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Multinuclear Metal Complexes of Schiff Base

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Multinuclear metal complexes of the type [M_2(3-FSA-PDA)$_2$·nH_2O] and [M_4(3-FSA-PDA)$_2$·nH_2O]where 3 FSA-PDA is a schiff base, derived from 3-formylsalicyclic acid and *p*-phenylene diamine; M = copper(II), nickel(II) and cobalt(II), n = 2 or 4 have been isolated. These have been characterized on the basis of elemental analysis, spectral studies, magnetic and conductivity measurements and thermal analyses. In case of binuclear complexes the metal ions are attached to the inner coordination sphere having N_2O_2-chromosphore. They have planar/ tetrahedral geometry around them with a slightly lower magnetic moment values at room temperature, while in case of tetra nuclear complexes the inner coordination sphere and outer having N_2O_2 and O_4^- chromophores, respectively. They show strong anti ferromagnetic interaction due to the presence of an oxo-bridge. Both bi and tetranuclear complexes are non-electrolytes in dioxane as evidenced from their low molar conductance values. IR and thermal analyses data of the tetranuclear complexes suggest the presence of coordinated water molecules.

Key Words: Multinuclear complexes, Schiff base.

INTRODUCTION

There are some report[1,2] of mono and binuclear metal complexes of 3-formyl salicylic acid (3-FSA) its Schiff bases with alkylamines and diamines. It is also established in those complexes that the phenolic oxygen acts as a briding group while the carboxylate oxygen and mononitrogen are coordinated to the metal ions. But in case of the complexes of 3-FSA and its schiff bases with monoamines, the organic constituents remain *trans* to each other (Fig. 1).

However, in the complexes of the schiff bases derived from 3-FSA and diamines such as ethylene diamine a *cis*-configuration with respect to the imino-nitrogen and carboxylate oxygen is formed (Fig. 2).

In the above type of complexes the inside coordination site has N_2O_2-chromophore, whereas the outside coordination site has O_4-chromophore and because of the hetero coordinating atoms they have different ligand field strengths.

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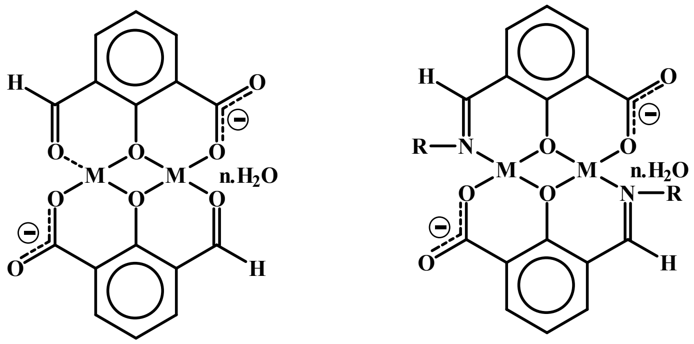


Fig.1

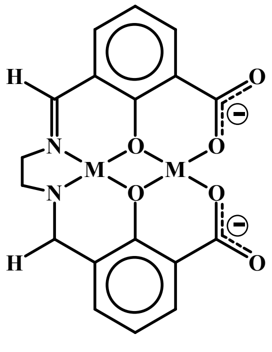


Fig.2

In the present communication we report the synthesis and structure elucidation of some bi- and tetranuclear metal complexes with a Schiff base derived from the condensation product of 3-FSA and *p*-phenylene diamine. It is expected that in these complexes the metals ions would be in different stereochemistry.

EXPERIMENTAL

All the chemicals used were of analaR grade. Solvents were used as supplied.

Preparation of 3-formyl salicyclic acid (3-FSA): 3-Formylsalicylic acid (3-FSA) was prepared following the method of Duff and Bills[3].

Attempts were made to preparate the schiff base by condensing 3-FSA and *p*-phenylene diamine but could not be achieved. Hence complexes were prepared *in situ* by taking different quantities of the metal salts and keeping *p*-phenelene diamine and 3-FSA stoichiometric ratio.

Preparation of binuclear copper(II) complex: To a mixed solution (water and dioxane) of sodium carbonate (0.106 g), 3-FSA (0.154 g) and *p*-phenylene diamine (11 g) an aqueous solution of copper acetate monohydrate (0.200 g) was added. The resultant solution was heated to 60ºC on a water bath for a while and then refluxed for a period of 0.5 h, when greenish microcrystalline solids appeared. It was cooled and filtered, thoroughly washed with hot water and dried in vaccum and analyzed.

Preparation of tetranuclear copper(II) complex: To a mixed solution (water and dioxane) of sodium carbonate (0.106 g), 3-FSA (0.154 g) and *p*-phenylene diamine (11 g) aqueous solution of copper acetate monohydrate (0.200 g) was added. The resultant solution was heated to 60ºC on a water bath for a while and then refluxed for a period of 0.5 h, when greenish microcrystalline solids appeared. It was cooled and filtered, thoroughly washed with hot water and dried in vaccum and over fused $CaCl_2$ and then analyzed.

The binuclear and tetranuclear complexes of nickel(II) and cobalt(II) were prepared in a similar manner. The metal contents in the complexes have been determine by standard methods. Carbon, hydrogen and nitrogen contents of the complexes were estimated using a MLW-CHN microanalyzer. The analytical data of the complexes are presented in Table-1.

TABLE-1
ANALYTICAL DATA OF THE COMPLEXES

Complex	Yield (%)	m.p. (ºC)	μ_{eff} (BM).	Ω_m mho cm^2 mol^{-1}	Found (Calcd.) (%)			
					M	C	H	N
Cu_4(3-FSA-PDA)$_2$ $4H_2O$	81	> 250	0.84	12.00	22.92 (22.41)	16.11 (46.97)	2.19 (2.14)	4.01 (4.98)
Ni_4(3-FSA-PDA)$_2$ $4H_2O$	72	> 250	1.98	9.20	21.62 (21.69)	45.11 (45.98)	2.17 (2.10)	4.73 (4.88)
Co_4 (3-FSA-PDA)$_2$ $4H_2O$	68	> 250	2.92	10.30	21.91 (21.75)	45.17 (45.35)	2.22 (2.10)	4.01 (4.88)
Cu_2 (3-FSA-PDA)$_2$ $2H_2O$	70	> 250	1.82	11.00	21.89 (22.41)	44.81 (45.98)	1.91 (1.98)	4.87 (4.93)
Ni_2 (3-FSA-PDA)$_2$ $2H_2O$	68	> 250	--	10.70	22.12 (21.75)	45.33 (45.66)	1.82 (1.79)	4.22 (4.18)
Co_2 (3-FSA-PDA)$_2$ $2H_2O$	61	> 250	4.25	12.10	22.65 (21.82)	45.31 (45.24)	2.22 (2.18)	4.12 (4.18)

Infrared spectra in KBr pellets were recorded on a Perkin-Elmer 398 spectrophotometer. Reflectance spectra were recorded on a Carry-2390 spectrophotometer. Room temperature magnetic susceptibilities were measured by Guoy method. Thermogravimetric analyses were carried bout by a netzch -429, simultaneous recording of TGA and DTA Thermoanalyser at a heating rate of 10ºC min^{-1} in air. Around 50-100 mg of the sample was used in each case.

RESULTS AND DISCUSSION

The complexes have the composition, $[M_2(3\text{-FSA-PDA})_2\cdot nH_2O]$ and $[M_4(3\text{-FSA-PDA})_2\cdot nH_2O]$ where 3-FSA-PDA is a schiff base prepared *in situ* by the condensation of 3-FSA and *p*-phenelene diamine and n = 2 and 4. All the complexes are microcrystalline having high melting points. They are insoluble in common organic solvents. But freshly prepared complexes are soluble in DMF, DMSO and dioxane. The molar conductance values of the complexes in dioxane are negligibly small suggesting them to be non-electrolytes. The complexes are quite stable under normal conditions and can be stored for long. However, they are decomposed with alkalies and acids.

Since the Schiff could not be isolated, the spectra of the ligand could not be recorded. Hence the spectra of the complexes are compared with the spectra of the starting materials and other related compounds. The binuclear as well as the tetranuclear complexes exhibit an identical spectral pattern. On scanning the IR spectra of the complexes no bands in the vicinity of 3300-3100 and 1690 cm^{-1} due to →NH and →C=O, respectively were observed with the suggestion that condensation has taken place[4]. Instead, a strong band 1635 cm^{-1}, attributed to →C=N has been observed[5]. This value is comparatively at a higher frequency than the usual →C=N value. The shifting of the band to higher frequency region led us to believe that the azomethine group takes part in complexation. The next structurally important band is due to →C-OH which is generally observed at 1320 cm^{-1}. However, the band has undergone a hypsochromic shift indicating the participation of C-OH in complexation. A carboxylate group may be coordinated to the metal ion either in a unidentate or a bidentate manner. In the present context we observe two bands 1605 and 1345 cm^{-1}. The large difference (COO^-) by 260 cm^{-1} is indicative of the monodentate nature of the carboxylate group[6]. However, in binuclear complexes and band due to COO^- remain undisturbed as observed in case of tetranuclear complexes. In the high frequency region, a very broad band centered at 3450 cm^{-1} has been assigned to the presence of coordinated water molecules[7-10]. This has further been supported by the additional[9] band at 850 cm^{-1}. A moderately strong band at 1012 cm^{-1} corresponding to →N-N has been observed. The band position is at a lower frequency than those observed for hydrazone complexes.

The low frequency region of the spectra of complexes furnishes some vital information regarding the mode of the coordination of the ligand with the metal centre. The coordination through oxygen and nitrogen atom is further supported by the appearance of additional bands in the spectra of the complexes. In the region 440 and 480 cm^{-1} assignable to →N-N and →N-O, rspectively[10,11].

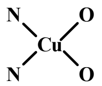
Electronic and magnetic properties of complexes

Binuclear complexes: The ligand field band for copper(II) complex is observed at 18,200 cm^{-1} which is in agreement with the band observed for N,N'-salicyledeneethylene-diaminato copper(II) and N,N'-disalicylidene-propylene-diaminato copper(II) complexes. This has been assigned to $^2E_g \rightarrow ^2T_{2g}$ transition. The room temperature magnetic moment is 1.82 BM. The magnetic property and electronic spectra imply that the copper (II) ion in the present complex has N_2O_2 coordinating similar to the salicyledene-aminato copper(II) complexes[12].

The reflectance spectra of the nickel(II) complex shows a single band 18,600 cm^{-1} which corresponds to the band reported for N,N'-salicylideneethylenediaminato nickel(II)[12]. Further, the complex is diamagnetic, suggesting a square plannar stereochemistry around the metal ion.

The cobalt(II) complex exhibited two bands at *ca.* 8,180 and 14,750 cm^{-1} assignable to $^4A_2$ (F) $\rightarrow$ $^4T_1$ (F) and $^4A_2$ (F) $\rightarrow$ $^4T_1$ (P) transitions, respectively. The spin only magnetic moment value and spectral data suggest, a tetrahendral environment around the cobalt(II) ion.

Tetranuclear complexes

The reflectance spectra of the copper (II) complex exhibits two bands in the visible region. The second high-energy band is well in accordance with the band for CuH_2FSA-en (where); HFSA-en is Schiff base drived from 3-FSA and ethylenediamine. The position of this practically equal to the band for N,N'-disalicylidene-*o*-phenylenediaminato copper(II)[13,14]. Therefore, the second band was tentatively assigned to the inside copper(II) having CuN_2O_2 chromosphere[14,15]. Sinn *et al.*[15] have found that dichloro [N,N'-disalicylidenetrimethylenediaminato copper(II)] has a band at 18,200 cm^{-1}. This fact implies that the coplanarity of the unit 

In [N,N'-disalicylidenetrimethylenediaminato copper(II)] is enhanced on forming a binuclear complex bridge by phenolic oxygen[13,14]. Therefore the band at 18950 cm^{-1} found in the present study for copper(II) is attributed to the Cu-N_2C_2 chromosphere. On the other hand, the first lower energy band 15,290 cm^{-1} is tentatively assigned to the outside copper(II) ion. The transitions involving the inside and outside copper(II) ions have been tentatively assigned to $^4E_g \rightarrow ^2T_{2g}$. Further, the magnetic moment (0.82 BM) of the complex at room temperature is found to be abnormal. It may be due to partial spin pairing between the copper(II) ions through the formation of an oxobridge.

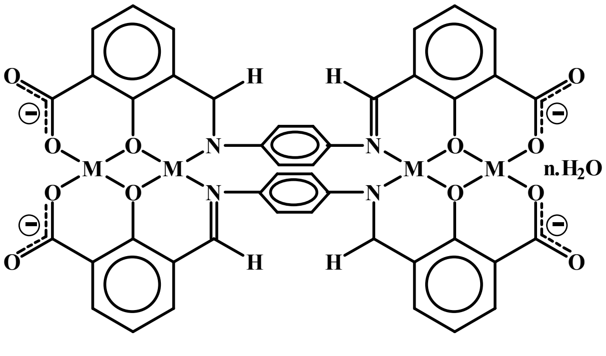
The reflectance spectrum of the tetranuclear nickel(II) complex has three *d-d* bands in the visible region. The band 18,450 cm^{-1} seems to correspond to the band for the mononuclear nickel(II) ion in an octahedral environment. Accordingly, the coordination of water from apical position was supported for the outside nickel(II) ion. The band around 10,000 and 14,970 cm^{-1} were assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}$, respectively.

The magnetic moment calculated per nickel (II) ion is much lower than the spin only value. This may be explained by (I) antiferromagnetic spin pairing between paramagnetic nickel(II) ions or (ii) formation of a complex containing one diamagnetic and one paramagnetic nickel(II) ions. The electronic spectra of the complex support the later observation.

The electronic spectra of cobalt(II) complex, $Co_4(3FAS\text{-}PDA)_24H_2O$: show three bands in the visible region. The high frequency band observed 18.000 cm^{-1} probably arises from $^4T_{2g}$ (F) → $^4T_{2g}$ (P) in an *ca.* octahedral environment. The other low frequency bands 7,220 cm^{-1} and 15,000 cm^{-1} have been tentatively assigned to $^4A_2$ (F) → $^4T_1$ (F) and $^4A_2$ (F) → $^4T_1$ (P) transitions, respectively for a cobalt(II) ion in an tetrahedral environment.

The magnetic moment value for a cobalt(II) ion is less than the calculated value. This may be due to the antiferromagnetic spin exchange interaction between two metal ions.

On the basis of the above discussion, the following structure where Cu(II), Co(II) or Ni(II), has been proposed for the tetranuclear metal complexes.



Thermal analysis

Since the IR spectra of the complexes indicted the presence of water molecule, thermal analysis was carried out to ascertain their nature. The thermograms of all the complexes exhibited an identical pattern of decomposition in each series of the complexes. In the case of binuclear complex of copper(II) the first weight loss was encountered at 90ºC. The weight loss corresponds to two molecules of water of crystallization. A stable product continues to exist up to 310ºC after which the complex starts breaking, finally decomposition to the metal oxides. All the other complexes show an identical pattern of thermal behaviour. However the tetranuclear complexes show a different pattern thermal decomposition. In case of tetranuclear copper(II) complex, the first decomposition starts at 100ºC supported by an endothermic peak at the same temperature. The weight loss corresponds to the loss of two molecules of water and may be due to[16,17] the loss of lattice water. After the elimination of lattice water a stable product continues to exit till the complexes starts losing weight at 310ºC, in a single step supported by an endothermic peak at the same temperature in the DTA thermogram. The occurrence of the endothermic peak may be due to bond breaking. Such as behaviour are characteristics of coordinated water in the same chemical environment[18]. The decomposition proceeds slowly from 210-780ºC with a final residue corresponding to the formation of metal oxides. The thermal stability of the complexes of both the series is in the order Ni > Cu > Co.

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