>1610</td>
<td>1490</td>
<td>1655</td>
<td>1565</td>
</tr>
<tr>
<td>[Ni(aa)(tca)]</td>
<td>1570</td>
<td>1515</td>
<td>1620</td>
<td>1470</td>
</tr>
<tr>
<td>[Ni(aa)(tca)(2-pic)]</td>
<td>1560</td>
<td>1510</td>
<td>1595</td>
<td>1465</td>
</tr>
<tr>
<td>[Ni(aa)(tca)(tu)(_2)]</td>
<td>1565</td>
<td>1515</td>
<td>1595</td>
<td>1465</td>
</tr>
<tr>
<td>[Ni(aa)(tca)(2-pic-NO)(_2)]</td>
<td>1560</td>
<td>1510</td>
<td>1610</td>
<td>1460</td>
</tr>
<tr>
<td>[Ni(aa)(tca)(tu)(_2)]</td>
<td>1568</td>
<td>1512</td>
<td>1608</td>
<td>1465</td>
</tr>
</tbody>
</table>

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* decomposes without melting.
** % Sulphur, 13.04/(13.54).
* * decomposes without melting.
Table 3—Thermogravimetric Measurements of Mixed Ligand Complexes of Copper(II) and Nickel(II)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Initial decomposition temp. °C</th>
<th>TGA</th>
<th>% Loss</th>
<th>Species formed</th>
<th>DTA peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>220-330</td>
<td>51.30</td>
<td>Cu(aa)(tca)_{0.5}</td>
<td>Endo.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>330-395</td>
<td>60.84</td>
<td>Cu(aa)(tca)_{0.25}</td>
<td>Endo.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>395-490</td>
<td>65.86</td>
<td>Cu(aa)</td>
<td>Endo.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>490-660</td>
<td>83.12</td>
<td>CuO</td>
<td>Exo.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120-180</td>
<td>48.81</td>
<td>Cu(aa)(tca)_{0.5}</td>
<td>Exo.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180-225</td>
<td>57.59</td>
<td>Cu(aa)(tca)_{0.25}</td>
<td>Endo.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>225-400</td>
<td>74.16</td>
<td>Cu(aa)_{0.5}</td>
<td>Exo.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400-540</td>
<td>88.36</td>
<td>CuO</td>
<td>Exo.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>540-660</td>
<td>86.33</td>
<td>CuO</td>
<td>Exo.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>240-475</td>
<td>74.74</td>
<td>Ni(aa)_{0.5}</td>
<td>Exo.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>475-530</td>
<td>79.80</td>
<td>Ni(aa)_{0.25}</td>
<td>Exo.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>530-600</td>
<td>82.40</td>
<td>NiO</td>
<td>Exo.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600-700</td>
<td>86.11</td>
<td>NiO</td>
<td>Exo.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180-250</td>
<td>48.90</td>
<td>Ni(aa)(tca)_{0.5}</td>
<td>Endo.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>250-435</td>
<td>56.72</td>
<td>Ni(aa)(tca)_{0.25}</td>
<td>Exo.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>435-490</td>
<td>65.19</td>
<td>Ni(aa)</td>
<td>Exo.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>490-675</td>
<td>85.32</td>
<td>NiO</td>
<td>Exo.</td>
</tr>
</tbody>
</table>

or endothermic peak closely agrees with the calculated loss in weight indicating the authenticity of the formulations of the mixed ligand complexes.

Acknowledgement

The authors sincerely thank Dr. D. V. Ramana Rao, Professor and Head, P. G. Department of Chemistry, Regional Engineering College, Rourkela for encouragement and the Management, Rourkela Steel Plant for facilities.

References

Bimetallic Tetramorpholine-4-carbodithioates of Copper(II) & Nickel(II) with Zinc(II) Cadmium(II) or Mercury(II)

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Bimetallic tetramorpholine-4-carbodithioates of the composition, MM'(mcdt)4 where M = Cu(II) or Ni(II); M' = Zn(II), Cd(II) or Hg(II); and mcdt = morpholine-4-carbodithioate have been prepared and characterised on the basis of chemical analyses, molar conductances, magnetic moments, IR and electronic spectral data. Square-planar stereochemistry around Cu(II) and Ni(II) has been proposed for these polymeric complexes.

Bimetallic tetradithiocarbamates were not known till Aggarwal et al. reported1 recently the preparation of the complexes, M Cd(dtc)4 where M = oxovanadium(IV), Mn(II), Fe(II), Co(II), Ni(II), Cu(II) or Zn(II) and dtc = piperidine-1-carbodithioate or diethyldithiocarbamate. Further, these complexes are expected to exhibit enhanced antifungal activity. It was, therefore, deemed worthwhile to prepare some more bimetallic complexes using morpholine-4-carbodithioate and study their antifungal and structural aspects. The present note reports the synthesis and structural elucidation of the complexes, MM'(mcdt)4 where M = Cu(II) or Ni(II); M' = Zn(II), Cd(II) or Hg(II); and mcdt = morpholine-4-carbodithioate.

All the chemicals used were of AR grade. Sodium morpholine-4-carbodithioate was isolated as described2 earlier. Its purity was checked by sulphur estimation (Found: 34.25% ; calc.: 34.7%). Bimetallic tetramorpholine-4-carbodithioates were prepared using appropriate metal nitrates according to the literature method. The metals and sulphur were estimated3 by standard methods. Physico-chemical data were recorded using Systronic direct reading conductometer - 303, Gouy balance, Perkin Elmer IR - 577 and Elico CL-24 spectrophotometers.

The analytical, conductivity and magnetic moment data are reported in Table 1. The results of elemental analyses are in conformity with the formulation, MM'(mcdt)4. All the copper and nickel complexes are chocolate-brown and green amorphous powders respectively. They are insoluble in water and common organic solvents and do not melt up to 250°C. These properties are characteristic of either ionic or polymeric nature of the complexes.

The negligibly small molar conductance values (0.09-0.52 mhos cm2 mol−1) of 10−3 M solution of these complexes in nitrobenzene suggest them to be nonelectrolytes. Hence, the complexes under report are presumably polymers. The magnetic susceptibility measurements at room temperature show that the nickel(II) complexes are diamagnetic. The copper(II) complexes are paramagnetic (1.72-1.75 B.M.) as expected for a 3d9 ion having one unpaired electron.

Two main stretching modes of dithiocarbamate moiety in morpholine-4-carbodithioate, νS (C=S)4-6 and ν(C=N)6-7 have been taken into consideration in order to determine the denticity of the ligand. In monodentate dithiocarbamate, νS (C=S) occurs as a doublet near 1000 cm−1 whereas a single distinct band is expected in the same region in case of bidentate dithiocarbamate. Further, ν(C=N) in case of monodentate behaviour shifts to lower wave numbers or remains unchanged whereas it undergoes a shift to higher wave numbers in case of bidentate behaviour.

The electronic spectra of the complexes have been recorded in chloroform medium. Copper(II) complexes display a d-d transition in the region 600-610 nm and a strong charge-transfer band at 428-436 nm presumably due to square-planar geometry around

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found (calc.), %</th>
<th>μeff (B.M.)</th>
<th>λM (mhos)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuZn(mcdt)4</td>
<td>8.04 8.52 32.82 1.75 0.15</td>
<td>(8.17) (8.41) (32.01)</td>
<td></td>
</tr>
<tr>
<td>CuCd(mcdt)4</td>
<td>8.25 13.12 30.82 1.72 0.09</td>
<td>(7.71) (13.64) (31.12)</td>
<td></td>
</tr>
<tr>
<td>CuHg(mcdt)4</td>
<td>6.32 21.08 27.47 1.73 0.20</td>
<td>(6.96) (21.99) (28.11)</td>
<td></td>
</tr>
<tr>
<td>NiZn(mcdt)4</td>
<td>8.16 7.95 32.89 Diamag. 0.52</td>
<td>(7.60) (8.46) (33.21)</td>
<td></td>
</tr>
<tr>
<td>NiCd(mcdt)4</td>
<td>7.25 13.09 30.95 Diamag. 0.48</td>
<td>(7.16) (13.72) (31.31)</td>
<td></td>
</tr>
<tr>
<td>NiHg(mcdt)4</td>
<td>7.08 21.95 27.95 Diamag. 0.30</td>
<td>(6.47) (22.11) (28.26)</td>
<td></td>
</tr>
</tbody>
</table>

Table 1—Characterisation Data of Bimetallic Complexes

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copper(II). Nickel(II) complexes exhibit one broad absorption band at 620 nm indicative of square-planar stereochemistry. The diamagnetic nature of nickel(II) complexes also supports square-planar environment around nickel(II). Further, the visible spectra of Cu M' (mcdt)$_4$ and Ni M' (mcdt)$_4$ complexes resemble those of square-planar complexes, Cu(mcdt)$_2$ and Ni(mcdt)$_2$ respectively thus confirming square-planar geometry around copper(II) and nickel(II).

In view of the aforesaid discussion, square-planar geometry around copper(II) and nickel(II) may be proposed for these polymeric bimetallic complexes (structure I).

The authors are grateful to Prof. D.V. Ramana Rao, Head, P.G. Department of Chemistry, Regional Engineering College, Rourkela for encouragement and the management of Rourkela Steel Plant, Rourkela for experimental facilities.

References
Hetero-binuclear Schiff Base Complexes of Copper(II) & Nickel(II) with Zinc(II) or Cadmium(II)

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Hetero-binuclear Schiff base complexes of the types \([CuL_2M_2X_2]^{-}\) and \([NiL'MX_2]^{-}\), where \(LH = \text{Schiff base derived from salicylaldehyde and ammonia; } M = \text{Zn(II) or Cd(II); } X = \text{Cl}^-, \text{NO}_3^-, \text{or } \text{ClO}_4^-\) and \(L'H_2 = \text{Schiff base derived from salicylaldehyde and o-phenylenediamine have been prepared and characterised by elemental analyses, spectral data (IR and electronic) and magnetic susceptibility measurements. Square-planar configuration around Cu(II) and Ni(II) has been proposed for these complexes.}

Although considerable attention has been paid to the study of homo-bi- and tri-nuclear transition metal complexes of Schiff bases, reports on heteronuclear transition metal complexes of such ligands are few. In continuation of our recent report on some bimetallic tetra-(morpholine-4-carbonates), we report in the present note the results of our investigations on a few hetero-binuclear Schiff base complexes of the types \([CuL_2M_2X_2]^{-}\) and \([NiL'MX_2]^{-}\), where \(LH = \text{Schiff base derived from salicylaldehyde and ammonia; } M = \text{Zn(II) or Cd(II); } X = \text{Cl}^-, \text{NO}_3^-, \text{or } \text{ClO}_4^-\) and \(L'H_2 = \text{Schiff base derived from salicylaldehyde and o-phenylenediamine.}

All the chemicals used were of AR grade.

Preparation of \([CuL_2M_2X_2]^{-}\)

The parent complex, \([CuL_2]^{-}\), was prepared according to the reported method by refluxing tetraammine-copper(II) complex (in solution) with ethanolic solution of salicylaldehyde in 1:2 molar ratio for one hour. The green coloured compound thus obtained was filtered, washed with ethanol and ether and dried in vacuo. The purity of the complex was established by estimating copper and nitrogen [Found: Cu, 20.41; N, 8.60. CuC_14_4H_11_4N_2O_2 requires: Cu, 20.93; N, 9.22%].

A suspension of \([CuL_2]^{-}\) in chloroform was then added to a solution of zinc(II) or cadmium(II) salt in ethanol in 1:1 stoichiometric ratio and the mixture was refluxed for 2 hr. The resulting solid compounds were filtered, washed several times with chloroform and finally dried in vacuo.

Preparation of \([NiL'MX_2]^{-}\)

The Schiff base, \(L'H_2\), was prepared as reported. The parent complex, \([NiL']^{-}\), was obtained as chocolate-red solid by refluxing nickel(II) chloride hexahydrate with the Schiff base \((L'H_2)\) in 1:1 molar ratio in ethanol medium for 1.5 hr followed by cooling. The resulting solid was filtered, washed with ethanol and ether and dried in vacuo. Its purity was checked by determining nickel and nitrogen contents [Found: Ni, 15.80; N, 7.43. Ni C_{30}H_{40}N_2O_2 requires: Ni, 15.92; N, 7.59%].

A solution of \([NiL']^{-}\) in chloroform was then mixed with an ethanol solution of zinc(II) or cadmium(II) salt in 1:1 stoichiometric ratio and the mixture was refluxed for 1.5 hr. The resulting solid compounds were filtered, washed thoroughly with chloroform and then dried in vacuo.

The purity of the isolated complexes was ascertained by elemental analyses. Copper, nickel, zinc, cadmium and chloride were estimated by standard methods. Carbon and hydrogen were estimated microanalytically. Magnetic measurements were carried out by a Gouy balance using \([Co(NCS)_4]^{-}\) as the calibrant. The diamagnetic corrections were made using Pascal's constants. IR spectra were recorded on a Perkin Elmer spectrophotometer-577 in the range 4000-600 cm\(^{-1}\) in KBr. Electronic spectra of the complexes were recorded in the solid state with the help of a Unicam SP-500 spectrophotometer using nujol mull technique.

Analytical data (Table 1) support the proposed formulations of the complexes. All the copper and nickel complexes are amorphous powders having high melting points (> 250°C). They are almost insoluble in water and common organic solvents.

The room temperature magnetic moment values of the present Cu(II) complexes (1.82-2.08 B.M.) correspond to the presence of one unpaired electron. However, no specific conclusion regarding their stereochemistry can be drawn from the magnetic moment data. All the Ni(II) complexes are found to be diamagnetic, suggesting their square-planar geometry.

The parent Cu(II) complex, \([CuL_2]^{-}\), exhibits IR bands at 3290, 3255, 1610 and 1515 cm\(^{-1}\) which may be attributed to \(\nu(N-H), \nu(C=O)\) and \(\nu(C-O)\) respectively. In the parent Ni(II) complex, \([NiL']^{-}\), \(\nu(C=O)\) and \(\nu(C-O)\) appear at 1595 and 1503 cm\(^{-1}\) respectively. These data suggest that the metal is...
Table 1—Analytical and Physical Data of Hetero-binuclear Schiff Base Complexes of Copper(II) & Nickel(II) with Zinc(II) or Cadmium(II)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Ni/Cu</th>
<th>Zn/Cd</th>
<th>Zn/H</th>
<th>Cd/H</th>
<th>Found (calc. %)</th>
<th>M_{eff.} (B.M.)</th>
<th>Magnetic nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NiLZnCl₂]</td>
<td>Reddish-yellow</td>
<td>11.02</td>
<td>12.48</td>
<td>47.11</td>
<td>2.38</td>
<td>13.88</td>
<td>do</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>[NiLZn(NO₃)₂]</td>
<td>Deep-red</td>
<td>(11.62)</td>
<td>(12.94)</td>
<td>(47.52)</td>
<td>(2.77)</td>
<td>(14.04)</td>
<td>do</td>
<td></td>
</tr>
<tr>
<td>[NiLZn(ClO₄)₂]</td>
<td>Orange</td>
<td>9.10</td>
<td>10.98</td>
<td>37.24</td>
<td>2.08</td>
<td>12.12</td>
<td>do</td>
<td></td>
</tr>
<tr>
<td>[NiLCdCl₂]</td>
<td>Orange-red</td>
<td>(9.27)</td>
<td>(10.32)</td>
<td>(37.91)</td>
<td>(2.21)</td>
<td></td>
<td></td>
<td>do</td>
</tr>
<tr>
<td>[NiLCd(NO₃)₂]</td>
<td>Orange</td>
<td>10.25</td>
<td>19.00</td>
<td>39.11</td>
<td>2.01</td>
<td>12.84</td>
<td>do</td>
<td></td>
</tr>
<tr>
<td>[NiLCd(ClO₄)₂]</td>
<td>Orange</td>
<td>(9.70)</td>
<td>(18.57)</td>
<td>(39.66)</td>
<td>(2.31)</td>
<td></td>
<td></td>
<td>do</td>
</tr>
<tr>
<td>[CuL₂ZnCl₂]</td>
<td>Grey</td>
<td>14.32</td>
<td>13.98</td>
<td>37.85</td>
<td>2.14</td>
<td>15.69</td>
<td>2.08</td>
<td></td>
</tr>
<tr>
<td>[CuL₂Zn(NO₃)₂]</td>
<td>Leaf-green</td>
<td>(14.44)</td>
<td>(14.86)</td>
<td>(38.19)</td>
<td>(2.72)</td>
<td>(16.12)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[CuL₂Zn(ClO₄)₂]</td>
<td>Yellowish-green</td>
<td>(12.89)</td>
<td>(13.26)</td>
<td>(34.08)</td>
<td>(2.43)</td>
<td></td>
<td>do</td>
<td>1.95</td>
</tr>
<tr>
<td>[CuL₂CdCl₂]</td>
<td>Grey</td>
<td>(11.78)</td>
<td>(11.51)</td>
<td>(29.58)</td>
<td>(2.11)</td>
<td></td>
<td></td>
<td>1.82</td>
</tr>
<tr>
<td>[CuL₂Cd(NO₃)₂]</td>
<td>Yellowish-green</td>
<td>(13.70)</td>
<td>(22.68)</td>
<td>33.98</td>
<td>2.59</td>
<td>14.20</td>
<td>1.92</td>
<td></td>
</tr>
<tr>
<td>[CuL₂Cd(ClO₄)₂]</td>
<td>Pale-green</td>
<td>(11.76)</td>
<td>(20.18)</td>
<td>30.68</td>
<td>1.86</td>
<td>12.12</td>
<td>2.05</td>
<td></td>
</tr>
</tbody>
</table>

Coordinated through C=N and C−O in both the parent complexes. The involvement of phenolic groups in the chelate formation is further confirmed by the absence of νOH in both the parent complexes. The occurrence of ν(C−O) bands at 1535-1540 and 1515-1530 cm⁻¹ in the [CuL₂MX₂] and [NiL₂MX₂] complexes respectively compared to that of the parent complexes [CuL₂] and [NiL₂] respectively at 1515 and 1503 cm⁻¹, suggests bridging through phenolic O. Other bands due to Schiff base in the parent complexes are also modified slightly (5-10 cm⁻¹) in the heterobinuclear complexes. The absence of ν₃ band of ionic nitrate around 1360 cm⁻¹ and the presence of two strong bands at ~1510 and ~1300 cm⁻¹ due to νas NO₃ and νs NO₃ respectively, reveal the undentate nature of coordinated nitrate groups in the nitrate complexes. The perchlorate complexes of Ni(II) exhibit three sharp bands in the region ~1100 cm⁻¹ supporting the coordinated nature of perchlorate group. Further, the absence of a broad band in the region 1100 cm⁻¹ in the IR spectra of Cu(II) complexes definitely suggests the coordinated behaviour of ClO₄⁻.

The solid state electronic spectra of [CuL₂MX₂] type of complexes in nujol mull exhibit a strong charge-transfer band at 27.7 kK and a d−d transition around 16.4 kK assignable to overlapping transitions ²B₁g→²A₁g, ²B₁g→²B₂g, and ²B₁g→²E₂g in a square planar environment around Cu(II), in conformity with the diamagnetic nature of the complexes. Further, the electronic spectra of the complexes [CuL₂MX₂] and [NiL₂MX₂] resemble those of square-planar complexes [CuL₂] and [NiL₂] respectively.

Hence, on the basis of analytical, magnetic moment, IR and electronic spectral data and stereochemical
consideration\textsuperscript{3,12} the following structures (I & II) are suggested for the present hetero-binuclear Schiff base complexes.

The authors are thankful to Prof. D.V. Ramana Rao, Head of the Chemistry Department, Regional Engineering College, Rourkela for his interest, the management of Rourkela Steel Plant for providing necessary facilities and to the RSIC and CDRI, Lucknow for running IR spectra of the complexes.

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CATIONIC NICKEL (III) COMPLEXES OF NN AND ONNO DONORS

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(Received 6 November, 1982)

A survey of literature reveals that not much work has been done on the complexes of nickel(III). Recently Das and Ramana Rao have reported the formation of low-spin square planar nickel (III) complexes of SS donor ligand, [Ni(mdtc)$_2$]X where mdtc$^-$ = morpholine dithiocarbamate and X = Cl, Br or I. The title investigation describes the synthesis, physico-chemical properties and probable structure of four cationic nickel (III) complexes of NN and ONNO donors, [Ni(dmg)$_2$X]$_2$H$_2$O and [Ni(ensal)]X (dmgH$^-$ = dimethyl glyoxime, ensalH$_3$ = NN ethylene bis(salicylideneimine) and X = Cl or Br) formed by the oxidation of [Ni(dmg)$_2$] and [Ni(ensal)] respectively with halogens in suitable media.

EXPERIMENTAL

All the chemicals were of chemically pure grade. Bis(dimethyl glyoximato) nickel(II) was prepared by the standard method. The schiff base, ensalH$_3$ was prepared by condensing salicylaldehyde with ethylenediamine in the molar ratio 1:2 in ethanol and recrystallising from benzene. The complex, [Ni(ensal)]$^-$ was isolated by the method reported earlier.

Chlorination—Pure and dry chlorine gas was passed very slowly through a suspension of [Ni(dmg)$_2$] or [Ni(ensal)] in CC$_4$ with constant shaking till a slight change in colour of the suspension was noticed. It was then corked and kept over night.

Bromination—A very dilute solution of bromine in CS$_2$ was added drop by drop to a suspension of [Ni(dmg)$_2$] or [Ni(ensal)] in CC$_4$ with constant shaking till a change in colour of the suspension was noticed. It was then corked and kept over night. The resulting complexes were suction filtered, washed with CC$_4$ or CS$_2$ followed by ether and finally dried in vacuo.

ANALYSES AND PHYSICAL MEASUREMENTS.

Metal and halogen content of the complexes were determined gravimetrically by standard methods. Molar conductance of the complexes in acetonitrile at $10^{-4}$ M concentr-
tration was measured with a Toshniwal conductivity bridge type CLO102. Magnetic susceptibility measurements were made at room temperature on a Gouy balance using Hg Co(NCS)₄ as calibrant and experimental magnetic susceptibilities were corrected for diamagnetism. IR spectra were recorded in KBr in 4000-400 cm⁻¹ region on a Perkin Elmer IR spectrophotometer model-397 calibrated with polystyrene. Electronic spectra of the complexes in acetonitrile were recorded on Elico model CL 24 spectrophotometer.

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>Colour</th>
<th>( \mu ) eff (B. M.)</th>
<th>( \Delta M ) (mhos)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ni} (\text{dmg})_2] \text{Cl. 2H}_2\text{O})</td>
<td>Reddish Violet</td>
<td>2.38</td>
<td>74.5</td>
</tr>
<tr>
<td>([\text{Ni} (\text{dmg})_2] \text{Br. 2H}_2\text{O})</td>
<td>Blood red</td>
<td>1.97</td>
<td>87.1</td>
</tr>
<tr>
<td>([\text{Ni} (\text{ensal})] \text{Cl})</td>
<td>Brick red</td>
<td>2.17</td>
<td>77.4</td>
</tr>
<tr>
<td>([\text{Ni} (\text{ensal})] \text{Br})</td>
<td>Orange</td>
<td>1.88</td>
<td>77.5</td>
</tr>
</tbody>
</table>

These do not melt even at 250°. On analysis, values for % M and % halogen were found to be satisfactory.

**RESULTS AND DISCUSSIONS**

The observed and calculated analytical data (Table 1) show close resemblance within the experimental limits. All the complexes do not melt upto 250°C. The complex are insoluble in water and common organic solvents but sparingly soluble in acetonitrile. These complexes have room temperature magnetic moments of 1.88-2.38 B.M. suggesting square planar geometry around Ni³⁺ which is isoelectronic with Co²⁺. All the complexes liberate iodine from KI solution indicating the presence of higher oxidation state of the metal ion. The molar conductance values of 74.5-87.1 mhos for these complexes indicate their 1:1 electrolytic nature.

The IR bands of diagnostic importance assigned for the present complexes are discussed. The bands at 1560 cm⁻¹ and 1240 & 1100 cm⁻¹ in the IR spectra of dimethylglyoximato complexes are assigned to \( \nu(C=\text{N}) \) and \( \nu(N-O) \) respectively. These complexes display bands in the region 3375-3350 cm⁻¹ which may be attributed to OH stretching vibration associated with inter or intra molecular hydrogen bonding. Bending mode of H—O—H appears in the region 1630-1625 cm⁻¹ in these two complexes. Further, these dimethylglyoximato complexes suffer weight loss equivalent to two water molecules per mole of the Ni(III) complex at ~110°C suggesting the presence of lattice water. In case of
M. Daki and A. K. Das

$[\text{Ni(ensal)} \times \text{complexes}, \quad \nu(\text{C=N}) \quad \text{and} \quad \nu(\text{C-O}) \text{are noticed in the regions} \ 1610-1605\ \text{and} \ 1315\ \text{cm}^{-1} \text{respectively. These observations closely agree with the IR spectra of similar complexes reported earlier. The band at} \approx 465\ \text{cm}^{-1} \text{in all these complexes may be assigned to metal-nitrogen stretching frequency.}$

Nickel(III) is isoelectronic with cobalt (II) having $3d^7$ electronic configuration. It is reported that square planar cobalt (II) complexes display electronic spectral bands around 10255 cm$^{-1}$ and 15870 cm$^{-1}$. In the present investigation the complexes in acetonitrile exhibit bands in the regions, 10800—11000 cm$^{-1}$ and 16000—16200 cm$^{-1}$ which are assigned to $d_{x^2-y^2} \rightarrow d_{yz}$ and $d_{yz} \rightarrow d_{xy}$ transitions respectively in square planar geometry around Ni$^{3+}$ ion. Based on analytical data and physicochemical studies, square planar structure may be proposed for all these trivalent nickel complexes.

Thanks are due to Prof. D. V. Ramana Rao, P. G. Department of Chemistry, Regional Engineering College, Rourkela for encouragement and to the management of Rourkela Steel plant for providing laboratory facilities.

**Summary**

Four low spin cationic complexes of nickel (III) having the compositions $[\text{Ni(dmg)}_2 \times \text{complexes,} \quad \times \text{dmgH = dimethylglyoxime, ensalH} = \text{NN ethylene bis (salicylideneimine) and} \ X = \text{Cl or Br have been isolated by the oxidation of} \ [\text{Ni(dmg)}_2 \ X.\text{2H}_2\text{O and} \ [\text{Ni(ensal)} \ X \text{respectively with halogen in suitable media. Based on analytical, magnetic, conductance, infrared and electronic spectral data square planar structure has been proposed for these trivalent nickel complexes.}$

**References**