CHAPTER : X

SPECIALISED REFERENCE BOOKS
AND LIST OF PUBLICATIONS
SPECIALISED REFERENCE BOOKS


LIST OF PUBLICATIONS

1. Polymetallic Complexes, X.
Cobalt(II), Nickel(II), Copper(II), Zinc(II), Cadmium(II) and Mercury(II) complexes with a chelating azodye ligand, 5-(2'-hydroxyphenyldiazo)acetoacetanilide.


2. Manganese(II), Cobalt(II), Nickel(II), Copper(II) and Mercury(II) Complexes with 5-(2'-hydroxyphenyldiazo)salicylaldehyde.


3. Mixed Ligand Complexes of Co(II), Cu(II), Zn(II), Cd(II) and Hg(II) with acetoacetanilide and isoquinoline.


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complexes with chelating tridentate ONO donor Schiff bases.


10. Polymetallic Complexes: XIX.
Doubly bidentate ON-OO donor ligand derived from 3-(2' -carboxy-
phenylazo)-acetoacetanilide and complexes with cobalt(II),
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Ind. J. Chem. (Communicated).

11. Polymetallic Complexes: XVI.
ON-NO doubly bidentate Schiff base complexes of cobalt(II),
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Inst. of Chemists (India).
Vol. 60, May 1988, pp. 97-98

12. Polymetallic Complexes: X
Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) complexes
with 1,5-diphenyl-3-(2'-hydroxyphenyl)formazan and 1-phenyl- 
3,5-di(2'-hydroxyphenyl)formazan.


-ooxo:-
POLYMETALLIC COMPLEXES, X

COBALT(II), NICKEL(II), COPPER(II), ZINC(II), CADMIUM(II) AND MERCURY(II) COMPLEXES WITH A CHELATING AZOYE LIGAND, 5-(o-HYDROXYPHENYLDIAZ0)-ACETOACETANILIDE

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5-(o-Hydroxyphenyldiazo)acetoacetanilide, a chelating bi-bidentate azodye is capable of forming a number of peculiar polymeric complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions. The complexes have been characterised on the basis of elemental analysis, conductance, magnetic susceptibility, i.r. and electronic spectral data. From the PK values of the ligand different binding sites have been identified. Cobalt(II) and nickel(II) complexes are octahedral, copper(II) complex is square planar and zinc(II), cadmium(II) and mercury(II) complexes are tetrahedral.

Introduction

Azodyes are well known for their antiseptic properties [1, 2] and some are also used as chemotherapeutic agents [3]. Potentiometric and spectrophotometric studies on Co(II), Ni(II) and Cu(II) chelates have been reported [4]. Some of the basic azodyes are used for dyeing foodstuffs and preservatives [5] as redox indicators [6] in acid-base titrations. Keeping all the above observations in view the present paper reports the preparation and characterisation of a new dibasic bi-bidentate chelating azodye, 5-(o-hydroxyphenyl diazo)acetoacetanilide which exhibits keto-enol tautomerism (A), (B) and its complexation behaviour with divalent metal ions like Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II).

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Experimental

All the chemicals were of A. R. grade. The azodye ligand was prepared by the method.

Preparation of the complexes

The metal chlorides in EtOH were added separately to an ethanolic solution of the azodye ligand in 1:1 ratio and the reaction mixture was refluxed for 1 h. On cooling saturated ammonia was added dropwise under stirring and the metal chelates separated were filtered, washed with EtOH, Et₂O and dried in vacuum.

Metal and nitrogen contents in the complexes were determined by standard methods. Conductance was measured in 10⁻³ M dimethylformamide solution of the complexes. Magnetic susceptibility measurements were made on solid samples by the Gouy method. The i.r. data were recorded in KBr phase on a Perkin-Elmer 398 spectrophotometer. The electronic spectra were recorded in 10⁻³ M DMF solution of the complexes using Hilger and Edwards spectrophotometer. The PK values of the ligand were measured by PH titration curve on a digital PH meter, Ellico-Li-120 India. Analysis, conductance, magnetic susceptibility and i.r. spectral data are compiled in Table I.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Found M%</th>
<th>Calcd. M%</th>
<th>Molar Mass (g mol⁻¹)</th>
<th>μ (B.M.)</th>
<th>v(C=O) (PHen.)</th>
<th>v(C=O) (Alt.)</th>
<th>v(C=N=N)</th>
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<td>1640</td>
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<td>1340</td>
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</table>

LH₂ = 5-(o-hydroxyphenyldiazo)acetoacetanilide

Results and Discussion

The complexes under report have the compositions [ML₂H₂O]₆, a [M'L]₆ where M = cobalt(II), nickel(II), M' = copper(II), zinc(II), chromium(II), mercury(II), LH₂ = 5-(o-hydroxyphenyldiazo)acetoacetanilide. The cobalt(II) complex in dark brown, copper coffee colour, zinc, cadmium and mercury complexes are white. All the complexes possess high melting points and are insoluble in common organic solvents but very feebly soluble in DMF in agreement with the non-electrolytic behaviour of the complexes (Table I).
The PK values of the ligand are 2.95, 10.1 and 11.2 as estimated from H-titration curve in which the pkI value was found to be 7.3. The above values are attributable to enol, phenol and → NH⁺ groups, respectively, indicating that in the alkaline medium (pH = 11.9) these sites are available for coordination.

The i.r. spectra of the bi-bidentate azodye ligand and its complexes are informative. The band at 1640 cm⁻¹ in the ligand may be ascribed to O—O vibration. The shift of about 20 cm⁻¹ from the amidic C=O of 1660 cm⁻¹ is in agreement with the moderate O—H...O intramolecular hydrogen bonding in the ligand. The band observed at about 1620 cm⁻¹ in the metal chelates may be attributed to amidic carbonyl oxygen coordinated to the metal ions. The band at 1600 cm⁻¹ may be ascribed to υ(C=O) vibration. Bands at 1200 and 1370 cm⁻¹ in the free azodye may be assigned to the ν and phenolic C—O vibrations, respectively. Decrease of these frequencies to lower frequency regions in the metal chelates are indicative of coordination of both enolic and phenolic oxygen atoms to the metal ions. The broad band at 3060 cm⁻¹ in the free ligand may be assigned to ᵃ(OH) vibrations, red, due to intramolecular O—H...N and O—H...O hydrogen bonding in the metal chelates this band disappears showing the deprotonation of enolic and enolic hydroxyl groups. A sharp band at 1500 cm⁻¹ in the azodye be attributed to υ(—N=N—) and shifting of this frequency to lower energy (about 1450 cm⁻¹) on complexation [7, 8] indicates the bonding of the azo nitrogen atoms to the metal atoms. In case of nickel(II) complex the presence of coordinated water molecules is shown [9, 10] by the observation of two sharp peaks at 3350 and 3200 cm⁻¹ followed by two sharp peaks at 880 and 760 cm⁻¹ assigned as the OH stretching, rocking and wagging vibrations, respectively. But in case of cobalt(II) complex one broad band occurs at 3300 cm⁻¹ followed by another weak band at 850 cm⁻¹ assigned to OH stretching and rocking vibrations, respectively, showing the presence of coordinated water molecules. The conclusive evidence of bonding is ascertained by the occurrence [11] of υ(M—O) and υ(M—N) bands at about 470 and 520 cm⁻¹, respectively. Hence the azodye behaves as a bi-bidentate and bonded through the potential donor O—N=N—O atoms.

The magnetic moment data show that cobalt(II), nickel(II) and copper(II) complexes are paramagnetic with μₚeff. values 4.9, 3.3 and 1.8 B.M., respectively, revealing octahedral (O₆) geometry in cobalt(II) and nickel(II) complexes and a square planar (D₄h) stereochemistry in the copper(II) complex.

The electronic spectrum of the copper(II) complex shows a broad band at 14 850 cm⁻¹ assignable [12—15] to the 2E → 2T₁ transition indicating square planar geometry. In case of cobalt(II) complex three bands are...
observed at 8 550, 17 200 and 20 500 cm\(^{-1}\) assignable to the transitions \(^4T_2g(F) \rightarrow ^4T_{2g}(F), \rightarrow ^4A_{2g}(F)\), and \(\rightarrow ^4T_{1g}(F)\), respectively. On the basis of band positions, magnetic moment values and spectral parameters like \(D_q\), \(B\) and \(\beta_{35}\), the dark brown coloured complex is presumed to be octahedral. The nickel(II) complex exhibits three bands at 8 950, 14 520 and 24 200 cm\(^{-1}\) attributable to the transitions \(^3A_{2g}(F) \rightarrow ^3T_{2g}(F), \rightarrow ^3T_{1g}(F)\) and \(\rightarrow ^3T_{2g}(F)\), respectively. The complex is suggested to be octahedral based upon its band position, magnetic moment and spectral parameter values which are in agreement with those reported in the literature. The zinc, cadmium(II) and mercury(II) complexes presumably are tetrahedral.

The following structure (C) can be suggested for the metal complex:

![Structure diagram]

The authors are grateful to Dr S. Guru for his helpful suggestions.

REFERENCES


Manganese(II), Cobalt(II), Nickel(II), Copper(II) & Mercury(II) Complexes with 5-(2-Hydroxyphenyldiazo)salicylaldehyde

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5-(2-Hydroxyphenyldiazo)salicylaldehyde, a chelating bis-bidentate azodye, forms polymeric complexes with manganese(II), cobalt(II), nickel(II), copper(II) and mercury(II) ions. These compounds have been characterised on the basis of elemental analysis, conductance, magnetic susceptibility, IR and electronic spectral and molecular weight data. Cobalt(II) and manganese(II) complexes are octahedral, nickel(II) and copper(II) complexes are square-planar and the mercury(II) complex possess tetrahedral geometry. All the complexes are polymeric in nature.

Although many complex compounds with azodyes as ligands have been reported, little work has been done on the complexes of chelating bis-bidentate azodyes. The present note reports the preparation and characterisation of a new dibasic bis-bidentate chelating azodye, 5-(2-hydroxyphenyldiazo)salicylaldehyde, and its complexes with divalent metal ions manganese, cobalt(II), nickel(II), copper(II) and mercury(II).

All the chemicals used were of AR grade. The azodye ligand was prepared by the usual method. The metal chelates were isolated by reacting ethanolic solutions of the metal chloride and the ligand in stoichiometric proportion and refluxing for 0.5 h. The products were filtered, washed with EtOH, Et2O and dried in vacuo.

Metal, nitrogen, carbon and hydrogen contents of the complexes were estimated by standard procedures. Conductances were measured using $10^{-3} M$ dimethylformamide solutions of the complexes. Magnetic susceptibility measurements were made on solid samples by the Gouy method at room temperature. The IR spectra were recorded in KBr phase on a Perkin-Elmer 398 spectrophotometer. The electronic spectra were recorded using $10^{-3} M$ DMF solutions of the polymeric complexes on a Hilger and Watt Uvispek spectrophotometer. Molecular weights of the complexes were determined by the Rast method. Analysis, magnetic susceptibility and molecular weight data are recorded in Table 1.

All the complexes have high melting points (> 280°C) and are insoluble in common organic solvents but sparingly soluble in dimethylformamide. Non-electrolytic nature of the complexes is indicated by their low conductance values (5-9 ohm$^{-1}$cm$^2$mol$^{-1}$).

The structurally important IR bands like $\nu$(C=O), $\nu$(C-O), $\nu$(-N=N-), $\nu$(M-O) and $\nu$(M-N) have been assigned which throw light on the structural features of the new azodye ligand and its mode of bonding to the metal ions. A broad band at 3450 cm$^{-1}$ in the free ligand is ascribed to $\nu$(OH) vibration, lowered due to intramolecular O...H...O and O...H...N hydrogen bonding. The disappearance of this band in metal chelates is indicative of deprotonation of phenolic hy-

Table 1—Analytical, Colour, Magnetic Moment and Molecular Weight Data

<table>
<thead>
<tr>
<th>Compound</th>
<th>(Colour)</th>
<th>Found (Calc.) %</th>
<th>$\mu_{eff}$ (B.M.)</th>
<th>Molec. weight</th>
<th>Found (Calc.)</th>
</tr>
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<td>Deep brown</td>
<td>11.3 64.3 3.98</td>
<td>—</td>
<td>238</td>
<td>—</td>
</tr>
<tr>
<td>[CoL$_2$H$_2$O]$_n$</td>
<td>17.2 8.1 46.4 3.5</td>
<td>4.8</td>
<td>638.00</td>
<td></td>
<td></td>
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<tr>
<td>[Reddish brown]</td>
<td>(17.5) (8.36) (46.58) (3.58)</td>
<td>—</td>
<td>(665.86)</td>
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<tr>
<td>NiL$_n$</td>
<td>Red</td>
<td>19.3 9.2 52.1 2.5</td>
<td>—</td>
<td>545.00</td>
<td></td>
</tr>
<tr>
<td>[CuL]$_n$</td>
<td>Coffee colour</td>
<td>20.8 9.1 51.3 2.4</td>
<td>1.7</td>
<td>578.00</td>
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</tr>
<tr>
<td>[MnL$_2$H$_2$O]$_n$</td>
<td>(20.9) (9.22) (51.40) (2.63)</td>
<td>—</td>
<td>(603.00)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Deep brown]</td>
<td>(16.5) (8.44) (47.14) (3.62)</td>
<td>5.5</td>
<td>622.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[HgL]$_n$</td>
<td>Dark grey</td>
<td>45.3 6.2 55.3 1.7</td>
<td>—</td>
<td>835.00</td>
<td></td>
</tr>
</tbody>
</table>
| LH$_2$ = 5-(2-Hydroxyphenyldiazosalicylaldehyde)


66.
droxyl groups and consequent dibasic nature of the ligand. The band occurring at 1340 cm\(^{-1}\) in the ligand may be assigned to \(\nu(C-O)\) vibration which shifts to higher frequency region (\(\sim 1350\) cm\(^{-1}\)) on complexation indicating bonding through both the phenolic oxygen atoms. The ligand shows a band at 1540 cm\(^{-1}\) due to the \(\nu(N-N)\) mode. In the metal chelates this frequency is lowered to \(\sim 1530\) cm\(^{-1}\) indicating the bonding of the azo nitrogen to the metal atom. The \(\nu(C-N)\) vibration appearing at 1490 cm\(^{-1}\) in the ligand suffers a downward shift of \(\sim 10\) cm\(^{-1}\) thereby supporting the coordination of one of the azo nitrogen atoms to the metal ion. The observation of a band at 1640 cm\(^{-1}\) in the azodye is due to the \(\nu(C-O)\), and on complexation it shifts to \(\sim 1620\) cm\(^{-1}\) showing the bonding of the carbonyl oxygen atom to the metal atom.

In the case of cobalt(II) and manganese(II) complexes, presence of coordinated water molecule is shown\(^3\) by the occurrence of a broad band near 3400 cm\(^{-1}\) followed by two weak bands at \(\sim 860\) and \(\sim 760\) cm\(^{-1}\) assigned to the OH stretching, rocking and wagging vibrations, respectively. The conclusive evidence of bonding is provided by the occurrence\(^4\) of \(\nu(M-O)\) and \(\nu(M-N)\) bands at \(\sim 450\) and \(510\) cm\(^{-1}\) respectively in the far IR spectra of the complexes.

The cobalt(II), copper(II) and manganese(II) complexes exhibit magnetic moment values expected for an octahedral stereochemistry. The degree of polymerization of the metal complexes was found to be 2.

The electronic spectrum of cobalt(II) complex shows bands at 9010, 18350 and 21250 cm\(^{-1}\) assignable to \(4T_{1g}(F) \rightarrow 4T_{2g}(G), 4A_{2g}(F) \rightarrow 4T_{1g}(P)\) transitions respectively. The calculation of spectral parameters like \(B(832\) cm\(^{-1}\), 10 \(Dq(9340)\) cm\(^{-1}\), \(\beta_{5g}(0.85)\) and \(\nu_{c}/\nu_{e}(2.01)\) suggests an octahedral structure\(^5\). The nickel(II) complex exhibits two bands at 16500 and 17600 cm\(^{-1}\) attributable to the transitions \(1A_{1g} \rightarrow 1B_{1g}\) and \(1E_{g}\) respectively which are consistent with a square-planar configuration\(^6\). The diamagnetic nature of the complex also supports this formulation. Mn(II) complex shows four electronic absorption bands at 18400, 22500, 24350 and 27600 cm\(^{-1}\) assignable to \(6A_{1g} \rightarrow 4T_{1g}(G), 4T_{2g}(G), 4E_{g}\) and \(4T_{2g}(D)\) transitions, respectively, suggesting\(^8\) a high-spin octahedral configuration for the complex. Copper(II) complex exhibits a broad absorption band at 14100 cm\(^{-1}\) indicating a square planar geometry\(^9\).

On the basis of above considerations, it is suggested that the azodye ligand behaves as a bisbidentate dibasic (LH\(_2\)) anion bonding to the metal ions through two phenolic oxygen, diazo nitrogen and carbonyl oxygen atoms. The following tentative structure (A) can be proposed for the repeating unit of the polymeric metal chelates.

The authors are thankful to Dr. B. Pradhan, Assistant Professor, R.E.C., Rourkela for supplying magnetic data and Prof. G.B. Behera for the IR spectra of the compounds.

References
Mixed Ligand Complexes of Co(II), Cu(II), Zn(II), Cd(II) & Hg(II) with Acetoacetanilide & Isoquinoline

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Received 9 January 1986; revised 14 July 1986; accepted 12 August 1986

Fifteen mixed ligand complexes of Co(II), Cu(II), Zn(II), Cd(II) and Hg(II) containing acetoacetanilide and isoquinoline as donors have been prepared. These compounds have been characterised on the basis of their elemental analysis, conductance, magnetic susceptibility, TGA, IR and electronic spectral data.

Study of mixed ligand complexes has aroused a lot of interest in recent years. Although much work has been done on β-ketones, β-ketoesters and α-hydroxyarylcarboxyls, very little work has been reported with β-ketoamides. Earlier we have reported1-4 a number of tetra-, penta-, hexa- and octa-coordinated Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) mixed ligand complexes. The present study reports the preparation and characterisation of mixed ligand complexes of Co(II), Cu(II), Zn(II), Cd(II) and Hg(II) with a monobasic bidentate oxygen donor (acetoacetanilide) and a neutral monodentate nitrogen donor (isoquinoline). All the chemicals used were of AR grade.

[MX(acacNXIQ)]

These compounds were prepared by reacting ethanolic solutions of the metal salt, acetoacetanilide and isoquinoline in 1:1:1 molar ratio. The reaction mixture was refluxed over a water-bath for about 0.5 hr. Concentrated ammonia was added dropwise with stirring to the moderately hot solution when the mixed ligand complexes separated out.

[CoBr(acacN)(IQ)(H2O)] and [Co(NO3)3(acacN)(IQ)(H2O)]

These compounds were prepared by reacting an ethanolic solution of cobalt(II) bromide (2.19 g), or cobalt(II) nitrate (2.9 g) with acetoacetanilide (1.7 g) and isoquinoline (1.3 ml) followed by dropwise addition of ammonia. The compounds thus prepared were filtered, washed with ethanol several times, then with ether, and dried in vacuo.

The conductance measurements of the complexes were carried out in acetone solution (10−3 M). Magnetic susceptibility measurements were made by the Gouy method. Infrared spectra were recorded on a Perkin-Elmer 398 spectrophotometer. Electronic spectra were recorded in acetone solution (10−2 M) using Hilger and Watt Uvispec spectrophotometer. Thermogravimetric analysis was carried out using an instrument manufactured by Hungarian Optical Works, Hungary at a heating rate of 10°C min−1. The characterisation data of the complexes are given in Table 1.

The complexes reported in the present investigation have the compositions [MX(acacN)(IQ)] and [M'Y(acacN)(IQ)(H2O)] where M = Co(II), Cu(II), Zn(II), Cd(II), Hg(II), X = Cl, Br, SCN, NO3, M' = Co(II), Y = Br and NO3, acacN = acetoacetanilide anion, and IQ = isoquinoline. Non-electrolytic nature of the complexes is indicated by the low ΛΜ values (7.0-12.5 mhos cm2 mol−1).

In the infrared spectra of acetoacetanilide, bands appearing at 1630, 1590 and 1150 cm−1 may be attributed to ν(C=O), ν(C=C) and ν(C−O) vibrations respectively. In the mixed ligand complexes these bands are observed at ~1620, ~1580 and ~1050 cm−1 indicating coordination of acetoacetanilide moiety to the metal ions through both amidic and enolate oxygen atoms. Conclusive evidence of metal-oxygen bond is provided5 by a band at ~440 cm−1 in the far infrared spectra of all the complexes. The sharp band observed at 2900 cm−1 due to ν(N−H) in the spectrum of acetoacetanilide remains unchanged in the spectra of the mixed ligand complexes showing non-coordination of acetoacetanilide nitrogen to the metal ions. A band at ~510 cm−1 in the infrared spectra of the mixed ligand complexes may be ascribed to bonding of isoquinoline nitrogen atom to the metal ions. The metal halogen stretching frequencies, however, fall beyond the range of the instruments used. In the case of nitrate and bromo complexes of cobalt(II), one broad band is observed at 3450 cm−1 followed by a sharp peak at 650 cm−1 indicating the presence of coordinated water molecule in the complexes. In the case of cobalt(II) and copper(II) nitrate complexes, strong bands are observed at ~1850 and ~1250 cm−1 which are indicative6-7 of unidentate coordination of the nitrate group. In the case of thiocyanato complex of Co(II), ν(C−N) and ν(C−S) band appeared at ~2070 and ~830 cm−1 respectively indicating M−NCS type of bonding. In the spectra of Zn(II) and Cd(II) complexes ν(C−N) and ν(C−S) appear at ~2030 and 720 cm−1 respectively which are indicative of M−SCN bonding of the thiocyanato group.

Electronic spectral band positions of cobalt(II)
Table 1—Characterisation Data of the Mixed Ligand Complexes

<table>
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<th>Compound</th>
<th>Colour</th>
<th>Elemental Analysis</th>
<th>μ_{eff} (B.M.)</th>
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<tr>
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<td></td>
<td>Found(Calc), %</td>
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</tr>
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<td>[CoCl(LXIQ)]</td>
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<td>6.91</td>
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<tr>
<td></td>
<td>(185)</td>
<td>(12.19)</td>
<td>(7.01)</td>
</tr>
<tr>
<td>[Co SCN(LXIQ)]</td>
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<td>13.75</td>
<td>9.72</td>
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<td>(&gt;250)</td>
<td>(13.96)</td>
<td>(9.95)</td>
</tr>
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<td>6.80</td>
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<td>(145)</td>
<td>(9.96)</td>
<td>(7.10)</td>
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<td>[CoNO3Cl(LXIQ)]</td>
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<td>(165)</td>
<td>(9.77)</td>
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<td>[CoCl(LXIQ)0]</td>
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<td>(6.98)</td>
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<td>[CuCl(LXIQ)]</td>
<td>Green</td>
<td>14.36</td>
<td>9.54</td>
</tr>
<tr>
<td></td>
<td>(155)</td>
<td>(14.69)</td>
<td>(9.75)</td>
</tr>
<tr>
<td>[CuN03(LXIQ)]</td>
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<td>14.36</td>
<td>9.54</td>
</tr>
<tr>
<td></td>
<td>(155)</td>
<td>(14.69)</td>
<td>(9.75)</td>
</tr>
<tr>
<td>[ZnCl(LXIQ)]</td>
<td>Yellowish white</td>
<td>15.75</td>
<td>6.72</td>
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<tr>
<td></td>
<td>(152)</td>
<td>(16.19)</td>
<td>(6.90)</td>
</tr>
<tr>
<td>[ZnBr(LXIQ)]</td>
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<td>14.14</td>
<td>6.05</td>
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<td></td>
<td>(180)</td>
<td>(14.50)</td>
<td>(6.21)</td>
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<tr>
<td>[Zn SCN(LXIQ)]</td>
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<td>15.82</td>
<td>9.54</td>
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<tr>
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<td>(182)</td>
<td>(15.24)</td>
<td>(9.80)</td>
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<tr>
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<td>White</td>
<td>24.51</td>
<td>6.05</td>
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<td>(152)</td>
<td>(24.82)</td>
<td>(6.18)</td>
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<td>(5.14)</td>
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<td>(8.76)</td>
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<td>(200)</td>
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<td>(185)</td>
<td>(37.06)</td>
<td>(5.17)</td>
</tr>
</tbody>
</table>

LH = Acetoacetanilide, IQ = Isoquinoline

complexes (Sl. Nos. 1 and 2 of Table 1) together with their high molar extinction coefficients (1200) and low μ_{eff} values (4.45 BM) are suggestive9,10 of a tetrahedral configuration of these two complexes. The spectra of bromo and nitrato complexes of cobalt(II) suggest an octahedral stereochemistry around the cobalt(II) ions10,11. The high μ_{eff} values (5.1 BM) and low extinction coefficient values support this inference. The two copper(II) complexes exhibit a broad absorption band around 14000 cm⁻¹ suggesting a square planar stereochemistry12–14. The room temperature magnetic moment values (1.81 and 1.88 BM Table 1) also favour the square-planar configuration15.

Thermogravimetric analysis data of two representative compounds are reported here. The complex [CoCl(LXIQ)] is quite stable at room temperature. It is found to lose the isoquinoline molecule in the range of 140-540°C, registering a mass loss of 32.23% (theoretical 32.33%). This mass loss is supported by the endothermic peak at 420°C on the DTA curve. The compound [CoBr(LXIQ)(H2O)] loses the water molecule along with one molecule of isoquinoline registering a mass loss of 25.2% (theoretical 25.2%) as observed from TGA curve. This is well supported by the sharp endothermic peak at 300°C on the DTA curve. The compound loses the other molecule of isoquinoline in the range of 450-630°C with a mass loss of 48.3% (theoretical 48.7%). This is supported by the exothermic peak at 560°C on the DTA curve.

The Zn(II), Cd(II) and Hg(II) complexes are presumably tetrahedral.

References
13 Orgel L E, J chem Phys, 23 (1956) 6.
15 Sacconi L & Ciampolini M, J chem Soc; (1964) 278.
MIXED LIGAND COMPLEXES OF COBALT (II), NICKEL (II), COPPER (II), ZINC (II), CADMIUM (II), MERCURY (II) AND MANGANESE (II)

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(Received 12 May, 1986)

In continuation of our earlier work on the study of schiff base complexes1-3 of divalent metal ions, the present paper reports the preparation and characterisation of some mixed ligand complexes of Co (II), Ni (II), Cu (II), Zn (II), Cd (II), Hg (II) and Mn (II) with a bidentate ON donor schiff base derived from salicylaldehyde with sulphanilic acid and \( \gamma \)-picoline.

EXPERIMENTAL AND DISCUSSION

The schiff base was synthesized by refluxing salicylaldehyde with sulphanilic acid (1:1) ratio in ethanolic medium over a water bath for 2 hrs. It was then filtered, washed with ethanol and air-dried. The metal complexes were prepared by refluxing metal salts, the schiff base and \( \gamma \)-picoline (1:2:2 ratio) in ethanol for 2 hrs. The solid complexes thus separated were kept for 24 hrs and then filtered, washed with ethanol, ether and dried in vacuo.

Analysis and physical measurements were done as in our earlier communication.2

The complexes have the compositions [M\( \text{L}_2\text{L}_2' \)] and [M'\( \text{L}\text{CIL}_2' \)] where M=Co(II), Ni (II), Cu (II), Mn (II), Zn (II), LH = schiff base derived from salicylaldehyde and sulphanilic acid, L' = \( \gamma \)-picoline, M' = Cd (II), Hg (II). All the complexes have low molar conductance values in acetone (\( \lambda_m \approx 7.5 - 10.5 \) mhos cm\(^2\) mole\(^{-1}\)) indicating non-electrolytic nature of the complexes. Magnetic moment values of Co (II), Ni (II), Mn (II) and Cu (II) are 5.1, 3.7, 5.9 and 1.87 B. M. respectively indicating octahedral configuration. In case of schiff base the absorption bands observed at 1640 and 1500 cm\(^{-1}\) may be ascribed to \( \nu(C=\text{N}) \) (imine) and \( \nu(C-O) \) (phenolic) vibration respectively. In adducts these bands are observed at 1590-1605 cm\(^{-1}\) (C=\text{N}) and 1480-1490 cm\(^{-1}\) (C-O) indicating the bonding of the schiff base to the metal ions through imino nitrogen and phenolic oxygen atoms. The \( \gamma \)-picoline adducts show bands in the 1620-1425 cm\(^{-1}\) region assignable to \( \nu(C=\text{C}) \) and \( \nu(C=\text{N}) \) vibration and a change of about 10 cm\(^{-1}\) indicates the bonding of \( \gamma \)-picoline to the metal ions.
The Cu(II) complexes exhibit one broad band at 14950 cm\(^{-1}\) indicating a distorted octahedral configuration. Electronic spectrum of the Co(II) complex shows bands at 8600, 18100 and 19350 cm\(^{-1}\) suggesting some amount of tetragonal distortion. The Ni(II) complex exhibits bands at 11150, 16500 and 22500 cm\(^{-1}\) characteristic of octahedral Ni(II) complex. Mn(II) complex shows two bands at 18500, 22700, 24450 and 27700 cm\(^{-1}\) supporting an octahedral structure.

The Zn(II) complex possesses an octahedral geometry and Cd(II), Hg(II) complexes are tetrahedral in configuration.

The authors are thankful to Prof. R. C. Acharya, Head of Chemistry Department, G. M. College for facilities.

REFERENCES

COBALT (II), NICKEL (II), COPPER (II), ZINC (II) AND MERCURY (II) COMPLEXES WITH CHELATING TRIDENTATE ONN DONOR SCHIFF BASE

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(Received 2 July, 1986)

In continuation of our earlier study\(^3\) on the schiff base complexes, the present paper reports the preparation of a new ONN tridentate schiff base and its complexation behaviour with Co (II), Ni (II), Cu (II), Zn and Hg (II) ions.

EXPERIMENTAL AND DISCUSSION

The metal chelates were prepared by reacting ethanolic solution of metal (II) chlorides with the schiff base in 1 : 2 molar ratio. The reaction mixture was refluxed over a waterbath for about 1 hr. On cooling conc. ammonia was added dropwise when the metal chelates separated out. These were then filtered, washed with ethanol, ether and dried in vacuo.

All analysis and physical measurements were done as in our earlier communication\(^1\).

Non-electrolytic nature of the complexes is indicated from the low $\Lambda$ values. In the i. r. spectrum of the ligand $\nu$ (C=N) appears at 1595 cm\(^{-1}\) and shifting of this band to higher frequency region (1600-1605 cm\(^{-1}\)) in the metal chelates indicates the bonding\(^2\) of imine nitrogen atom to the metal ions. In case of metal complexes $\nu_{as}$ (COO) and $\nu_{as}$ (COO) appear at 1535-1540 cm\(^{-1}\) and 1370-1375 cm\(^{-1}\) and a difference of ca. 160 cm\(^{-1}\) indicates the monodentate nature of the carboxylate group\(^8\). In case of ligand $\nu$ (N—O) appears at 1030 cm\(^{-1}\) and a positive shift of ca. 10 cm\(^{-1}\) (1040-1045 cm\(^{-1}\)) in the metal chelates is diagnostic of oxime nitrogen co-ordination\(^4\). The broad band at ca. 3450 cm\(^{-1}\) in the ligand and in complexes can be assigned to $\nu$ (OH) vibration which indicates that oximino —OH group is free and not bonded to metal ions.

In the electronic spectrum of the cobalt (II) complex, three absorption bands are observed at 8450, 17100 and 19500 cm\(^{-1}\) attributable to $^4T_{1g}$ (F) $\rightarrow$ $^6T_{1g}$ (F), $\rightarrow$ $^4A_{2g}$ (F) and $\rightarrow$ $^4T_{1g}$ (P) transitions respectively in conformity with an octahedral configuration. The high $\mu$\(_\text{eff}\) value of 5.0 B. M. supports this formulation. The electronic spectrum of the copper (II) complex show the band at 21,000 cm\(^{-1}\), suggestive of distorted octahedral configuration. The $\mu$\(_\text{eff}\) value of 1.79 B. M. is indicative of the presence of one unpaired
electron. In case of nickel (II) complex, two bands appear at 22,400 and 26,700 cm⁻¹ assignable to \(^1A_{2g} \rightarrow ^1A_{2g}\) and \(^1B_{2g} \rightarrow \) transitions respectively in conformity with a square planar configuration\(^5\). The dimagnetic nature of the red coloured complex supports this stereochemistry.

The zinc (II) and mercury (II) complexes are presumably four co-ordinated with a tetrahedral geometry around the metal ions.

**Summary**

Five complexes have been synthesized having the compositions \([\text{CoL}_2]\), \([\text{CuL}_2]\), \([\text{NiLCl}]\), \([\text{ZnLCl}]\) and \([\text{HgLCl}]\) where \(\text{LH} = \text{Schiff base derived from diacetylmonoxime and glycine. The cobalt (II) complex is octahedral, copper (II) distorted octahedral, nickel (II) square planar, zinc (II) and mercury (II) complexes are tetrahedral in configuration.**

**References**

POLYMETALLIC COMPLEXES: PART XVIII.
COBALT(II), NICKEL(II), COPPER(II), ZINC(II), CADMIUM(II) AND MERCURY(II) COMPLEXES CONTAINING A CHELATING AZO DYE, 
N,N'-BIS[3-(2'-HYDROXYPHENYLazo)ACETOACETANILIDE| ETHYLENE-DIAMINE.

Bipin B. Mahapatra* and Dillip K. Das
Department of Chemistry, G.M. College,
Sambalpur - 768 004, Orissa, INDIA.

SUMMARY

Six polymeric complexes have been isolated with the octadentate ligand having \( \text{O N-ONNO-N O} \) donor atoms. All the complexes have high melting points, are insoluble in common organic solvents and amorphous. The cobalt(II), nickel(II) and copper(II) complexes are found to be pseudo-octahedral whereas a tetrahedral structure is suggested for zinc(II), cadmium(II) and mercury(II) complexes. The characterisation is made on the basis of analysis, conductance, magnetic susceptibility, i.r. and electronic spectral data.

INTRODUCTION

The azo dyes possess both antiseptic and chemotherapeutic properties.\(^1\),\(^2\) They are also used as preservatives and for dyeing food stuffs and as redox indicator.\(^3\),\(^4\) In continuation of our earlier studies
on the azo dye complexes,\(^5\) we report here the preparation of a new octadentate azo dye and six metal complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions.

**EXPERIMENTAL**

All the chemicals were of AR grade. The compound \(N,N'\)-bis(acetoacetanilide)ethylenediamine was prepared following a reported method.\(^8\)

**Preparation of the azo dye.** The diazonium chloride obtained from o-aminophenol (1.1 g) by a common method\(^9\) was slowly added to the NaOH solution (30 ml) of the above compound (3.78 g) kept inside an ice-salt bath with constant stirring. The red coloured azo dye precipitated and was then filtered, washed with water thoroughly and then dried in air. It was finally recrystallised from hot ethanol solution by slow cooling in an ice bath. Yield 2.5 g (55 %), melting point 250\(^\circ\)C.

Calculated for \(C_{34}H_{34}O_4N_8\): C, 66.01%; H, 5.50%; N, 18.12%.

Found: C, 65.15%; H, 5.32%; N, 17.95%.

**Preparation of the complexes.** An EtOH solution (30 ml) of the ligand (6.18 g) was mixed with an EtOH solution (20 ml) of the metal chloride (1:3 ratio) and the mixture was refluxed for 1/2-1 hr over a water bath. Upon cooling, a few drops of conc. ammonia were added slowly with stirring causing the metal complexes to precipitate. These were then filtered, washed with ethanol, ether and dried in vacuo.

The physical measurements were accomplished by the following standard procedures. Metal contents in the complex were determined by the EDTA-titration method using Eriochrome-Black-T as indicator at the pH range 10 while the nitrogen and halogen contents were determined by semimicro-Kjeldahl and semimicro-sodium-ethanolamine procedures,
respectively. Conductance was measured in $10^{-3}$ M EDTA solutions of the complex using a Toshniwall conductivity bridge. Magnetic susceptibilities were measured on solid samples by the Gouy Method. The i.r. spectra were recorded in KBr pellets on a Perkin-Elmer 398 spectrophotometer. The electronic spectra of the complexes were recorded on $10^{-2}$ M DMF solutions using a Hilger and Watt Uvispeck spectrophotometer.

Analysis, conductance, magnetic susceptibility data are recorded in Table 1 while i.r. spectral and ligand field parameters data are recorded in Table 2.

RESULTS AND DISCUSSION

The formation of complexes obtained is due to the following thermochemical equation involving the metal chlorides and the title ligand $LH_2$:

\[(i) \quad 3MCl_2 + LH_2 + aq \xrightarrow{\Delta} [M_3LCl_4(H_2O)_4]^2 + 2HCl \]
\[ [M = \text{Co(II), Ni(II), Cu(II)}] \]

\[(ii) \quad 3MCl_2 + LH_2 + aq \xrightarrow{\Delta} [M_3LCl_2(H_2O)_2]^2Cl_2 + 2HCl \]
\[ [M = \text{Zn(II), Cd(II), Hg(II)}] \]

All the complexes are amorphous and have high melting points and are insoluble in solvents like methanol, ethanol, benzene etc., but sparingly soluble in dimethyl formamide, in which the cobalt, nickel and copper complexes are found to be non-electrolytes but the zinc, cadmium and mercury complexes are found to be 1:2 electrolytes (Table 1).

In the i.r. spectrum of the ligand, the broad band appearing at $3250 \text{ cm}^{-1}$ may be assigned to $\nu(\text{OH})$ lower in energy from $3450 \text{ cm}^{-1}$ due to intramolecular O-H.....N hydrogen bonding. The disappearance of this band in metal complexes is indicative of phenolic oxygen coordination to the metal ions. The band at $1375 \text{ cm}^{-1}$ in the free ligand may be
Table 1. Analysis, Magnetic Susceptibility and Conductance Data

<table>
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<th>Compound</th>
<th>Colour</th>
<th>M.P. (°C)</th>
<th>Yields in %</th>
<th>% M Found</th>
<th>% M Calcd.</th>
<th>% C Found</th>
<th>% C Calcd.</th>
<th>% H Found</th>
<th>% H Calcd.</th>
<th>% N Found</th>
<th>% N Calcd.</th>
<th>% Cl Found</th>
<th>% Cl Calcd.</th>
<th>B.M</th>
<th>Ω effective</th>
<th>Δ Conductance cm² mol⁻¹</th>
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</thead>
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<td>-</td>
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<td>66.01</td>
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<td>17.95</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>C₄H₄N₂O₂Cl₂</td>
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<td>45</td>
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<td>40</td>
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<td>50</td>
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<td>38.62</td>
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<td>6.7</td>
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<td></td>
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<td></td>
<td>19.49</td>
<td>19.81</td>
<td>40.90</td>
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<td>9.99</td>
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<td>42.86</td>
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<td>9.88</td>
<td>10.16</td>
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<td>105.0</td>
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</table>

LH₂ = N,N'-bis[3-(2'-hydroxyphenylazo)acetoacetilidem]ethylenediamine.
ascribed to the $\nu$(C=O) vibration and a bathochromic shift of $\sim$15 cm$^{-1}$ in the metal complexes shows the bonding of phenolic oxygen atoms to the metal ions. The $-\text{N}=\text{N}-$ frequency in the ligand is observed at 1500 cm$^{-1}$ and is shifted to $\sim$1430 cm$^{-1}$ in the chelates, indicating the bonding of one of the azo nitrogen atoms to the metal ions. The band at 1620 cm$^{-1}$ in the ligand may be proposed for a $\nu$(C=O) vibration. The bathochromic shift of $\sim$40 cm$^{-1}$ from the amide C = O of 1660 cm$^{-1}$ is in agreement with moderate C = O .... H - N hydrogen bonding. In metal chelates it appears at 1610 cm$^{-1}$ thereby showing amide oxygen coordination to the metal ions. The strong absorption band appearing at 3150 cm$^{-1}$ in the free ligand can be assigned to $\nu$(NH) of the ethylenediamine part of the ligand supporting the ketoamine structure (1). Broadening and splitting of this band in the metal complexes show their linkage to the metal ions. The conclusive evidence of bonding of the oxygen and nitrogen atoms to the metal ions is indicated by the appearance of bands at $\sim$450 and $\sim$500 cm$^{-1}$ assignable to $\nu$(M-O) and $\nu$(M-N) vibrations, respectively, in the far i.r. spectra of the complexes.

The $\mu_{\text{eff}}$ values of the Co(II), Ni(II) and Cu(II) complexes are found to be 3.1, 3.7 and 1.8 B.M., respectively, indicating a pseudo-$O^4$ geometry around the metal ions. The other complexes are found to be diamagnetic in nature.

The electronic transition of the cobalt(II) complex exhibits three d-d bands at 8152(11), 16074(22) and 19386(30) cm$^{-1}$ which may be attributed$^{12}$ to the transitions $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)(\nu_1)$, $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)(\nu_2)$ and $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)(\nu_3)$, respectively. The position of absorption, low intensity and values of spectral parameters like B, $\beta$, $\gamma_2/\gamma_1$, 10 Dq, 6% support an octahedral geometry around the cobalt(II) ion (Table 2). The electronic spectrum of the nickel(II)
Table 2. Spectral and Ligand Field Parameters Data

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\gamma_1^\text{cm}^{-1}$</th>
<th>$\gamma_2^\text{cm}^{-1}$</th>
<th>$\gamma_3^\text{cm}^{-1}$</th>
<th>$\gamma_{\text{C-O}}$</th>
<th>$\gamma_{\text{N-N}}$</th>
<th>$\gamma_{\text{M-O}}$</th>
<th>$\gamma_{\text{M-N}}$</th>
<th>$10 \text{ Dq cm}^{-1}$</th>
<th>B cm$^{-1}$</th>
<th>$\gamma_{2/\gamma_1}$</th>
<th>$\delta$</th>
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<tbody>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>1500</td>
<td>1600</td>
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<tr>
<td>[Co$_3$LCl$_4$(H$_2$O)$_6$]</td>
<td>8135</td>
<td>16074</td>
<td>19386</td>
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<td>450</td>
<td>300</td>
<td>7922</td>
<td>779</td>
<td>0.802</td>
<td>1.97</td>
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<tr>
<td>[Ni$_3$LCl$_4$(H$_2$O)$_6$]</td>
<td>12640</td>
<td>20457</td>
<td>25825</td>
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<td>445</td>
<td>305</td>
<td>11640</td>
<td>760</td>
<td>0.793</td>
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</tr>
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<td>14604</td>
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<td>760</td>
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<td>1430</td>
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<td>1605</td>
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<td>1435</td>
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<td>1610</td>
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<td>[Hg$_3$LCl$_2$(H$_2$O)$_2$]Cl$_2$</td>
<td>1355</td>
<td>1430</td>
<td>445</td>
<td>305</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1610</td>
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complex is consistent with octahedral geometry, showing three d-d transitions at 12640(6.5), 20475(9.5) and 23825(17.5) cm\(^{-1}\) assignable to the \(3A_2g(F)\rightarrow 3T_2g(F)(\nu_1)\), \(3A_2g(F)\rightarrow 3T_1g(F)(\nu_2)\) and \(3A_2g(F)\rightarrow 3T_1g(F)(\nu_3)\) transitions, respectively. The energy of the first band corresponds to 10 Dq in case of the Ni(II) complex. The calculation of spectral parameters supports the octahedral stereochemistry for the Ni(II) complexes.\(^{13}\) The copper(II) complex shows three shoulder bands at 12750(25.5), 14604(39) and 20572(59) cm\(^{-1}\) assignable to the \(2B_{1g}\rightarrow 2A_{1g}, 2B_{1g}\rightarrow 2B_{2g}\) and \(2B_{1g}\rightarrow 2B_{2g}\) transitions, respectively. Due to Jahn-Teller distortion in the Eg ground state, the Cu(II) ion in the complex displays distorted octahedral geometry.\(^{14}\)

The Zn(II), Cd(II) and Hg(II) complexes are polymeric in nature and presumably possess tetrahedral stereochemistry, based upon analytical, conductance and i.r. spectral data.

The three possible structures (1,2,3) of the azo dye ligand and the tentative structure of the metal complexes (4) and (5) are represented below.

(1) Ketoamine
(2) Ketoimine

(3) Hydrogen bonded

(4) \( M = \text{Co}^{II}, \text{Ni}^{II}, \text{Cu}^{II} \)
(5) $N = \text{Zn(II), Cd(II), Hg(II)}$

REFERENCES


Received: 2 September, 1987
Accepted: 24 August, 1988
Referee I: J. A. Burke, Jr.
Referee II: M. J. Maroney
SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY

Dear Sir:

Your manuscript entitled: Polymetallic Complexes Part XVIII.
Cobalt(II), Nickel(II), Copper(II) . . .

[] has been received. We shall notify you regarding the publication of the paper as soon as possible.

X has been accepted for publication and will appear in issue # 10 (1988).

K. Moedritzer
Monsanto Company
St. Louis, MO 63167 USA
Synthesis and characterisation of some Co (II), Ni (II), Cu (II) and Cd (II) complexes with ON-NO donor doubly-bidentate Schiff base N,N'-bis (benzoin) 4,4'-diaminodiphenylmethane are reported in this paper.

Experimental and Discussion

Metal complexes were prepared by refluxing ethanolic solution of the metal salts with the Schiff base in dioxan in 1:1 molar ratio on water-bath for 1 hr. The complexes, separated out on cooling were filtered, washed with ethanol, ether and dried in vacuo.

Metal and nitrogen contents were determined by standard methods. Conductances were measured in dimethylformamide (10⁻³ M solution). The magnetic moments of Co (II), Ni (II) and Cu (II) complexes were measured by Gouy method. IR spectra were recorded on KBr discs on a Perkin Elmer 398 spectrophotometer and electronic spectra were recorded on a Hilger-watt Uvispeck spectrophotometer using nujol as mulling agent. Molecular weight measurements were carried out by the Rast method using camphor as the solvent.

The complexes synthesized have the compositions [M₂L₂.4H₂O] and [M₄L₄] where M = Co (II), Ni (II), Cu (II) ; M' = Cd (II) ; LH₂ = N,N'-bis (benzoin) 4,4'-diaminodiphenylmethane. Cobalt complex is brown, nickel green, copper green and cadmium complex is light yellow in colour. All the complexes are amorphous in natures and are insoluble in common organic solvents but sparingly soluble in DMF. The complexes are found to be non-electrolytes in DMF medium (5.0-9.5 mhos cm² mole⁻¹). The percentage of metal, nitrogen and the molecular weight of the compounds were duly verified by analysis.

Sub-normal magnetic moments of Co (II), Ni (II) and Cu (II) complexes (2.65, 2.21 and 1.34 B. M. respectively) show magnetic interactions between the metal ions present in the polymeric compounds.

The Schiff base acts as a ON-NO donor doubly bidentate ligand. In the i.r. spectrum of the Schiff base, two bands of medium intensity are observed at 3400 and
98 POLYMERIC COMPLEXES

3030 cm\(^{-1}\) assigned to intramolecular O-H...N hydrogen bond (\(\nu\) OH). These bands disappear in the metal complexes indicating deprotonation of enolic OH groups. The appearance of bands at 1670 and 1255 cm\(^{-1}\) in the ligand spectrum may be ascribed to \(\nu\) (C = N) and \(\nu\) (C – O) vibrations respectively. A bathochromic shift of these bands (Ca 1600 and 1250 cm\(^{-1}\)) in the metal complexes indicate the bonding of the ligand to the metal ions through the imine nitrogen and hydroxyl oxygen atoms. In the spectra of Co(II), Ni(II) and Cu(II) complexes, a broad band appears at 3200-3400 cm\(^{-1}\) followed by other peaks at 1400 and 830 cm\(^{-1}\) assignable to OH stretching, bending and rocking vibrations respectively confirming the presence of coordinated water molecules. The conclusive evidence of bonding is obtained by the observation of bands at Ca 510 and 450 cm\(^{-1}\) attributable to \(\nu\) (M – N) and \(\nu\) (M – O) vibrations respectively.

The electronic spectrum of the Co(II) complex exhibit a broad band at 8300 cm\(^{-1}\) and medium strong band at 17150 and 19450 cm\(^{-1}\) assignable to \(^4\text{T}_{1g}(F) \rightarrow ^4\text{T}_{2g}(F)\) (\(\nu_2\)), \(^4\text{A}_{2g}\) (\(\nu_3\)) and \(\rightarrow ^4\text{T}_{1g}(P)\) (\(\nu_3\)) transition respectively, supporting a distorted octahedral configuration for the complex. The electronic spectrum of the Ni(II) complex shows three absorption bands at 8800, 15200 and 24950 cm\(^{-1}\) attributable to \(^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(F)\), \(\rightarrow ^3\text{T}_{1g}(F)\) and \(\rightarrow ^3\text{T}_{1g}(P)\) transitions respectively. The spectral parameters suggest a distorted octahedral geometry around the complex. The Cu(II) complex exhibits a single broad asymmetric band at 16250 cm\(^{-1}\) which may arise due to \(^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}(\nu_1) \rightarrow ^2\text{B}_{2g}(\nu_2)\) and \(\rightarrow ^2\text{E}_g(\nu_3)\) transitions supporting a distorted octahedral configuration for the complex.

The molecular weight data support the dimeric composition of all the complexes.

SUMMARY

Four complex compounds of the composition [M\(_2\)L\(_2\).4H\(_2\)O] and [M\(_3\)L\(_2\)] have been prepared where M = Co(II), Ni(II), Cu(II) and M' = Cd(II), LH\(_2\) = N, N'-bis (benzoin)-4,4'-diaminodiphenylmethane. The Co(II), Ni(II) and Cu(II) complexes have been characterised to possess a distorted octahedral geometry and the Cd(II) complex, a tetrahedral stereochemistry around the metal ions on the basis of analysis, conductance, magnetic susceptibility, i. r. and electronic spectral data.

REFERENCES

SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY

Date: 3 - 9 - 88

Dear Sir:

Your manuscript entitled: Polymetallic Complexes, Part XM

REvised MANuSCRIPT

has been received. We shall notify you regarding the publication of the paper as soon as possible.

[ ] has been accepted for publication and will appear in issue #__________________________.

K. Moedritzer
Monsanto Company
St. Louis, MO 63167 USA
In continuation of our earlier reports on the study of fungitoxic activity of complex compounds having mono- and bi-pyrazolones as ligands, the present paper deals with the synthesis of a Schiff base by reacting furfuraldehyde with 4-amino-2,3-dimethyl-1-phenylpyrazole-5-one and preparation and characterisation of its CoII, NiII, CuII, ZnII, CdII and HgII complexes.

Experimental

All the chemicals used were of A.R. grade.

Preparation of Schiff base: Ethanolic solutions of 4-amino-2,3-dimethyl-1-phenylpyrazole-5-one and furfuraldehyde in 1:1 molar ratio were mixed and refluxed over a water-bath for 2 h. The Schiff base that separated out on cooling the mixture was filtered, washed with ethanol, air-dried and analysed, m.p. 198°.

Preparation of complexes: The Schiff base dissolved in dioxane and the metal chlorides in ethanol were mixed in 1:1 ratio and refluxed at 120° for ~2 h. The complexes that separated out on keeping the solution overnight were filtered, washed with ethanol, air-dried and analysed, m.p. 120° for ~2 h. The complexes that separated out on cooling the mixture were 0.78.

The electronic spectra of CoII complex exhibited bands at 8700, 17500 and 21540 cm⁻¹ attributable to three spin-allowed transitions at 9465, 15100 and 25540 cm⁻¹ assignable to the OH stretching vibration, respectively.

Results and Discussion

All the complexes have the composition [MLCl₄.H₂O], where, M = CoII, NiII, CuII, ZnII, CdII, HgII; L = Schiff base. The cobalt complex was pink, nickel complex greenish yellow, copper complex coffee-coloured, zinc complex white, cadmium complex yellow and mercury complex grey in colour. Low molar conductances indicate non-electrolytic nature of the complexes. In the ligand, vC–O band appearing at 1640 cm⁻¹ undergoes a bathochromic shift of ca 10–20 cm⁻¹ in the metal complexes indicating the bonding of the Schiff base to the metal ion through carbonyl oxygen. The lowering of vC–N ligand band (1595 cm⁻¹) to ca 1580 cm⁻¹ in the complexes showed the azomethine nitrogen coordination to the metal ions. The ligand vC–O (furan ring) band (1020 cm⁻¹) shifted to ca 940 cm⁻¹ in the metal complexes, suggesting the involvement of furan oxygen atom to the metal atoms. The sharp far-IR band at ca 500 cm⁻¹ of the complexes was assigned to the metal–oxygen (furan) ring stretching vibration. The 1460 and 1420 cm⁻¹ bands appearing both in the ligand and the complexes were attributed to the bending vibration of the pyrazole skeleton. The presence of coordinated water molecule in all the metal complexes is shown by the appearance of bands at ca 3300–3450 cm⁻¹ followed by another peak at ca 840–860 cm⁻¹ assignable to the OH stretching and rocking vibrations, respectively.

The µeff values of the CoII, NiII and CuII complexes were found to be 5.0, 3.12 and 1.78 B.M., respectively, indicating an octahedral geometry around the metal ions.

The uv-visible spectra of the ligand exhibited two bands at 273 (36630) and 337 nm (29673 cm⁻¹) assignable to π–π* and n–π* transitions, respectively. The electronic spectra of the NiII complex exhibited three spin-allowed transitions at 9465, 15100 and 25540 cm⁻¹ assignable to A₂g→E₄g, A₂g→T₁g (v₂) and A₄g→T₁g (v₂), respectively. The spectral parameter B has been calculated by utilising the equation, B = (ν₂ + ν₃ – 3ν₁)/15. The lower value of B (816 cm⁻¹) indicates considerable covalent nature of the metal–ligand bond. The lowering of νC–O/νC=O ratio (1.59) from 1 h shows high-spin octahedral configuration for the complex. The value of covalency parameter (β) was found to be 0.78.

The electronic spectra of CoII complex exhibited bands at 8700, 17500 and 21540 cm⁻¹ attributable to three spin-allowed transitions at 9465, 15100 and 25540 cm⁻¹ assignable to A₂g→E₄g, A₂g→T₁g (v₂) and A₄g→T₁g (v₂), respectively. The spectral parameter B has been calculated by utilising the equation, B = (ν₂ + ν₃ – 3ν₁)/15. The lower value of B (816 cm⁻¹) indicates considerable covalent nature of the metal–ligand bond. The lowering of νC–O/νC=O ratio (1.59) from 1 h shows high-spin octahedral configuration for the complex. The value of covalency parameter (β) was found to be 0.78.

The electronic spectra of CoII complex exhibited bands at 8700, 17500 and 21540 cm⁻¹ attributable to three spin-allowed transitions at 9465, 15100 and 25540 cm⁻¹ assignable to A₂g→E₄g, A₂g→T₁g (v₂) and A₄g→T₁g (v₂), respectively. The spectral parameter B has been calculated by utilising the equation, B = (ν₂ + ν₃ – 3ν₁)/15. The lower value of B (816 cm⁻¹) indicates considerable covalent nature of the metal–ligand bond. The lowering of νC–O/νC=O ratio (1.59) from 1 h shows high-spin octahedral configuration for the complex. The value of covalency parameter (β) was found to be 0.78.
to the transitions $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow ^4T_{4e}(F)$, respectively. The ligand field parameters like $B_1 (818 \text{ cm}^{-1})$, $10Dq (9020 \text{ cm}^{-1})$, $v_3/v_2$ (0.02), $B_2$ (0.84) and (19.04) along with higher $\mu_{\text{eff}}$ value (Table 1) suggest an octahedral stereochemistry.

The Co$^{II}$ complex showed one broad band at (13 900—15 800 cm$^{-1}$) (185) cm$^{-1}$ which can be assigned to $^2E_g \rightarrow ^2T_{2g}$ transition which is a characteristic of distorted octahedral configuration$^1$.

Acknowledgement

The authors wish to record their sincere thanks to Prof. M. K. Chakravatry, Principal and to Prof. R. C. Acharya, Chemistry Head, G. M. College, Sambalpur, for their encouragement.

References

POLYMETALLIC COMPLEXES : PART XVIII.
COBALT(II), NICKEL(II), COPPER(II), ZINC(II), CADMIUM(II) AND MERCURY(II) COMPLEXES CONTAINING A CHELATING AZO DYE, N,N'-BIS[3-(2'-HYDROXYPHENYLazo)ACETOACETANILIDE]ETHYLENEDIAMINE.

Bipin G. Mahapatra* and Dillip K. Das
Department of Chemistry, G.M. College,
Sambalpur - 768 004, Orissa, INDIA.

SUMMARY

Six polymeric complexes have been isolated with the octadentate ligand having \[\text{O} \quad \text{N-ONNO-N} \quad \text{O}\] donor atoms. All the complexes have high melting points, are insoluble in common organic solvents and amorphous. The cobalt(II), nickel(II) and copper(II) complexes are found to be pseudo-octahedral whereas a tetrahedral structure is suggested for zinc(II), cadmium(II) and mercury(II) complexes. The characterisation is made on the basis of analysis, conductance, magnetic susceptibility, i.r. and electronic spectral data.

INTRODUCTION

The azo dyes possess both antiseptic and chemotherapeutic properties.\(^1,2\) They are also used as preservatives and for dyeing food stuffs and as redox indicator.\(^3,4\) In continuation of our earlier studies on the azo dye complexes,\(^5,7\) we report here the preparation of a new octadentate azo dye and six metal complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions.

EXPERIMENTAL

All the chemicals were of AR grade. The compound \(\text{N,N'}\text{-bis(acetoacetanilide)ethylendiamine}\) was prepared following
a reported method.\textsuperscript{8}

**Preparation of the azo dye.** The diazonium chloride obtained from o-aminophenol (1.1 g) by a common method\textsuperscript{9} was slowly added to the NaOH solution (30 ml) of the above compound (3.78 g) kept inside an ice-salt bath with constant stirring. The red coloured azo dye precipitated and was then filtered, washed with water thoroughly and then dried in air. It was finally recrystallised from hot ethanol solution by slow cooling in an ice bath. Yield 2.5 g (55 %), melting point 250°C.

Calculated for $\text{C}_{34}\text{H}_{34}\text{O}_{4}\text{N}_8$: C, 66.01%; H, 5.50%; N, 18.12%.

Found: C, 65.15%; H, 5.32%; N, 17.95%.

**Preparation of the complexes.** An EtOH solution (30 ml) of the ligand (6.18 g) was mixed with an EtOH solution (20 ml) of the metal chloride (1:3 ratio) and the mixture was refluxed for 1/2-1 hr over a water bath. Upon cooling, a few drops of conc. ammonia were added slowly with stirring causing the metal complexes to precipitate. These were then filtered, washed with ethanol, ether and dried in vacuo.

The physical measurements were accomplished by the following standard procedures. Metal contents in the complex were determined by the EDTA-titration method using Eriochrome-Black-T as indicator at the pH range 10 while the nitrogen and halogen contents were determined by semimicro-Kjeldahl and semimicro-sodium-ethanolamine procedures, respectively. Conductance was measured in $10^{-3}$ M EDTA solutions of the complex using a Toshiiwall conductivity bridge. Magnetic susceptibilities were measured on solid samples by the Gouy Method. The i.r. spectra were recorded in KBr pellets on a Perkin-Elmer 398 spectrophotometer. The electronic spectra of the complexes were recorded on $10^{-2}$ M DMF solutions using a Hilger and Watt Uvispeck spectrophotometer.

Analysis, conductance, magnetic susceptibility data are recorded in Table 1 while i.r. spectral and ligand field parameters data
are recorded in Table 2.

**RESULTS AND DISCUSSION**

The formation of complexes obtained is due to the following thermochemical equation involving the metal chlorides and the title ligand LH₂:

(i) \[3 \text{MCI}_2 + \text{LH}_2 + \text{aq} \xrightarrow{\Delta} [\text{M}_3 \text{LCl}_4 (\text{H}_2\text{O})_6] + 2\text{HCl}\]

\[\text{M} = \text{Co(II), Ni(II), Cu(II)}\]

(ii) \[3 \text{MCI}_2 + \text{LH}_2 + \text{aq} \xrightarrow{\Delta} [\text{M}_3 \text{LCl}_2 (\text{H}_2\text{O})_2] \text{Cl}_2 + 2\text{HCl}\]

\[\text{M} = \text{Zn(II), Cd(II), Hg(II)}\]

All the complexes are amorphous and have high melting points and are insoluble in solvents like methanol, ethanol, benzene etc., but sparingly soluble in dimethyl formamide, in which the cobalt, nickel and copper complexes are found to be non-electrolytes but the zinc, cadmium and mercury complexes are found to be 1:2 electrolytes (Table 1).

In the i.r. spectrum of the ligand, the broad band appearing at 3250 cm⁻¹ may be assigned to \(\nu(\text{OH})\) lower in energy from 3450 cm⁻¹ due to intramolecular O-H...N hydrogen bonding. The disappearance of this band in metal complexes is indicative of phenolic oxygen coordination to the metal ions. The band at 1375 cm⁻¹ in the free ligand may be ascribed to the \(\nu(\text{C-O})\) vibration and a bathochromic shift of \(~45 \text{ cm}^{-1}\) in the metal complexes shows the bonding of phenolic oxygen atoms to the metal ions. The \(\text{N} = \text{N}\)-frequency in the ligand is observed at 1500 cm⁻¹ and is shifted to \(~1430 \text{ cm}^{-1}\) in the chelates, indicating the bonding of one of the azo nitrogen atoms to the metal ions.\(^{10,11}\) The band at 1620 cm⁻¹ in the ligand may be proposed for a \(\nu(\text{C=O})\) vibration. The bathochromic shift of \(~40 \text{ cm}^{-1}\) from the amicid C = O of 1660 cm⁻¹ is in agreement with moderate C = O ... H - N hydrogen bonding. In metal chelates it appears at 1610 cm⁻¹ thereby showing amicid oxygen coordination.
to the metal ions. The strong absorption band appearing at 3150 cm⁻¹ in the free ligand can be assigned to $\nu$(NH) of the ethylenediamine part of the ligand supporting the ketoamine structure (I). Broadening and splitting of this band in the metal complexes show their linkage to the metal ions. The conclusive evidence of bonding of the oxygen and nitrogen atoms to the metal ions is indicated by the appearance of bands at ~450 and ~500 cm⁻¹ assignable to $\nu$(M–O) and $\nu$(M–N) vibrations, respectively, in the far i.r. spectra of the complexes.

The $\mu_{\text{eff}}$ values of the Co(II), Ni(II) and Cu(II) complexes are found to be 5.1, 3.7 and 1.8 A.M., respectively, indicating a pseudo-O₆ geometry around the metal ions. The other complexes are found to be diamagnetic in nature.

The electronic transition of the cobalt(II) complex exhibits three d-d bands at 8152(11), 16074(22) and 19386(30) cm⁻¹ which may be attributed to the transitions $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)(\gamma)$, $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)(\gamma)$ and $^4T_{1g}(F) \rightarrow ^4T_{2g}(P)(\gamma)$, respectively. The position of absorption, low intensity and values of spectral parameters like B, $\beta$, $\gamma$, 10 Dq, 6% support an octahedral geometry around the cobalt(II) ion (Table 2). The electronic spectrum of the nickel(II) complex is consistent with octahedral geometry, showing three d-d transitions at 12640(6.5), 20475(9.5) and 25825(17.5) cm⁻¹ assignable to the $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)(\gamma)$, $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)(\gamma)$ and $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)(\gamma)$ transitions, respectively. The energy of the first band corresponds to 10 Dq in case of the Ni(II) complex. The calculation of spectral parameters supports the octahedral stereo-chemistry for the Ni(II) complexes. The copper(II) complex shows three shoulder bands at 12750(25.5), 14604(35) and 20572(54) cm⁻¹ assignable to the $^2B_{1g} \rightarrow ^2A_{1g}$, $^2B_{1g} \rightarrow ^2B_{2g}$ and $^2B_{1g} \rightarrow ^2B_{2g}$ transitions, respectively. Due to Jahn-Teller distortion in the Eg ground state, the
Cu(II) ion in the complex displays distorted octahedral geometry.\textsuperscript{14} The Zn(II), Cd(II) and Hg(II) complexes are polymeric in nature and presumably possess tetrahedral stereochemistry, based upon analytical, conductance and i.r. spectral data.

The three possible structures (1, 2, 3) of the azo dye ligand and the tentative structure of the metal complexes (4) and (5) are represented below.

(1) Ketoamine

(2) Ketoimine
(4) $M = \text{Co(II), Ni(II), Cu(II)}$

(5) $N = \text{Zn(II), Cd(II), Hg(II)}$
REFERENCES

Table 1. Analysis, Magnetic Susceptibility and Conductance Data

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<th>Compound</th>
<th>Colour</th>
<th>M.P. (°C)</th>
<th>Yields in %</th>
<th>% M Found Calcd.</th>
<th>% C Found Calcd.</th>
<th>% H Found Calcd.</th>
<th>% N Found Calcd.</th>
<th>% Cl Found Calcd.</th>
<th>( \mu_{\text{eff}} ) B.M.</th>
<th>( \Delta ) mhos cm(^2) mol(^{-1} )</th>
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<tr>
<td>LH2</td>
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<td>-</td>
<td>65.75</td>
<td>5.32</td>
<td>17.95</td>
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<td>( \text{C}<em>{34}\text{H}</em>{34}\text{O}_{4}\text{N}_8 )</td>
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<td></td>
<td></td>
<td></td>
<td>(66.01)</td>
<td>(5.50)</td>
<td>(18.12)</td>
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<td>Grey (&gt;250)</td>
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<td>17.5 (17.82)</td>
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<td>( \text{[Cu}_3\text{LCl}_6\text{(H}_2\text{O})_6] )</td>
<td>Green (&gt;250)</td>
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<td>18.86 (19.02)</td>
<td>38.20 (38.62)</td>
<td>2.90 (3.03)</td>
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<td>( \text{[Zn}_3\text{LCl}_6\text{(H}_2\text{O})_2\text{Cl}_2] )</td>
<td>Yellowish white (&gt;250)</td>
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<td>19.49 (19.81)</td>
<td>40.90 (41.21)</td>
<td>2.98 (3.23)</td>
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<td>12.97 (14.32)</td>
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</tr>
<tr>
<td>( \text{[Cd}_3\text{LCl}_6\text{(H}_2\text{O})_2\text{Cl}_2] )</td>
<td>Brown (&gt;250)</td>
<td></td>
<td>45</td>
<td>29.42 (29.81)</td>
<td>35.80 (36.07)</td>
<td>2.52 (2.82)</td>
<td>9.65 (9.99)</td>
<td>12.10 (12.53)</td>
<td>-</td>
<td>98.0</td>
</tr>
<tr>
<td>( \text{[Cd}<em>3\text{C}</em>{34}\text{H}_{36}\text{O}_6\text{N}_8\text{Cl}_4] )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{[Hg}_3\text{LCl}_6\text{(H}_2\text{O})_2\text{Cl}_2] )</td>
<td>Greyish brown (&gt;250)</td>
<td></td>
<td>40</td>
<td>42.86 (43.12)</td>
<td>28.78 (29.23)</td>
<td>1.98 (2.29)</td>
<td>7.89 (8.02)</td>
<td>9.88 (10.16)</td>
<td>-</td>
<td>105.0</td>
</tr>
<tr>
<td>( \text{[Hg}<em>3\text{C}</em>{34}\text{H}_{36}\text{O}_6\text{N}_8\text{Cl}_4] )</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

LH2 = N,N'-bis[3-(2'-hydroxyphenylazo)acetoacetanilide]ethylenediamine.
In continuation of our earlier reports on the study of fungitoxicity of complex compounds having mono- and bi-pyrazolones as ligands, the present paper deals with the synthesis of a Schiff base by reacting fufuraldehyde with 4-amino-2,3-dimethyl-1-phenylpyrazole-5-one and preparation and characterisation of its Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes.

Experimental

All the chemicals used were of A.R. grade.

Preparation of Schiff base: Ethanolic solutions of 4-amino-2,3-dimethyl-1-phenylpyrazole-5-one and fufuraldehyde in 1:1 molar ratio were mixed and refluxed over a water-bath for 2 h. The resulting Schiff base that separated out on cooling the mixture was filtered, washed with ethanol, air-dried and analysed, m.p. 198\(^\circ\).

Preparation of complexes: The Schiff base dissolved in dioxane and the metal chlorides in ethanol were mixed in 1:1 ratio and refluxed at 120\(^\circ\) for ~ 2 h. The resulting Schiff base that separated out on cooling the mixture was filtered, washed with ethanol, air-dried and analysed.

Conductance of 10\(^{-8}\)M solutions in dimethyl formamide were measured using a Toshniwal conductivity bridge. Magnetic moments \(\mu\) were determined by Gouy method at room temperature (300 K). Infrared spectra (KBr) were recorded using a Perkin-Elmer 221 spectrophotometer and electronic spectra of 10\(^{-8}\)M solution of the complexes in DMF on a Hilger Wollaston spectrophotometer. The results are given in Table 1.

<table>
<thead>
<tr>
<th>Table 1—Analytical and Magnetic Data of Complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compd.*</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>[CoLCl(_2).H(_2)O]</td>
</tr>
<tr>
<td>[NiLCl(_2).H(_2)O]</td>
</tr>
<tr>
<td>[ZnLCl(_2).H(_2)O]</td>
</tr>
<tr>
<td>[CdLCl(_2).H(_2)O]</td>
</tr>
<tr>
<td>[HgLCl(_2).H(_2)O]</td>
</tr>
</tbody>
</table>

* L = Schiff base derived from fufuraldehyde and 4-amino-2,3-dimethyl-1-phenylpyrazole-5-one (C\(_9\)H\(_{10}\)N\(_2\)O\(_2\)).

Results and Discussion

All the complexes have the composition [MLCl\(_2\).H\(_2\)O], where, M = Co\(^{II}\), Ni\(^{II}\), Cu\(^{II}\), Zn\(^{II}\), Cd\(^{II}\), Hg\(^{II}\); L = Schiff base. The cobalt complex was pink, nickel complex greenish yellow, copper complex coffee-coloured, zinc complex white, cadmium complex yellow and mercury complex grey in colour.

Low molar conductances indicate non-electrolytic nature of the complexes. In the ligand, \(\nu\text{C}=\text{O}\) band appearing at 1 640 cm\(^{-1}\) undergoes a bathochromic shift of ca 10-20 cm\(^{-1}\) in the metal complexes indicating the bonding of the Schiff base to the metal ion through carbonyl oxygen. The lowering of \(\nu\text{C}={\text{N}}\) ligand band (1 595 cm\(^{-1}\))\(^{14-16}\) to ca 1 580 cm\(^{-1}\) in the complexes showed the azomethine nitrogen coordination to the metal ions. The ligand \(\nu\text{C}={\text{N}}\) (furan ring) band (1 020 cm\(^{-1}\))\(^{14-16}\) to ca 940 cm\(^{-1}\) in the complexes showed the azomethine nitrogen coordination to the metal ions.

The ligand \(\nu\text{C}={\text{O}}\) (furan ring) band (1 020 cm\(^{-1}\)) shifted to ca 940 cm\(^{-1}\) in the metal complexes, suggesting the involvement of furan oxygen atom to the metal atoms. The sharp far-infrared bands at ca 500 cm\(^{-1}\) of the complexes was assigned to the metal-oxygen (furan) ring stretching vibration\(^{16}\). The 1 460 and 1 420 cm\(^{-1}\) bands appearing both in the ligand and the complexes were attributed to the bending vibration of the pyrazole skeleton\(^{16}\). The presence of coordinated water molecule in all the metal complexes is shown\(^{16}\) by the appearance of bands at ca 2 900-3 450 cm\(^{-1}\) followed by another peak at ca 840–860 cm\(^{-1}\) assignable to the OH stretching and rocking vibrations, respectively.
The \( \mu_{	ext{eff}} \) values of the Co\( ^{III} \), Ni\( ^{II} \) and Cu\( ^{II} \) complexes were found to be 5.0, 3.12 and 1.78 B.M., respectively, indicating an octahedral geometry around the metal ions\(^{14,15}\).

The uv-visible spectra of the ligand exhibited two bands at 273 (36 630) and 337 nm (29 673 cm\(^{-1}\)) assignable to \( \pi-\pi^* \) and \( n-\pi^* \) transitions respectively.

The electronic spectra of the Ni\( ^{II} \) complex exhibited three spin-allowed transitions at 9 465, 15 100 and 25 540 cm\(^{-1}\) assignable to \( ^4A_{2g} \rightarrow ^4T_{2g} \) \( (\nu_1) \), \( ^4A_{2g} \rightarrow ^4T_{1g} (F)(\nu_2) \) and \( ^4A_{2g} \rightarrow ^4T_{1g} (P)(\nu_3) \), respectively.

The spectral parameter \( B \) has been calculated\(^1\) by utilising the equation, \( B = (\nu_2 + \nu_3 - 3\nu_1)/15 \). The lower value of \( B \) (816 cm\(^{-1}\)) indicates considerable covalent nature of the metal–ligand bond\(^{18}\). The lowering of \( \nu_2/\nu_3 \) ratio (1.59) from 1.8 shows high-spin octahedral configuration for the complex. The value of covalency parameter \( (\beta) \) was found to be 0.78.

The electronic spectra of Co\( ^{III} \) complex exhibited bands at 8 700, 17 500 and 21 540 cm\(^{-1}\) attributable to the transitions \( ^4T_{2g} (F) \rightarrow ^4T_{1g} (F) \) and \( ^4T_{2g} (F) \rightarrow ^4T_{1g} (P) \), respectively. The ligand field parameters like \( B \) (818 cm\(^{-1}\)), \( D_q \) (9 020 cm\(^{-1}\)), \( \nu_2/\nu_3 \) (0.02), \( \beta_{3g} \) (0.84) and (19.04) along with higher \( \mu_{	ext{eff}} \) value (Table 1) suggest an octahedral stereochemistry.

The Co\( ^{III} \) complex showed one broad band at \( (13 900–15 800 \text{ cm}^{-1}) \) (185) cm\(^{-1}\) which can be assigned to \( \Delta E \rightarrow \Delta T_{eg} \) transition which is a characteristic of distorted octahedral configuration\(^{19}\).

**Acknowledgement**

The authors wish to record their sincere thanks to Prof. M. K. Chakravarty, Principal and to Prof. R. C. Acharya, Chemistry Head, G. M. College, Sambalpur, for their encouragement.
NOTES

Cobalt-, Nickel-, Copper-, Zinc-, Cadmium- and Mercury-(ll) Complexes
with a Tridentate ONO Donor Schiff Base

BIPIN B. MAHAPATRA*, D. PANDA, DILLIP K. DAS,
B. K. PATEL and S. C. CHAUDHURY

Department Chemistry, G. M. Collage, Sambalpur-768 004
Manuscript received 21 August 1987, revised 3 June 1988, accepted 11 June 1988.

In continuation of our earlier reports1-8 on the study of fungitoxicity of complex compounds having mono- and bi-pyrazolones as ligands, the present paper deals with the synthesis of a Schiff base by reacting furfuraldehyde with 4-amino-2,3-dimethyl-1-phenylpyrazole-5-one and preparation and characterisation of its CoIII, NiIII, CuIII, ZnII, CdII and HgII complexes.

Experimental

All the chemicals used were of A.R. grade.

Preparation of Schiff base: Ethanolic solutions of 4-amino-2,3-dimethyl-1-phenylpyrazole-5-one and furfuraldehyde in 1:1 molar ratio were mixed and refluxed over a water-bath for 2 h. The resulting Schiff base that separated out on cooling the mixture was filtered, washed with ethanol, air-dried and analysed, m.p. 198°.

Preparation of complexes: The Schiff base dissolved in dioxane and the metal chlorides in ethanol were mixed in 1:1 ratio and refluxed at 120° for ~2 h. The complexes that separated out on keeping the solution overnight were filtered, washed with ethanol, ether and dried under reduced pressure and analysed.

Conductance of 10-4 M solutions in dimethyl formamide were measured using a Toshniwal conductivity bridge. Magnetic moments \( \mu_{eff} \) were determined by Gouy method at room temperature (300 K). Infrared spectra (KBr) were recorded using a Perkin-Elmer 221 spectrophotometer and electronic spectra of 10-4 M solution of the complexes in DMF on a Hilger Watt Usvispec spectrophotometer. The results are given in Table I.

Results and Discussion

All the complexes have the composition \([MCl_xH_2O]_y\), where, \(M=Co^{lll}, Ni^{lll}, Cu^{lll}, Zn^{lll}, Cd^{lll}, Hg^{lll}\); \(L=Schiff\, base\). The cobalt complex was pink, nickel complex greenish yellow, copper complex coffee-coloured, zinc complex white, cadmium complex yellow and mercury complex grey in colour. Low molar conductances indicate non-electrolytic nature of the complexes. In the ligand, \(v_C-O\) band appearing at 1 640 cm \(^{-1}\) undergoes a bathochromic shift of ca 10-20 cm \(^{-1}\) in the metal complexes indicating the bonding of the Schiff base to the metal ion through carbonyl oxygen. The lowering of \(v_{C=O}\) ligand band (1 595 cm \(^{-1}\)) to ca 1 580 cm \(^{-1}\) in the complexes showed the azomethine nitrogen coordination to the metal ions. The ligand \(v_C-O\) (furan ring) band\(^8\) (1 020 cm \(^{-1}\)) to ca 940 cm \(^{-1}\) in the metal complexes, suggesting the involvement of furan oxygen atom to the metal atoms. The sharp far-ir band at ca 500 cm \(^{-1}\) of the complexes was assigned to the metal–oxygen (furan) ring stretching vibration\(^{10-11}\). The 1 460 and 1 420 cm \(^{-1}\) bands appearing both in the ligand and the complexes were attributed to the bending vibration of the pyrazole skeleton\(^{12}\). The presence of coordinated water molecule in all the metal complexes is shown\(^8\) by the appearance of bands at ca 3 300-3 450 cm \(^{-1}\) followed by another peak at ca 840-860 cm \(^{-1}\) assignable to the OH stretching and rocking vibrations, respectively.

The \(\mu_{eff}\) values of the CoIII, NiIII and CuIII complexes were found to be 5.0, 3.12 and 1.78 B.M., respectively, indicating an octahedral geometry around the metal ions\(^{14-16}\).

The UV-visible spectra of the ligand exhibited two bands at 273 (36 630) and 337 nm (29 673 cm \(^{-1}\)) assignable to \(\pi-\pi^*\) and \(\pi-n^*\) transitions, respectively. The electronic spectra of the NiII complex exhibited three spin-allowed transitions at 9 465, 15 100 and 25 540 cm \(^{-1}\) assignable to \(^3A_{eg}→^3T_{2g} (\pi_1), ^3A_{eg}→^3T_{1g} (\pi_1)\) and \(^3A_{eg}→^3T_{2g} (\pi_2)\), respectively. The spectral parameter \(B\) has been calculated\(^{17}\) by utilising the equation, \(B=(v_{v}+v_2−3v_1)/15\). The lower value of \(B\) (816 cm \(^{-1}\)) indicates considerable covalent nature of the metal–ligand bond\(^{18}\). The lowering of \(v_{v}/v_1\) ratio (1.59) from 1.8 shows high-sun octahedral configuration for the complex. The value of covalency parameter (\(B\)) was found to be 0.78.

The electronic spectra of CoII complex exhibited bands at 8 700, 17 500 and 21 540 cm \(^{-1}\) attributable

---

### Table I—Analytical and Magnetic Data of Complexes

<table>
<thead>
<tr>
<th>Compd.</th>
<th>Analysis %</th>
<th>Found/(Calcd.)</th>
<th>(\mu_{eff})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Metal</td>
<td>N</td>
<td>B.M.</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoLCl(_2).H(_2)O)</td>
<td>19.49</td>
<td>9.45</td>
<td>5.0</td>
</tr>
<tr>
<td>NiLCl(_2).H(_2)O)</td>
<td>19.80</td>
<td>9.85</td>
<td>9.12</td>
</tr>
<tr>
<td>CuLCl(_2).H(_2)O)</td>
<td>14.26</td>
<td>9.55</td>
<td>1.78</td>
</tr>
<tr>
<td>ZnLCl(_2).H(_2)O)</td>
<td>14.85</td>
<td>9.20</td>
<td>—</td>
</tr>
<tr>
<td>CdLCl(_2).H(_2)O)</td>
<td>32.60</td>
<td>9.89</td>
<td>—</td>
</tr>
<tr>
<td>HgLCl(_2).H(_2)O)</td>
<td>44.60</td>
<td>9.02</td>
<td>—</td>
</tr>
</tbody>
</table>

\(L=Schiff\, base\) derived from furfuraldehyde and 4-amino-2,3-dimethyl-1-phenylpyrazole-5-one (\(C_8H_6N_2\)).
to the transitions $^4T_{2g} (F) \rightarrow ^4T_{2g} (F)$ and $^4T_{1g} (F) \rightarrow ^4T_{1g} (F)$, respectively. The ligand field parameters like $B$ (818 cm$^{-1}$), $Dq$ (9 020 cm$^{-1}$), $\beta_{2g}$ (0.82), $\beta_{2g}$ (0.84) and (19.04) along with higher $\mu_{\text{eff}}$ value (Table 1) suggest an octahedral stereochemistry.

The Co$^{II}$ complex showed one broad band at (13 900 - 15 800 cm$^{-1}$) (185) cm$^{-1}$ which can be assigned to $^4A_g \rightarrow ^2T_{2g}$ transition which is a characteristic of distorted octahedral configuration$^{19}$.

Acknowledgement

The authors wish to record their sincere thanks to Prof. M. K. Chakrabarty, Principal and to Prof. R. C. Acharya, Chemistry Head, G. M. College, Sambalpur, for their encouragement.

References

A series of metal complexes containing salicylidene amino acids as ligands have been reported by Nayak et al. Dutta and his coworkers have prepared mixed chelates of salicylidene amino acids and bidentate nitrogen donors. The present paper describes the synthesis of two dibasic ONO tridentate Schiff bases, acetophenone glycine and acetophenone alanine and their complexation behaviour with Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) ions.

Experimental:

All the chemicals used were of A.R. grade. The Schiff bases acetophenone glycine (LH₂) and acetophenone alanine (L'H₂) were prepared by condensing orthohydroxyacetophenone (1.4 ml.) in ethanol (50 ml.) with glycine (0.75 g) and alanine (0.89 g) at ~105°C respectively for about 1 hr. The metal complexes were prepared by refluxing the Schiff bases with metal(II) chloride or acetate in the 1:1 ratio for about 1/2 hr. After cooling conc. ammonia was added dropwise. The precipitated complexes were filtered, washed with ethanol.
and ether and finally dried in vacuo.

Elemental analysis and physicochemical measurements were done as per procedure described earlier.  

Results and discussion

Low molar conductance ($\Lambda_M$) of all the complexes (Table 1), measured in DMF, indicates the nonelectrolytic nature. In the i.r. spectra in KBr phase the Schiff bases showed $\gamma$(C=N) at 1590 cm$^{-1}$ (LH$_2$) and 1595 cm$^{-1}$ (L$'$H$_2$). A hypsochromic shift of Ca 5-15 cm$^{-1}$ in the metal complexes indicated bonding of the azomethine nitrogen to the metal ions. The ligands show stretching frequencies at Ca. 3450 cm$^{-1}$ [$\gamma$(OH)] which appears at Ca. 3100-3350 cm$^{-1}$ in the complexes. The $\gamma$(C-O) band at 1320 cm$^{-1}$ of free ligand was observed, at Ca. 1530 and 1535 cm$^{-1}$ in the complexes indicated monodentate coordination of phenolic oxygen atom to the metal ions. The $\delta_3$ and $\delta_2$ vibrations of the carboxylate group for Fe(II), Co(II), Ni(II) and Cu(II) complexes (of LH$_2$) appear at Ca. 1540 and 1430 cm$^{-1}$ and at Ca. 1470 cm$^{-1}$ and 1360 cm$^{-1}$ (of L$'$H$_2$) respectively with a difference of Ca 110 cm$^{-1}$, suggestive of bidentate coordination of the carboxylate group. In case of Zn(II) and Hg(II) complexes the frequency difference is Ca. 155 cm$^{-1}$ indicating monodentate nature of the carboxylate group. The presence of coordinated water in Fe(II), Co(II), Cu(II) and Hg(II) complexes was indicated by a broad band at Ca. 3400 cm$^{-1}$ followed by a sharp band at Ca. 870 cm$^{-1}$ assignable respectively to stretching and rocking vibrations of OH moiety. The 430 and 510 cm$^{-1}$ bands
are assigned to $\nu(M-O)$ and $\nu(M-N)$ respectively.

A sharp endothermic peak on the DTA curve of the 
Co(II) complex $[\text{Co}_2\text{L}_2\cdot 4\text{H}_2\text{O}]$ suggested the loss of four water 
molecules at 240°C.

Molecular weight of iron(II), cobalt(II), Nickel(II) 
and copper(II) complexes suggests dimeric nature of these 
complexes while those of Zn(II) and Hg(II) complexes suggest 
monomeric species.

Electronic spectra of cobalt(II) complexes showed 
three bands at $\sim 8600$, $\sim 18000$ and $\sim 19500$ cm$^{-1}$ attributable to $^{4}T_{1g}(F) \rightarrow ^{4}T_{2g}(F)$, $^{4}A_{2g}(F) \rightarrow ^{4}T_{1g}(P)$ transitions respectively suggesting for an octahedral configuration.
The $\mu_{\text{eff}}$ value of the complexes were around 2.91 B.M. indicating 
magnetic interaction between the metal ions. Two bands at 
24300 and 27000 cm$^{-1}$ attributable to $^{1}A_{1g} \rightarrow ^{1}A_{2g}$ and 
$^{1}B_{1g}$ transitions respectively were observed for the nickel(II) 
complexes showing square planar configuration which is in 
conformity with the diamagnetic nature of the complexes.

Sub-normal magnetic moment (1.2 B.M.) of the copper(II) complexes 
indicated the Cu-Cu interaction. The Cu(II) complexes showed 
one broad asymmetric band $\sim 13150$ cm$^{-1}$ suggesting a tetragonally 
distorted structure.

From the shape of the ESR spectrum of the Cu(II)-LH$_2$ 
complex at the X-band, it is evident that the symmetry around 
the Cu(II) in the unit cell of the complex is tetragonal.
An elongated octahedral, with $d_{x^2-y^2}$ ground state. The $G$ value has been calculated to be 2.77. It is found that when this $G$ value lies in between 5.0 and 3.5, the 'g' values will be near to molecular 'g' values and when they lie outside this range, the 'g' values indicate strong exchange interaction among magnetically inequivalent Cu(II) ions in the unit cell. Since the 'G' value for the present complex fall beyond this range, the 'g' values indicate the existence of more than one magnetically inequivalent molecules with exchange interaction among Cu(II) ions. Hence these 'g' values represent the overall symmetry of these molecule in the unit cell\textsuperscript{12} (Table 2).

The ESR data (Table 2) at RT at $\nu$ band indicate the existence of two species with axial symmetry.

Acknowledgement

Authors are thankful to Prof. K.C. Acharya and Dr. S. Guru, Department of Chemistry, G.M. College, Sambalpur for providing some facilities and Prof. M. Narasimhacharry, Dept. of Physics, Osmania University for his interpretation of ESR spectra.
References

**TABLE 1: ANALYTICAL DATA MOLECULAR WEIGHT AND MOLAR CONDUCTANCE VALUES OF THE COMPLEXES**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Analysis $X$: Found/(Calcd.)</th>
<th>Molar Conductance $\Omega^{-1} cm^2 mol^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{LH}_2$</td>
<td>Yellow</td>
<td>182 (193)</td>
<td>$6.69$ (7.23)</td>
</tr>
<tr>
<td>$\text{L'}\text{H}_2$</td>
<td>Light Yellow</td>
<td>198 (207)</td>
<td>$6.31$ (6.76)</td>
</tr>
<tr>
<td>$[\text{Fe}_{2}\text{L}_2\cdot\text{H}_2\text{O}]$</td>
<td>Brown</td>
<td>545.00 (571.68)</td>
<td>4.58 (4.89)</td>
</tr>
<tr>
<td>$[\text{Fe}_{2}\text{L}_2\cdot\text{H}_2\text{O}]$</td>
<td>Yellowish Brown</td>
<td>566.00 (599.68)</td>
<td>4.31 (4.66)</td>
</tr>
<tr>
<td>$[\text{Co}_{2}\text{L}_2\cdot\text{H}_2\text{O}]$</td>
<td>Buff</td>
<td>546.00 (571.86)</td>
<td>4.57 (4.89)</td>
</tr>
<tr>
<td>$[\text{Co}_{2}\text{L}_2\cdot\text{H}_2\text{O}]$</td>
<td>Reddish Brown</td>
<td>569.88 (599.68)</td>
<td>4.32 (4.66)</td>
</tr>
<tr>
<td>$[\text{Ni}_{2}\text{L}_2]$</td>
<td>Red</td>
<td>458.00 (499.42)</td>
<td>5.41 (5.60)</td>
</tr>
<tr>
<td>$[\text{Ni}_{2}\text{L}_2]$</td>
<td>Red</td>
<td>509.90 (527.42)</td>
<td>5.16 (5.30)</td>
</tr>
<tr>
<td>$[\text{Cu}_{2}\text{L}_2\cdot\text{H}_2\text{O}]$</td>
<td>Blue</td>
<td>568.86 (581.00)</td>
<td>4.85 (4.81)</td>
</tr>
<tr>
<td>$[\text{Cu}_{2}\text{L}_2\cdot\text{H}_2\text{O}]$</td>
<td>Greenish Blue</td>
<td>589.25 (609.00)</td>
<td>4.26 (4.59)</td>
</tr>
<tr>
<td>$[\text{ZnL}_2]$</td>
<td>White</td>
<td>418.00 (447.37)</td>
<td>6.07 (6.25)</td>
</tr>
<tr>
<td>$[\text{ZnL}_2]$</td>
<td>White</td>
<td>449.00 (475.37)</td>
<td>5.42 (5.89)</td>
</tr>
<tr>
<td>$[\text{HgL.H}_2\text{O}]$</td>
<td>Pale Yellow</td>
<td>382.00 (409.39)</td>
<td>3.17 (3.41)</td>
</tr>
<tr>
<td>$[\text{HgL'}\cdot\text{H}_2\text{O}]$</td>
<td>Yellow</td>
<td>397.00 (423.59)</td>
<td>3.01 (3.55)</td>
</tr>
<tr>
<td>Band</td>
<td>$g$ values</td>
<td>$g_{11}$</td>
<td>$g_1$</td>
</tr>
<tr>
<td>------</td>
<td>------------</td>
<td>---------</td>
<td>------</td>
</tr>
<tr>
<td>X</td>
<td>2.230</td>
<td>2.083</td>
<td>2.77</td>
</tr>
<tr>
<td>Q</td>
<td>2.235 (A)</td>
<td>2.074 (A)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.105 (B)</td>
<td>2.074 (B)</td>
<td></td>
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</tbody>
</table>
POLYMETALLIC COMPLEXES PART XVI.
ON-NO DOUBLY BIDENTATE SCHIFF BASE COMPLEXES OF COBALT (II), NICKEL (II), COPPER (II) AND CADMIUM (II):
BIPIN B. MAHAPATRA AND DILIP K. DAS

Department of Chemistry, G. M. College, Sambalpur—768 004, Orissa,
(Received 3 June, 1987)

Synthesis and characterisation of some Co (II), Ni (II), Cu (II) and Cd (II)
complexes with ON-NO donor doubly-bidentate schiff base, \( N,N'-\text{bis (benzoin) 4,4'-diamino-diphenylmethane} \) are reported. In this paper,

**EXPERIMENTAL AND DISCUSSION.**

Metal complexes were prepared by refluxing ethanolic solution of the metal salts
with the schiff base in dioxan in 1 : 1 molar ratio on water-bath for 1 hr. The complexes
separated out on cooling were filtered, washed with ethanol, ether and dried in vacuo.

Metal and nitrogen contents were determined by standard methods. Conductance
were measured in dimethylformamide (10^{-4} \text{ M solution}). The magnetic moments of Co (II),
Ni (II) and Cu (II) complexes were measured by Gouy method. IR spectra were recorded
on KBr discs on a Perkin Elmer 398 spectrophotometer and electronic spectra were recorded
on a Hilger-watt Univeck spectrophotometer using nujol as mulling agent. Molecular
weight measurements were carried out by the Rast method using camphor as the solvent.

The complexes synthesized have the compositions \([M_2L_2 \cdot 4H_2O]\) and \([M'L_3]\),
where M = Co (II), Ni (II), Cu (II) ; \( M' = \text{Co (II)} \); \( LH_2 = N,N'-\text{bis (benzoin) 4,4'-diamino-diphenylmethane} \). Cobalt complex is brown, nickel green, copper green and cadmium complex is light yellow in colour. All the complexes are amorphous in nature and are insoluble in common organic solvents but sparingly soluble in DMF. The complexes are found to be non-electrolytes in DMF medium (5.0-9.5 mhos cm\(^{-1}\) mole\(^{-1}\)). The percentage of metal, nitrogen and the molecular weight of the compounds were duly verified by analysis.

Sub-normal magnetic moments of Co (II), Ni (II) and Cu (II) complexes (2.65, 2.21 and 1.34 B. M. respectively) show magnetic interactions between the metal ions present in the polymeric compounds.

The schiff base acts as a ON-NO donor doublybidentate ligand. In the IR spectrum of the schiff base, two bands of medium intensity are observed at 3400 and
3030 cm$^{-1}$ assigned to intramolecular O-H-N hydrogen bond ($\nu$-OH). These bands disappear in the metal complexes indicating deprotonation of enolic OH groups. The appearance of bands at 1670 and 1255 cm$^{-1}$ in the ligand spectrum may be ascribed to $\nu$ (C = N) and $\nu$ (C – O) vibrations respectively. A bathochromic shift of the bands (Ca 1600 and 1250 cm$^{-1}$) in the metal complexes indicate the bonding of the ligand to the metal ions through the imine nitrogen and hydroxyl oxygen atoms$^3$. In the spectra of Co (II), Ni (II) and Cu (II) complexes, a broad band appears at 3200-3400 cm$^{-1}$ followed by other peaks at 1400 and 830 cm$^{-1}$ assignable to OH stretching, bending and rocking vibrations respectively confirming the presence of coordinated water molecules$^{6}$. The conclusive evidence of bonding is obtained by the observation of bands at Ca 510 and 450 cm$^{-1}$ attributable to $\nu$ (M – N) and $\nu$ (M – O) vibrations respectively.

The electronic spectrum of the Co(II) complex exhibit a broad band at 8300 cm$^{-1}$ and medium strong band at 17150 and 19450 cm$^{-1}$ assignable to $^4T_{1g}(F) \rightarrow ^4T_{1g}(F)$ ($\nu_1$), $^4A_{1g} (\nu_2)$ and $^4T_{1g} (F)$ ($\nu_3$) transition respectively, supporting a distorted octahedral configuration for the complex$^4$. The electronic spectrum of the Ni(II) complex shows three absorption bands at 8800, 15200 and 24950 cm$^{-1}$ attributable to $^3A_{1g} \rightarrow ^3T_{1g} (F)$, $^3T_{1g} (F)$ and $^3T_{1g} (F)$ transitions respectively. The spectral parameters suggest a distorted octahedral geometry around the complex$^4$. The Cu(II) complex exhibits a single broad asymmetric band at 16250 cm$^{-1}$ which may arise due to $^2B_{1g} \rightarrow ^2A_{1g} (\rho_1) \rightarrow ^2B_{1g} (\rho_2)$ and $^2B_{1g} (\rho_2)$ transitions supporting a distorted octahedral configuration for the complex$^5$. The molecular weight data support the dimeric composition of all the complexes.

**SUMMARY**

Four complex compounds of the composition [M$_4$L$_2$·4H$_2$O] and [M$_4$L$_4$] have been prepared where M = Co(II), Ni(II), Cu(II) and M' = Cd(II), LH$_2$ = N, N'-bis (benzoin)-4,4'-di aminodiphenylmethane. The Co(II), Ni(II) and Cu(II) complexes have been characterised to possess a distorted octahedral geometry and the Cd(II) complex, a tetrahedral stereochemistry around the metal ions on the basis of analytical, conductance, magnetic susceptibility, i.r. and electronic spectral data.

**REFERENCES**