Communications

Binuclear Complexes Involving Quadridentate Schiff Bases of 3-Formylsalicylic Acid

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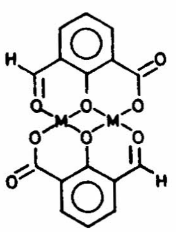
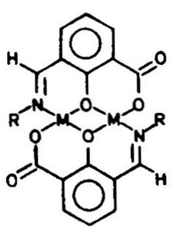
Complexes of the type MLH_2 (M=bivalent metal ions) with the quadridentate Schiff bases LH_4 (derived from 3-aldehydosalicylic acid and diamines) can function as dibasic ligands and a series of bimetallic complexes of the type $[(ML)M'(L')_2]n.H_2O$ (where M'=bivalent metal ions; $L'=H_2O$ or nothing; and n=0-5) have been isolated in the solid state. Structure (V) has been suggested on the basis of elemental analyses, infrared and electronic spectra and magnetic susceptibilities.

IT has been demonstrated that 3-formylsalicylic acid (= $FSA\text{-}H_2$) and its Schiff bases with mono- and diamines are versatile chelating ligands[1]. It has been observed that $FSA\text{-}H_2$ can function either as monobasic bidentate ligand (utilizing its formyl and hydroxyl groups), or as dibasic bidentate ligand (utilizing its hydroxyl and carboxyl groups) (Dey, K., *et al.*, unpublished work). It can also function as a bridging (dibasic) tridentate ligand as shown in I. Schiff bases of $FSA\text{-}H_2$ with alkyl or aryl mono-amines can form chelates of the following types II and III. On the other hand, Schiff bases of $FSA\text{-}H_2$ with diamines (aliphatic or aromatic) can form complexes of the type IV (M = stands for bivalent metals).

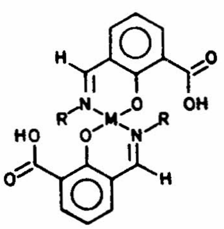
The complexes (III and IV) can easily form alkali and alkaline earth metal salts, which have been isolated in the solid states and their analytical utilities have been explored (Dey, K., Sen, S. K. & Bhar, J. K., unpublished work).



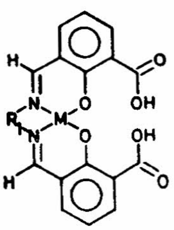
I



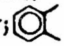
II



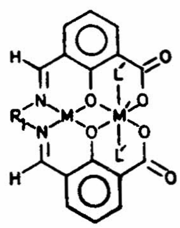
III



$R_1=(CH_2)_n$ (n=2or3); $-CH_2CH(OH)CH_2-$;



IV



V

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Our recent studies showed that the complexes of the type IV (henceforth MLH_2, where LH_4 stands for the Schiff bases derived from $FSA\text{-}H_2$ and diamines) can function as dibasic ligands under suitable reaction conditions, and in fact, we have isolated a series of bimetallic complexes of the type (V) having the composition $[(ML)M'L'_2]$ (where M' stands for bivalent metals, and L' stands for water or nothing) by reacting MLH_2 with $M'X_2$ (X = halides or acetate) in the presence of requisite amount of KOH or LiOH in water. Elemental analyses (Table 1) support the formulation of the new chelates. Some of the bimetallic complexes are found to have water of crystallization.

The colour of the bimetallic complex is different from the colour of the corresponding mononuclear complex. As, for example, the colour of $NiLH_2$ is red, while the colour of (NIL)VO is yellow. Besides, the colour of $(CuL)Ni.3H_2O$ is quite different from that of $Cu_2L.2H_2O$ (yellow-brown) and that of $Ni_2L.3H_2O$ (red). The colour of $VOLH_2$ is orange-yellow, while the colour of $(VOL)Ni.2H_2O$ is grey-yellow.

In the infrared spectrum of MLH_2 the band due to the free carboxyl group was observed at 1700-1715 cm^{-1}. On the other hand, this band could not be seen in the spectrum of $[(ML)M'L'_2]$. Instead, a new band appeared at 1530-1560 cm^{-1}, which may be attributed to the carboxylate group. Bridging phenolic νC—O may appear in this region, which appears around 1500 cm^{-1} in the uncomplexed Schiff base and around 1640 cm^{-1} when attached to a single metal ion (non-bridging)[2]. Therefore, one should be careful in interpreting these bands. Detailed infrared spectral analyses are yet to be done.

The electronic absorption spectra of these chelates also support the formation of heterobinuclear complexes (V). As, for example, the complex (VOL)Cu (where $R_1 = CH_2CH_2$, and L = nothing in V) shows bands (in $CHCl_3$ solution) at 38·5, 37·0 (sh), 28·5, 17·8, 16·4 (sh), and 13·8 kK, while the parent complex $VOLH_2$ shows bands (in the same solvent) at 37·0, 28·6, 19·3, 16·2 (sh), 14·0 kK. The band around 16·4 kK may be assigned to the (CuO_4)-chromophore[3]. The bands in the range 28·13 kK may be assigned to the *d-d* bands of the $VO(N_2O_2)$-chromophore[4].

The room temperature magnetic moments of these heterobinuclear complexes are very interesting. The μ_{eff} values of the complexes (VOL)Ni and (VOL)Pd are found to be 1·68 and 1·72 BM respectively. This supports the presence of oxo-vanadium (IV) (a d^1-system) species in these heterobinuclear chelates, where Ni^{2+} or Pd^{2+} (d^8-system) remains as spin-paired having square-planar geometry. However, the dihydrate $[(VOL)Ni(H_2O)_2]$ was found to be strongly paramagnetic (μ_{eff} = 5·00 BM at room temperature). This accounts for the presence of a

TABLE 1 — ELEMENTAL ANALYSES AND MAGNETIC MOMENTS OF SOME BINUCLEAR COMPLEXES, $(ML)M'(L')(H_2O)_n$*

(Calculated values are given in parentheses)

Sl No.	M	M′	R_1 (in structure V)	L′	Found (%)† M	M′	N	μ_{eff} (BM)	Temp. °C
1	VO^{2+}	Ni^{2+}	$-(CH_2)_2$	H_2O $n=2$	9·30 (9·92)	10·95 (11·48)	5·71 (5·45)	1·84 (total)	29·5
2	VO^{2+}	Ni^{2+}	$-(CH_2)_3$	H_2O $n=1$	9·82 (10·01)	11·12 (11·51)	5·23 (5·50)	3·68 (total)	29·5
3	VO^{2+}	Ni^{2+}	$-O-C_6H_4$	H_2O $n=5$	8·12 (8·30)	9·82 (9·53)	4·46 (4·54)	4·04 (total)	29·7
4	VO^{2+}	Cu^{2+}	$-(CH_2)_2$	H_2O $n=2$	9·52 (9·83)	12·43 (12·26)	5·25 (5·40)	0·75 (per atom)	30·5
5	VO^{2+}	Cu^{2+}	$-(CH_2)_3$	H_2O $n=1$	9·28 (9·83)	12·98 (12·24)	5·12 (5·38)	0·77 (per atom)	30·5
6	VO^{2+}	Cu^{2+}	$-O-C_6H_4$	H_2O $n=1$	8·98 (9·30)	11·82 (11·58)	5·23 (5·10)	0·65 (per atom)	30·5
7	VO^{2+}	Pd^{2+}	$-(CH_2)_2$	H_2O $n=1$	9·15 (9·40)	20·13 (19·50)	5·32 (5·14)	1·38 (total)	31·0
8	VO^{2+}	Pd^{2+}	$-(CH_2)_3$	H_2O $n=2$	8·45 (8·87)	18·63 (18·43)	5·20 (4·87)	1·32 (total)	31·0
9	VO^{2+}	Pd^{2+}	$-O-C_6H_4$	—	8·23 (8·90)	17·89 (18·56)	4·98 (4·88)	1·15 (total)	30·0
10	Ni^{2+}	VO^{2+}	$-(CH_2)_2$	H_2O $n=1$	12·89 (13·43)	11·23 (11·67)	6·42 (6·40)	Completely diamagnetic	29·6
11	Ni^{2+}	VO^{2+}	$-(CH_2)_3$	H_2O $n=2$	10·53 (10·18)	9·92 (10·46)	5·78 (6·17)	3·64 (total)	29·5
12	Ni^{2+}	VO^{2+}	$-O-C_6H_4$	H_2O $n=2$	10·78 (10·45)	8·85 (9·08)	4·90 (5·07)	2·92 (total)	29·6
13	Cu^{2+}	VO^{2+}	$-(CH_2)_2$	H_2O $n=1$	11·82 (12·24)	8·93 (9·83)	4·89 (5·38)	1·01 (per atom)	27·6
14	Cu^{2+}	VO^{2+}	$-O-C_6H_4$	H_2O $n=4$	11·12 (10·82)	8·23 (8·70)	4·27 (4·77)	0·89 (per atom)	28·0
15	Cu^{2+}	Ni^{2+}	$-(CH_2)_2$	H_2O $n=2$	(12·45)	(11·50)	(5·49)	—	—
16	Cu^{2+}	Ni^{2+}	$-(CH_2)_3$	H_2O $n=2$	(12·12)	(11·19)	(5·34)	—	—
17	Ni^{2+}	Cu^{2+}	$-(CH_2)_2$	H_2O $n=2$	(11·50)	(12·45)	(5·49)	—	—
18	Ni^{2+}	Cu^{2+}	$-(CH_2)_3$	H_2O $n=2$	(11·19)	(12·12)	(5·34)	—	—
19	Cu^{2+}	Cu^{2+}	$-(CH_2)_2$	—	(26·52)	—	(5·85)	—	—
20	Cu^{2+}	Cu^{2+}	$-(CH_2)_3$	H_2O $n=2$	24·22 (24·68)	—	5·55 (5·44)	0·76 (per atom)	32·0

*We have also isolated bimetallic complexes with $M=VO^{2+}$, UO_2^{2+}, MoO_2^{2+}, Zn^{2+} and Cd^{2+} with anyone of these as M′.
†Calculated values are given in parentheses.

spin-free d^8-system along with a d^1-system without any spin-spin interaction in the complex $[(VOL)Ni(H_2O)_2]$. Electronic spectra also support the presence of (NiO_6)-chromophore in the complex. Similar observations were made when $M = Cu^{2+}$ and $M' = Ni^{2+}$. However, the heterobinuclear complexes (containing $M = VO^{2+}$ or Cu^{2+} and $M' = Cu^{2+}$ or VO^{2+}) showed reduced μ_{eff} values at room temperature (μ values were observed ~1·6 BM per molecule). This is an evidence (but not proof) of strong antiferromagnetic interactions between the $d^1(VO^{2+})$ and $d^9(Cu^{2+})$ systems, similar to that has been observed[2] in all analogous heterobinuclear species containing two paramagnetic ions. However, cryomagnetic studies are yet to be made by us.

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