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Synthesis, structure, spectra and magnetic properties of the unsymmetrical oxo-bridged complex $[Fe_2O(OAsPh_3)_4Cl_3]_2[Fe_2OCl_6].2CH_3CN$

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Abstract—A new unsymmetrical (μ-oxo)diiron(III) complex $[Fe_2O(OAsPh_3)_4Cl_3]_2[Fe_2OCl_6].2CH_3CN$ (I), where $OAsPh_3$ is triphenylarsine oxide, has been prepared by several ways and characterized by X-ray structural analysis, elemental analysis, spectral and magnetic methods. The complex (I) is formed simultaneously with another two complexes of the composition $[Fe_2O(OAsPh_3)_4Cl_3][FeCl_4].CH_3CN$ (II) and $[Fe(OAsPh_3)_4Cl_2]$ $[FeCl_4]$ (III). In compound (I) the complex cation has one Fe atom coordinated by four $OAsPh_3$ which form a plane, and the oxo-bridged ligand occupies an apex and form a square pyramid configuration about the second iron atom. In the complex anion each Fe atom is tetrahedrally coordinated by three chlorine atoms and the oxo bridge. The magnetic properties have been investigated in the 4.2–300 K temperature range and these data correspond to the EPR spectra. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: iron(III) complexes; unsymmetrical oxo-bridged complexes; triphenylarsine oxide; magnetism; spectroscopic data; structure.

We are interested in the formation of iron complexes with triphenylphosphine oxide ($OPPh_3$) by autocatalytic oxidation of PPh_3 by dioxygen to $OPPh_3$ in the presence of some iron salts and corresponding anions [1–5]. In spite of the simplicity of the PPh_3-system we have explored the $AsPh_3$-system, too. How-

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Abbreviations: acac: acetylacetonate; acacen: N,N′-ethylenebis(acetylacetonylideneiminate); bpy: 2,2′-bipyridine; Bz: benzyl; cbpN: 2-hydroxy-5-chlorobenzophenone with 1,5,9- triazanonane; $C_6H_{15}N_3$: 1,4,7-triazacyclononane; Cl-dipic: 4-chloro-2,6-pyridinedicarboxylate; dbat: 7, 16-dihydro-6, 8, 16, 17-tetramethyldibenzo[b,i][1,4,8,11] tetraazacyclotetradecinate; dmso: dimethylsulfoxide; dsit: S-methyl-N^1,N^4-di(salicyliden)isothiosemikarbazidate-S,N^1,N^4; $Fe(cp)_2$: ferrocenium; $hbpz_3$: hydrotris-1-pyrazolylborate; hfacac: hexafluoroacetylacetonate; hp: hemiporphyrazinate; Me: methyl; 2-Mequin: 2-methyl-8-hydroxyquinolinate; mim: 1-methylimidazole; n5: N-(hydroxyethyl)-N,N′,N′-tris(2-benzimi-dazolylmethyl)-1,2-diaminoethane; n6: N,N,N′,N′-tetrakis((2-benzimidazolyl)methyl)ethanediamine: N-n-propyl-sal: N-n-propylsalicylideneiminate; N-p-Cl-Ph-sal: N-p-chlorophenylsalicylaldiminate; nta: nitrilotriacetate; odm: 5,15-dimethyl-2,3,7,8,12,13,17,18-octaethylporphinate; o-xy: o-xylene; pc: phthalocyaninate; phen: 1,10-phenanthroline; py: pyridine; salen: 1,2-bis(salicylideneaminato)ethane(2-); taab: tetrabenzo[b,f,j,n][1,5,9,13] tetraazacyclohexadecane; 3-tBusaltmen: 2,3-dimethyl-2,3-bis(3-tert-butylsalicylideneamino)butane(2-); tetren: tetraethylenepentaamine; tpa: tris(2-pyridylmethyl)amine; tmpyp: tetrakis(1-methylpyridinium-4-yl) porphyrinate(2-); tpc: 7,8-dihydroxo-5,10,15,20-tetraphenylporphyrinate; tpp: 5,10,15, 20-tetraphenylporphyrinate(2-); tpp(F_5): 5,10,15,20-tetrakis-pentafluorophenylporphinate(2-).

ever, in the later case we have found that besides the monomeric Fe(III) complex there are also formed the diiron(III) complexes. The monomeric [Fe(OAsPh$_3$)$_4$Cl$_2$][FeCl$_4$] salt is known which was prepared by direct reaction of FeCl$_3$ with OAsPh$_3$ in ethanol [6] or toluene under anaerobic conditions [7]. Two oxo-bridged diiron salts: [Fe$_2$O(OAsPh$_3$)$_4$Cl$_3$]$_2$[Fe$_2$OCl$_6$].2CH$_3$CN (I) and [Fe$_2$O(OAsPh$_3$)$_4$Cl$_3$] [FeCl$_4$].CH$_3$CN (II) have different anions. The [(OAsPh$_3$)$_4$FeOFeCl$_3$]$^+$ cation is the first nonbiological unsymmetrical oxo-bridged Fe(III) complex ion with penta- and tetracoordinated iron atoms. However, until to-date, in all the known oxo-bridged Fe(III) complexes both Fe(III) atoms are tetracoordinated [8–20], pentacoordinated [21–37], hexacoordinated [38–48] or even heptacoordinated [49]. There are examples [50–53], in which two non-equivalent Fe(III) atoms, (viz. hexa- and tetra- coordinated) are bridged by a single O atom. It is known [54] that unsymmetrical Fe–O–Fe bridge angle is present in a class of dinuclear iron proteins. The (μ-oxo)-diiron(III) complexes have been prepared by several ways and are characterized by spectral and magnetic methods as well as by X-ray analysis. (The compound (II) has been characterized by us previously [55]).

EXPERIMENTAL

Preparations of the compounds

Complexes of the composition, [Fe$_2$O(OAsPh$_3$)$_4$Cl$_3$]$_2$[Fe$_2$OCl$_6$].2CH$_3$CN (I) [Fe$_2$O(OAsPh$_3$)$_4$Cl$_3$] [FeCl$_4$]. CH$_3$CN (II) and [Fe(OAsPh$_3$)$_4$Cl$_3$][FeCl$_4$] (III) are formed simultaneously and amounts of the individual complexes are dependent on the reaction conditions. These complexes were prepared by several ways:

Method 1

Solution of OAsPh$_3$ (2.575 g, 8.0 mmol) in ethanol (ca. 70 ml) or toluene (ca. 100 ml) was added to FeCl$_3$ (0.648 g, 4.0 mmol) at room temperature and the resulting mixture stirred for 2 h. The yellow product which precipitated was filtered out and recrystallized from acetonitrile. The individual complexes were separated by fractional crystallization using acetonitrile, yielding the following three products;

1. [Fe$_2$O(OAsPh$_3$)$_4$Cl$_3$]$_2$[Fe$_2$OCl$_6$].2CH$_3$CN (I) as the least soluble complex (dark yellow sticks). Found: C, 51.56; H, 3.60; Cl, 12.90; Fe, 9.65. Calcd. for C$_{148}$H$_{126}$As$_8$Cl$_{12}$Fe$_6$N$_2$O$_{11}$: C, 51.3; H, 3.7; Cl, 12.3; Fe, 9.7%.
2. [Fe$_2$O(OAsPh$_3$)$_4$Cl$_3$][FeCl$_4$].CH$_3$CN (II) as more soluble complex (yellow needles). Found: C, 50.76; H, 3.59; N, 0.83; Cl, 14.22; Fe, 9.46. Calcd. for C$_{74}$H$_{63}$As$_4$Cl$_7$Fe$_3$NO$_5$: C, 50.45; H, 3.60; N, 0.80; Cl, 14.09; Fe, 9.51%.
3. [Fe(OAsPh$_3$)$_4$Cl$_2$][FeCl$_4$] (III) as the most soluble complex (light yellow plates). Found: C, 53.58; H, 3.78; Cl, 13.41; Fe, 6.67. Calc. for C$_{72}$H$_{60}$O$_4$As$_4$Cl$_6$Fe$_2$: C, 53.60; H, 3.75; Cl, 13.18; Fe, 6.92%.

When the reaction mixture is kept under argon, the complex (III) is a major fraction. However, when the raw product is slowly recrystallized from hot CH$_3$CN in the presence of O$_2$, both dimeric complexes (I + II) are formed in larger amounts.

Method 2

Solutions of acetonitrile (ca. 30 ml) and 0.70 ml of a 36% solution (by weight) of aqueous HCl (8.0 mmol) ($T = 333$ K) containing excess iron powder (0.33 g, 5.9 mmol) and AsPh$_3$ (1.23 g, 4.0 mmol) were stirred for about 2 days under a dioxygen atmosphere. The completion of the oxidation of AsPh$_3$ to OAsPh$_3$ was ascertained by comparing the electronic absorption spectrum of the reaction solution with the spectrum of pure OAsPh$_3$ which exhibits four absorption bands with the maxima at 252, 259, 262 and 270 nm. The resulting mixture was filtered (mainly from Fe$_2$O$_3$) and separated by fractional crystallization using CH$_3$CN by the same procedure of *Method* 1. In this case complex (III) was a minor fraction. Both dimeric complexes were obtained in equally amounts.

Method 3

AsPh$_3$ (0.61 g, 2.0 mmol) dissolved in ca. 40 ml CH$_3$CN was transfered to FeCl$_3$ (0.17 g, 1.0 mmol) in the reaction vessel. The contents were stirred and heated to a temperature of ~333 K under a O$_2$ atmosphere for ca. 2 days. Monitoring of the reaction course and fractional crystallization were done in the manner as mentioned above. In this case the dimers were obtained in larger amounts than complex (III) and were suitable for X-ray analyses.

Method 4

Fe$_2$(SO$_4$)$_3$.7H$_2$O (1.10 g, 2.1 mmol) and KCl (0.60 g, 8.0 mmol) were placed into a thermostated vessel, the acetonitrile solution (ca. 30 ml) of AsPh$_3$ (1.23 g, 4.0 mmol) was added and the mixture was stirred under O$_2$ for about 2 days. The course on this reaction was monitored according to the manner mentioned above. After the oxidation, the K$_2$SO$_4$ as a by-product was filtered out. The crude product was separated by fractional crystallization, too. The complex (II) was the major product.

Method 5

The acetonitrile solution (30 ml) of complex (III) (0.41 g, 0.25 mmol) was stirred for about 10 h under

O_2 in a thermostated vessel ($T = 323\,\text{K}$). The dark-yellow solution containing all the complexes was separated by fractional crystallization (see *Method* 1). The amount of (II) was larger than that of (I).

Elemental analyses confirm the composition of the separated complexes (*Method* 2 to 5). Elemental analyses were carried out using a Carlo-Erba C,H,N,S-O (EA 1108) analyser.

Spectroscopic studies

Infrared spectra were recorded using Philips Analytical PU 9800 FTIR spectrometer in Nujol mulls on KBr plates over 4000–200 cm^{-1} range. Electronic spectra were recorded on Specord M 40 spectrophotometer by Carl Zeiss. Resonance Raman spectra were recorded on a Bruker ER 200 E-SRC spectrometer. Electron paramagnetic resonance (EPR) spectrum was measured with X-band Radiopan SE/X spectrometer for powder. Solid sample of Mn(II) in MgO was used as the reference and the magnetic field was calibrated with a nuclear magnetometer MJ 110R.

Magnetic measurements

Magnetic susceptibility of the polycrystalline samples of the compounds were measured by the Faraday method in the temperature range 4.2–293 K, using a sensitive Sartorius M-25D electrobalance. Susceptometer was equipped with Oxford Instruments CF-1200 continuous-flow cryostat and an electromagnet operating at 6.25 kG. The calibrant employed was $HgCo(NCS)_4$ [56], for which the magnetic susceptibility taken as $16.44 \times 10^{-6}\,\text{cm}^3\,\text{g}^{-1}$. The correction for diamagnetism of the constituent atoms was calculated using Pascal's constants [57] and found to be $-928 \times 10^{-6}\,\text{cm}^3\,\text{mol}^{-1}$ and $-1820 \times 10^{-6}\,\text{cm}^3\,\text{mol}^{-1}$ per molecule of complexes I and II, respectively. The value $N\alpha = 0$ ($\text{cm}^3\,\text{mol}^{-1}$) was used for the temperature independent paramagnetism of the compounds. The effective magnetic moment was calculated from the equation, $\mu_{\text{eff}} = 2.83 \times (\chi_{\text{M}} \times \text{T})^{1/2}$ (B.M.). The value of the exchange parameters were determined by least-square procedure, and the minimization of the function:

$$R = \sum_{i=1}^{n} (\chi_i^{\exp t1} - \chi_i^{\text{calcd}})^2 / (\chi_i^{\exp t1})^2$$

was the criterion used to determine the best fit.

Table 1. Crystal and structure refinement data for $[(Ph_3AsO)_4FeOFeCl_3]_2[Fe_2OCl6].2CH_3CN$ (I)

Formula	$C_{148}H_{126}As_8Cl_{12}Fe_6N_2O_{11}$
M_r	3468.4
Crystallographic system	triclinic
a (Å)	13.523(11)
b (Å)	13.618(12)
c (Å)	24.009(15)
α (°)	76.17(7)
β (°)	87.93(7)
γ (°)	59.53(9)
V (Å^3)	3681(7)
F(000)	1740
Space group	$P\bar{1}$
Z	1
T (K)	120(2)
λ (Å)	0.71069
ρ_{calcd}. (g cm^{-3})	1.565(4)
ρ_{meas}. (g cm^{-3})	1.469
μ (cm^{-1})	26.4
No. of reflcns collcd.	9014
No. of obsd. reflcns	6690(I $> 3\sigma$)
$R\ (= \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.0371
wR^2	0.0985
w	$1/[(\sigma^2(F_o^2) + 0.067P)^2 + 10.4P$

X-ray structure determination

$[Fe_2O(OAsPh_3)^4Cl_3]_2[Fe_2OCl_6].2CH_3CN$ (I) A well-formed dark yellow crystal was affixed to the end of glass fiber using silicone grease and transferred to the goniostat where it was cooled to 120 K for data collection ($4° < 2\Theta < 44°$) (Table 1). Standard inert atmosphere techniques were used. A systematic search of a limited hemisphere of reciprocal space located no symmetry or systematic absences indicating a triclinic space group. Subsequent solution and refinement of the structure confirmed the proper space group to be $P\bar{1}$. The structure was solved by direct methods and refined by SHELXL-93 program [58]. The phenyl ring H-atoms were included in geometrically calculated positions and the acetonitrile H-atoms were not determined from final difference map. No absorption correction was applied. A final difference map was essentially featureless, the largest peaks being in the vicinity of the As atoms. The high values of anisotropic temperature factors for acetonitrile molecules may suggest partially disorder of these molecules. Bond lengths and angles, atomic coordinates, displacement parameters and lists of structure factors for (I) are deposited.

RESULTS AND DISCUSSION

Anhydrous $FeCl_3$ and $OAsPh_3$ interact rapidly in several solvents (e.g. ethanol [6], toluene [7], acetonitrile) to afford yellow solutions. When the interaction is carried out under anaerobic conditions, the complex (III) is formed as a major product. However, in the presence of oxygen the I and II complexes are also formed, (*Method* 1). A similar mixture of these 3 complexes were also obtained when the following reactants were used as the starting compounds:

$\mathrm{Fe{-}HCl{-}AsPh_3{-}O_2}$ (*Method* 2)
$\mathrm{FeCl_3{-}AsPh_3{-}O_2}$ (*Method* 3)
$\mathrm{Fe_2(SO_4)_3.7H_2O{-}KCl{-}AsPh_3{-}O_2}$ (*Method* 4)
$\mathrm{[Fe(OAsPh_3)_4Cl_2][FeCl_4]{-}O_2}$ (*Method* 5)

Autocatalytic oxidation of $\mathrm{AsPh_3}$ to $\mathrm{OAsPh_3}$ by $\mathrm{O_2}$, which has taken place in the Methods 2, 3 and 4, were used for the preparation of mainly diiron complexes. During oxidation of $\mathrm{AsPh_3}$ mentioned reaction systems consumed $\mathrm{O_2}$, what was demonstrated by measurements of dioxygen uptake on the apparatus described previously [1].

Both the complexes (I) and (II) are built with identical cationic forms (Fig. 1), different anions ($\mathrm{FeCl_4^-}$ [55] and $\mathrm{Fe_2OCl_6^{2-}}$ (Fig. 2)) and acetonitrile solvate molecules. Selected bond distances and angles of the complex (I) are given in Tables 2 and 3, respectively. The complex cations of (I) and (II) have similar structures. They contain two unsymmetrical iron(III) μ-oxo species (Fig. 1). The Fe(1) atom is coordinated by four $\mathrm{OAsPh_3}$ ligands which form a distorted square pyramide configuration about the Fe(1). The Fe(2) is tetrahedrally coordinated by three chlorine atoms and the oxo bridge. They differ significantly with Fe–O–Fe bond angle of 161.0(3)° in (II) and of 170.3(3)° in (I). The Fe(2)–O(5) bonds of 1.759(4) Å in (II) and 1.776(4) Å in (I) are slightly shorter than the Fe(1)–O(5) bonds (1.784(4) Å in (II) and 1.779(4) Å in (I)), as expected. Both lengths, as well as the Fe–O–Fe angle, fall in the range of values observed for the diiron(III) μ-oxo analogues (Table 5). The bond lengths for Fe(2)–Cl in (II) (average 2.204(3) Å) are identical with those observed in the $[(n5)\mathrm{FeOFeCl_3}]^+$ cation (average 2.203(3) Å) [52] and they are the slightly shorter than Fe(2)–Cl bond lengths in (I) (average 2.218(4) Å). To our knowledge, the Fe–($\mathrm{OAsPh_3}$) fragment has not been characterized previously.

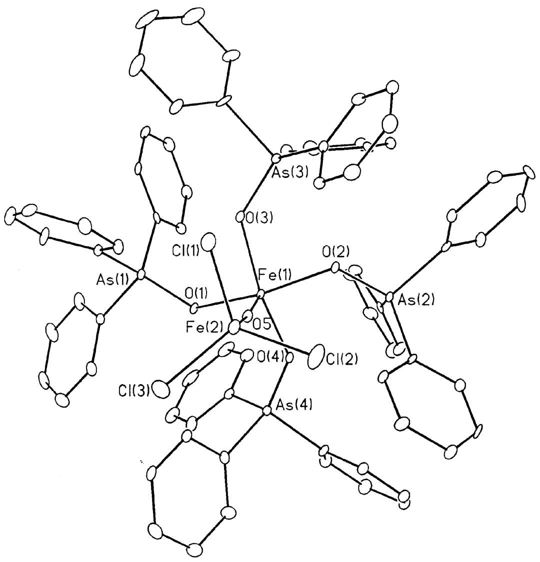

Fig. 1. The overall view of $\mathrm{[(OAsPh_3)_4FeOFeCl_3]^+}$ cation in (I).

Table 2. Selected bond lengths (Å), bond angles (°) and torsion angles (°) for $\mathrm{[(Ph_3AsO)_4FeOFeCl_3]^+}$ in (I).

Fe(1)...Fe(2)	3.543(3)
Fe(1)–O(1)	1.972(4)
Fe(1)–O(2)	1.974(4)
Fe(1)–O(3)	1.993(5)
Fe(1)–O(4)	2.002(5)
Fe(1)–O(5)	1.779(4)
Fe(2)–O(5)	1.776(4)
Fe(2)–Cl(1)	2.223(4)
Fe(2)–Cl(2)	2.213(2)
Fe(2)–Cl(3)	2.219(3)
As(1)–O(1)	1.682(4)
As(2)–O(2)	1.691(4)
As(3)–O(3)	1.680(4)
As(4)–O(4)	1.675(4)
As(1)–O(1)–Fe(1)	136.6(3)
As(2)–O(2)–Fe(1)	129.7(3)
As(3)–O(3)–Fe(1)	133.6(3)
As(4)–O(4)–Fe(1)	138.2(3)
O(1)–Fe(1)–O(5)	105.1(2)
O(2)–Fe(1)–O(5)	106.5(2)
O(3)–Fe(1)–O(5)	103.4(2)
O(4)–Fe(1)–O(5)	105.2(2)
O(1)–Fe(1)–O(2)	148.4(2)
O(1)–Fe(1)–O(3)	87.9(2)
O(1)–Fe(1)–O(4)	87.0(2)
O(2)–Fe(1)–O(3)	84.8(2)
O(2)–Fe(1)–O(4)	84.9(2)
O(3)–Fe(1)–O(4)	151.4(2)
Fe(1)–O(5)–Fe(2)	170.3(3)
O(5)–Fe(2)–Cl(1)	110.6(2)
O(5)–Fe(2)–Cl(2)	111.2(2)
O(5)–Fe(2)–Cl(3)	112.2(2)
Cl(1)–Fe(2)–Cl(2)	105.4(2)
Cl(1)–Fe(2)–Cl(3)	106.3(2)
Cl(2)–Fe(2)–Cl(3)	110.9(2)
Cl(1)–Fe(2)–O(5)–Fe(1)	15.8(15)
Cl(2)–Fe(2)–O(5)–Fe(1)	−100.9(15)
Cl(3)–Fe(2)–O(5)–Fe(1)	134.3(15)
Fe(2)–O(5)–Fe(1)–O(1)	−110.8(15)
Fe(2)–O(5)–Fe(1)–O(2)	69.1(15)
Fe(2)–O(5)–Fe(1)–O(3)	−19.5(15)
Fe(2)–O(5)–Fe(1)–O(4)	158.2(15)
O(5)–Fe(1)–O(1)–As(1)	94.6(4)
O(5)–Fe(1)–O(2)–As(3)	102.6(4)
O(5)–Fe(1)–O(3)–As(3)	104.6(4)
O(5)–Fe(1)–O(4)–As(4)	82.4(4)

In (II) the Fe(3) atom in the $\mathrm{[FeCl_4]^-}$ anion is tetrahedrally coordinated by four chlorine atoms (Fe–Cl range from 2.158(4) Å to 2.180(3) Å and Cl–Fe–Cl angles from 108.0 to 111.6(2)° what is typically for these anions [59].

The iron atoms in the oxo-bridged dinuclear $\mathrm{[Cl_3Fe{-}O{-}FeCl_3]^{2-}}$ anion in (I) each possess a slightly

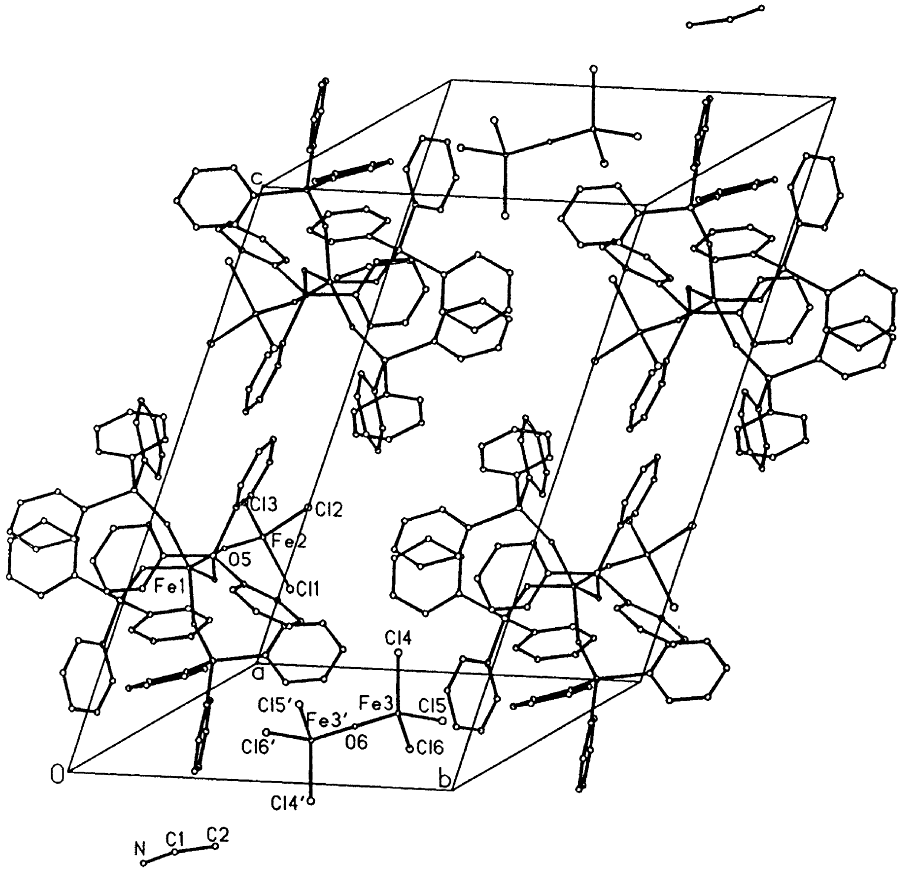

Fig. 2. The packing in the (I) crystal (approximately along the Fe...Fe axis).

Table 3. Selected bond lengths (Å), bond angles (°) and torsion angles (°) for $Fe_2OCl_6^{2-}$ in (I)

Fe(3)...Fe(3^{i})	3.512(3)
Fe(3)–Cl(4)	2.232(3)
Fe(3)–Cl(5)	2.208(3)
Fe(3)–Cl(6)	2.218(4)
Fe(3)–O(6)	1.756(2)
Cl(4)–Fe(3)–Cl(5)	108.5(2)
Cl(4)–Fe(3)–Cl(6)	106.2(2)
Cl(4)–Fe(3)–O(6)	112.5(2)
Cl(5)–Fe(3)–Cl(6)	111.2(2)
Cl(5)–Fe(3)–O(6)	109.2(2)
Cl(6)–Fe(3)–O(6)	109.3(2)

Symmetry code: (I) $1-x$, $1-y$, $-z$.

distorted tetrahedral ligand environment. The bond distances of the anion agree with those of the compounds investigated so far. The Fe–O–Fe angle is relatively large (Table 5).

Table 4 summarized infrared spectroscopic data of three Fe(III)–$OAsPh_3$ complexes. In the IR spectra of these complexes showed that ν(As–O) bands are shifted to lower energies compared with the free $OAsPh_3$, as the result of $OAsPh_3$ coordination. The dimeric complexes I and II have a strong new absorption at 849 cm^{-1} and 841 cm^{-1}, respectively. It is attributed to the asymmetric Fe–O–Fe stretching vibration (ν_{as}). Intense absorption in the region 800–860 cm^{-1} is commonly used as diagnostic criterion for identification of the oxo-monobridged Fe(III) complexes [8, 52]. The bands assigned to the symmetric Fe–O–Fe stretching vibration (ν_s) observed at 415 (I) and at 411 cm^{-1} (II) are within the range expected for these monobridged structures [60]. The Fe–O–Fe vibrations of I and II correlate with bond angles; the Fe–O–Fe angles can be predicted within 10° from knowledge of ν_s and ν_{as} [60]. In the infrared spectrum the Fe–O–Fe frequencies are nearly identical with those observed in the Raman spectrum. Whereas ν_{as}(Fe–O–Fe) are stronger and ν_s(Fe–O–Fe) are weaker in the IR spectra of I and II, in the Raman spetra the stretching vibration intensities are opposite. Infrared bands at

Table 4. Characteristic IR data (cm^{-1}) for the Fe(III)–$OAsPh_3$ complexes

Compound	ν(As–O)	ν(FeOFe)		ν($FeCl_4^-$)	ν($FeCl_3$)	
		ν_{as}	ν_s		ν_{as}	ν_s
III	869s 828s	—	—	380s	—	—
II	860s 828s	841s	411m	382s	369m	307m
I	881s 830vs	849vs	415m	—	363vs	314m

363 (I) and 369 cm^{-1} (II) are assigned to the respective Fe–Cl_3 asymmetric stretch by comparison with $[Fe_2OCl_6]^{2-}$ and bands at 314 (I) and 307 cm^{-1} (II) are assigned similarly to the symmetric $FeCl_3$ mode in agreement with literature data [51]. IR spectra of II and III show a characteristic strong band at 383 and 380 cm^{-1} (ν_3) of $FeCl_4^-$, respectively [8].

In Table 5 are summarized selected structural data for μ-oxo-bridged dimeric Fe(III) compounds. As can be seen, the mean Fe–O(bridge) bond distance increases with increasing coordination number in the sequence: 1.754 Å (tetra coordinated) < 1.771 Å (penta coordinated) < 1.786 Å (hexa coordinated), as expected. The Fe–O–Fe bridge angles in the series of tetra-, penta- and hexa-coordinated species are well comparable, i.e. they are in the range of 147.7 to 180°, of 142.7 to 180° and of 146.6 to 180°, respectively. There are relationships between the Fe–O–Fe bridge angle and Fe–Fe distances. When the former closses the latter is shortened.

The anion $FeCl_4^-$ is a strong paramagnet with $S = 5/2$ spin, but the $Fe_2OCl_6^{2-}$ ion is a molecular antiferromagnet. Using the theoretical equation [61]

$$\chi_M = \left(\frac{N_g^2 \mu_B^2}{kT}\right) \times \left(\frac{2e^{2x} + 10e^{6x} + 28e^{12x} + 60e^{20x} + 110e^{30x}}{1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x} + 11e^{30x}}\right)$$

(where χ_M was corrected for diamagnetism, and $TIP = 0$ and $\chi = J/kT$) and X- ray data (this work) for $Fe_2OCl_6^{2-}$ in the crystal lattice of the complex (I), the relation $\chi_{Fe_2OCl_6^{2-}} = f(T)$ was prepared (Fig. 3). The magnetic interaction in a dimer is expressed by the Heisenberg–Dirac–van Vleck Hamiltonian, $H_{HDVV} = -2J_{S_aS_b}$, where $\hat{S}_a$ and $\hat{S}_b$ are the spins of the magnetically interacting iron(III) ions ($\hat{S}_a = \hat{S}_b = 5/2$).

The cationic forms observed in both the complexes indicate lack of any symmetry and a difference in the bridging angle Fe–O–Fe, 170.3° and 161.0° for the complexes I and II, respectively.

In the crystal lattice of the complex II two magnetically isolated paramagnetic forms exist, which confirms the absence of the maximum on the experimental curve $\chi_M = f(T)$ up to 4.2 K. A weak anomaly observed in the region 4.2–20 K and the value $\Theta \sim -2.5$ K may suggest weak antiferromagnetic superexchange interaction. The relation between molar magnetic susceptibility and the magnetic moment for both the complexes as a function of temperature enables us to compare their properties (Fig. 4; magnetic data are given for whole molecular system.). Both the complexes indicate a relation typical for a paramagnet, although the magnetic effect for the complex (II) is stronger (Table 6).

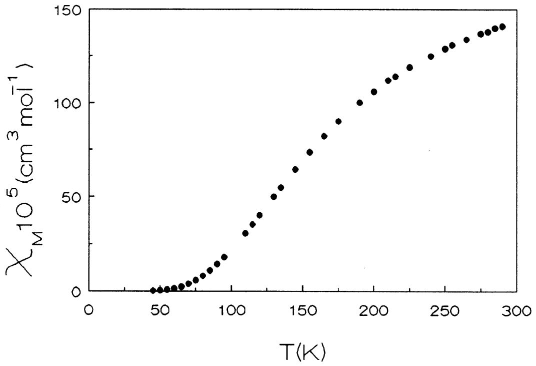

Fig. 3. Plots of the magnetic susceptibility versus T for $Fe_2OCl_6^{2-}$ anions calculated for $g = 2$, $J = -170\ cm^{-1}$, diamagnetic correction $= -188.\ 10^{-6}\ cm^3 mol^{-1}$.

In the EPR spectrum of the complex (II) only one

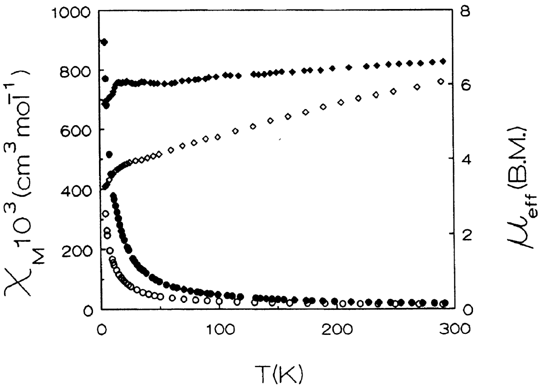

Fig. 4. Experimental magnetic susceptibility and magnetic moment vs. temperature for $[(OAsPh_3)_4FeOFeCl_3][FeCl_4]$ (●, ◆) and $[(OAsPh_3)_4FeOFeCl_3]_2[Fe_2OCl_6]$ (o, ◇), respectively.

Table 5. Selected structural data for μ-oxo-bridged dimeric Fe(III) compounds[a]

Complex	Chromophore		Fe–L (Å)	Fe–Fe (Å) Fe–O–Fe (°)		L–Fe–L (°)	Ref.
$(Ph_4P)_2\,[Fe_2OCl_6]$	$FeCl_3O$	μO	1.744 (4,0)	not given	Cl, Cl[b]	108.4 (2,1.5)	[8]
		Cl[b]	2.210 (2,6)	170.4 (4)	μO, Cl	110.5 (2,1.5)	
$(Ph_4P)_2\,[Fe_2OCl_6]\cdot 2CH_2Cl_2$	$FeCl_3O$	μO	1.740 (1)	3.480	Cl, Cl	108.1 (1,8)	[9]
		Cl	2.211 (2,11)	180.0	μO, Cl	110.8 (1,2.6)	
$(BzPh_3P)_2[Fe_2OCl_6]$	$FeCl_3O$	μO	1.760 (3,3)	3.467(2)	Cl, Cl	108.7 (1,2.5)	[8],[10]
		Cl	2.216 (2,21)	160.2 (5)	μO, Cl	110.3 (2,2.2)	
$(BzPhMe_2N)_2[Fe_2OCl_6]$	$FeCl_3O$	μO	1.766 (5,9)	3.393(1)	Cl, Cl	109.5 (1,1.8)	[11]
		Cl	2.210 (2,14)	147.7(3)	μO, Cl	109.4 (2,1.5)	
$(Hpy)_2[Fe_2OCl_6]\cdot py$	$FeCl_3O$	μO	1.755 (3,0)	3.428(3)		not given	[8],[10],[12]
		Cl	2.214	155.6 (7)			
$(Ph_4As)_2[Fe_2OCl_6]$	$FeCl_3O$	μO	1.74 (3)	3.469[d]		not given	[8],[13]
		Cl	2.207	170.8 (5)			
$[(Ph_3P)_2CSe]_2[Fe_2O$-	$FeCl_3O$	μO	1.752(2)	3.504		not given	[14]
$Cl_6]\cdot 4CH_2Cl_2$		Cl	not given	180.0			
$(BzEt_3N)_2[Fe_2OCl_6]$	$FeCl_3O$	μO	1.755 (5,3)	not given		not given	[8]
		Cl	2.219	155.3 (3)			
$[FeCl(dmso)_5][Fe_2OCl_6]$	$FeCl_3O$	μO	1.760 (8,6)	not given	Cl, Cl	109.0 (2,1.5)	[15]
		Cl	2.203 (4,11)	150.3 (4)	μO, Cl	109.8(3, 2.9)	
$[FeCl(dmso)_5][Fe_2OCl_6]$	$FeCl_3O$	μO	1.776 (5,2)	3.401[d]	Cl, Cl	109.3 (1,1.5)	[15]
(at 103 K)		Cl	2.223 (2,9)	146.5 (2)	μO, Cl	109.5 (1,2.0)	
$[FeCl(dmso)_5][Fe_2OCl_6]$	$FeCl_3O$	μO	1.763 (7,0)	not given	Cl, Cl	109.2 (1,1.4)	[15]
(at 223 K)		Cl	2.216(4,14)	149.7(4)	μO, Cl	109.7 (2,1.9)	
$[FeCl(dmso)_5][Fe_2OCl_6]$	$FeCl_3O$	μO	1.737(7,6)	3.374[d]	Cl, Cl	108.8 (2,2.8)	[15]
(at 343 K)		Cl	2.190(3,9)	152.7(4)	μO, Cl	110.0(3,2.8)	
$[Fe(phen)_3][Fe_2OCl_6]\cdot dmf$	$FeCl_3O$	μO	1.75 (2,1)	3.455(7)	Cl, Cl	109.1 (2,2.0)	[16]
		Cl	2.22 (2,2)	161.6 (9)	μO, Cl	109.9 (5,3.3)	
$[Fe(bpy)_3][Fe_2OCl_6]$	$FeCl_3O$	μO	1.752(11,12)	3.374[d]		not given	[17]
		Cl	2.209(6,16)	148.9(7)			
$[Fe(bpy)_3][Fe_2OCl_6]$	$FeCl_3O$	μO	1.765(3,1)	3.394[d]	Cl, Cl	108.69(5,1.92)	[18]
(at 223 K)		Cl	2.222(1,1.6)	148.1(2)	μO, Cl	110.2(10,1.0)	
$[Fe(cp)_2]_2[Fe_2OCl_6]$	$FeCl_3O$	μO	1.749(4,0)	3.455(5)	Cl, Cl	108.4(2,1.3)	[19]
		Cl	2.197(5,7)	162.1(5)	μO, Cl	110.5(4,5)	
$[Fe_2O(OAsPh_3)_4Cl_3]_2$–	$FeCl_3O$	μO	1.756(2,0)	3.512(3)	Cl, Cl	108.6(2,2.6)	this work
$[Fe_2OCl_6]\cdot 2MeCN$	(anion)	Cl	2.219(4,13)	180.00	μO, Cl	110.3(2,2.2)	
(at 120 K)							
$[Fe(cp)_2]_2[Fe_2OBr_6]$	$FeBr_3O$	μO	1.752(2,0)	not given	Br, Br	108.8(1,2.4)	[20]
		Br	2.347(4,7)	159.8(4)	μO, Br	110.2(4,1.3)	
$[Fe_2O(2\text{-}Mequin)_4]\cdot CHCl_3$	FeO_3N_2	O	1.925(14,15)	3.451[d]	O, O	123.4(6)	[21]
		μO	1.781(11,21)	151.6(7)	μO, O	118.3(5,5)	
		N	2.184(14,4)		N, N	160.9(5)	
					O, N	79.3(5,1.3)	
					μO, N	91.8(5,2.1)	
						99.4(5,1)	
$[Fe_2O(N\text{-}p\text{-}ClPh\text{-}sal)_4]$	FeO_3N_2	O	1.89(2,3)	3.53	O, O	127.1(7,2.6)	[22]
		μO	1.77(1,1)	175(1)	μO, O	116.4(7,3.0)	
		N	2.16(2,5)		N, N	168.6(7,1.1)	
					O, N	87.7(7,3.5)	
					μO, N	95.7(7,2.3)	
$[Fe_2O(N\text{-}n\text{-}propyl\text{-}sal)_4]$	FeO_3N_2	O	1.93(2,1)	not given	μO, O	114(2,3)	[23]
		μO	1.77(1,1)	164(5)	O, N	86(1,1)	
		N	2.14(2,1)		μO, N	98(2,4)	
$[Fe_2O(acacen)_2]\cdot CH_2Cl_2$[c]	FeO_3N_2	O	1.962(8,7)	not given	O, O	87.6(3,2)	[24]
		μO	1.783(7,14)	154.6(4)	μO, O	108.6(4,2.6)	
		N	2.077(9,29)		N, N	79.1(4,1.2)	
					O, N	87.0(4,8)	
					μO, N	145.7(4,5.6)	
						105.2(4,3.0)	

continued

Table 5—*continued.*

Complex	Chromophore		Fe–L (Å)	Fe–Fe (Å) Fe–O–Fe (°)		L–Fe–L (°)	Ref.
$[Fe_2O(acacen)_2]\cdot CH_2Cl_2$ [c]	FeO_3N_2	O	1.955(8,5)	not given	O, O	88.5(3,8)	[24]
		μO	1.780(7,5)	155.6(5)	μO, O	109.3(4,3.8)	
		N	2.080(9,18)		N, N	79.1(4,6)	
					O, N	86.5(4,6)	
					μO, N	145.4(4,5.8)	
						104.6(4,2.9)	
$[Fe_2O(salen)_2]\cdot 2py$	FeO_3N_2	O	1.92(1,2)	3.391	μO, O	109.6(5,2.3)	[25]
		μO	1.78(1,0)	144.6(6)	O, N	85.4(5,3)	
		N	2.12(2,1)		μO, N	145.4(5,4.7)	
						103.3(5,3.0)	
$[Fe_2O(salen)_2]\cdot CH_2Cl_2$	FeO_3N_2	O	1.94(3,0)	not given	O, O	95(4)	[26]
		μO	1.80(5,0)	144(2)	N, N	76(4)	
		N	2.12(3,1)		O, N	86(4,1)	
$[Fe_2O(3\text{-}tBusaltmen)_2]$	FeO_3N_2	O	1.923(4,8)	3.551	O, O	92.49(19,15)	[27]
		μO	1.779(4,5)	173.45(27)	N, N	75.80(22,2)	
		N	2.124(5,19)		O, N	85.10(19,78)	
						136.02(18,1.80)	
						149.02(19,1.08)	
$[Fe_2O(dsit)_2]\cdot 2H_2O$	FeO_3N_2	O	1.912(4,10)	3.481(4)	O, O	93.3(2,4)	[28]
		μO	1.769(3,0)	156.4(2)	N, N	72.6(2,2)	
		N	2.104(5,3)		O, N	86.2(2,1.7)	
$[Fe_2O(dbat)_2]\cdot MeCN$	FeN_4O	μO	1.792(1,1)	3.397[d]	N, N	83.32(7,5.36)	[29]
		N	2.053(2,11)	142.75(9)	μO, N	140.19(7,1.01)	
						109.91(7,1.51)	
$[Fe_2O(tpp)_2]$	FeN_4O	μO	1.763 (1)	not given	N, N	86.8 (3,4)	[30]
		N	2.087 (6,11)	174.5(1)	N, N	152.5 (2,1.4)	
					μO, N	103.7 (2,4.0)	
$[Fe_2O(tpp)_2]$ (at 122 K)	FeN_4O	μO	1.759(1,0)	3.516[d]	N, N	86.9(4,0)	[31]
		N	2.081(3,0)	176.1(2)		153(2,0)	
$[Fe_2O(NCH_3tpp)(tpp)]ClO_4$ (at 133 K)	FeN_4O	μO	1.767(4)	not given	N, N	87.4 (2,9)	[32]
		N	2.067(6,12)	165.4(3)	μO, N	155.4(2,1.4)	
	FeN_4O	μO	1.740(4)		N, N	102.3(2,2.6)	
		MeN	2.257(5)		μO, N	86.1(2,2.4)	
		N	2.058(6,8)			149.7(2,4)	
						105.0(2,5.5)	
$[Fe_2O(tpc)_2]\ 4CHCl_3$ (at 143 K)	FeN_4O	μO	1.755(5,8)	3.510(8)	N, N	86.8(2,3)	[33]
		N	2.084(5,18)	180	μO, N	152.5(3,3.5)	
						103.7(1,1.8)	
$[Fe_2O(odm)_2]$	FeN_4O	μO	1.752(1)	3.504[d]	N, N	86.5(2,2.8)	[34]
		N	2.065(4,12)	178.5(6)	μO, N	104.4(2,1.6)	
$[Fe_2O(tmpyp)_2](ClO_4)_8\cdot 4H_2O$ (at 118 K)	FeN_4O	μO	1.750(2)	not given	N, N	87.2(4,4)	[35]
		N	2.081(9,15)	175.1(7)	μO, N	154.2(4,2)	
						102.2(4,1.2)	
$[Fe_2O(tpp(F_5))_2]$ (at 173 K)	FeN_4O	μO	1.775(1,0)	3.550	μO, N	105.1(3,1.6)	[36]
		N	2.088(7,16)	178.4(5)			
$[Fe_2O(taab)_2(MeO)_4]$	FeN_4O	μO	1.777(4,6)	3.552(1)	N, N	88.7(2,3.3)	[37]
		N	2.064(5,68)	176.3(3)	μO, N	93.2(2,2.5)	
						115.6(2,4.4)	
$[Fe_2O(Cl\text{-}dipic)_2(H_2O)_4]\cdot 4H_2O$	FeO_5N	O	2.075(3,22)	3.545(1)	O, O	89.3(1,6)	[38]
		μO	1.773(3,1)	180	μO, O	149.1(1,3)	
		N	2.105(3,3)		O, N	175.1(1,2)	
					μO, N	98.9(1,6.6)	
						81.1(1,6.6)	
						180	
$Ba[Fe_2O(nta)_2(H_2O)_2]\cdot 4H_2O$	FeO_5N	O	2.05(1,14)	not given	μO, O	103.5(5)	[39]
		μO	1.82(1,1)	153.2(6)	O, N	78.1(4)	
		N	2.23(1,0)				

continued

Table 5—*continued.*

Complex	Chromophore	Fe–L (Å)		Fe–Fe (Å) Fe–O–Fe (°)	L–Fe–L (°)		Ref.
$[Fe_2O(phen)_2(H_2O)_6]$–$(NO_3)_4 \cdot 4H_2O$	FeO_4N_2	O	2.068(5,86)	3.506(2)	O, O	86.9(2,9.7)	[40]
		μO	1.775(4,10)	162.0(3)	μO, O	94.6(2,1.9)	
		N	2.155(6,12)			175.7(2,1.2)	
					N, N	76.8(2,4)	
					O, N	89.3(2,4.6)	
						164.8(2,2.1)	
					μO, N	97.4(2,2.6)	
$[Fe_2O(MeC(CH_2NCMe$–$CH_2C(CF_3)_2))_2(CH_2NH_2)_2]$	FeO_3N_3	O	1.972(2,20)	3.468(1)	O, O	99.7(1,5.0)	[41]
		μO	1.811(1)	146.6(2)	μO, O	99.9(1)	
		N	2.231(3,82)		N, N	81.2(1,7.4)	
					O, N	85.7(1,3.9)	
						162.8(1,2.2)	
					μO, N	94.4(1,4.5)	
						166.0(1)	
$[Fe_2O(cbpN)_2] \cdot 3o$-xy	FeO_3N_3	μO	1.806(3,2)	3.440^d		not given	[42]
		O	not given	144.5(2)			
		N					
$[Fe_2O(C_6H_{15}N_3)_2)(acac)_2]$–$(ClO_4)_2$	FeO_3N_3O	μO	2.007(5,11)	3.512(2)	O, O	89.1(2,2)	[43]
		N	1.787(5,5)	158.6(3)	μO, O	98.9(2,1.2)	
			2.178(7,51)		N, N	78.0(3,1.7)	
					O, N	90.5(3,6.7)	
						163.7(3,2.3)	
					μO, N	96.2(3,4.1)	
						170.5(2,8)	
$[Fe_2O(hbpz_3)(hfacac)_2]$	FeO_3N_3	O	2.071(7,12)	3.537(2)		not given	[44]
		μO	1.776(7,2)	169.4(4)			
		N	2.127(9,82)				
$[Fe_2O(tetren)_2]I_4$	FeN_5O	μO	1.77(1,0)	3.531^d	N,N	73(1,1)	[45]
		N	2.25(5,13)	172		81(1,1)	
						91(4,2)	
						100(4,2)	
						160(2,9)	
					μO, N	155(2)	
						103(5,6)	
						88(1)	
$[Fe_2O(pc)_2)(mim)_2]$–$[Fe(pc)(mim)_2] \cdot 3Me_2CO$	FeN_5O	μO	1.749(1,0)	not given	N,N	89.6(4,2.0)	[46]
		$_{pc}$N	1.922(8,27)	175.1		178.3(4,1.0)	
		$_{im}$N	2.039(7,0)		μO, N	90.8(3,1.2)	
						178.9(4)	
$[Fe_2O(phen)_4(H_2O)_2]$–$(NO\ _3)_4 \cdot 5H_2O$	FeN_4O_2	μO	1.785(5,2)	3.49	N,N	82.5(3,8.4)	[47]
		O	2.024(9,3)	155.1(4)		158.2(3,9)	
		N	2.175(9,88)		μO, O	96.4(3,5)	
					O,N	91.0(3,7.6)	
						164.1(2,1.7)	
					μO, N	98.5(3,4.2)	
						172.5(3,1.0)	
$[Fe_2O(tpa)_2Cl_2](ClO_4)_2$	FeN_4OCl	μO	1.785(1,0)	3.565(2)	N,N	79.8(3,8.1)	[48]
		N	2.192(7,54)	174.7(5)		151.9(3)	
		Cl	2.298(2)		μO, N	93.4(3,1.2)	
						170.6(2)	
					N,Cl	98.7(2,8.8)	
						165.2(2)	
					μO, Cl	99.3(1)	
$[Fe_2O(NO_3)_4(bpy)_2]$ (at 201 K)	FeO_5N_2	O	2.191(2,70)	3.5510(7)	O, O	58.49(7,52)	[49]
		μO	1.7755(4)	180		75.09(7)	
		N	2.159(2,19)		μO, O	94.91(6,3.76)	
					N,N	75.02(8)	
					O,N	83.38(8,3.54)	
					μO, N	95.31(6)	
						169.19(6)	

continued

Table 5—*continued.*

Complex	Chromophore		Fe–L (Å)	Fe–Fe (Å) Fe–O–Fe (°)		L–Fe–L (°)	Ref.
$[Fe_2O(OAsPh_3)_4Cl_3]$–$[FeCl_4]\cdot MeCN$	$FeCl_3O$	Cl	2.204(3,14)	3.494(3)	Cl, Cl	108.4(2,2.4)	[55]
		μO	1.759(4)	161.0(3)	μO, Cl	110.5(2,9)	
	FeO_5	O	1.976(4,21)		O, O	86.2(2,9)	
		μO	1.784(4)		μO, O	150.1(3,3.5)	
						105.0(2,2.4)	
$[Fe_2O(OAsPh_3)_4Cl_3]_2$–$[Fe_2OCl_6]\cdot 2MeCN$ (at 120 K)	$FeCl_3O$	Cl	2.218(4,5)	3.543(3)	Cl, Cl	107.5(2,3.4)	this work
		μO	1.776(4)	170.3(3)	μO, Cl	111.3(2,9)	
	FeO_5 (cation)	O	1.985(5,17)		O, O	86.2(2,1.7)	
		μO	1.779(4)			149.9(2,1.5)	
					μO, O	105.1(2,1.7)	
$[Fe_2O(n6)Cl_3]Cl\cdot 0.5$–$HCl\cdot 3H_2O\cdot 2EtOH$	$FeCl_3O$	Cl	2.201(4,13)	3.440(2)	Cl, Cl	109.0(2,6)	[50]
		μO	1.745(7)	153.2(4)	μO, Cl	109.9(3,1.3)	
	FeN_5O	aN	2.32(1,4)		aN,aN	77.9(3)	
		iN	2.08(1,3)		iN, iN	93.5(4,3.8)	
		μO	1.791(7)			162.4(3)	
					aN, iN	83.0(3,5.7)	
						152.7(3)	
					iN, μO	99.5(3,5.2)	
					aN, μO	101.3(3)	
						172.7(3)	
$[Fe_2O(n5)Cl_3]Cl\cdot 2EtOH$	$FeCl_3O$	Cl	2.203(3,5)	3.411(1)	Cl, Cl	110.1(1,2.5)	[51] [52]
		μO	1.751(4)	149.5(3)	μO, Cl	108.8(2,2.4)	
	FeN_5O	aN	2.320(5,37)		aN, aN	78.0(2)	
		iN	2.095(6,19)		iN, iN	91.9(2,2.5)	
		μO	1.784(4)			162.0(2)	
					aN, iN	81.2(2,8.7)	
						149.5(2)	
					iN, μO	101.4(2,7.5)	
					aN, μO	100.6(2)	
						172.6(2)	
$[Fe_2O(n5)Br_3]Br\cdot 2EtOH$	$FeBr_3O$	Br	2.348(3,19)	3.408(3)	Br, Br	109.8(1,2.0)	[52]
		μO	1.726(9)	150.6(4)	μO, Br	109.1(3,3.2)	
	FeN_5O	aN	2.31(1,3)		aN, aN	78.2(4)	
		iN	2.09(1,2)		iN, iN	92.0(4,2.3)	
		μO	1.797(9)			162.1(4)	
					aN, iN	81.2(4,7.7)	
						150.1(4)	
					iN, μO	101.3(4,7.3)	
					aN, μO	100.6(4)	
						172.7(3)	
$[Fe_2O(hp)_2(H_2O)]$	FeN_4O	N	1.986(10,5)	3.52	N, N	87.9(3,4)	[53]
			2.193(11,13)	180		148.6(4)	
		μO	1.739(6)			164.6(4)	
					μO, N	101.7(3,4.0)	
	FeN_4O_2	N	2.098(11,108)		N, N	89.8(4,1)	
		O	2.212(6)			171.9(4,1.5)	
		μO	1.782(6)		O, N	94.1(3,7)	
					μO, N	85.9(3,7)	

[a] Where more than one chemically equivalent distance or angle present, the mean value is tabulated. The first number in parenthesis is e.s.d., the second is maximum deviation from the mean value.

[b] The chemical identity of coordinated atom/ligand is specified in these columns.

[c] There are two crystallographically independent molecules.

[d] It indicates that the distance was calculated trigonometrically [60].

Table 6. Magnetic data

Compound	Temperature $T(K)$	Magnetic susceptibility $\chi_M \times 10^6$ (cm^3 mol^{-1})	Magnetic moment μ_{eff} (B.M.)
$[Fe_2O(OAsPh_3)_4Cl_3][FeCl_4].CH_3CN$	4.2 292	894000 18700	5.48 6.62
$[Fe_2O(OAsPh_3)_4Cl_3]_2[Fe_2OCl_6].2CH_3CN$	4.2 290	319000 25800	3.28 6.06

single line is present, with $g = 2.04$ (room temperature and 77 K).

The EPR spectrum of the cation of complex (I) presents one single line with $g = 2.06$ and two additional weak lines with $g = 4.34$ and 6.08 at room temperature. It suggests a doublet ground state $< \pm 1/2$ I with admixture of $< \pm 3/2$ I and $< \pm 5/2$ I states.

The magnetic data for the $[(Ph_3AsO)_4FeOFeCl_3]^+$ cation, indicated only one unpaired electron per every Fe(III) centre, in a core of Fe(III) [D_{4h} deformed]–O–Fe(III) [T_d deformed]).

Further, the magnetic data at temperatures lower than 20 K are identical with the expected magnetism exclusively for the cation and indicate a singlet ground state and upper triplet state.

However, for complex II calculation of the magnetic moment of the cation was found to be impossible because we have not any possibility to estimate magnetism of the isolated $FeCl_4^-$ anion. It was imposible, too, to compare magnetic properties of $[(Ph_3AsO)_4FeOFeCl_3]^+$ cations from crystal lattice of the complexes I and II.

We also prepared another unsymmetrical oxo-bridged diiron(III) complexes with $[(Ph_3AsO)_4FeOFeBr_3]^+$ cation and study of their properties is in progress.

Atomic coordinates, displacement factor coefficients, full list of bond length and angles and lists of F_o/F_c values have been deposited as supplementary data with the Editor, from whom copies are available on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

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