

## X-ray Diffraction, Magnetic Moments, Electron Spin Resonance & Other Spectral Properties of Complexes of Iron(III) Halides with Bis(tertiaryphosphine/arsine Oxides)

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Received 26 November 1984; accepted 18 December 1984

A series of complexes of bis(tertiaryphosphine/arsine oxides)(L-L) with iron(III) chloride and bromide of general composition,  $[\text{Fe}(\text{L-L})_2\text{Cl}][\text{FeCl}_4]_2$  and  $[\text{Fe}(\text{L-L})_2\text{Br}_2][\text{FeBr}_4]$  have been synthesized. These have been characterized with the help of elemental analysis, spectral data [IR, far IR, UV-visible (solid), ESR], conductivity and TGA data, magnetic moments and powder X-ray diffraction patterns. The complexes are high-spin exhibiting normal magnetic behaviour.

In our previous paper<sup>1</sup>, we described the preparation and characterization of the complexes of 1,1-methylene(mdpo)-, 1,2-ethylene(edpo)-, 1,4-tetramethylene(tmdpo)- and 1,6-hexamethylene(hmdpo)-bis(diphenylphosphine oxides) with iron(III) chloride and nitrate. As an extension the complexes of mdpo, edpo, tmdpo and hmdpo with iron(III) bromide and those of edao and tmdao (arsine

analogues of edpo and tmdpo) with iron(III) chloride and bromide have now been prepared and characterized.

While the preparation of bis(tertiaryphosphine oxide) derivatives has been reported earlier, the arsine analogues, edao (m.p. 177-78°) and tmdao (m.p. 254°) were prepared by the method reported earlier<sup>1,2</sup>. The methods of preparation of complexes and the description of various techniques employed were the same as reported earlier<sup>1</sup>.

The iron(III) chloride complexes of edao and tmdao are yellow in colour, have 3:2 metal to ligand ratio and have been formulated as  $[\text{Fe}(\text{L-L})_2\text{Cl}][\text{FeCl}_4]_2$  on the basis of conductance measurements in nitrobenzene (Table 1). The iron(III) bromide complexes have 1:1 (metal-ligand) stoichiometry and are either red or reddish brown in colour. Their molar conductances in the range 16-25 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> support the formulation,  $[\text{Fe}(\text{L-L})_2\text{Br}_2][\text{FeBr}_4]$  (Table 1)<sup>1,3,4</sup>. The complexes decompose around the melting points of the ligands.

In the IR spectra of the complexes, the  $\nu(\text{PO})$  and  $\nu(\text{AsO})$  modes of the free ligands undergo shift to lower wavenumbers on coordination,  $\Delta\nu$  being 32-65 cm<sup>-1</sup> and 30-35 cm<sup>-1</sup> respectively. However,  $\nu(\text{As-C})_{\text{aromatic}}$  remains unaffected probably due to the presence of the bulky polarizable arsenic atoms which may satisfy the acidic requirements of the metal via the oxygen

Table 1—Elemental Analyses, Magnetic Moments, Molar Conductances and ESR g-Values of the Complexes

| Complex   | m.p.<br>(°C) | Found (Calc.) %  |                |                  | $\Lambda_m$<br>(ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> ) | $\mu_{\text{eff}}$<br>(B.M.) | $g_{\text{eff}}$  |
|---|--------------|------------------|----------------|------------------|---|------------------------------|-------------------|
|   |              | C                | H              | Fe               |   |                              |                   |
| $[\text{Fe}(\text{edao})_2\text{Cl}][\text{FeCl}_4]_2$                                      | 148          | 41.75<br>(40.97) | 2.62<br>(3.15) | 10.93<br>(11.02) | 55  | 6.02                         | 2.02              |
| $[\text{Fe}(\text{tmdao})_2\text{Cl}][\text{FeCl}_4]_2$                                     | 128          | 43.16<br>(42.52) | 4.45<br>(3.54) | 10.01<br>(10.60) | 37  | 5.80                         | 2.02<br>4.18      |
| $[\text{Fe}(\text{mdpo})_2\text{Br}_2][\text{FeBr}_4] \cdot 2\text{H}_2\text{O}^{\text{a}}$ | 298(d)       | 40.70<br>(41.90) | 3.44<br>(3.44) | 8.12<br>(7.67)   | 25  | 6.06                         | 2.05              |
| $[\text{Fe}(\text{edpo})_2\text{Br}_2][\text{FeBr}_4]$                                      | 265          | 42.25<br>(42.94) | 3.43<br>(3.30) | 7.85<br>(7.71)   | 25  | 6.14                         | 2.04              |
| $[\text{Fe}(\text{tmdpo})_2\text{Br}_2][\text{FeBr}_4]$                                     | 204          | 44.01<br>(44.50) | 3.46<br>(3.60) | 7.96<br>(7.42)   | 17  | 6.10                         | 2.00,<br>6.64     |
| $[\text{Fe}(\text{hmdpo})_2\text{Br}_2][\text{FeBr}_4]$                                     | 114          | 46.38<br>(46.03) | 4.18<br>(4.09) | 7.60<br>(7.16)   | 16  | 6.10                         | 2.04,<br>5.66     |
| $[\text{Fe}(\text{edao})_2\text{Br}_2][\text{FeBr}_4] \cdot 2\text{H}_2\text{O}^{\text{a}}$ | 176          | 37.81<br>(37.80) | 3.72<br>(3.12) | 7.14<br>(6.73)   | 19  | 5.82                         | 2.14 <sup>b</sup> |
| $[\text{Fe}(\text{tmdao})_2\text{Br}_2][\text{FeBr}_4]$                                     | 102          | 39.27<br>(39.92) | 3.84<br>(3.82) | 7.03<br>(6.65)   | 17  | 6.10                         | —                 |

(a) Water is present as lattice water.

(b) Five-line spectrum with g centered at 2.14.

donor atom. The water present in two complexes is simply lattice water as shown by IR and TG data.

In the far IR spectra of the complexes of edao and tmdao with iron(III) chloride, the  $\nu_3$  modes characteristic of  $[\text{FeCl}_4]^-$  appear around  $370\text{ cm}^{-1}$  (see ref. 3,4). The cations,  $[\text{Fe}(\text{L-L})_2\text{Cl}]^{2+}$  show  $\nu(\text{Fe-Cl})$  modes at  $240\text{--}245\text{ cm}^{-1}$  indicating that chlorine is acting as a bridge and the coordination number is six instead of five. Similarly, the  $\nu_3$  modes of  $[\text{FeBr}_4]^-$  appear at  $280\text{--}285\text{ cm}^{-1}$  and  $\nu_{\text{as}}(\text{Fe-Br})$  due to  $[\text{Fe}(\text{L-L})_2\text{Br}_2]^+$  occur in the range  $210\text{--}230\text{ cm}^{-1}$  indicating *trans* disposition of the bromine atoms in agreement with literature<sup>3-5</sup>. No tentative assignment of  $\nu(\text{Fe-O})$  modes was possible<sup>4,6</sup>.

The powder X-ray diffraction patterns of the complexes of iron(III) bromide indicate them to be crystalline but not isomorphous. However, the edao and tmdao complexes of iron(III) chloride are isomorphous. All the complexes are paramagnetic and  $\mu_{\text{eff}}$  values lie in the range 5.80-6.14 B.M. characteristic of high-spin  $d^5$ -configuration<sup>3,4</sup>. The reflectance spectra of the complexes show spin-forbidden transitions  ${}^6A_1 \rightarrow {}^4T_1(G)$ ,  ${}^4T_2(G)$ ;  ${}^4A_1(G)$ ,  ${}^4E(G)$ ; and  ${}^4T_2(D)$  in the range  $11600\text{--}18500\text{ cm}^{-1}$  as weak to medium intensity bands, characteristic of  $[\text{FeX}_4]^-$  moiety. The ligand to metal charge transfer bands occur in the region  $18900\text{--}26300\text{ cm}^{-1}$  as strong bands<sup>1,3,5,7-10</sup>.

The ESR spectrum of the complex of tmdao with iron(III) chloride displays a strong signal at 3295 G with  $g_{\text{eff}} = 2.02$  supporting the presence of tetrahedral ion  $[\text{FeCl}_4]^-$  (ref. 4). The other signal of medium intensity occurs at 1625 G with  $g_{\text{eff}} = 4.18$  indicating rhombic symmetry for the cation,  $[\text{Fe}(\text{L-L})_2\text{Cl}]^{2+}$ . The complex of edao with iron(III) chloride, however, shows a strong broad signal at 3290 G with  $g_{\text{eff}} = 2$ . The other signal with  $g = 4.27$ , often a weak signal, has not been detected in the spectrum<sup>11</sup>. However, the isomorphism with the complex of tmdao as shown by X-ray; supports a structure similar to that of  $[\text{Fe}(\text{tmdao})_2\text{Cl}][\text{FeCl}_4]_2$ .

The complex of tmdpo with iron(III) bromide shows a strong signal at a  $g$ -value of  $\sim 2.00$ , corresponding to the anion,  $[\text{FeBr}_4]^-$  and a weak signal with  $g$ -value of 6.64 corresponding to *trans*-octahedral cation,  $[\text{Fe}(\text{tmdpo})_2\text{Br}_2]^+$  (see ref. 1). Similarly, the ESR spectrum of the complex of hmdpo exhibits signals with  $g = 2.04$  and 5.66. It may be noted that the complex  $[\text{Fe}(\text{hmdpo})_2\text{Cl}_2][\text{FeCl}_4]$  also gave similar  $g$ -values<sup>1</sup>. The ESR spectra of the complexes of mdpo and edpo with iron(III) bromide exhibit only one strong broad signal having  $g_{\text{eff}}$  value of 2.05. This implies that in the formulation,  $[\text{Fe}(\text{L-L})_2\text{Br}_2][\text{FeBr}_4]$ , there must be exchange interaction between the cation and the anion as observed in similar complexes reported in literature<sup>1,2</sup>. The ESR spectrum of the complex of edao displays a five-line pattern with  $g$ -value centered at 2.14 indicating symmetric environment around the iron atom with less zero-field splitting.

One of us (HSC) is thankful to the Guru Nanak Dev University for research facilities and to the UGC, New Delhi for the award of a teacher fellow. We are also thankful to Prof G Mehta of the University of Hyderabad for the ESR spectra.

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