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Synthesis and Characterization of Mono and Homo-Dinuclear, Cobalt(II), Nickel(II) and Copper(II) Complexes of the Schiff Base Derived from 3-Formylsalicyclic Acid and Hydroxylamine Hydrochloride

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Mono and homo-dinuclear cobalt(II), nickel(II) and copper(II) complexes of the type of M{3fsa)$_2$-HyAm}(H_2O)$_n$ and M_2{(3fsa)$_2$-HyAM}(H_2O)$_n$ respectively, where {(3fsa)$_2$-HyAm} is a Schiff base derived from 3-formyl salicylic acid and hydroxylamine hydrochloride, n = 0, 1, 2, ... etc., have been isolated and characterized. The dinuclear cobalt(II) complex has been found to have a mixed spin state consisting of a high spin and a low spin cobalt(II) ion. Although strong antiferromagnetic spin exchange interaction has been observed between the metal ions of dinuclear copper(II) complex, the dinuclear nickel(II) complex exhibits slightly lower magnetic moment value corresponding to two unpaired electrons. The mononuclear cobalt(II) and copper(II) complexes are paramagnetic while the mononuclear nickel(II) exhibits diamagnetic character. The reflectance spectra of all the complexes are consistent with observed magnetic moment values. IR spectra, thermal analysis and low molar conductance values fully agree with the proposed structures. The complexes have been evaluated as possible fungicides. The dinuclear complexes show higher percentage of inhibition as compared to the mononuclear ones. Copper(II) complexes of both the series exhibit maximum fungitoxicity.

INTRODUCTION

Coordination compounds with multimetal centres with magnetic interactions are of considerable importance in the domain of metalloenzymes and homogeneous catalysis[1–5]. Schiff-bases derived from 3-formylsalicylic acid and diamines are of considerable importance in the preparation of mononuclear complexes[6], heterodinuclear complexes[7] and mixed spin complexes[8]. Considering the importance of such systems, we are engaged in isolation and characterisation of a few more mono and dinuclear metal complexes with the Schiff base derived from 3-formylsalicylic acid (3-fsaH_2) and hydroxylamine hydrochloride. The metal ions of these complexes are supposed to have different stereochemistries and spin states.

EXPERIMENTAL

Chemicals used were either of BDH or E. Merck quality. Metal salts and solvents were used without further purification.

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Preparation of 3-formylsalicylic acid (3-fsaH_2): 3-fsaH_2 was prepared using the literature method[9].

Preparation of 3-oximinomethylsalicylic acid (3-oxm): A mixture of 3-fsaH_2 (1 m), hydroxylamine-hydrochloride (1 m) and sodium hydroxide (1.5 m) in water (100 mL) was slightly warmed at *ca.* 40°C for 24 h. The clear solution was then cooled and acidified with cold dilute sulphuric acid (1 : 4 by vol.), when 3-oxm separated out in the form of colourless crystals. This was washed with cold water and recrystallized from warm water containing some iron-free charcoal. The product was dried at room temperature (m.p. 193°C).

Preparation of mono and dinuclear complexes: A warm acidified solution of appropriate metal(II) acetate (1 m for mononuclear and 2 m for dinuclear) was added to an alcoholic solution of 3-oxm (2 m), and to this dilute ammonia was added dropwise to maintain the pH *ca.* 4.5. The resultant solution was kept on the water bath for about 10–15 min when the complex appeared slowly. It was then filtered, washed thoroughly with alcoholic-water and finally dried over vacuum.

The metal contents in the complexes have been determined by standard methods. Carbon, hydrogen and nitrogen contents of the complexes were estimated using a MLW-CHN microanalyser. The analytical data of the complexes are presented in Table-1.

TABLE-1

ANALYTICAL DATA OF THE COMPLEXES DERIVED FROM 3-FORMYLSALICYLIC ACID AND HYDROXYLAMINE HYDROCHLORIDE

Complexes	μ_{eff} (B.M.)	% Found (Calcd.)			
		M	C	N	H
$[Cu_2((3\text{-fsa})_2\text{-HyAm})(H_2O)_2](H_2O)_2$	0.81	21.84	34.09	4.89	3.05
		(22.91)	(34.42)	(5.01)	(3.22)
$[Ni_2((3\text{-fsa})_2\text{-HyAm})(H_2O)_2](H_2O)_3$	1.89	20.34	33.61	4.71	3.39
		(20.76)	(33.95)	(4.95)	(3.53)
$[Co_2((3\text{-fsa})_2\text{-HyAm}](H_2O)_3$	4.83	20.98	35.79	5.01	2.79
		(22.23)	(36.24)	(5.28)	(3.02)
$[Cu((3\text{-fsa})_2\text{-HyAm}](H_2O)_2$	1.98	13.61	41.18	5.86	3.33
		(13.82)	(41.78)	(6.09)	(3.48)
$[Ni((3\text{-fsa})_2\text{-HyAm}](H_2O)$	—	13.09	43.42	6.21	2.87
		(13.44)	(43.96)	(6.41)	(3.20)
$[Co((3\text{-fsa})_2\text{-HyAm}](H_2O)$	1.96	13.29	43.70	6.31	2.99
		(13.48)	(43.96)	(6.40)	(3.20)

IR spectra in KBr pellets were recorded on a Perkin-Elmer spectrophotometer. Reflectance spectra were recorded on a Cary-2390 spectrophotometer. Room temperature magnetic susceptibilities were measured by Gouy method and thermal analyses were carried out by Netsch-429. Simultaneous recordings of TGA and DTA were carried out at a heating rate of 10°C min^{-1} in air using 50–100 mg of the smaple in each case.

RESULTS AND DISCUSSION

Complexes of both the series are coloured. Although they are soluble in DMF and DMSO to a considerable extent, the low molar conductance values in DMF suggest them to be non-electrolytes. Most of the complexes decompose above 250°C before melting.

IR Spectral Studies

All the complexes and the ligand exhibit two broad and smooth bands at 3485 and 3355 cm^{-1}, which may be assigned to the combined ν(O—H) mode of intramolecular hydrogen bonded structure involving the N—OH group. However, in the metal complexes it broadens which may be due to the presence of coordinated water molecules involving hydrogen bonding[10, 11]. The persistence of these bands indicates the ligand to be coordinated in its uncharged state with respect to the oxime group.

The ligand band due to ν(C═N) undergoes a downward shift and is observed at *ca.* 1620 cm^{-1} in the complexes, suggesting the participation of azomethine group in complexation. Further the band at 1420 cm^{-1} due to ν(N—O) shows an upward shift and appears as a strong band at 1440 cm^{-1} supporting coordination of oxime group[11, 12].

Out of the three bands that are observed in the range of 1200 to 1000 cm^{-1}, the middle one is the strongest and represents ν(N—O).[13] On comparison of the spectra of the ligand (3-oxm) and its complexes, with certain reported oxime complexes, we are of the opinion that the oxygen atom of the N—OH group does not participate in coordination.

The hypsochromic shift of the band due to ν(C—OH), which is generally observed at 1320 cm^{-1}, indicates the participation of the phenolic oxygen in complexation[14].

A carboxylate group may be coordinated to the metal ion either in a unidentate or in a bidentate manner. Two bands are observed at 1590 and 1350 cm^{-1} and the large difference in (ΔCOO^-) of 240 cm^{-1} is indicative of the monodentate nature of the carboxylate group[7]. However, the bands observed at *ca.* 1700–1680 cm^{-1} for mononuclear complexes may be assigned to the free carboxylic group[2].

The appearance of a band at 840 cm^{-1} due to $\rho(H_2O)$ further suggests the presence of coordinated water molecules[1].

The appearance of two additional low frequency bands in the region 470–430 cm^{-1} is assignable to ν(M—N) and ν(M—O) respectively, further supporting our earlier observation of the coordination through the nitrogen and oxygen atoms of the ligand [15, 16].

Thermal Analyses

The natures of the water molecules, indicated in the IR spectra were further ascertained by thermal analyses. The first weight losses for mononuclear copper(II) and nickel(II) complexes were encountered at *ca.* 85°C supported by a broad endothermic peak at the same temperature in the DTA curve, corresponding to two and one molecule of water of crystallisation respectively[17, 18].

However, the first weight loss for mononuclear cobalt(II) complex, that occurred at *ca.* 125°C supported by a broad endothermic peak at the same temperature in the DTA curve, is the characteristic of coordinated water molecule.

The DTA thermograms of the dinuclear complexes exhibited the characteristics of both coordinated water as well as water of crystallisation. Loss of water of crystallisation has been observed in the range of 70° to 80°C. The elimination of coordinated water for copper(II) and nickel(II) complexes occurred in a single step supported by a broad endothermic peak at 125°C and 130°C respectively. Simultaneous elimination of water molecules suggests them to be in the same chemical environment[19]. However, the loss of water molecules in case of the dinuclear cobalt(II) complex is a two-step process, one at 125°C corresponding to loss of one molecule of coordinated water (exactly at the same temperature as the mononuclear cobalt(II) complex) and the other at 135°C corresponding to the loss of two molecules of co-ordinated water. Both the complexes finally decompose to their metal oxides and in both the series the thermal stabilities of the complexes are in the order of Cu > Ni > Co.

Mononuclear complexes

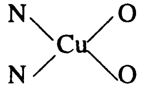
The single band observed at 18,050 cm^{-1} for the mononuclear copper(II) complex is well in agreement with the band for N,N′-salicylidene-ethylenediaminatocopper(II)[20]. This absorption is assignable to $^2E_g \rightarrow {}^2T_{2g}$ transition. Moreover, the room temperature magnetic moment value of the present complex of 1.96 B.M. implies a planar structure similar to the corresponding N,N′-salicylideneethylenediaminatocopper(II) complex having the same N_2O_2 chromophore.

Only one band is observed in the ligand field spectra of diamagnetic mononuclear nickel(II) complex at 18,450 cm^{-1} which corresponds well with the band for the diamagnetic-N,N′-salicylideneethylenediaminatonickel(II) complex with a planar N_2O_2 chromophore[20]. Hence, it is imperative that the present mononuclear nickel(II) complex has also a planar environment around the nickel(II) ion.

The mononuclear cobalt(II) complex exhibits bands at 6,150, 9,400, 13,810 and 16,230 cm^{-1}. The room temperature magnetic moment value of 1.94 B.M. is in accordance with the cobalt(II) ion in the low-spin state. It is known that[21] N,N′-salicylideneethylenediaminatocobalt(II), [Co(Salen)], reacts with pyridine (Py) to form [Co(salen)Py)], where cobalt(II) ion is in the low-spin state with a tetragonal-pyramidal geometry around it, exhibiting reflectance bands at 6000, 9000, 13500 and 16000 cm^{-1}. This suggests that the present mononuclear cobalt(II) complex may also have a similar tetragonal pyramidal structure—the water molecule occupying the apical position—since pyridine does not differ much from water in ligand field strength[8].

Dinuclear complexes

The spectral pattern and the room temperature magnetic moment values of this series of complexes are substantially different from that of the mononuclear ones.

The dinuclear copper(II) complex shows two bands in the visible region. The high energy band is well in agreement with the band for CuH_2fsa-en (where H_2fsa-en is a Schiff base derived from 3-$fsaH_2$) and ethylene diamine). Practically the position of this band is similar to the band for N,N′-disalicylidene-*o*-phenylenediaminatocopper(II)[20]. Therefore this high energy band has been tentatively assigned to the inner copper(II) possessing a N_2O_2-chromophore. It was observed[22] that dichloro(N,N′-disalicylidenetrimethylenediaminato-copper(II) has a d-d band at 17,100 cm^{-1}. This indicates the coplanarity of the unit  in N,N′-disalicylidenetrimethylene diaminato copper(II) is enhanced on forming a dinuclear complex bridged by phenolic oxygen. Hence, the band at 17,725 cm^{-1} is attributed to Cu-N_2O_2 chromophore. On the other hand the low energy band at 15,175 cm^{-1} is tentatively assigned to the 'outer' copper(II) ion. Transitions involving the 'inner' and the 'outer' copper(II) ion have been tentatively assigned to $^2E_g \rightarrow {}^2T_{2g}$. Further, the subnormal room temperature magnetic moment value of 0.81 B.M. may be due to super exchange process operating between the P_x orbitals of the two copper(II) ions through the oxo-bridge.

Three d-d bands are observed in the reflectance spectrum of the dinuclear nickel(II) complex. The band at 18,345 cm^{-1} is well in agreement with the band for mononuclear nickel(II) complex. The rest two bands at 14,900 and 9,950 cm^{-1} are indicative of an octahedral environment around the nickel(II) ion. Accordingly, coordination of two water molecules from apical positions is suggested for 'outer' nickel(II) ion. The two bands at 14,900 and 9,950 cm^{-1} are assigned to $^3A_{2g} \rightarrow {}^3T_{1g}$ and $^3A_{2g} \rightarrow {}^3T_{2g}$ transitions respectively. The observed magnetic moment value for nickel(II) ion is less than the spin only value. This might either be due to the antiferromagnetic spin-pairing between the two paramagnetic nickel(II) ions or formation of a complex with one diamagnetic and one paramagnetic nickel(II) centre. The electronic spectra favour the latter possibility.

Several spectral bands are observed in the region 6,000 to 20,000 cm^{-1} in the spectrum of dinuclear cobalt(II) complex. Since it has already been established that the complex CuCo(3-fsa-R)$(H_2O)_{2-3}$ (where R is a diamine) has an 'outer' cobalt(II) ion in a pseudooctahedral environment[7], it is likely that the 'outer' cobalt(II) ion in our present dinuclear cobalt(II) complex may also have a pseudooctahedral structure, coordinated by water molecules from the apical positions. It is known[21] that N,N′-disalicylideneethylenediaminatocobalt(II), [Co(Salen)(Py)], where cobalt(II) ion is in the low spin state, has a tetragonal-pyramidal geometry with pyridine at the apex. Hence, it is likely that the present dinuclear cobalt(II) complex also has a structure composed of an 'inner' low spin tetragonal-pyramidal and spin-free 'outer' pseudooctahedral cobalt(II) ion, since pyridine does not differ much from water in ligand field strength.

The reflectance spectra of CuCo(3-fsa-R)$(H_2O)_{2-3}$ (where R is a diamine) shows bands at 8,300, 11,000 and 19,200 cm^{-1} for 'outer' cobalt(II) ion[8]. On the other hand[23, 24], the spectra of 'inner' cobalt(II) in $[Co_2(3fsa)_2$-HyAm$(H_2O)_3]$ should be similar to that of [Co(salen)(Py)] which has d-d bands at 6000, 9000, 13,500 and 16,000 cm^{-1}. The reflectance spectrum of $[Co_2(3fsa)_2\text{-HyAm}(H_2O)_3]$ shows five bands at 6890, 8480, 13,350, 16,225 and 18,300 cm^{-1} which can be interpreted in terms of the superimposition of the spectra of five coordinate 'inner' and six-coordinate 'outer' cobalt(II) ion. Hence, no conclusive assignments of the bands could be made.

The room temperature magnetic moment value of $[Co_2(3\text{-fsa})_2\text{-HyAm}(H_2O)_3]$ was found to be 4.89 BM. It is known that the low spin cobalt(II) and the high spin cobalt(II) (octahedral) have magnetic moments in the range of 1.9 to 2.8 BM and 4.3 to 5.2 BM respectively[25]. Therefore, the expected magnetic moment values for high spin dinuclear cobalt(II), mixed spin dinuclear cobalt(II) and low-spin dinuclear cobalt(II) are in the range of 6.1 to 7.4, 4.7 to 5.9 and 2.7 to 4.0 BM respectively, only if no spin interaction is operating between the cobalt(II) ions. So, the present complex may be mixed-spin dinuclear or magnetically coupled high-spin dinuclear. The electronic spectra favour the former observation.

On the basis of the above discussions we propose the following structures for mononuclear (Fig. 1) and dinuclear (Fig. 2) metal(II) complexes.

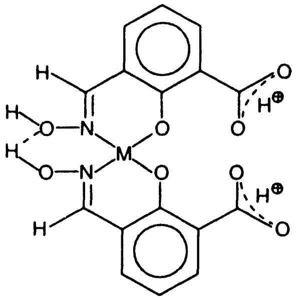


Fig. 1

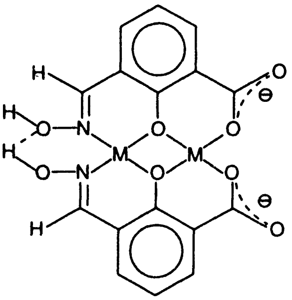


Fig. 2

Fungicidal screening

All the complexes have been screened as possible fungitoxides against the fungal pathogens *Fusarium oxysporium* and *Helminthosporium oryzae*. The screening has been carried out by Horsfall method[26] in different concentrations. The

TABLE-2

Complexes	*Helminthosporium oryzae* % of inhibition over control					*Fusarium oxysporium* % inhibition over control				
	100	200	400	800	1000	100	200	400	800	1000
Mononuclear copper(II)	12.4	19.0	24.7	58.6	67.4	11.7	17.4	23.4	54.0	66.1
Mononuclear nickel(II)	8.9	12.4	16.2	51.0	52.2	7.6	11.4	15.4	27.9	48.9
Mononuclear cobalt(II)	11.1	14.2	21.2	38.4	48.9	12.2	16.4	25.2	43.0	54.7
Dinuclear copper(II)	18.2	25.1	32.4	62.3	79.0	16.1	23.9	32.1	63.4	74.8
Dinuclear nickel(II)	13.1	15.2	19.2	32.9	56.1	15.3	18.4	21.2	40.4	63.0
Dinuclear cobalt(II)	14.3	18.4	24.2	41.5	59.7	12.8	16.4	22.5	34.9	57.2

amount of goumination or growth inhibition was determined after inoculation of the fungal spores into czapexdox agar-agar media. Spores were also inoculated onto the agar-agar media containing the text sample. The whole system was kept in an incubator for five days. The percentage of inhibition was calculated as follows:

$$\% \text{ inhibition} = 100(P - Q)/P$$

where P = area of colony growth without the test sample and Q = area of colony growth with the test sample. The results have been presented in Table-2.

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