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Synthesis and Characterization of $[Fe_2OX_6]^{2-}$ (X = Cl, Br, I) Complexes. Crystal and Molecular Structure of $(BzPh_3P)_2[Fe_2OCl_6]$

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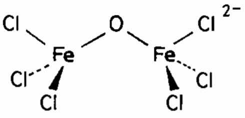
Abstract

Improved and simple methods for the preparation of $[Fe_2OX_6]^{2-}$ (X = Cl Br I) complexes are described. The complexes were obtained in high and purified yields as the $BzPh_3P^+$ or R_4N^+ salts. An X-ray crystallographic study of $(BzPh_3P)_2[Fe_2OCl_6]$ revealed a structure for the complex anion in which the two iron atoms are linked by a μ-oxo bridge and the terminal coordination sites are occupied by the chloride ligands. Mössbauer and infrared spectra for the complexes are reported.

Introduction

Oxo-bridged dimeric iron centers are of particular importance in the aqueous chemistry and biochemistry of iron. Iron-proteins that contain the $[Fe_2O]^{4+}$ core have been found in the invertebrate non-heme oxygen carriers hemerythrin [1] and myohemerythrin [1b 2] in ribonucleotide reductase [2], and in interoferring and bovine spleen purple acid phosphatase [4]. On the other hand there are many known and well characterized synthetic oxo-bridged binuclear iron complexes [5]. Among these the simple oxo-bridged binuclear complex **1**, featuring both iron atoms in tetrahedral coordination and chlorine atoms as non-bridging ligands, has been obtained by partial hydrolysis of $FeCl_3$ in nonaqueous solvents and isolated as the pyridinium [6] and $[(Ph_3P)_4C_2Se]^{2+}$ salts [7]. Recently an improved method for the synthesis of $(Et_4N)_2[Fe_2OCl_6]$ using the silyl reagent $NaOSiMe_3$ has been reported [8].



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In view of the simplicity of the $[Fe_2OCl_6]^{2-}$ unit and its potential use as a precursor in the assembly of more complex molecules [9], as synthetic analogues of hemerythrin, we report here on improved and particularly simple methods for the preparation of the different members of the series $[Fe_2OX_6]^{-2}$, where X = Cl, Br, I. Of these the bromo and iodo derivatives are new compounds We also report on the structural characterization of the $(BzPh_3P)_2[Fe_2OCl_6]$ complex because of its high stability and its easy isolation from aqueous solution.

Experimental

Preparation of Compounds

All reagents and solvents were obtained from commercial sources and used without further purification. Benzyltriphenyl phosphonium chloride or bromide were prepared by refluxing triphenylphosphine with equivalent amounts or benzylchloride or benzylbromide in toluene for twelve hours. After cooling the crystalline products were filtered and dried in air. Benzyltriphenylphosphonium iodide was obtained from the corresponding chloride by a metathetical reaction. Elemental analyses for C, H, N were performed by the analytical service laboratory of the N.R.C. Demokritos. Halides were determined potentiometrically by standard methods. Iron was determined spectrophotometrically as the 1,10-phenanthroline complex.

$(BzPh_3P)_2[Fe_2OCl_6]$

(a) To a stirred solution of 3.88 g (10 mmol) of $BzPh_3PCl$ in 20 ml of ethanol were added dropwise 3.2 g (12 mmol) of $FeCl_3 \cdot 6H_2O$ in 30 ml of water. The resulting mixture was left for 3–4 h whereupon red crystals were deposited. They were collected by filtration, washed with water and dried in air. The pure product (3.2 g, 69%) can be recrystallized from acetonitrile (50 °C) yielding diamond shape, shiny red crystals. *Anal.* Calc. for $C_{50}H_{44}Cl_6Fe_2OP_2$: C, 57.34; H, 4.23, Cl, 20.31; Fe, 10.66. Found: C, 57.80; H, 4.21; Cl, 20.40; Fe, 10.32%.

(b) A suspension of 0.64 g (5 mmol) of $FeCl_2$ and 1.94 g (5 mmol) of $BzPh_3PCl$ in 30 ml CH_3CN was refluxed for 12 h. The resulting solution was filtered while hot to remove any unreacted starting materials, and the filtrate was left for 12 h at room temperature. During this time well shaped, red shiny

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crystals were deposited which were collected by filtration, washed with ether and dried in air. The product was 1.2 g (46%). *Anal.* Calc. for $C_{50}H_{44}Cl_6Fe_2OP_2$: C, 57.34; H, 4.23. Found C, 57.42; H, 4.20%.

$(BzMe_3N)_2[Fe_2OCl_6]$

To a stirred solution of 1.85 g (10 mmol) of $BzMe_3NCl$ in 30 ml ethanol were added dropwise 2.70 g (10 mmol) of $FeCl_3 \cdot 6H_2O$ in 20 ml of ethanol and 1.02 g (10 mmol) of Et_3N (or equivalent amount of any other available amine) in 30 ml ethanol. After thirty minutes of stirring the honey colored crystals were collected, washed with alcohol and ether and dried in air. The yield was 2.80 g (43.6%). It can be recrystallized from acetonitrile–ether with almost quantitative recovery. *Anal.* Calc. for $C_{20}H_{32}Cl_6Fe_2N_2O$: C, 37.48; H, 5.03; Cl, 33.18; Fe, 17.42; N, 4.36. Found: C, 37.62; H, 5.21; Cl, 33.52; Fe, 17.21; N, 4.21%.

$(BzEt_3N)_2[Fe_2OCl_6]$

This complex was prepared in a manner similar to that described for the $BzMe_3N^+$ salt. Starting with 2.7 g (10 mmol) of $FeCl_3 \cdot 6H_2O$, 2.28 g (10 mmol) of $BzEt_3NCl$ and 1.02 g (10 mmol) of Et_3N, 2.7 g (74%) of a yellow solid were obtained. *Anal.* Calc. for $C_{26}H_{44}Cl_6Fe_2N_2O$: C, 43.07; H, 6.11; Cl, 29.33; Fe, 15.40; N, 3.86. Found: C, 43.45; H, 5.98; Cl, 29.20; Fe, 15.55; N, 3.61%.

$(Et_4N)_2[Fe_2OCl_6]$

This was also prepared according to the procedure for the Me_3BzN^+ salt. From 2.7 g (10 mmol) of $FeCl_3 \cdot 6H_2O$, 1.66 g (10 mmol) of Et_4NCl and 1.02 g (10 mmol) of Et_3N, 1.52 g (65%) of a yellow–brown solid were obtained. This was recrystallized from acetonitrile–ether affording gold brown crystals. *Anal.* Calc. for $C_{16}H_{40}Cl_6Fe_2N_2O$: C, 31.98; H, 6.71; Cl, 35.40; Fe, 18.59; N, 4.66. Found: C, 32.23; H, 7.00; Cl, 35.18; Fe, 18.20; N, 4.40%.

$(BzPh_3P)_2[Fe_2OBr_6]$

This compound was prepared according to the method (b) for the preparation of $(BzPh_3P)_2[Fe_2OCl_6]$. A suspension of 1.08 g (5 mmol) of $FeBr_2$ and 2.17 g (5 mmol) of $BzPh_3PBr$ in 30 ml of CH_3CN were refluxed for 6 h. The resulting solution was filtered, and the filtrate was left for two days at room temperature. During this time, large diamond-shaped crystals were obtained and dried in air. The yield was 2.0 g (61%). *Anal.* Calc. for $C_{50}H_{44}Br_6Fe_2OP_2$ C, 45.70; H, 3.37; Br, 36.48; Fe, 8.50. Found: C, 45.12; H, 3.50; Br, 36.63; Fe, 8.70%.

$(BzPh_3P)_2[Fe_2OI_6]$

A solution of 1.27 g (5 mmol) of FeI_2 in 50 ml of ethyl alcohol was prepared by refluxing 1.27 g of iodine with an excess of iron powder (0.400 g) followed by filtration. To the resulting solution were added a few drops of a 30% solution of H_2O_2. After a few seconds a vigorous reaction took place and a yellow–brown solid precipitated. This was collected, washed with ether and dried in air. It was recrystallized from 30 ml acetonitrile (50 °C) affording 1.9 g (47.6%) shiny red crystals. *Anal.* Calc. for $C_{50}H_{44}Fe_2I_6OP_2$: C, 37.61; H, 2.77; Fe, 6.99; I, 47.72. Found: C, 37.32; H, 2.91; Fe, 7.10; I, 47.25%.

Physical Measurements

Mössbauer spectra were recorded by using a conventional constant acceleration spectrometer. The source was ^{57}Co (Rh). Infrared spectra were recorded in KBr on a Perkin-Elmer Model 283 spectrophotometer.

X-ray Data of $(BzPh_3P)_2[Fe_2OCl_6]$

Preliminary oscillation and Weissenberg photographs showed that the space group was $P2_1/C$. The crystal was mounted on a $P2_1$ Syntex diffractometer and the cell parameters, Table I, were calculated by least-squares refinement of the setting angles of 20 automatically centered reflections ($20° < 2\theta < 23°$). The intensities of 3 standard reflections monitered regularly during data collection showed no decay. The data were reduced with the SHELX-76 program [10] which was also used for all subsequent calculations. Atomic scattering factors, as well as values for $\Delta f'$ and $\Delta f''$ for all nonhydrogen atoms, were taken from the International Tables [11]. Lorentz and polarization but no absorption corrections were applied. The structure was solved by the heavy-atom method. Fourier syntheses revealed the positions of all other atoms. However, all hydrogen atoms were placed in calculated positions and during the refinement they were riding on their respective carbon atoms. The phenyl groups were refined as rigid bodies (C–C = 1.385 Å, C–C–C = 120 and C–H = 1.00 Å) with anisotropic thermal parameters for each carbon atom. For each phenyl group the five hydrogen atoms had their isotropic thermal parameters tied to a free variable which was refined. All other atoms had anisotropic thermal parameters. Refinement was carried out by blocked full-matrix least-squares calculation in which $\Sigma w\Delta^2$ was minimized. One block contained the anion $[Fe_2OCl_6]^{2-}$ and one cation $BzPh_3P^+$ and the other block the second cation $BzPh_3P^+$. The weight for each reflection was initially unity and in the final cycles given by $w = 1/(\sigma(F_o)^2 + cF_o^2)$ where $c = 0.0003$ was chosen such that the average values for $w\Delta^2$ for ranges of increasing F_o were almost constant. The last two cycles of refinement included an empirical isotropic extinction parameter, and they converged to an $R = (\Sigma \| F_o| - |F_c\| / \Sigma |F_o|)$ of 0.0389 and $R_w = [\Sigma w \| F_o| - |F_c\|^2 / \Sigma w |F_o|^2]^{1/2}$ of 0.0450. A final

TABLE I. Summary of Crystal and Intensity Collection Data

Compound	$(BzPh_3P)_2[Fe_2OCl_6]$	$(BzPh_3P)_2[Fe_2OBr_6]$
Formula	$C_{50}H_{44}Cl_6Fe_2OP_2$	$C_{50}H_{44}Br_6Fe_2OP_2$
Molecular weight	1047.3	1313.5
a (A)	20.477(2)	20.839(6)
b (A)	13.489(2)	13.593(3)
c (A)	19.196(2)	19.609(5)
β (deg)	111.78(1)	111.69(2)
V (A^3)	4923.3	
Z	4	
D_{calc} (g/cm^3)	1.412	
D_{meas} (g/cm^3)	1.40	
Space group	$P2_1/C$	
Crystal dimensions (mm)	0.15 radius	
Crystal shape	sphere	
Radiation	Mo K$\bar{\alpha}$, Zr-filtered	
μ (cm^{-1})	9.66	
Scan type	$\theta/2\theta$	
Scan speed ($2\theta°$/min)	variable, 1 to 10	
Scan range (deg)	0.8 below Ka_1 to 0.8 above Ka_2	
Background counting (s)	0.6 × scan time	
2θ limit (deg)	47	
Data collected/unique	8317/7326	
Data used	5309 with $I \geqslant 2.5\sigma(I)$	
Data form	*hkl and $\bar{h}kl$*	
Data/parameter	5309/443	
R	0.0389	
R_w	0.0450	

difference Fourier map showed no peak greater than 0.35 e/Å^3. Positional and U_{eq} parameters are given in Table II.

TABLE II. Final Positional Parameters and U_{av} ($\times 10^4$) with Estimated Standard Deviations in Parentheses. $U_{av} = U_{11} + U_{22} + U_{33}$

Atom	x	y	z	U
Fe1	1936(3)	3873(4)	4818(3)	478
Fe2	7254(3)	3824(4)	4824(3)	424
Cl11	2189(1)	3401(1)	3847(1)	977
Cl12	784(1)	4006(1)	4451(1)	826
Cl13	2295(1)	2283(1)	717(1)	744
Cl21	6614(1)	1172(1)	530(1)	834
Cl22	6543(1)	3514(1)	3648(1)	615
Cl23	8050(1)	2360(1)	261(1)	756
P1	9394(1)	1474(1)	2747(1)	436
P2	4223(1)	1315(1)	2678(1)	430
O	7653(2)	4987(2)	4843(2)	700
C1	8603(2)	784(3)	2215(2)	514
C11	7625(2)	1470(2)	2530(2)	652
C12	7176(2)	1460(2)	2920(2)	886
C13	7202(2)	685(2)	3403(2)	911
C14	7679(2)	−80(2)	3496(2)	762
C15	8128(2)	−71(2)	3107(2)	573
C16	8101(2)	704(2)	2623(2)	438
C21	8974(1)	2713(2)	3656(1)	620
C22	8728(1)	3603(2)	3824(1)	738
C23	8649(1)	4415(2)	3358(1)	752
C24	8818(1)	4338(2)	2725(1)	724
C25	9064(1)	3449(2)	2557(1)	570
C26	9143(1)	2636(2)	3022(1)	445
C31	10025(1)	4764(2)	1489(1)	526
C32	9556(1)	4236(2)	895(1)	643
C33	9129(1)	4729(2)	255(1)	652
C34	9171(1)	5750(2)	210(1)	669
C35	9639(1)	6278(2)	804(1)	577
C36	10066(1)	5785(2)	1444(1)	455
C41	9686(1)	1329(2)	1447(1)	573
C42	10105(1)	1470(2)	1031(1)	706
C43	10744(1)	1956(2)	1346(1)	775
C44	10963(1)	2301(2)	2077(1)	675
C45	10543(1)	2160(2)	2492(1)	595
C46	9905(1)	1674(2)	2177(1)	474
C51	2811(2)	970(2)	3358(2)	649
C52	2576(2)	593(2)	3895(2)	800
C53	2682(2)	−397(2)	4096(2)	810
C54	3023(2)	−1010(2)	3761(2)	783
C55	3257(2)	- 633(2)	3224(2)	649
C56	3152(2)	357(2)	3023(2)	469
C61	5089(1)	615(2)	4082(1)	619
C62	5610(1)	4(2)	4553(1)	692
C63	5926(1)	−697(2)	4254(1)	637
C64	5722(1)	−786(2)	3483(1)	684

(continued)

TABLE II. *(continued)*

Atom	*x*	*y*	*z*	*U*
C65	5201(1)	-175(2)	3012(1)	568
C66	4885(1)	525(2)	3311(1)	458
C71	4851(1)	2909(2)	3581(1)	501
C72	4863(1)	3851(2)	3872(1)	564
C73	4246(1)	4390(2)	3687(1)	620
C74	3617(1)	3986(2)	3211(1)	608
C75	3605(1)	3044(2)	2920(1)	497
C76	4222(1)	2505(2)	3105(1)	425
C81	4001(1)	1278(2)	1153(1)	531
C82	4197(1)	1459(2)	547(1)	666
C83	4851(1)	1862(2)	661(1)	641
C84	5309(1)	2085(2)	1382(1)	652
C85	5113(1)	1904(2)	1987(1)	576
C86	4459(1)	1501(2)	1873(1)	421
C2	3366(2)	732(3)	2386(2)	489

Results and Discussion

The $[Fe_2OX_6]^{2-}$ complexes (X = Cl, Br, I) with different counterions were prepared according to reactions 1–3 from common reagents in highly purified yields.

$$2FeCl_3{\cdot}6H_2O + 2BzPh_3PCl \xrightarrow{EtOH} (BzPh_3P)_2[Fe_2OCl_6] + 2HCl + 6H_2O \qquad (1)$$

$$2FeCl_3{\cdot}6H_2O + 2BuNH_2 + 2R_4NCl \xrightarrow{EtOH} (R_4N)_2[Fe_2OCl_6] + 2BuNH_3Cl + 5H_2O \qquad (2)$$

$$2FeX_2 + 2BzPh_3PX + \tfrac{1}{2}O_2 \xrightarrow{MeCN} (BzPh_3P)_2[Fe_2OX_6] \qquad (3)$$

Reactions 1 and 2 demonstrate the intrinsic stability of the $[Fe_2OCl_6]^{2-}$ unit as a hydrolysis product of ferric chloride. It is noteworthy that the $BzPh_3P^+$ salt of this dimer was obtained in excellent yield from aqueous reaction mixtures. Reaction 3 involves the use of a divalent iron halide and the corresponding benzyl triphenylphosphonium halide for the assembly of the $(BzPh_3P)[Fe_2OX_6]$ complexes. Without intending to comment as to the mechanism of this reaction, it is likely that air oxidation leads to the formation of the $[Fe_2O]^{4+}$ core in anhydrous medium. The preparation of $(BzPh_3P)_2[Fe_2OI_6]$ from FeI_2 and $BzPh_3PI$ was accomplished by using hydrogen peroxide as oxidant. It is also appropriate to note that the $(BzPh_3P)_2[Fe_2OI_6]$ complex is the first molecule, to our knowledge, which contains three iodine atoms bonded to trivalent iron and which is quite stable at room temperature. The tetrahedral $(R_4N)[FeI_4]$ molecule, with iron in a tetrahedral environment of four iodine atoms, is known but stable only at low temperatures [12].

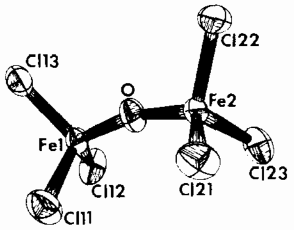

Fig. 1. View of the coordination environment of μ-oxo-bis-(trichloroferrate(III)) anion.

TABLE III. Bond Lengths (A) and Angles (deg) in the Anion of $(BzPh_3P)_2[Fe_2OCl_6]$

Distances			
Fe1–O	1.757(3)	Fe2–O	1.763(3)
Fe1–Cl11	2.205(2)	Fe2–Cl21	2.207(2)
Fe1–Cl12	2.207(1)	Fe2–Cl22	2.226(1)
Fe1–Cl13	2.237(2)	Fe2–Cl23	2.212(2)
Angles			
Cl11–Fe1–O	109.7(2)	Cl21–Fe2–O	111.1(2)
Cl11–Fe1–Cl12	108.2(1)	Cl21–Fe2–Cl22	107.9(1)
Cl11–Fe1–Cl13	109.7(1)	Cl21–Fe2–Cl23	106.9(1)
Cl12–Fe1–O	110.8(1)	Cl22–Fe2–O	108.1(1)
Cl12–Fe1–Cl13	108.0(1)	Cl22–Fe2–Cl23	111.2(1)
Cl113–Fe1–O	110.4(2)	Cl23–Fe2–O	111.4(2)

Description of the Structure of $(BzPh_3P)_2[Fe_2OCl_6]$

The structural features of the $BzPh_3P^+$ cation are very similar to those reported [13] and it will not be discussed here. The anion $[Fe_2OCl_6]^{2-}$ appears in three previous structures with different cations, *i.e.*, pyridinium [6], tris(1,10-phenanthroline)iron(II) [14] and tetraphenylphosphonium*. The present determination confirms the tetrahedral geometry about each iron atom and the bridging of the two irons by an oxygen atom, Fig. 1. Pertinent structural parameters are shown in Table III. Although there is very good agreement in the bond lengths and angles for the $[Fe_2OCl_6]^{2-}$ anion in all four structures, there is a large variation in the conformations, Table IV*. As can be seen from Table IV (see also Fig. 1) the conformation of one $FeCl_3$ unit with respect to the other $FeCl_3$ unit and to the $\mathrm{Fe}\overset{\mathrm{O}}{\diagup\,\diagdown}\mathrm{Fe}$ plane varies greatly. The Cl13–Fe1–Fe2–Cl22 torsion angle

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*The structure of $[Fe_2OCl_6]^{2-}$ with Ph_4P^+ is not included in Table IV because it is disordered and it appears as if the oxygen atom occupies a center of symmetry.

TABLE IV. Comparison of some Structural Parameters in $[F_2OCl_6]^{2-}$

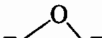
	This study	Reiff[a]	Drew[b]
Fe1–Fe2 (A)	3.467(2)	3.455(7)	3.428(3)
Fe1–O (A)	1.757(3)	1.76(2)	1.755(3)
Fe2–O (A)	1.762(3)	1.74(2)	d
Fe1–O–Fe2 (deg)	160.2(5)	161.6(9)	155.6(7)
Fe1–O–Fe2/Cl13–Fe1–O[c]	35.4	25.9	12.4
Fe1–O–Fe2/Cl22–Fe2–O[c]	26.1	−45.5	d
Cl13–Fe1–Fe2–Cl22[e]	10.2	75.5	0[d]

[a] Ref. 14. [b] Ref 6 [c] Angle (deg) between the two planes defined by the respective three atoms. [d] The O atom is on a mirror plane. [e] Torsion angle (deg).

TABLE V. Infrared and Mössbauer Parameters

Compound	Fe–O–Fe (cm^{-1})	Fe–X (cm^{-1})	T (K)	IS[a] (cm^{-1})	ΔE_Q ($mm\ s^{-1}$)	A_{II}/A_I[b]
$(BzPh_3P)_2[Fe_2OCl_6]$	860s	350s, 308m	300	0.225	1.20	1.05
			77	0.329	1.24	1.02
$(BzMe_3N)_2[Fe_2OCl_6]$	843s	355s, 310m	300	0.220	1.20	1.50
			77	0.316	1.28	1.16
$(BzEt_3N)_2[Fe_2OCl_6]$	868s	360s, 308m	300	0.224	1.27	1.21
			77	0.324	1.31	1.06
$(Et_4N)_2[Fe_2OCl_6]$	858s	360, 310m	300	0.233	1.34	1.18
			77	0.328	1.37	1.03
$(BzPh_3P)_2[Fe_2OBr_6]$	830m	270m	300	0.221	1.37	1.03
			77	0.318	1.39	
$(BzPh_3P)_2[Fe_2OI_6]$	835m		300	0.216	1.42	
			77	0.315	1.43	

[a] With respect to Fe metal at room temperature. [b] Relative peak amplitudes.

varies from 0° to 10.2° to 75.5°. We also note that bonds Fe1–Cl13 and Fe2–Cl22 are longer than the other four Fe–Cl bonds by more than ten standard deviations. These chlorine atoms, Cl13 and Cl22, are the ones which together with the Fe atoms define a mean plane closest to the  plane, Fig. 1. The same effect, although not as clear as in the present study, is also observed in the Drew and Reiff structures. The $(BzPh_3P)_2[Fe_2OBr_6]$ complex is isostructural to the chloro derivative and its unit cell parameters are shown in Table I.

Infrared Spectra

The important features of the spectra are found around 860 cm^{-1} where the asymmetric Fe–O–Fe stretching vibration is expected to occur. Strong absorption in this region is commonly used as diagnostic criterion for identification of the cation of (μ-oxo) diiron complexes [16]. All complexes reported here exhibit an intense broad band around 860 cm^{-1} as indicated in Table V.

The local symmetry around each iron atom in the $[Fe_2OX_6]^{2-}$ anion is C_{3v} and, hence, two IR active Fe–X vibrations are expected. In line with this assignment we have observed two absorptions in the 450–400 cm^{-1} region, Table V, in the several chloro derivatives of the series. Absorption in this region is absent in the bromo or iodo derivatives of the series. A strong absorption at 270 cm^{-1} by the $[Fe_2OBr_6]^{2-}$ anion is attributed to one of the two expected Fe–Br antisymmetric vibrations; the other apparently occurs below 250 cm^{-1} and hence it is not detected by our instrument.

Mössbauer Spectra

The Mössbauer spectra at 300 K and 77 K of all complexes consist of quadrupole doublet in agreement with previous observations [6, 7]. The quadrupole interaction of all complexes does not show any significant temperature variation between 300 K and 77 K. However, the spectra of the chloro derivatives exhibit a marked peak asymmetry at 300 K which decreases significantly at 77 K. Because of strong intramolecular exchange coupling ($J \simeq 90$

cm^{-1}) [6] these dimeric oxo molecules even at room temperature populate mainly the diamagnetic, $S_{\mathrm{TOTAL}} = 0$, ground state, and hence the peak asymmetry cannot be due to electronic spin relaxation. The observed line asymmetry is likely associated with anisotropy of the recoil-free fraction of the absorber iron nuclei (Goldanskii-Karyagin effect). This is not unexpected in view of the anisotropic coordination environment of each iron in a dimeric molecule. This argument is supported by the different degree of line asymmetry observed in the various chloro derivatives with different stabilizing countercations, Table V.

The isomer shift values at 77 K of all complexes fall in the range 0.3 to 0.6 mm s^{-1} associated with each iron in a $S = 5/2$ spin state [17]. The isomer shift values are somewhat smaller than those of other reported μ-oxo-complexes [18]. This difference is attributed to the greater covalent character of the bonds in tetrahedral *vs.* octahedral complexes [17]. The quadrupole splittings are very similar for all complexes, and although they are large compared to those of simple high-spin iron compounds, they are near to the values reported for other oxygen-bridged binuclear high-spin iron(III) compounds [18]. The large quadrupole splittings reflect the electronic asymmetry about the Fe ion arising from a strong Fe–O bond and weakened Fe–halide bonds. Most of the tetrahedral, spin-free $[\mathrm{FeX_4}]^-$ salts do not show any measurable quadrupole splitting because of the equivalent iron–halogen bonds [17].

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