

Preparation & Spectral & Magnetic Properties of Some Five-coordinate Binuclear Iron(III) Complexes

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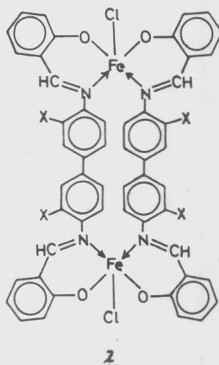
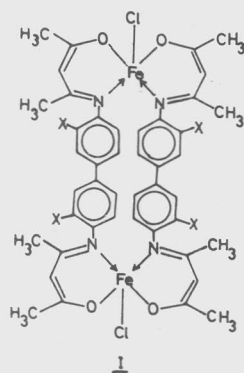
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Binuclear iron(III) complexes of tetradentate schiff base ligands, derived from the condensation of diamines with pentane-2,4-dione or salicylaldehyde, have been prepared and studied by magnetic and spectral techniques. The electronic spectral data and magnetic moment values together with Mössbauer data suggest a five-coordinate, square-pyramidal geometry for the iron centre.

Iron(III) complexes of schiff base ligands have been the subject of several studies¹⁻⁹. Among these are complexes with unusual coordination numbers and polynuclear complexes. Both six-coordinate and five-coordinate complexes are common. Many of the oxygen-bridged dimeric complexes show interesting magnetic properties due to antiferromagnetic coupling^{10,11}. Spectral and magnetic properties of the complexes have been used in identifying the geometry and other structural characteristics of these complexes.

In continuation of our investigations on binuclear systems, several binuclear iron(III) complexes have been synthesised using two types of binucleating ligand systems. These ligands have been obtained by condensing 4,4'-diaminobiphenyls with acetylacetone or salicylaldehyde. The possible structures of these complexes are shown in 1 and 2.



A, X=H
B, X=OCH₃
C, X=CH₃

Materials and Methods

The ligands in series 1 were prepared by refluxing a mixture of diamine (0.05 M), pentane-2,4-dione

(0.1 M) and one drop of conc. HCl in benzene (150 ml) for about 12 hr. Water was removed azeotropically and the reaction mixture on concentration and cooling gave the corresponding ligand. Series 2 ligands were synthesised by mixing warm methanolic solutions of diamine (0.05 M) and salicylaldehyde (0.1 M), which on cooling precipitated out the ligands as orange solids.

The iron(III) complexes were prepared by mixing warm solution of ligand in dichloromethane and anhydrous ferric chloride in methanol (1:1 molar ratio). The dark reddish-brown solution so obtained was concentrated to get highly impure material which was treated repeatedly with hexane to get the solid complex. Recrystallisation was done from acetone-hexane mixture.

The compounds were analysed for C, H and N by the microanalytical methods and for Fe by the oxine method¹². The analytical data for the iron compounds, with the expected values in brackets are: **1A** [C, 60.01 (60.37); H, 4.89 (5.03); N, 6.0 (6.40); Fe, 13.76 (13.89)]; **1B** [C, 57.50 (57.9); H, 4.92 (5.23); N, 5.10 (5.63); Fe, 12.56 (12.09)]; **1C** [C, 61.34 (61.89); H, 5.38 (5.58); N, 5.84 (6.01); Fe, 12.30 (12.99)]; **2A** [C, 64.20 (64.8); H, 3.42 (3.74); N, 5.44 (5.81); Fe, 13.09 (12.52)]; **2B** [C, 62.38 (62.07); H, 3.80 (4.06); N, 5.48 (5.17); Fe, 11.45 (11.04)]; **2C** [C, 65.61 (65.97); H, 4.01 (4.31); N, 5.10 (5.49); Fe, 11.26 (11.78)].

IR spectra were recorded on a Perkin Elmer 297 spectrophotometer. Molecular weight determinations were carried out by osmotic pressure method on a Knauer Osmometer. PAR 6001 Photo Acoustic Spectrometer was used for solid state electronic spectral measurements and CARY 17D or Shimadzu UV 200S instruments were used for recording solution spectra. Magnetic moment measurements were done by Gouy method on a Bruker BM-6 susceptibility set-

up. Mössbauer spectra were recorded employing a constant acceleration Elscint drive in conjunction with a multichannel analyzer (Promeda). In all cases, a 25 mCi $^{57}\text{Co}/\text{Rh}$ was used as source and sodium nitroprusside as the calibrant. Electrochemical studies were carried out on a PAR Model 370 electrochemistry system using a three electrode assembly.

Results and Discussion

The ligands were characterized by analytical and spectral methods before using them for the preparation of complexes. The ligands are binucleating and hence require two metal ions for coordination. The oxidation state of iron is satisfied by the presence of a negative ion, in this case a chloride ion. The presence of chloride has been established by the qualitative analysis of chloride in the complex. Molecular weight determinations were carried out in methanol for compounds of **1**. The values were very low (~ 150) which did not correspond to either mononuclear or binuclear species. It appears that the compound decomposes in this medium. These measurements could not be done for compounds of series **2** as they were insoluble in common organic solvents. The analytical data of the complexes agree well with their structural formulations. Conductivity measurements in acetonitrile and nitromethane gave results much lower than the values expected for 1:1 or 1:2 electrolytes.¹³ This implies that the chloride atoms are in the first coordination sphere. The identical behaviour of *A*, *B*, *C* complexes of both **1** and **2** series shows that OCH_3 group in *B* does not participate in any bond formation.

IR data

The IR spectra of both the ligands and complexes have a number of peaks in the region $1600\text{--}600\text{ cm}^{-1}$. A weak IR band at $\sim 960\text{ cm}^{-1}$ can be observed for pentane-2,4-dione based complexes. This band is not clearly defined for complexes of **2** series. For monomeric five-coordinate complexes of the type $\text{Fe}(\text{Salen Cl})_2\text{MeNO}_2$, a weak IR band appears in this region. On the other hand, for iron systems, where Fe—O—Fe type bonding exists (dimeric and six-coordinate), a strong IR band is observed^{2,14} at $\sim 850\text{ cm}^{-1}$. Fe—O—Fe type bonding results if the molecule is dimeric in nature or has oxo type bridges between the two metal centres. The latter possibility in both **1** and **2** can be ruled out because of the large internuclear distance. Metal-metal distance¹⁵ in binuclear copper(II) systems from the same ligand system has been found to be $\sim 12\text{ \AA}$. Absence of a strong IR band at $\sim 850\text{ cm}^{-1}$ shows the absence of Fe—O—Fe type bond and hence of dimer formation

Table 1—Spectral and Magnetic Data of the Iron(III) Complexes of the Types **1** and **2**

Compd	μ_{eff} (B.M.) ^a	Electronic spectra $\nu(\text{cm}^{-1})$		Mössbauer data (SNP)	
				δ (mm s^{-1})	Δ (mm s^{-1})
1A	5.86	b	20,000	0.65	0.59
1B	5.97	10,000	22,730	0.62	0.52
1C	6.03	11,235	23,810	0.62	0.58
2A	5.9	b	20,000	0.67	0.70
2B	6.10	b	20,000	0.67	0.70
2C	5.83	b	25,000	0.66	0.67

^aper metal atom

^bnot observed

thereby showing the absence of hexacoordination through sharing of an oxygen atom.

Magnetic moments

The room temperature magnetic moment values of the complexes are shown in Table 1. The μ_{eff} values are in the range 5.9–6.1 B.M. This clearly shows that the ground state is sextet with $S=5/2$. This ground state configuration is possible both for a five- or a six-coordinate geometry. The μ_{eff} values for the five-coordinate complexes^{6,14} ($\sim 5.9\text{ B.M.}$) overlap considerably with those of the six-coordinate complexes¹⁶ and hence these values alone cannot be taken as a criterion in identifying the geometry around the iron centres. However, iron(III) compounds of the type $\text{Fe}(\text{acac})_2\text{Cl}$ and $\text{Fe}(\text{Salen Cl})_2\text{MeNO}_2$, similar to the present complexes, are known to have five-coordinate square-pyramidal geometries with μ_{eff} values of $\sim 5.8\text{ B.M.}$ Comparing the present binuclear complexes with them, a similar five-coordinate square-pyramidal geometry can be suggested for these binuclear systems also. The near identical μ_{eff} values close to the spin-only value for $S=5/2$ also suggest the absence of strong metal-metal interaction. This is not surprising considering the large metal-metal separation ($\sim 12\text{ \AA}$), the nonplanarity of the biphenyl system and the noncoplanarity of the coordination sites and the metal centre. Binuclear copper complexes of comparable structure also do not show any significant antiferromagnetic interaction¹⁷. Variable temperature susceptibility measurements on one compound upto liquid nitrogen temperature did not show any deviation in its μ_{eff} values.

Spectral data

The electronic spectral band positions of all the iron complexes recorded in solid phase are shown in

Table 1. All of them have very intense bands at $\sim 27,000\text{ cm}^{-1}$ which are identified as originating from the ligand part of the compounds. In addition, for 1 type complexes, there is a weak band at $\sim 10,000\text{ cm}^{-1}$ and a strong shoulder at $\sim 20,000\text{ cm}^{-1}$. For 2 type complexes, only the shoulder at $\sim 20,000\text{ cm}^{-1}$ is observed. For six-coordinate iron(III) complexes all *d-d* transitions are forbidden and hence generally absorption peaks are not observed. For five coordinate complexes, two reasonably intense *d-d* transitions are expected^{18,19} at $\sim 20,000\text{ cm}^{-1}$ and $25,000\text{ cm}^{-1}$. The positions can vary depending on the ligand systems.

Mössbauer data

All the compounds show an asymmetric Mössbauer doublet at room temperature. The striking feature of the Mössbauer spectrum of the square-pyramidal complexes is the distinct asymmetry exhibited by the two lines⁴. This happens since long spin-lattice relaxation times are associated with ^6S electronic ground states; spin-spin relaxation dominates the behaviour of ferric compounds. When these relaxation times are comparable with the Larmor precession times, a broadening of the peak or asymmetry in peak heights is noticeable²⁰. The isomer shift and quadrupole split values for the complexes are collected in Table 1. The magnitude of Δ is 0.52 to 0.70 mm s^{-1} . For some comparable five-coordinate iron systems, the values in mm s^{-1} are^{14,20}: $\text{Fe}(\text{acac})_2\text{Cl}$, 1.0 ; $[\text{Fe}(\text{Salen})\text{Cl}]\text{MeCN}$, 0.83 ; $[\text{Fe}(\text{Salen})\text{Br}]\text{MeCN}$, 0.54 . They all have square-pyramidal geometry. For six-coordinate dimeric iron complexes¹⁶ of the type $[\text{Fe}(\text{Salen})\text{Cl}]_2$ having $\text{Fe}-\text{O}-\text{Fe}$ type bridge, Δ value is $\sim 1.45\text{ mm s}^{-1}$. Although there is overlap in the Δ values of five- and six-coordinate geometries, the Mössbauer data are more in agreement with a five-coordinate geometry than a six-coordinate geometry.

Liquid nitrogen temperature Mössbauer spectra have been recorded for sample systems, **1B**, **1C**, **2A** and **2B**. As the temperature is lowered, the asymmetry of the peaks increases and at liquid nitrogen temperature only a broad peak is observed. This in general can be explained as due to an increase in the spin-relaxation times.

Cyclic voltammetric (CV) experiments were tried in acetonitrile for all the complexes. However, they showed only ill-defined CV profiles both in the negative and positive potential ranges. It was not possible to derive any conclusions from these experiments.

The spectral and magnetic data, although they support a five-coordinate geometry, can also be

discussed on the basis of six-coordinate geometry. However, the six-coordinate geometry is not favoured for the following reasons: (i) valency requirement of the central iron atom does not permit the presence of any anion at the sixth coordination position and the analytical data do not support presence of any neutral molecules at this position, (ii) six-coordination by sharing of a ligand oxygen by another molecule (dimer formation) similar to that in $[\text{Fe}(\text{Salen})\text{Cl}]_2$ is discounted due to the absence of $\text{Fe}-\text{O}-\text{Fe}$ IR band and on the basis of other experimental data, and (iii) comparable systems like $\text{Fe}(\text{acac})\text{Cl}$ and $\text{Fe}(\text{Salen})\text{Cl}.\text{MeCN}$, etc., have five-coordinate square-pyramidal geometry. These considerations together with spectral and magnetic data presented in the earlier sections support a five-coordinate geometry for the iron centre in these binuclear complexes.

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