

## Spectral & Magnetic Studies on Bimetallic Complexes of Nickel(II) & Cobalt(II)

N S BIRADAR, M C DIVAKAR & T M AMINABHAVI\*

Department of Chemistry, Karnatak University, Dharwad 580 003

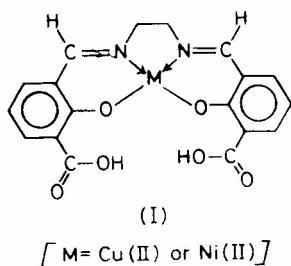
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Using Ni(II) or Cu(II) complex with the schiff base derived from 3-formylsalicylic acid and ethylenediamine as the starting parent complex, a few bimetallic complexes of copper(II) and nickel(II) with tetravalent metal ions such as silicon(IV), tin(IV), tellurium(IV) and titanium(IV) have been prepared. The complexes have been characterised by elemental analyses, conductivity measurements, spectral and magnetic results.

As a part of an ongoing research programme for the synthesis of bimetallic complexes of biological importance, we are currently investigating binuclear transition metal complexes with schiff bases<sup>1-3</sup>. Literature survey reveals that there are only a few reports on the binuclear copper(II) and nickel(II) complexes with schiff bases derived from 3-formylsalicylic acid<sup>4,5</sup>. To the best of our knowledge, no binuclear complexes of transition metals with 3-formylsalicylic acid-ethylenediamine schiff base and tetravalent metal ions such as silicon(IV), tin(IV), tellurium(IV) and titanium(IV) have been synthesized. In this investigation, an attempt has been made to synthesize a few bimetallic complexes of copper(II) and nickel(II) with 3-formylsalicylic acid-ethylenediamine schiff base and chlorides of silicon(IV), tin(IV), tellurium(IV) and titanium(IV).

### Materials and Methods

All the chemicals used in this study were of reagent grade. The ligands(I), namely, copper(II) and cobalt(II) complexes with the schiff base ethylenediamine-3-formylsalicylic acid were prepared according to literature methods<sup>6,7</sup>.



The bimetallic complexes were prepared by mixing in equimolar ratio the respective ligands(I) with Sn(IV), Si(IV), Te(IV) or Ti(IV) chlorides in dry benzene. The mixture was allowed to stand for several hours with occasional shaking. The separated bright coloured

bimetallic complexes were filtered, washed with dry benzene and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

Elemental analyses were carried out by standard methods<sup>8</sup>. Copper in the complexes was estimated as the pyridine thiocyanate salt and nickel was estimated as dimethylglyoximate. Tellurium was determined as the metal. Silicon, tin and titanium were estimated as their oxides by a direct ignition method. Chloride in the complexes was determined as silver chloride by the gravimetric technique and nitrogen content was estimated by the micro-Kjeldahl's method.

Conductivities were measured in dimethylformamide (DMF) using an Elico-CM-82 conductivity bridge with a cell having a cell constant of 0.829 cm<sup>-1</sup>. All conductivity measurements were made at room temperature using 10<sup>-3</sup> M solutions of the complexes.

The infrared(IR) spectra from 4000 to 200 cm<sup>-1</sup> were recorded in KBr using a Perkin-Elmer 180 spectrophotometer. Magnetic measurements at room temperature were made on a Gouy balance using Hg[Co(CNS)<sub>4</sub>] as a calibrant. Electronic spectra were recorded on a Unicam Sp-800 Ultraviolet spectrophotometer in the region 12500-50000 cm<sup>-1</sup>.

### Results and Discussion

All the complexes are coloured and amorphous in nature. They are insoluble in common organic solvents except DMF and DMSO. The elemental analyses as shown in Table 1 agree with a 1:1 (metal:ligand) stoichiometry. The conductivity data (1-30 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>) indicate non-electrolytic behaviour of the complexes in solution.

Ray and Sen<sup>9</sup> classified the tetra-coordinated complexes of copper(II) into two groups, one having the  $\mu_{\text{eff}}$  values between 1.72 and 1.82 B.M. and the other having  $\mu_{\text{eff}}$  values in the range 1.9-2.2 B.M. They attributed a planar  $dsp^2$  structure to the first group and tetrahedral  $sp^3$  or planar  $sp^2d$  configuration to the

Table 1—Analytical and Physical Data of Ligands and Complexes

| Ligand/Complex                  | Found (Calc.), % |                |                  |                  | $\mu_{\text{eff.}}$<br>(B.M.) | Electronic<br>transitions<br>( $\text{cm}^{-1}$ ) |
|---------------------------------|------------------|----------------|------------------|------------------|-------------------------------|---------------------------------------------------|
|                                 | Cu/Ni            | N              | Cl               | M'               |                               |                                                   |
| Cu(H <sub>2</sub> fsaen)        | 14.06<br>(14.16) | 6.13<br>(6.19) | —                | —                | 1.78                          | 14,710<br>27,780<br>37,200                        |
| Cu(fsaen).Si(IV)Cl <sub>2</sub> | 12.21<br>(12.45) | 5.28<br>(5.45) | 13.66<br>(13.62) | 5.23<br>( 5.45)  | 1.72                          | 16,130(sh)<br>27,750<br>37,000                    |
| Cu(fsaen).Sn(IV)Cl <sub>2</sub> | 10.65<br>(10.58) | 4.48<br>(4.63) | 11.48<br>(11.57) | 19.72<br>(19.67) | 1.74                          | 16,140(sh)<br>27,780<br>37,200                    |
| Cu(fsaen).Te(IV)Cl <sub>2</sub> | 10.28<br>(10.42) | 4.50<br>(4.56) | 11.71<br>(11.40) | 20.92<br>(20.81) | 1.71                          | 16,130(sh)<br>27,760<br>37,100                    |
| Cu(fsaen).Te(IV)Cl <sub>2</sub> | 12.01<br>(12.12) | 5.28<br>(5.34) | 13.49<br>(13.55) | 8.98<br>( 9.16)  | 1.69                          | 16,140(sh)<br>27,780<br>37,200                    |
| Ni(H <sub>2</sub> fsaen)        | 13.12<br>(13.19) | 6.25<br>(6.26) | —                | —                | 2.89                          | 16,670<br>12,500<br>27,030<br>37,740              |
| Ni(fsaen).Si(IV)                | 11.32<br>(11.39) | 5.42<br>(5.50) | 13.92<br>(13.95) | 5.36<br>( 5.50)  | 1.91                          | 27,770<br>37,040                                  |
| Ni(fsaen).Sn(IV)                | 9.63<br>(9.67)   | 4.59<br>(4.67) | 11.79<br>(11.83) | 19.79<br>(19.83) | 1.26                          | 27,760<br>37,045                                  |
| Ni(fsaen).Te(IV)                | 9.31<br>(9.52)   | 4.50<br>(4.60) | 11.89<br>(11.66) | 20.98<br>(21.02) | 1.24                          | 29,410<br>37,740                                  |
| Ni(fsaen).Ti(IV)                | 11.23<br>(11.18) | 5.23<br>(5.40) | 13.54<br>(13.68) | 9.21<br>(9.25)   | 0.97                          | 27,720<br>37,045                                  |

M' = Si, Sn, Te, Ti.

second group. The crystal field theory predicts that copper(II) complexes have a marked orbital contribution to the magnetic moment only when the ground state is orbitally degenerate<sup>10</sup>. In square-planar symmetry, the ground state is not a degenerate one and hence the complex should possess a  $\mu_{\text{eff.}}$  value close to spin only value of 1.73 B.M. The values found in the present investigation are in accordance with the predicted results<sup>11,12</sup>.

In nickel(II) schiff base ligand,  $\mu_{\text{eff.}}$  is around 2.89 B.M. The bimetallic complexes containing nickel(II) show magnetic moments much lower than that expected even for one unpaired electron; the values suggest the presence of diamagnetic square planar nickel(II)<sup>13</sup>. It has been reported that all Ni-O<sub>4</sub> type complexes are paramagnetic, while Ni-S<sub>4</sub> and Ni-S<sub>2</sub>N<sub>2</sub> complexes are diamagnetic in the absence of steric strain. In the cases of Ni-O<sub>2</sub> and Ni-N<sub>2</sub> complexes, there is a distribution between spin paired and spin free forms depending on the nature of the ligand and the solvent effects<sup>14</sup>. These facts suggest a planar structure for the complexes under consideration.

#### Electronic spectra

The spectra of the ligands containing copper(II) exhibit three bands around 14,710, 27,780 and 37,200  $\text{cm}^{-1}$  resembling, to a large extent, the spectra of the hexacoordinated copper carboxylate complexes<sup>15</sup>. In the spectra of the bimetallic complexes, the important band around 14,700  $\text{cm}^{-1}$  loses its original intensity, almost taking the shape of a shoulder. This might be due to the steric restriction imposed by the tetravalent metal ion. The spectra of the complexes under study resemble those of the known square planar complexes<sup>16,17</sup>.

The electronic transitions observed for parent nickel(II) complexes (ligands) and the bimetallic complexes are also included in Table 1. The electronic spectrum of the ligand exhibits three spin allowed transitions around 12,500, 16,670 and 27,030  $\text{cm}^{-1}$  along with an extra band at 37,740  $\text{cm}^{-1}$ , which may be due to charge transfer. Since the spectrum is taken in the range 12,500-50,000  $\text{cm}^{-1}$ , the band due to  ${}^3T_{2g} \leftarrow {}^3A_{2g}$  i.e., the  $\nu_1$  transition could not be observed, but its position could be calculated on the basis of the other

two peaks<sup>18</sup>. The band noticed around  $27,030\text{ cm}^{-1}$  is attributed to the  ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$  transition ( $\nu_3$ ). Another band at  $12,500\text{ cm}^{-1}$  is assigned to  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  transition ( $\nu_2$ ).

In the spectra of the bimetallic complexes, the bands at  $12,500$  and  $16,670\text{ cm}^{-1}$  disappear leaving only one band at  $29,410\text{ cm}^{-1}$  along with a charge transfer band at  $37,740\text{ cm}^{-1}$ . Such a situation is characteristic of square planar nickel(II)<sup>19</sup>. The spectra also do not reveal any electronic transition below  $10,000\text{ cm}^{-1}$ , which is a further proof of the planar nickel(II).

#### Infrared spectra

In all the ligands, a band at  $2600\text{ cm}^{-1}$  is attributed to free hydroxy group. The  $\nu(\text{C}=\text{O})$  mode of free carboxyl group and the coordinated azomethine group are noticed respectively at  $1710$  and  $1650\text{ cm}^{-1}$ . The  $\nu_{\text{as}}(\text{COO})$  in combination with  $\text{C}=\text{C}/\text{C}=\text{N}$  stretching vibrations is assigned at  $1575\text{ cm}^{-1}$ . Bands at  $1270$  and  $570\text{ cm}^{-1}$  are respectively assigned to  $\nu(\text{C}=\text{O})$  (phenolic) and  $\nu(\text{Cu}-\text{N})$  modes.

In the spectra of bimetallic complexes containing copper(II), the bands due to free OH disappear suggesting that protons of the carboxylic groups have reacted with chlorine atoms of the tetravalent metal chlorides. The band due to  $\nu(\text{C}=\text{N})$  suffers a small negative shift indicating the strain imposed on ethylenediamine bridge. Even the band due to phenolic  $\nu(\text{C}-\text{O})$  undergoes a shift to lower region thus indicating its coordination to metal.

In the spectra of bimetallic complexes, the  $\nu(\text{Si}-\text{O})$ ,  $\nu(\text{Sn}-\text{O})$ ,  $\nu(\text{Te}-\text{O})$  and  $\nu(\text{Ti}-\text{O})$  are observed at  $860$ ,  $430$ ,  $420$  and  $420\text{ cm}^{-1}$  respectively. Similarly, the  $\nu(\text{Si}-\text{Cl})$ ,  $\nu(\text{Sn}-\text{Cl})$ ,  $\nu(\text{Te}-\text{Cl})$  and  $\nu(\text{Ti}-\text{Cl})$  vibrations are seen<sup>20</sup> respectively at  $520$ ,  $380$ ,  $375$  and  $360\text{ cm}^{-1}$ .

In the spectra of nickel(II) ligands, a broad band around  $2600\text{ cm}^{-1}$  as attributed to the intramolecularly hydrogen bonded OH group<sup>21</sup> and this band disappears from the spectra of bimetallic complexes thus indicating deprotonation and coordination of this group. This is also supported by the elemental analysis which shows the presence of only two chlorine atoms. A change in positions of the bands due to  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}=\text{N})$  during complexation indicates the coordination of the metal ion with oxygen of the phenolic C-O group and nitrogen of azomethine group with nickel(II)<sup>22</sup>.

The band at  $1300\text{ cm}^{-1}$  in the spectra of ligands is due to phenolic  $\nu(\text{C}-\text{O})$ . On complexation, this band is shifted to higher wave number region thus suggesting the involvement of phenolic oxygen in coordination with the tetravalent metal moiety. The  $\nu(\text{Ni}-\text{N})$  vibrations in the ligands are seen at  $560\text{ cm}^{-1}$  while these vibrations in the complexes are observed in the region  $530-550\text{ cm}^{-1}$ . The  $\nu(\text{Si}-\text{O})$ ,  $\nu(\text{Sn}-\text{O})$ ,  $\nu(\text{Te}-\text{O})$  and  $\nu(\text{Ti}-\text{O})$  modes are seen<sup>20</sup> respectively at  $870$ ,  $460$  and  $450\text{ cm}^{-1}$ . The bands at  $510$ ,  $350$ ,  $360$  and  $340\text{ cm}^{-1}$  are respectively attributed to  $\nu(\text{Si}-\text{Cl})$ ,  $\nu(\text{Sn}-\text{Cl})$ ,  $\nu(\text{Te}-\text{Cl})$  and  $\nu(\text{Ti}-\text{Cl})$  modes<sup>20</sup>.

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