

## Chemistry of Iron Complexes. Part 1. Synthesis, Characterization, and Structures of Iron(III) Complexes with Bis(tertiary phosphine oxides) †

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Bidentate bis(tertiary phosphine oxides) (L-L) such as *PP'*-methylene- (mdpo), *PP'*-ethylene- (edpo), *PP'*-tetramethylene- (tmdpo), and *PP'*-hexamethylene-bis(diphenylphosphine oxides) (hmdpo) on reaction with iron(III) chloride or nitrate in suitable organic solvents yield complexes of the types:  $[\text{Fe}(\text{L-L})_2\text{Cl}_2][\text{FeCl}_4] \cdot x\text{H}_2\text{O}$  ( $x = 0$  for all except hmdpo),  $[\text{Fe}(\text{L-L})(\text{ONO}_2)_3]$  (L-L = tmdpo or hmdpo),  $[\text{Fe}(\text{L-L})_2(\text{ONO}_2)_2][\text{NO}_3] \cdot \text{H}_2\text{O}$  (L-L = edpo), and  $[\text{Fe}_2(\text{L-L})_3(\text{ONO}_2)_4][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$  (L-L = mdpo). These complexes have been characterized by elemental analyses, i.r., far-i.r., u.v.-visible, e.s.r., and Mössbauer spectral data, molar conductance, thermogravimetric analysis, magnetic moments, and X-ray diffraction data. The cation  $[\text{Fe}(\text{L-L})_2\text{Cl}_2]^+$  has been assigned a *trans*-octahedral structure. The nitrate complex of mdpo has a dimeric trigonal bipyramidal cation while the complex of edpo has a *cis*-octahedral structure. The nitrate complexes of tmdpo and hmdpo also have trigonal bipyramidal structure.

Tertiary phosphines and their chalcogenides have been frequently used for the study of the co-ordination chemistry of a number of metal ions.<sup>1-3</sup> Tertiary phosphine oxides are finding extensive use in the extraction and separation of metal ions from aqueous acidic media such as for the lanthanides and actinides.<sup>4</sup> Although monotertiary-phosphine and -arsine oxides have been used to some extent for studying the co-ordination chemistry of iron(II) and iron(III), very little work has appeared in the literature dealing with their bidentate analogues.<sup>2,3,5</sup> Furthermore, iron-containing systems have great industrial and biological importance.<sup>5</sup> The lack of study on the co-ordination chemistry of iron has been chiefly due to its complex electronic spectra and hydrolytic nature of the complexes. However, availability of techniques like Mössbauer, e.s.r. etc. encourages detailed study on the complex chemistry of this important metal. In this paper, the new complexes of iron(III) chloride and nitrate with *PP'*-methylene-, *PP'*-ethylene-, *PP'*-tetramethylene-, and *PP'*-hexamethylene-bis(diphenylphosphine oxide) (mdpo, edpo, tmdpo, and hmdpo respectively) are described.

### Experimental

**Ligands.**—The ligands were prepared by the oxidation of the ditertiary phosphines with 30% hydrogen peroxide followed by recrystallization from a 1 : 1 methanol-water mixture.<sup>2</sup> (The melting points of the ligands are: mdpo, 176–178; edpo, 256–258; tmdpo, 246–247; and hmdpo, 196–197 °C.<sup>2,6</sup>)

**Complexes.**—The complexes were prepared by the addition of a hot solution of the ligand in chloroform to a hot iron(III) salt solution in an acetone-benzene mixture (5 : 1) (chloride) and absolute alcohol (nitrate). A yellow or red thick liquid separated out which solidified on treatment with light petroleum (b.p. 40–60 °C). The solid was washed several times with a mixture of the solvents used in the preparation.

**Techniques used.**—Carbon and hydrogen analyses were from the University College of Science, Calcutta, India. Iron was estimated spectrophotometrically.<sup>7</sup> The molar conductances of millimolar solutions of the complexes in nitrobenzene were measured with a Toshniwal conductivity bridge, type CIOI/02A. The i.r. spectra of the ligands as well as complexes were recorded in the range 4 600–650 cm<sup>-1</sup> (in

Nujol mulls or KBr pellets) using a spectromom-2000 instrument. The reflectance spectra (300–1 000 nm) of the complexes were recorded with a VSU-2P spectrophotometer. The far-i.r. spectra of the chloride complexes in the range 4 000–200 cm<sup>-1</sup> were recorded by Defence R and D Centre, Gwalior and those of the nitrate complexes in the range 4 000–100 cm<sup>-1</sup> by I.I.T., Madras. Magnetic susceptibility measurements on solid samples were carried out at room temperature using Gouy's method. The apparatus was calibrated with Hg[Co(NCS)<sub>4</sub>] and diamagnetic corrections were made employing Pascal's constants.<sup>8</sup> Mössbauer spectra were recorded with a MBS-35 Mössbauer spectrometer (ECIL, India) having a multichannel analyser (480 channels, MCA-28B type). The calibration was carried out with sodium nitroprusside at 25 ± 2 °C. The thermogravimetric analysis (t.g.a.) of the complexes was carried out with an instrument supplied by FCI unit Sindri, India. X-Ray photographs of the powdered samples were taken using a Debye-Scherrer camera of radius 57.3 mm; Cu-K<sub>α</sub> X-rays from a Phillips generator, type PW-1720 were used. The X-band (9.3 GHz) e.s.r. of powdered samples were recorded at the University of Hyderabad.

### Results and Discussion

Most of the complexes have a metal to ligand ratio of 1 : 1 while two complexes correspond to a 1 : 2 and 2 : 3 ratio (Table 1). The chloride complexes are yellow, whereas the nitrate complexes are light brown. The melting points of the complexes generally fall in the range of their respective ligands except that of hmdpo. The chloride complexes show a molar conductance of 11–16 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> in nitrobenzene. These values are less than expected for a 1 : 1 electrolyte, but are not too low to declare the complexes as non-electrolytes. Thus the complexes may be formulated as  $[\text{Fe}(\text{L-L})_2\text{Cl}_2]^+[\text{FeCl}_4]^-$  (L-L = bidentate ligand). Similar types of complexes have been reported with unidentate tertiary-phosphine and -arsine oxides and their chloride complexes also showed lower  $\Lambda_m$  values than those expected for 1 : 1 electrolytes.<sup>9,10</sup>

The nitrate complexes of mdpo and edpo have been formulated as  $[\text{Fe}_2(\text{mdpo})_3(\text{ONO}_2)_4][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$  and  $[\text{Fe}(\text{edpo})_2(\text{ONO}_2)_2][\text{NO}_3] \cdot \text{H}_2\text{O}$  on the basis of molar conductance. The corresponding complexes of tmdpo and hmdpo show conductances of 10 and 12 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, respectively and may be formulated as  $[\text{Fe}(\text{L-L})(\text{ONO}_2)_2][\text{NO}_3]$  (Table 2).

† Non-S.I. units employed: 1 G = 10<sup>-4</sup> T; B.M. ≈ 9.27 × 10<sup>-24</sup> A m<sup>2</sup>.

**Table 1.** Elemental analyses, m.p., and i.r. spectra (4 000–650 cm<sup>-1</sup>) of the complexes

Complex	Analysis <sup>a</sup> (%)			M.p./ °C	I.r. <sup>b</sup> /cm <sup>-1</sup>	
	C	H	Fe		v(P-C)	v(P=O)
[Fe(mdpo) <sub>2</sub> Cl <sub>2</sub> ][FeCl <sub>4</sub> ]	50.80 (51.80)	4.40 (3.90)	10.45 (9.70)	268 <sup>c</sup>	1 105s,sp	1 145s,sp 1 180m,sp
[Fe(edpo) <sub>2</sub> Cl <sub>2</sub> ][FeCl <sub>4</sub> ]	51.70 (52.65)	3.55 (4.05)	9.70 (9.45)	270 <sup>c</sup>	1 110s,sp	1 140s,sp 1 168s,sp
[Fe(tmdpo) <sub>2</sub> Cl <sub>2</sub> ][FeCl <sub>4</sub> ]	55.55 (54.10)	5.10 (4.50)	8.80 (9.00)	212	1 110s,sp	1 146s,sp 1 162s,sp
[Fe(hmdpo) <sub>2</sub> Cl <sub>2</sub> ][FeCl <sub>4</sub> ] 2H <sub>2</sub> O	54.30 (54.00)	5.20 (5.10)	8.30 (8.40)	112	1 105s,sp	1 139s,sp
[Fe <sub>2</sub> (mdpo) <sub>3</sub> (ONO <sub>2</sub> ) <sub>4</sub> ]- [NO <sub>3</sub> ] <sub>2</sub> ·2H <sub>2</sub> O	50.15 (50.80)	4.65 (3.95)	6.50 (6.35)	221 <sup>c</sup>	1 080s,sp	1 145s,sp 1 170m,sp
[Fe(edpo) <sub>2</sub> (ONO <sub>2</sub> ) <sub>2</sub> ]- [NO <sub>3</sub> ] <sub>2</sub> ·H <sub>2</sub> O	55.10 (55.70)	3.55 (4.45)	5.50 (5.00)	264	1 100s,sp	1 140s,sp 1 170 (sh)
[Fe(tmdpo)(ONO <sub>2</sub> ) <sub>3</sub> ]	47.45 (48.00)		8.40 (8.00)	121 <sup>c</sup>	1 090s,sp	1 134s,sp
[Fe(hmdpo)(ONO <sub>2</sub> ) <sub>3</sub> ]	51.80 (49.40)	5.05 (4.40)	7.05 (7.70)	140 <sup>c</sup>	1 090s,sp	1 138s,sp

<sup>a</sup> Calculated values in parentheses. <sup>b</sup> s = Strong, m = medium, sp = sharp, and sh = shoulder. <sup>c</sup> With decomposition.

**Table 2.** Far-i.r., Mössbauer,<sup>a</sup> magnetic moments, and molar conductance data

Complex	v(Fe-X) <sup>b,c</sup> cm <sup>-1</sup>	δ/mm s <sup>-1</sup>	Δ/mm s <sup>-1</sup>	μ <sub>eff.</sub> /B.M.	Λ <sub>m</sub> /ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
[Fe(mdpo) <sub>2</sub> Cl <sub>2</sub> ][FeCl <sub>4</sub> ]	380s,br 280m	0.60		6.10	11
[Fe(edpo) <sub>2</sub> Cl <sub>2</sub> ][FeCl <sub>4</sub> ]	375s,sp 280m	0.53		5.87	16
[Fe(tmdpo) <sub>2</sub> Cl <sub>2</sub> ][FeCl <sub>4</sub> ]	375s,sp 280m	0.63		6.10	16
[Fe(hmdpo) <sub>2</sub> Cl <sub>2</sub> ][FeCl <sub>4</sub> ] 2H <sub>2</sub> O	375s,sp 280m	<i>d</i>		6.02	15
[Fe(edpo) <sub>2</sub> (ONO <sub>2</sub> ) <sub>2</sub> ][NO <sub>3</sub> ] <sub>2</sub> ·H <sub>2</sub> O	286m,br 325m,br 284m,sp	<i>d</i>		5.94	20
[Fe(tmdpo)(ONO <sub>2</sub> ) <sub>3</sub> ]	258	0.58	0.67	6.00	10
[Fe(hmdpo)(ONO <sub>2</sub> ) <sub>3</sub> ]	270m,br 276m,br	<i>d</i>		6.05	12

<sup>a</sup> δ Values are relative to sodium nitroprusside. <sup>b</sup> X = Cl in the case of the chlorides and ONO<sub>2</sub> in the nitrates. <sup>c</sup> Other bands due to [FeCl<sub>4</sub>]<sup>-</sup> are either Raman active (~335 cm<sup>-1</sup>) or fall below 200 cm<sup>-1</sup>. <sup>d</sup> Poor absorption.

In the i.r. spectra, the v(PO) bands of free mdpo, edpo, tmdpo, and hmdpo occur at 1 205, 1 192 (doublet); 1 190, 1 180 (doublet); and 1 182 and 1 185 cm<sup>-1</sup> respectively while in the corresponding complexes v(PO) fall in the range 1 134–1 180 cm<sup>-1</sup> (either as doublets or singlets, Table 1). A decrease of the order of 22–52 cm<sup>-1</sup> is indicative of co-ordination through the oxygen atoms. The v(P-C) aromatic bands in the free ligands which lie in the range 1 125–1 130 cm<sup>-1</sup> show a negative shift of 20–35 cm<sup>-1</sup> on complexation which is somewhat more pronounced in the nitrate complexes than in the chloride complexes.<sup>11,12</sup> However, Sandhu and Sandhu<sup>13,14</sup> did not observe any shift in v(P-C) in edpo and tmdpo on complexation with cobalt(II) or nickel(II) halides. The presence of lattice water in the complexes is indicated by a broad band, v(OH), around 3 300–3 200 cm<sup>-1</sup> and δ(HOH) at 1 650 cm<sup>-1</sup> which was confirmed by t.g.a. data.

In the far-i.r. spectra, the strong v(Fe-Cl) bands in the range 375–380 cm<sup>-1</sup> are indicative of the characteristic [FeCl<sub>4</sub>]<sup>-</sup> anion which supports the formulation of the structure as [Fe(L-L)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>[FeCl<sub>4</sub>]<sup>-</sup>. The bands at 280 cm<sup>-1</sup> have been assigned as ν<sub>asym</sub>(Fe-Cl) in the *trans*-[Fe(L-L)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> system (Table 2).<sup>15</sup> On the basis of this formulation, two peaks corresponding to the octahedral cation [Fe(L-L)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>, and the

tetrahedral anion, [FeCl<sub>4</sub>]<sup>-</sup>, are expected in the Mössbauer spectrum. However, the Mössbauer spectra of these complexes show single broad peaks having isomer shift (δ) values in the range 0.53–0.63 mm s<sup>-1</sup> characteristic of high-spin iron(III) complexes. The two-site nature of these compounds has been obscured due to line-broadening which is always observed in high-spin iron(III) complexes. No bands can be unequivocally assigned as v(Fe-O) in agreement with previous findings for analogous complexes in the literature<sup>10,16</sup> (Table 2).

In the nitrate complexes of mdpo and edpo, bands occur in the range 1 330–1 340 cm<sup>-1</sup> which support the presence of ionic nitrates. No such band appeared in the complexes of tmdpo and hmdpo.<sup>10,17–20</sup> All these complexes show a ν<sub>3</sub> band splitting (1 395–1 260 cm<sup>-1</sup>) and the magnitude of splitting indicated that the nitrates are unidentate. Thus the complexes of tmdpo and hmdpo do not contain ionic nitrate and their Λ<sub>m</sub> values of 10 and 12 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> respectively appear to be due to ionization of the complexes in nitrobenzene. In the far-i.r. spectra, each nitrate complex shows two bands in the range 258–325 cm<sup>-1</sup> attributable to v(Fe-ONO<sub>2</sub>) in agreement with a similar assignment to the complex, [Fe(OPPh<sub>3</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>], which has a *trans* trigonal-bipyramidal structure.<sup>10</sup> The

**Table 3.** Electronic absorption bands ( $\text{cm}^{-1}$ ) of the complexes

Complex	<i>d-d</i> bands	Assignment	Charge-transfer bands
[Fe(mdpo) <sub>2</sub> Cl <sub>2</sub> ][FeCl <sub>4</sub> ]	19 230 (sh)	<sup>6</sup> A <sub>1</sub> → <sup>4</sup> A <sub>1</sub> (G), <sup>4</sup> E(G)	23 270s, br, 28 570m
[Fe(edpo) <sub>2</sub> Cl <sub>2</sub> ][FeCl <sub>4</sub> ]	19 230 (sh)	<sup>6</sup> A <sub>1</sub> → <sup>4</sup> A <sub>1</sub> (G), <sup>4</sup> E(G)	25 000s, br
[Fe(tmdpo) <sub>2</sub> Cl <sub>2</sub> ][FeCl <sub>4</sub> ]	20 850w	<sup>6</sup> A <sub>1</sub> → <sup>4</sup> T <sub>2</sub> (D)	23 270s, 26 310s, 27 780 (sh)
[Fe(hmdpo) <sub>2</sub> Cl <sub>2</sub> ][FeCl <sub>4</sub> ·2H <sub>2</sub> O]	20 850w	<sup>6</sup> A <sub>1</sub> → <sup>4</sup> T <sub>2</sub> (D)	23 270s, 26 310s, 27 780 (sh)
[Fe <sub>2</sub> (mdpo) <sub>3</sub> (ONO <sub>2</sub> ) <sub>4</sub> ][NO <sub>3</sub> ] <sub>2</sub> ·2H <sub>2</sub> O	17 540w	<sup>6</sup> A <sub>1</sub> → <sup>4</sup> T <sub>2</sub> (G)	25 670s, 27 020 (sh)
	20 410w	<sup>6</sup> A <sub>1</sub> → <sup>4</sup> T <sub>2</sub> (D)	
[Fe(edpo) <sub>2</sub> (ONO <sub>2</sub> ) <sub>2</sub> ][NO <sub>3</sub> ]			21 740s, 23 270w, 26 310s
[Fe(tmdpo) <sub>2</sub> (ONO <sub>2</sub> ) <sub>3</sub> ]			21 740s, 23 270w, 26 310s
[Fe(hmdpo)(ONO <sub>2</sub> ) <sub>3</sub> ]	16 000w	<sup>6</sup> A <sub>1</sub> → <sup>4</sup> T <sub>2</sub> (G)	25 000s
	17 540w		
	20 410m	<sup>6</sup> A <sub>1</sub> → <sup>4</sup> T <sub>2</sub> (D)	

**Table 4.** Main bands in X-ray diffraction powder patterns of the complexes

Complex	<i>d</i> -lines <sup>*</sup> /Å
[Fe(mdpo) <sub>2</sub> Cl <sub>2</sub> ][FeCl <sub>4</sub> ]	8.57(35), 7.71(40), 5.93(10), 5.14(20), 4.535(100), 4.28(30), 3.85(5), 3.67(30), 3.35(20), 2.86(50)
[Fe(edpo) <sub>2</sub> Cl <sub>2</sub> ][FeCl <sub>4</sub> ]	9.071(60), 8.116(65), 6.425(80), 5.392(35), 4.819(40), 4.307(70), 4.283(75), 3.725(50), 3.505(10), 3.352(20), 2.977(15), 2.659(90), 2.417(80), 2.281(10), 2.154(20), 1.623(75), 1.460(35)
[Fe(tmdpo) <sub>2</sub> Cl <sub>2</sub> ][FeCl <sub>4</sub> ]	7.559(30), 6.590(40), 5.507(5), 4.509(50), 4.168(20), 3.725(10), 2.545(60), 2.271(50), 2.142(30), 2.040(25), 1.554(50)
[Fe(hmdpo) <sub>2</sub> Cl <sub>2</sub> ][FeCl <sub>4</sub> ·2H <sub>2</sub> O]	2.649(70), 2.402(60), 2.241(40), 2.13(10), 1.627(70), 1.452(20), 1.346(10)
[Fe(edpo) <sub>2</sub> (ONO <sub>2</sub> ) <sub>2</sub> ][NO <sub>3</sub> ] <sub>2</sub> ·H <sub>2</sub> O	8.380(50), 6.704(60), 5.140(80), 4.911(40), 4.673(45), 4.483(40), 4.331(45), 4.016(50), 3.914(45), 3.473(50), 3.281(45), 2.315(60), 2.136(70), 2.013(50), 1.932(30), 1.827(20), 1.698(40), 1.455(50)
[Fe(tmdpo)(ONO <sub>2</sub> ) <sub>3</sub> ]	7.998(30), 4.911(40), 4.356(50), 3.914(60), 3.725(10), 3.521(15), 3.382(10), 3.109(20), 2.877(15), 2.672(95), 2.448(10), 2.387(90), 2.248(80), 2.142(60), 2.034(10), 1.740(10), 1.616(90), 1.515(20), 1.440(75), 1.353(10), 1.307(10)
[Fe(hmdpo)(ONO <sub>2</sub> ) <sub>3</sub> ]	5.507(10), 3.761(10), 3.569(20), 3.047(10), 2.845(5), 2.696(20), 2.659(100), 2.440(10), 2.365(95), 2.216(90), 2.118(40), 2.029(10), 1.908(30), 1.736(10), 1.616(95), 1.447(80), 1.346(20), 1.302(10)

\* Intensities are given in parentheses.

Mössbauer spectrum of the nitrate complex of mdpo shows a doublet with  $\delta$  0.56  $\text{mm s}^{-1}$  and  $\Delta$  0.70  $\text{mm s}^{-1}$  which indicates that the cation [Fe<sub>2</sub>(mdpo)<sub>3</sub>(ONO<sub>2</sub>)<sub>4</sub>]<sup>2+</sup> probably has a dimeric trigonal-bipyramidal structure involving bridging through one of the ligands.<sup>21</sup> The nitrate complex of tmdpo also shows a doublet with  $\delta$  and quadrupole splitting ( $\Delta$ ) values of 0.58 and 0.67  $\text{mm s}^{-1}$  respectively, which supports a trigonal-bipyramidal structure (Table 2). The nitrate complex of hmdpo did not show a Mössbauer absorption, but probably has a structure analogous to that of tmdpo. The complex of edpo also did not show a Mössbauer absorption and it is likely that the cation [Fe(edpo)<sub>2</sub>(ONO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> has an octahedral structure. It may be noted here that Cox *et al.*<sup>22</sup> could not observe Mössbauer spectra of iron(III) nitrate complexes with N-donors.

Magnetic moments ( $\mu_{\text{eff.}}$ ) of the chloride complexes lie in the range 5.87–6.10 B.M. while those of nitrate complexes in the range 5.86–6.05 B.M. These data conform to the high-spin *d*<sup>5</sup> configuration (Table 2).<sup>5</sup> The charge-transfer bands have been assigned in the range 21 740–28 570  $\text{cm}^{-1}$  which dominate the electronic spectrum. The *d-d* bands are fewer in number than expected and some appear to have been masked or undetected by the instrument (Table 3).<sup>9a,23-27</sup> The chloride complexes show transitions at 19 230  $\text{cm}^{-1}$  [<sup>6</sup>A<sub>1</sub> → <sup>4</sup>A<sub>1</sub>(G), <sup>4</sup>E(G)] and 20 850  $\text{cm}^{-1}$  [<sup>6</sup>A<sub>1</sub> → <sup>4</sup>T<sub>2</sub>(D)] which are characteristic of the [FeCl<sub>4</sub>]<sup>-</sup> ion.

The X-ray powder diffraction patterns (Table 4) show that the compounds are crystalline but not isomorphous with one another.

The X-band (9.3 GHz) e.s.r. spectrum of the chloride complex of hmdpo shows a very strong peak at 3 225 G having  $g_{\text{eff.}} = 2.06$  and another weak peak at 1 100 G having  $g_{\text{eff.}} = 6.04$ . The former value of  $g_{\text{eff.}}$  (2.06) corresponds to the [FeCl<sub>4</sub>]<sup>-</sup> group and the latter (6.04) to the *trans*-[Fe(hmdpo)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> cation. In the literature, a similar pattern has been observed for the complex *trans*-[Fe(OPPh<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>][FeCl<sub>4</sub>].<sup>10</sup> The e.s.r. spectrum of the chloride complex of edpo shows a very strong signal at 3 235 G with  $g_{\text{eff.}} = 2.05$ . This is possible if there is an exchange interaction in [Fe(edpo)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>[FeCl<sub>4</sub>]<sup>-</sup> as has been observed in the case of [Fe(Me<sub>2</sub>SO)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup>[FeCl<sub>4</sub>]<sup>-</sup> which also showed a single e.s.r. peak at  $g_{\text{eff.}} = 2$ .<sup>28</sup> The e.s.r. spectrum of the nitrate complex of edpo is somewhat complicated and it shows the prominent peak at 1 675 G with  $g_{\text{eff.}} \approx 4$ . This indicates that the cation [Fe(edpo)<sub>2</sub>(ONO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> has a distorted *cis* octahedral structure instead of a *trans* structure. In the latter case, it would have axial symmetry and  $g_{\text{eff.}} = 6$  is expected as is commonly observed for *trans*-[Fe(L)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> (L = OPPh<sub>3</sub>, etc.) systems.

In t.g.a., water was lost below 100 °C indicating that it was present as lattice water. The nitrate complexes are decomposed in the range 160–340 °C and the ligand molecules are lost slowly in the range 220–800 °C. The order of thermal stability of these complexes appears to be: tmdpo > edpo ≈ mdpo. In the case of the chloride complexes all the ligand molecules are lost in the range 150–700 °C. The loss of chloride in complexes of mdpo, tmdpo, and hmdpo is 33, 50, and 100% in the temperature range 400–800 °C. The order of thermal stability is reversed in this case, *i.e.* mdpo > tmdpo > hmdpo.

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