

observed in the $\nu(\text{C-N})$ region. The two bands at 1342 and 1315 in the ligand are assigned to $\nu(\text{C-N})$; these shift to 1320 and 1260 in the spectra of complexes indicating coordination of the nitrogen of the dimethyl group.

Compounds $\text{TiBr}_4 \cdot \text{Ampy} \cdot 2\text{BBr}_3$ and $\text{SnBr}_4 \cdot \text{Ampy} \cdot 2\text{BBr}_3$ — These compounds were obtained by the reaction of compounds $\text{MCl}_4 \cdot \text{Ampy}$ ($\text{M} = \text{Ti}$ or Sn) with BBr_3 . It is interesting to note that while all the four chlorine atoms get replaced by bromine, additional two molecules of BBr_3 get bonded to the tetrabromo complex resulting in the formation of compounds of the type $\text{MBr}_4 \cdot \text{Ampy} \cdot 2\text{BBr}_3$. Here BBr_3 seems to serve two functions i.e. (i) it acts as a brominating agent and (ii) it also acts as a Lewis acid where two molecules of BBr_3 coordinate with two available ring nitrogens on the ligand molecule.

The IR spectra of these bromo complexes in the region of $\nu(\text{C=O})$ and $\nu(\text{C-N})$ are similar to those of the parent chloro compounds.

It is interesting to observe that a medium band at 1090 for the ligand appears as an unshifted weak band in $\text{MCl}_4 \cdot \text{Ampy}$, but the same band shifts and splits into two bands at 1050 and 1040 in spectra of the bromo complexes. If the band at 1090 is associated with $\nu(\text{N-N})$ then the lowering and splitting of the band is not surprising as the coordination of BBr_3 molecules will considerably affect the $\nu(\text{N-N})$.

The most striking differences in the spectra of the bromo adducts as compared to the original chloro adducts appear in the region 960 to 800. Another medium band at 960 appearing in the bromo adducts neither appears in the spectrum of free ligand nor in the spectra of chloro adducts. It is, therefore, reasonable to assume that this band is associated with the coordination of BBr_3 . Vibrational frequencies ν_2 , ν_3 and ν_4 are reported¹¹ to be IR active for BBr_3 which appear at 375, 820 and 150 respectively. The band at 760 can be attributed to the combination band arising due to $\nu_3 + \nu_4$. Another medium-strong band at 840 appears only in the spectra of bromo adducts. The IR bands in the 886-840 region can be assigned to $\nu \text{B-N}$ frequencies. Jain and Rao⁴ have also assigned a band at 790 to $\nu \text{B-N}$ mode.

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References

1. JAIN, S. C. & RIVEST, R., *J. inorg. nucl. Chem.*, **29** (1967), 2787.
2. JAIN, S. C. & RIVEST, R., *J. inorg. nucl. Chem.*, **31** (1969), 399.
3. BOHUNOVSKY, O., JAIN, S. C. & RIVEST, R., *Can. J. Chem.*, **47** (1969), 1689.
4. JAIN, S. C. & RAO, G. S., *J. Indian chem. Soc.*, **53** (1976), 25.
5. JAIN, S. C. & RIVEST, R., *Can. J. Chem.*, **40** (1962), 2243.
6. JAIN, S. C. & RIVEST, R., *Can. J. Chem.*, **41** (1963), 2130.
7. AHUJA, H. S., KHAN, I. A., KUNTE, P. P. & RAO, G. S., *BARC Report*, No. 1 (1972), 174.
8. JAIN, S. C., GILL, M. S. & RAO, G. S., *J. Indian chem. Soc.*, **53** (1976), 537.

9. JAIN, S. C. & RIVEST, R., *Can. J. Chem.*, **45** (1967), 139.
10. JAIN, S. C. & HAJELA, B. P., *Indian J. Chem.*, **12** (1974) 843.
11. NAKAMOTO, K., *Infrared spectra of inorganic and coordination compounds* (John Wiley, New York), (1962), 90.

Synthesis of Schiff Base Derived from 2,4-Dihydroxyacetophenone & Ethanolamine & Structural Studies of Its Chelates with Cu(II), Ni(II), Co(II) & Fe(III)†

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Complexes of 1 : 1 stoichiometry of Fe(III), Co(II), Ni(II) and Cu(II) with the schiff base derived from 2,4-dihydroxyacetophenone and ethanolamine have been prepared and characterized. The metal to ligand ratio is 1 : 1 in all chelates. Cu(II) and Fe(III) complexes are suggested to have polynuclear and binuclear structures respectively, with oxygen bridges in an octahedral geometry. Co(II) and Ni(II) complexes have been assigned the trigonal bipyramidal and tetrahedral geometries. Cu(II) and Fe(III) complexes have low magnetic moments as compared to spin only values, due to antiferromagnetic interaction in solid state.

SCHIFF bases derived from simple aromatic aldehydes and ethanolamine act either as bidentate or tridentate with different metals. For example, N-hydroxyethylsalicylideneimine has been reported¹ as bidentate in Cu(II), Fe(III) complexes whereas in Ni(II) chelate it is shown² to act as a tridentate with oxygen of the alcoholic hydroxyl also participating in coordination without deprotonation. Recently boron³ and vanadyl⁴ chelates of schiff base derived from *o*-hydroxyacetophenone and aminoalcohols have been studied. Complexes of resacetophenone thiosemicarbazone⁵ etc. have been studied but no attempt has been made to synthesize and study the complexing behaviour of the schiff base resulting from resacetophenone (2, 4-dihydroxyacetophenone) and ethanolamine. In this note we report the synthesis of this schiff base (RETA) and its complexing behaviour towards Fe(III), Co(II), Ni(II) and Cu(II). Azomethine compounds of resacetophenone such as hydrazone⁶ are reported to be physiologically active. Preliminary screening of the presently synthesized chelates shows them to be physiologically active.

All the solvents and reagents used were of AR grade. Magnetic susceptibilities were determined at room temperature using Faraday technique. The metal estimation were done following standard procedures⁷.

For the preparation of the schiff base, a solution of ethanolamine (0.1 mol) was added to a solution

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NOTES

of resacetophenone (0.1 mol) in methanol (30 ml), and the contents refluxed for 2 hr. A crystalline yellow compound which separated out was filtered, washed with cold methanol several times and finally with pet. ether and dried *in vacuo*; m.p. 186°C (Found : C, 61.43; H, 6.59; N, 7.19. Required C, 61.53; H, 6.66 ; N 7.17%).

The chelates were prepared as follows : A hot solution of the ligand (0.01 mol) in aq. methanol (50%, v/v) was added slowly with stirring to the respective metal chloride solution (0.01 mol) in methanol (20 ml). The reaction mixture was refluxed for 1 hr, cooled, pH adjusted to 4-5 for Cu(II) chelate and around 8 for others and the solids thus separated were washed with cold methanol, pet. ether and finally dried *in vacuo*.

The complexes are coloured and stable in air. Cu(II) and Fe(III) chelates are sparingly soluble in dimethylformamide and dimethylsulphoxide whereas Co(II) and Ni(II) complexes are insoluble in most of the solvents. The metal to ligand ratio has been found to be 1:1 in all the chelates (Table 1).

The IR spectra of the chelates and the ligand, recorded in KBr on a Perkin-Elmer model 577 spectrophotometer, exhibit the following characteristic features (ν_{\max} in cm^{-1}). The ligand exhibits a broad band in the region 3300 to 2400 assignable to three hydroxyl groups, involved in multiple inter- and intramolecular hydrogen bonding. A broad peak at 1570 is attributed to hydrogen bonded $\nu(\text{C}=\text{N})$. The peaks observed at 1230, 1260 and 1070 are assigned to $\nu(\text{C}-\text{O})$ phenolic at positions 2 and 4, and alcoholic respectively⁸. The presence of a medium band at 890 is presumably characteristic of $-\text{OH} \dots \text{N}=\text{O}$ wagging similar to that of $-\text{OH} \dots \text{O}=\text{O}$ wagging.

The complexes of Cu(II) and Ni(II) exhibit a distinct band at 3450 assignable to free-OH at position-4. A broad trough in the region 3300-3000 for Ni(II) and 3600-3200 for Fe(III) and Co(II) complexes are assignable to coordinated water. This is further supported by a peak at 850. TG analysis further reveals that in Ni(II) and Fe(III) complexes the mass loss corresponds to one mol of water at 140°C whereas in the case of Co(II) complexes the mass loss corresponds to two mol of water in a single step at 160°C. In the IR spectra of Fe(III) and Co(II) complexes the peak due to free

$-\text{OH}$ at position-4 is assumed to be engulfed in the broad trough due to coordinated water. In the case of Cu(II) complex no such trough is observed, indicating the absence of coordinated water. The nature and higher range of the troughs when compared to ligand indicates the involvement of oxygen of phenolic group at position-2 in coordination. The upward shift of $\nu(\text{C}-\text{O})$ (phenolic at position-2) of the free ligand at 1230 by 10 cm^{-1} in all the complexes supports the coordination through the phenolic oxygen. The persistence of peak at 1260 in all the chelates indicates the non-participation of phenolic $-\text{OH}$ at position-4. The upward shift of $\nu(\text{C}=\text{N})$ by $15-20 \text{ cm}^{-1}$ shows the participation of nitrogen of azomethine group in coordination⁹. The disappearance of the free ligand band at 890 in all the chelates points to the disruption of $-\text{OH} \dots \text{N}=\text{O}$ bonding and coordination through phenolic oxygen and azomethine nitrogen. A red shift to the extent of 10 cm^{-1} of the free ligand $\nu(\text{C}-\text{O})$ (alcoholic) is observed in all the complexes indicating the participation of this oxygen of the alcoholic group in coordination. A few weak absorptions in the far IR region ($290-380 \text{ cm}^{-1}$) are probably due to $\nu\text{M}-\text{N}$, $\nu\text{M}-\text{O}$ and $\nu\text{M}-\text{Cl}$ bonds.

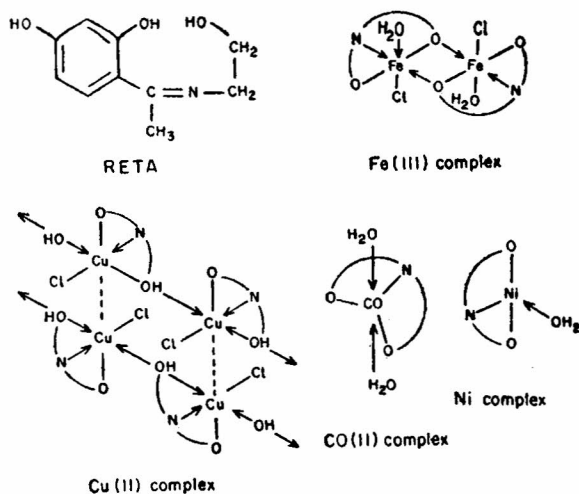
The magnetic moments for Cu(II) (1.5 B.M.) and Fe(III) (3.85 B.M.) chelates at room temperature are lower than the spin-only values. The low values may be attributed to antiferromagnetic interactions. Also the magnetic moments of these complexes decrease with the decrease in temperature as expected for antiferromagnetic complexes.

The electronic spectra of the chelates recorded as mulls on a Cary-14D spectrophotometer exhibit the following characteristic features (ν_{\max} in cm^{-1}). Cu(II) complex exhibits three bands around 15000, 27040 and 40000. The first band is assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ transition¹⁰ and the later two to charge transfer. A broad band in the region of 20000 is observed in Fe(III) chelate which is assigned to ${}^4T_{1g} \leftarrow {}^6A_{1g}$ transition¹¹. Another band at 25000 is presumed to arise from charge transfer.

On the basis of IR, magnetic and electronic data it is inferred that the schiff base acts as a tridentate with alcoholic oxygen acting as bridging centre in Cu(II) and Fe(III) chelates resulting in octahedral geometry. In case of Cu(II) complex which is prepared at lower pH (4-5) the schiff base acts as a

TABLE 1 — ANALYTICAL DATA OF THE CHELATES

Compound	Found (calc) (%)				
	C	H	N	Cl	Metal
[Fe(C ₁₀ H ₁₁ O ₃ N)(H ₂ O)Cl]	39.49 (39.68)	4.59 (4.69)	4.61 (4.63)	11.68 (11.71)	18.38 (18.40)
[Co(C ₁₀ H ₁₁ O ₃ N) (2H ₂ O)]	41.44 (41.42)	5.83 (5.20)	4.79 (4.82)	—	19.28 (20.09)
[Ni(C ₁₀ H ₁₁ O ₃ N)(H ₂ O)]	44.08 (44.09)	5.00 (4.82)	5.17 (5.19)	—	(21.62) (21.71)
[Cu(C ₁₀ H ₁₁ O ₃ N)Cl]	40.78 (40.95)	4.12 (4.09)	4.69 (4.77)	12.08 (12.11)	21.61 (21.67)



monobasic tridentate with the alcoholic oxygen coordinating without deprotonation² whereas in other chelates it is acting as a dibasic tridentate

The magnetic moment of (5.14 B.M.) for Co(II) complex is fairly higher than the reported spin-only value. The electronic bands at 15600 and 20000 and a weak band at 12900 are more in consistence with trigonal bipyramidal geometry than octahedral or planar disposition¹². The bands at 15600 and 20000 can be assigned respectively to ${}^4A'_2(P) \leftarrow {}^4A'_2(F)$ and ${}^4E''(P) \leftarrow {}^4A'_2(F)$ transitions¹⁰. The observed magnetic moment value (3.45 B.M.) for Ni(II) complex shows no probability of square planar or octahedral geometry¹³. Hence, it is proposed that the complex has tetrahedral disposition which is supported by electronic spectral band at 15380 assignable to ${}^3T_1(P) \leftarrow {}^3T_1(F)$ transition¹¹. The probable structures of the complexes are given in Fig. 1.

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References

- PODDAR, S. N., DEY, K., HALDAR, J. & NATHSARKAR., *J. Indian Chem. Soc.*, **47** (1970), 743.
- YAMADA, S., KUGE, Y. & YAMANOUCHI., *Bull. chem. Soc. Japant.*, **40** (1967), 1864.
- SINGH, H. & TANDON, J. P., *Indian J. Chem.*, **17 A** (1979), 620.
- SYAMAL, A. & KALE, K. S., *Indian J. Chem.*, **19A** (1980), 486.
- GERBERLEU, N. V., *Ser. Biol.-i-Khim. Nauk.*, **11** (1964), 3; *Chem. Abstr.*, **64** (1964), 9220.
- HANS ZIMMER., BENJAMIN GROSS H., HUGH GERLACH, E., KENNETH FRY, ANDREW PRONAY, C. & HORST SCHMANK., *J. org. Chem.*, **24** (1969), 1969.
- VOGEL, A. I., *Quantitative inorganic analysis* (Longmans, London) 1968.
- COLTHOP, N. B., DALY, L. H. & WIBERLY, S. E., *Introduction to infrared and Raman spectroscopy* (London, Academic Press), 1964, 274, 380.

- SRIVASTAVA, T. N., CHAUHAN, A. K. S. & DIWEDI, *Indian J. Chem.*, **19A** (1980) 269.
- LEVER, A. B. P., *Inorganic electronic spectroscopy* (Elsevier, London), 1968, 356.
- SUTTON, D., *Electronic spectra of transition metal complexes* (McGraw-Hill, New York), 1968, 146, 188.
- CIAMPOLINI, M. & SPERONI, G. P. S., *Inorg. Chem.*, **5** (1966), 45.
- COTTON, F. A. & WILKINSON G., *Advanced inorganic chemistry* (John Wiley and Sons), 1969, 883.

Dioxomolybdenum (VI) Complexes of Schiff Bases Derived from Salicylaldehyde, Substituted Salicylaldehydes & Benzoylhydrazide

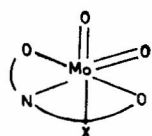
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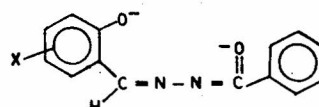
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Several new dioxomolybdenum(VI) complexes of schiff bases derived from salicylaldehyde, 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, 5-nitrosalicylaldehyde, 2-hydroxy-1-naphthaldehyde and benzoylhydrazide have been synthesised and characterized by elemental analyses, quantitative determination of ligand, IR, conductance, molecular weight and magnetic susceptibility measurements. The ligands behave as ONO donor dibasic tridentates and form complexes of the type $MoO_2L.H_2O$ (where LH_2 =schiff base). These complexes react with tetrahydrofuran (THF) to give the adducts, $MoO_2L.THF$. All the complexes are monomers, non-electrolytes and diamagnetic. The THF adducts are less stable than the aquo adducts. IR data indicate that the complexes possess *cis*- MoO_2 structure.

MOLYBDENUM is coordinated to nitrogen, oxygen and/or sulphur atoms in enzymes like nitrogenase, aldehyde oxidase, xanthine oxidase, sulphite oxidase, nitrate reductase and xanthine dehydrogenase¹. The valence of molybdenum varies depending on the nature of the enzyme, and the function of some redox enzymes is dependent on variable valence molybdenum cofactors. In order to understand the gross mechanism of enzyme activity, experiments on relatively small molecules are needed. We report here the synthesis of some model molybdenum coordination complexes of the type(I) with the dianions of tridentate ONO donor schiff bases(II) derived from benzoylhydrazide and salicylaldehyde or substituted salicylaldehyde and monodentate oxygen donor neutral ligand (X) like H_2O or tetrahydrofuran (THF). Not much work seems to have



I X = H_2O , THF



II. X=H, 5-Chloro, 5-Bromo, 5-Nitro, 5,6-Benzo