Inorg. Chem. **1993,** *32,* 520–525

The (μ-Oxo)bis[trichloroferrate(III)] Dianion Revisited

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Received May 27, 1992

From 11 published crystal structure determinations of salts containing the (μ-oxo)bis[trichloroferrate(III)] dianion the following structural features of the anion in the solid state are evident: (i) The structure is dependent on the nature of the respective countercation. (ii) The Fe–O–Fe bond angle spans a range from 146.5 to 170.8°; a linear Fe–O–Fe unit has not been experimentally verified. (iii) The Fe–O_{oxo} bond distances are within experimental error identical (1.756 Å). (iv) The geometry of the Cl_3FeO unit is approximately tetrahedral, but the symmetry is C_s; description in C_{3v} symmetry is in many instances not appropriate. (v) The two corner-sharing tetrahedra adopt different conformations depending on the nature of the countercation. The crystal structure of $[Ph_4P]_2[Fe_2Cl_6O]$ has been determined: space group $P\bar{1}$, $a = 9.847(3)$ Å, $b = 12.953(5)$ Å, $c = 21.099(5)$ Å, $\alpha = 85.12(3)°$, $\beta = 76.45(2)°$, $\gamma = 67.70(3)°$, and $Z = 2$. Five crystallographically well-characterized salts with Fe–O–Fe angles ranging from 148.1 to 170.8° have been investigated by infrared and Raman spectroscopy, and their magnetic susceptibilities have been measured in the temperature range 2.7–295 K. Antiferromagnetic exchange coupling between the ferric ions has been established in all cases. The coupling constant J was found to be 112 ± 5 cm^{-1} ($H = -2JS_1 \cdot S_2$; $S_1 = S_2 = {}^5/_2$) irrespective of the actual structure of the $[Fe_2Cl_6O]^{2-}$ anion. An angle dependence of the intramolecular antiferromagnetic coupling has not been detected within the experimental accuracy of our measurements.

Introduction

Drew, McKee, and Nelson reported in 1978 the synthesis, crystal structure, and magnetic properties of bispyridinium (μ-oxo)bis[trichloroferrate(III)]–pyridine, $[Hpy]_2[Fe_2Cl_6O]py$.[1] Since then, a number of other salts containing the (μ-oxo)bis[trichloroferrate(III)] dianion have been synthesized and crystallographically characterized.[1-18] We have listed those in Table I. Synthesis of this species has been achieved by a variety of methods yielding the dinuclear oxo-bridged complex in many instances as a serendipitously obtained side product. In 1985 Armstrong and Lippard published a convenient, high-yield synthesis of $[Et_4N]_2[Fe_2Cl_6O]$,[19] which is similar to the procedure published by Do, Simhon, and Holm.[20]

An important result of the crystal structure determinations has been the discovery that the geometry of the $[Fe_2Cl_6O]^{2-}$ anion in the solid state is dependent on the nature of the respective countercation. While both iron(III) ions are always tetrahedrally coordinated (Cl_3FeO) with little or no significant variation of the Fe–Cl and Fe–O bond distances and nearly ideal tetrahedral Cl–Fe–Cl and Cl–Fe–O bond angles, the Fe–O–Fe bond angle appears to vary between 146.5 and 180° (Table I) if the reported structural results from the literature are used in an uncritical manner. The two corner-sharing tetrahedra in the $[Fe_2Cl_2O]^{2-}$ anions adopt different positions relative to each other; there are a number of different conformations. The dinuclear $[Cl_3Fe\text{–}O\text{–}FeCl_3]^{2-}$ complex has in the past decade served as a paradigm for strong intramolecular antiferromagnetic spin exchange coupling between two high-spin ferric ions mediated by an oxo bridge.

Magnetochemical studies on a large number of dinuclear ferric complexes have unambiguously established that the magnitude of the antiferromagnetic spin exchange coupling constant J as defined by the spin Hamiltonian $H = -2JS_1 \cdot S_2$ ($S_1 = S_2 = {}^5/_2$) is strongly dependent on the Fe–O_{oxo} bond distance.[21,23] The shorter this bond, i.e. the larger the overlap of half-filled 3d orbitals of the ferric ions and a filled p orbital of the oxo bridge (magnetic superexchange pathway), the more efficiently are the unpaired spins of one Fe(III) ion coupled to those of the second Fe(III) ion in an antiparallel fashion. This invariably results in a diamagnetic $S = 0$ ground state for the (μ-oxo)diiron(III) complexes.

Several authors[22-24] have recently addressed the question of an Fe–O–Fe angular dependence of J. Mukherjee, Stack, and Holm

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[†] Ruhr-Universität Bochum.

[‡] Universität-Gesamthochschule Essen.

(1) Drew, M. G. B.; McKee, V.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1978,** 80.

(2) Solbrig, R. M.; Duff, L. L.; Shriver, D. F.; Klotz, I. M. *J. Inorg. Biochem.* **1982,** *17,* 69.

(3) Adler, J.; Ensling, J.; Gütlich, P.; Bominaar, E.; Guillin, J.; Trautwein, A. X. *Hyperfine Interact.* **1988,** *42,* 869.

(4) Schmidbaur, H.; Zybill, C. E.; Neugebauer, D. *Angew. Chem., Int. Ed. Engl.* **1983,** *22,* 156.

(5) Dehnicke, K.; Prinz, H.; Massa, W.; Pebler, J.; Schmidt, R. *Z. Anorg. Allg. Chem.* **1983,** *499,* 20.

(6) Juang, L.; Jiang, F.; Lu, J. *Huaxue Tongbao* **1984,** 14.

(7) Vasilevsky, I.; Stenkamp, R. E.; Lingafelter, E. C.; Rose, N. J. *J. Coord. Chem.* **1988,** *19,* 171.

(8) Reiff, W. M.; Witten, E. H.; Mottle, K.; Brennan, T. F.; Garafalo, A. R. *Inorg. Chim. Acta* **1983,** *77,* L83.

(9) Bullen, G. J.; Howlin, B. J.; Silver, J.; Fitzsimmons, B. W.; Sayer, I.; Larkworthy, L. F. *J. Chem. Soc., Dalton Trans.* **1986,** 1937.

(10) Boeyens, J. C. A.; Khan, F. B. D.; Neuse, E. W. S. *South Afr. J. Chem.* **1984,** *37,* 187.

(11) Carty, P.; Clare, K. C.; Creighton, J. R.; Metcalfe, E.; Raper, E. S.; Dawes, H. M. *Inorg. Chim. Acta* **1986,** *112,* 113.

(12) Petridis, D.; Terzis, A. *Inorg. Chim. Acta* **1986,** *118,* 129.

(13) Weiss, H.; Strähle, J. *Z. Naturforsch.* **1984,** *39b,* 1453.

(14) Healy, P. C.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1983,** *36,* 2057.

(15) Neuse, E. W.; Khan, F. B. W.; Berhalter, K.; Thewalt, U. *Crystallogr. Spectrosc. Res.* **1986,** *16,* 483.

(16) Ponomarev, V. I.; Arutyunyan, L. D.; Atovmyan, L. O. *Kristallografiya* **1984,** *29,* 910; *Sov. Phys. Crystallogr.* **1984,** *29,* 538.

(17) Gütlich, P.; Peters, K. Unpublished results.

(18) Neuse, W.; Meirim, M. G. *Transition Met. Chem.* **1984,** *9,* 205.

(19) Armstrong, W. H.; Lippard, S. J. *Inorg. Chem.* **1985,** *24,* 981.

(20) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1983,** *22,* 3809.

(21) Gorum, S. M.; Lippard, S. J. *Inorg. Chem.* **1991,** *30,* 1625.

(22) Mukherjee, R. N.; Stack, T. D. P.; Holm, R. H. *J. Am. Chem. Soc.* **1988,** *110,* 1850.

(23) Kurtz, D. M., Jr. *Chem. Rev.* **1990,** *90,* 585.

0020-1669/93/1332-0520$04.00/0

Table I. Compilation of Structural Data for Compounds Containing the $[Fe^{III}Cl_6O]^{2-}$ Anion[a]

compd	α(Fe–O–Fe), deg	Fe–O, Å	Fe–Cl, Å	sym[b]	disorder[c]	ref
$[Hpy]_2[Fe_2Cl_6O]py$	155.6(7)	1.755(3)	2.208–2.219	C_s	–/+	1
$[\{Ph_3P\}_2CSe]_2[Fe_2Cl_6O]$	180			C_i	+	4
$[Ph_4P]_2[Fe_2Cl_6O]\cdot 2CH_2Cl_2$	180	1.740(1)	2.206–2.222	C_i	+	5
$[Mg(dmf)_6][Fe_2Cl_6O]$[d]	180					6
$[Ph_4As]_2[Fe_2Cl_6O]$ (**5**)	170.8(5)	1.74(3)	2.204–2.210	C_2	+	7
$[Ph_4P]_2[Fe_2Cl_6O]$ (**4**)	170.4(4)	1.744(4), 1.744(4)	2.205–2.216		+	this work
$[BzEt_3N]_2[Fe_2Cl_6O]$ (**2**)	155.3(3)	1.752(5), 1.758(5)	2.206–2.231		–	17
$[Fe(phen)_3][Fe_2Cl_6O]\cdot dmf$	161.6(9)	1.76(2), 1.74(2)	2.204–2.23		+	8
$[Fe(\eta^5\text{-}Cp)_2]_2[Fe_2Cl_6O]$	162.4(9)	1.757(2)	2.204–2.193	C_s	+	9
	160.8(7)	1.754(2)	2.197(3) av	C_s	+	10
	162.1(5)	1.749(4)	2.190–2.201	C_s	+	11
$[BzPh_3P]_2[Fe_2Cl_6O]$ (**3**)	160.2(5)	1.757(3), 1.763(3)	2.205–2.237		–	12
$[Fe(bpy)_3][Fe_2Cl_6O]$ (**1**)	148.1(2)	1.764(3), 1.766(3)	2.216–2.238		–	13
	148.9(7)	1.763(11), 1.740(11)	2.201–2.225		–	14
$[PhBzMe_2N]_2[Fe_2Cl_6O]$	147.7(3)	1.757(5), 1.775(5)	2.202–2.223		–	15
$[FeCl(dmso)_5][Fe_2Cl_6O]$[e]	146.5(2)	1.778(4), 1.774(5)	2.214–2.231		+	16
	152.7(4)	1.754(7), 1.765(8)	2.297–2.211		+	

[a] Abbreviations: Hpy = pyridinium cation; py = pyridine; Ph = phenyl; dmf = dimethylformamid; Bz = benzyl; Et = ethyl; phen = *o*-phenanthroline; cp = cyclopentadienyl; bpy = 2,2′-bipyridine; dmso = dimethyl sulfoxide. [b] Crystallographically imposed symmetry of the $[Fe_2OCl_6]^{2-}$ anion. [c] + indicates orientational disorder of the $[Fe_2OCl_6]^{2-}$ anion as judged from published displacement parameters of the oxygen and/or chlorine atoms, +/– indicates disorder possible but not clearly documented; – indicates no disorder problems apparent. [d] Literature not available; data from: *Chem. Abstr.* **1984**, *101*, 560 (*101*:63979a). [e] Crystal structures determined at (a) 103 K and (b) 300 K.

have fully characterized a pair of corner-sharing biooctahedral ferric complexes with identical Fe–O_{oxo} distances but different Fe–O–Fe angles (145 and 173°) and concluded from careful temperature-dependent susceptibility measurements that *J* shows an angle dependence.[22] Que et al., on the other hand, have shown that in doubly bridged (μ-oxo)diferric complexes no such dependence is experimentally verifiable.[24]

In all these examples the complexes compared have different ligands and subtle unidentified effects may influence the magnitude of *J*. Therefore, it appeared to us very promising to study the Fe–O–Fe angle dependence of *J* in different salts containing the $[Cl_3Fe{-}O{-}FeCl_3]^{2-}$ anion.

Inspection of the existing literature on the magnetic properties of these salts immediately revealed that the available data are of insufficient quality to prove or disprove the above question. For instance, for $[Hyp]_2[Fe_2Cl_6O]py$ Drew et al.[1] reported a *J* value of $-92\ cm^{-1}$, which was calculated from temperature-dependent susceptibility data in the range 130–293 K. On the other hand, Adler et al.[3] reported for the same compound a *J* value of $-127\ cm^{-1}$ without providing experimental details.[25] In the same paper these authors report a *J* value of $-190.3\ cm^{-1}$ for $[\{(C_6H_5)_3P\}_2CSe]_2[Fe_2Cl_6O]$.[4] Taking the data in ref 3 where four different salts containing the $[Fe_2Cl_6O]^{2-}$ dianion have been investigated, one could—at least qualitatively—construct a dependence of *J* on the Fe–O–Fe bond angle.

We decided to determine or redetermine the spin exchange coupling constants of five salts which have been structurally well characterized (with no or small disorder problems). We also report the crystal structure of $[PPh_4]_2[Fe_2Cl_6O]$.

Experimental Section

Preparation of Salts Containing the $[Fe_2Cl_6O]^{2-}$ Anion. $[Fe^{II}(bpy)_3][Fe_2Cl_6O]$ (**1**) was prepared as described in ref 13; $[Ph_4As]_2[Fe_2Cl_6O]$ (**5**) as in ref 7.

Synthesis of [cation]$_2$[Fe$_2$Cl$_6$O] Salts (Cation = $[BzEt_3N]^+$ (2), $[BzPh_3P]^+$ (3), $[Ph_4P]^+$ (4)). To a filtered solution of $FeCl_2\cdot 4H_2O$ (0.96 g; 4.8 mmol) in dry methanol (45 mL) was added solid [cation]Cl (cation = $[Ph_4P]^+$, $[BzPh_3P]^+$) (4.0 mmol). After filtration the solution was allowed to stand in an open vessel in the presence of air at 22 °C for 2–3 days. Brown crystalline solids formed, which were collected by filtration and dried in air. The yields of the desired [cation]$_2$[Fe$_2$Cl$_6$O] salts were in the range 10–25% based on $FeCl_2\cdot 4H_2O$. Typically X-ray-quality crystals of high purity were obtained in this fashion.

Table II. Crystal Data for $[Ph_4P]_2[Fe_2OCl_6]$

formula	$C_{48}H_{40}Cl_6Fe_2OP_2$	*Z*	2
cryst system	triclinic	*T*	295
space group	$P\bar{1}$	fw	1019.1
a Å	9.847(3)	λ, Å	0.711 073
b, Å	12.953(5)	μ(Mo Kα), cm^{-1}	1.032
c, Å	21.099(5)	ρ_{calcd}, g cm^{-3}	1.398
α, deg	85.12(3)	$R(F_o)$[a]	0.0445
β, deg	76.45(2)	$R(F_o^2)$[b]	0.043
γ, deg	67.70(3)		

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R(F_o^2) = \{\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2\}^{1/2}$; $w^- = \sigma^2(F) + 0.0001F^2$.

$[BzEt_3N]_2[Fe_2Cl_6O]$ (**2**) was prepared similarly by combining a solution of $FeCl_2\cdot 4H_2O$ (0.35 g; 1.8 mmol) in CH_3OH (50 mL) and a solution of $[BzEt_3N]Cl$ (0.45 g; 2.0 mmol) in CH_3OH (50 mL).

X-ray Structure Determination. Intensities and lattice parameters of a brown, rhombohedrally shaped crystal of $[PPh_4]_2[Fe_2Cl_6O]$ were measured on a Siemens P4 diffractometer at 293 K (Table II) by using Mo Kα X-ray radiation. Intensities were corrected for Lorentz and polarization effects in the usual manner; an empirical absorption correction (ψ-scans) was carried out. The Siemens SHELXTL PLUS (VMS) program package was used. The structure was solved by using direct methods. The function minimized during full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(F) + 0.0001F^2$. Neutral-atom scattering factors and anomalous dispersion corrections were taken from ref 26. The positions of all phenyl hydrogen atoms were located in the final difference Fourier map and were included in the refinement with isotropic thermal parameters. The observed C–H distances are in the range 0.9–1.1 Å. All other non-hydrogen atoms were refined with anisotropic thermal parameters.

Physical Measurements. Temperature-dependent magnetic susceptibilities on powdered samples were measured either with a SQUID magnetometer (MPMS, Quantum Design) in the temperature range 2.7–295 K or by the Faraday method in the temperature range 77–295 K. Corrections for the diamagnetic response of the sample holder and for diamagnetic contributions of the samples (Pascal's constants) were carried out.

Infrared spectra were recorded on a Perkin-Elmer 1720 X FT-IR spectrometer in the range 4000–400 cm^{-1} (KBr disks). Spectra in the range 500–200 cm^{-1} were recorded on a Perkin-Elmer 1700 X FT-IR spectrometer (KBr disks). Raman spectra of solid samples were recorded on a Bruker NIR-FT Raman spectrometer (FRA-106) equipped with a germanium detector (liquid nitrogen cooling) and a Michelson interferometer (FT). A Nd–YAG laser (350 mW; 1064 nm) was used.

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(24) Norman, R. E.; Holz, R. C.; Ménage, S.; O'Connor, C. J.; Zhang, J. H.; Que, L., Jr. *Inorg. Chem.* **1990**, *29*, 4629.

(25) Susceptibility measurements were carried out in the temperature range 4–298 K. Gütlich, P. Private communication.

(26) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 99, 149.

Table III. Atom Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for the $[Fe_2Cl_6O]^{2-}$ Anion in $[Ph_4P]_2[Fe_2Cl_6O]$

atom	*x*	*y*	*z*	U_{eq}[a]
Fe(1)	5143(1)	1101(1)	2272(1)	52(1)
Fe(2)	3518(1)	3898(1)	2728(1)	52(1)
Cl(1)	6088(2)	882(1)	1209(1)	88(1)
Cl(2)	6887(2)	115(2)	2812(1)	96(1)
Cl(3)	3322(2)	443(2)	2504(1)	86(1)
Cl(4)	3179(2)	4119(1)	3791(1)	89(1)
Cl(5)	4810(2)	4890(2)	2189(1)	96(1)
Cl(6)	1270(2)	4556(2)	2494(1)	87(1)
O(1)	4479(5)	2500(3)	2499(2)	109(2)

[a] $U_{eq} = {}^1/_3 \sum_i \sum_j a_i^* a_j^* a_i a_j$.

Results and Discussion

Structure Determinations. A literature search revealed that the crystal structures of 11 different salts containing the $[Fe_2Cl_6O]^{2-}$ anion have been published since 1978. Pertinent data are compiled in Table I. Despite the apparent wealth of information available it is clear from a careful inspection of these data that many of these structure determinations have inherent crystallographic problems which do not allow an accurate assessment of even the true geometry of the $[Fe_2Cl_6O]^{2-}$ anion. In nearly all cases these problems are associated with crystallographically imposed site symmetry C_s, C_i, or C_2 of the anion which masks an orientational disorder of the anion. This is not always readily detected, but inspection of the thermal displacement parameters of the oxygen and chlorine atoms generally reveals this problem.

Three structure determinations are reported with an apparently linear Fe–O–Fe moiety. In ref 4 this has been taken as the first example for this geometry, but sufficient crystallographic data have not been provided to support this claim. Dehnicke et al.,[5] on the other hand, have clearly recognized the orientational disorder of a bent Fe–O–Fe unit in $[PPh_4]_2[Fe_2Cl_6O]\cdot 2CH_2Cl_2$ resulting in an apparently linear Fe–O–Fe group. They estimate a true Fe–O–Fe angle α of 167–172°. Data for the third structure[6] have not been available to us. Thus, the claim of the existence of an $[Fe_2Cl_6O]^{2-}$ anion with a *linear* Fe–O–Fe unit is not experimentally substantiated to date.

Since the structure determination of $[PPh_4]_2[Fe_2Cl_6O]\cdot 2CH_2Cl_2$[5] was also complicated by the presence of two solvate molecules of CH_2Cl_2, we decided to determine the structure of $[PPh_4]_2[Fe_2Cl_6O]$,[27] which does not contain additional solvate molecules in the crystal lattice. Interestingly, both salts crystallize in the same triclinic space group $P\bar{1}$ but with $Z = 2$ in our case and $Z = 1$ in Dehnicke's structure. Thus the $[Fe_2Cl_6O]^{2-}$ anion has no crystallographically imposed symmetry in the solvate-free salt. Table II summarizes crystal data for $[PPh_4]_2[Fe_2Cl_6O]$ (**4**). Table III gives atom coordinates of the $[Fe_2Cl_6O]^{2-}$ unit only, and Table IV lists bond distances and angles of the $[Fe_2Cl_6O]^{2-}$ anion. Figure 1 shows the structure of the dianion. The Fe–O–Fe angle α is 170.4(4)° in agreement with Dehnicke's estimate. Although the quality of the structure determination is good, the relatively large values of U_{eq} for the chlorine and, especially, the oxygen atom (Table III) do indicate some degree of orientational disorder of the dianion in the crystal lattice. Note that the cations $[Ph_4P]^+$ are not disordered since it has been possible to locate and refine the positions of the phenyl hydrogen atoms.

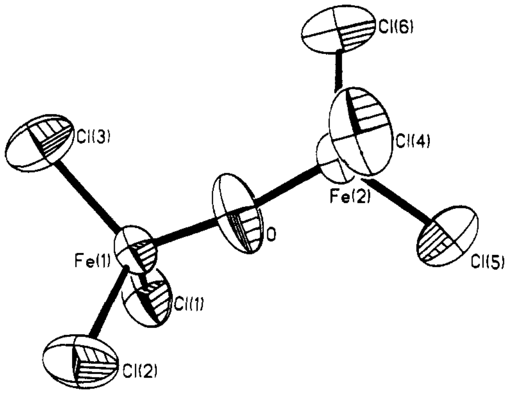

Figure 1. Structure of the $[Fe_2Cl_6O]^{2-}$ anion in crystals of $[Ph_4P]_2[Fe_2Cl_6O]$. Thermal ellipsoids are drawn at the 50% probability level.

Table IV. Bond Distances (Å) and Angles (deg) of the $[Fe_2Cl_6O]^{2-}$ Anion in $[Ph_4P]_2[Fe_2OCl_6]$

Fe(1)–Cl(1)	2.216(2)	Fe(2)–Cl(4)	2.215(2)
Fe(1)–Cl(2)	2.209(2)	Fe(2)–Cl(5)	2.208(2)
Fe(1)–Cl(3)	2.205(2)	Fe(2)–Cl(6)	2.208(2)
Fe(1)–O(1)	1.744(4)	Fe(2)–O(1)	1.744(4)
Cl(1)–Fe(1)–Cl(2)	109.9(1)	Cl(1)–Fe(1)–Cl(3)	107.0(1)
Cl(2)–Fe(1)–Cl(3)	108.4(1)	Cl(1)–Fe(1)–O(1)	111.2(2)
Cl(2)–Fe(1)–O(1)	109.0(2)	Cl(3)–Fe(1)–O(1)	111.3(2)
Cl(4)–Fe(2)–Cl(5)	109.8(1)	Cl(4)–Fe(2)–Cl(6)	107.2(1)
Cl(5)–Fe(2)–Cl(6)	108.2(1)	Cl(4)–Fe(2)–O(1)	111.3(2)
Cl(5)–Fe(2)–O(1)	109.1(2)	Cl(6)–Fe(2)–O(1)	111.1(2)
Fe(1)–O(1)–Fe(2)	170.4(4)		

Interestingly, Rose and co-workers[7] have reported the structure of the closely related salt $[Ph_4As]_2[Fe_2Cl_6O]$, which they refined in the monoclinic space group $C2/c$. Here the $[Fe_2Cl_6O]^{2-}$ anion has crystallographically imposed symmetry C_2. The Fe–O and Fe–Cl bond distances have unacceptably large estimated standard deviations, and the isotropic thermal displacement parameters of oxygen and chlorine atoms are very large. We suspect that either the space group has not been correctly established or that severe unresolved disorder problems prevail.

There are only two structures where the published information unambiguously rules out orientational disorder or other crystallographic problems: $[BzPh_3P]_2[Fe_2Cl_6O]$[12] and $[Fe(bpy)_3][Fe_2Cl_6O]$.[13] The present structure of $[Ph_4P]_2[Fe_2Cl_6O]$ may also be in this category, although, clearly, some small disorder prevails. The structure of $[BzEt_3N]_2[Fe_2Cl_6O]$[17] is not severely hampered by disorder problems, but the full data are as yet unpublished.[28] Interestingly, in all these cases the $[Fe_2Cl_6O]^{2-}$ anion does not possess crystallographically imposed symmetry.

Using these data alone it is possible to state unequivocally the following structural details of the $[Fe_2Cl_6O]^{2-}$ anion. First, the Fe–O–Fe bond angle is dependent of the nature of the countercation; it definitely spans the range 148.1–170.4°. There is no experimental proof for a linear Fe–O–Fe unit. Second, the Fe–O distances are within three times the estimated standard deviation identical (average 1.756 Å). But note the enormous difference in accuracy in two structure determinations reported independently by two groups for the same compound $[Fe(bpy)_3][Fe_2Cl_6O]$.[13,14] Third, it appears that the three Fe–Cl distances of one $FeCl_3O$ part of the dianion are not equivalent. This has been noted previously by Petridis and Terzis[12] for $[BzPh_3P]_2[Fe_2Cl_6O]$, who have pointed out that one Fe–Cl bond at one half-dimer is always significantly longer than the other two (manifestation of a structural trans influence of the oxo group?). Last, a significant variation in the conformation of two corner-sharing tetrahedra is observed.[12] Figure 2 shows this for the five structures considered here. The schematic representations are constructed by using published atom coordinates in the following fashion: The first Cl_3FeO half-dimer is always positioned so that the one tetrahedral face defined by three chlorine atoms coincides with the paper

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(27) Petridis and Terzis[12] had previously refrained from publishing their data on this species "because it is disordered and it appears as if the oxygen atom occupies a center of symmetry." This is not the case in our structure, but small orientational disorder of the $[Fe_2Cl_6O]^{2-}$ anion is observed.

(28) Crystal data for $[BzEt_3N]_2[Fe_2Cl_6O]$: orthorhombic space group *Pbca*; $a = 16.063(5)$, $b = 29.52(2)$, $c = 15.0(1)$ Å; $Z = 8$. We thank Dr. K. Peters (Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany) for this information prior to publication.

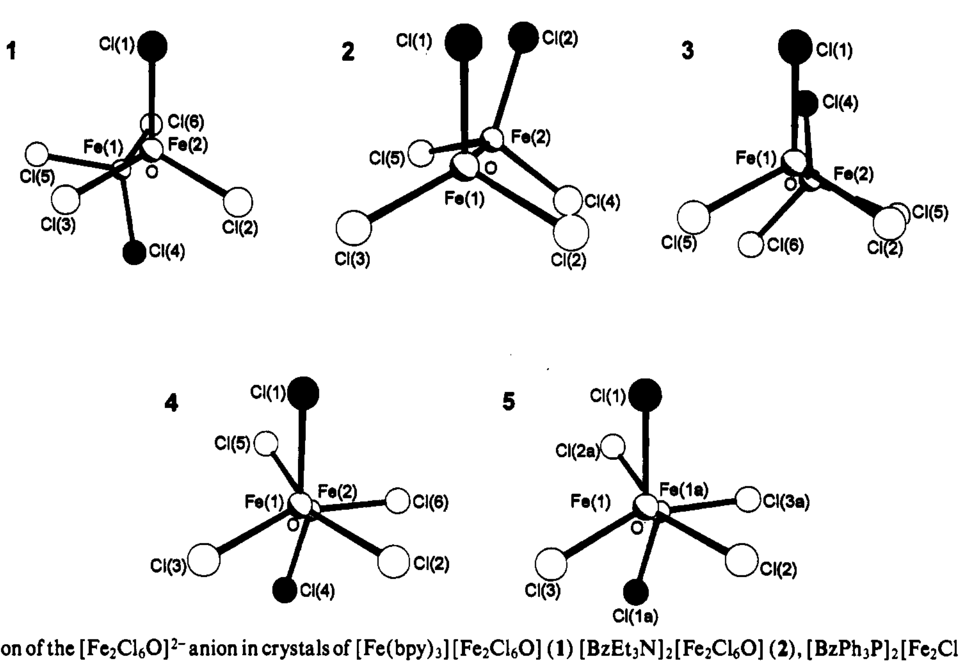


Figure 2. Conformation of the $[Fe_2Cl_6O]^{2-}$ anion in crystals of $[Fe(bpy)_3][Fe_2Cl_6O]$ (**1**) $[BzEt_3N]_2[Fe_2Cl_6O]$ (**2**), $[BzPh_3P]_2[Fe_2Cl_6O]$ (**3**), $[Ph_4P]_2[Fe_2Cl_6O]$ (**4**), and $[Ph_4As]_2[Fe_2Cl_6O]$ (**5**). Filled circles represent chlorine atoms which have the longest Fe–Cl distance in a Cl_3FeO unit. See text for an explanation of the unified representation of the $[Fe_2Cl_6O]^{2-}$ anions.

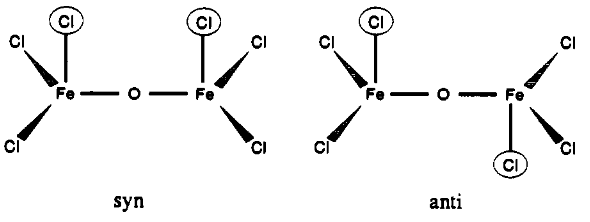
Table V. Vibrational Data for Complexes Containing the $[Fe_2Cl_6O]^{2-}$ Anion[a]

no.	cation	α(Fe–O–Fe), deg	ν_{as}(Fe–O–Fe), cm^{-1}		ν_s(Fe–O–Fe), cm^{-1}		$\nu_{as}(FeCl_3)$, cm^{-1}		$\nu_s(FeCl_3)$, cm^{-1}		δ(Fe–O–Fe), cm^{-1}	
			Ir	Ra	Ir	Ra	Ir	Ra	Ir	Ra	Ir	Ra
1	$[Fe(bpy)_3]^{2+}$	148.1	849 (vs)		465 (vw) 475 (vw)?	459 477	367 (sh) 360 (s)	369	317 (m)	317		
2	$[BzEt_3N]^+$	155.4	868 (vs)		463 (vw)	465	364 (s) 350 (ms)	362	315 (m)	308		202
3	$[BzPh_3P]^+$	160.2	866 (vs) 843 (vs)?		468 (m) 476 (m)	470	362 (s) 350 (ms)	358	319 (m)	304		239, 237, 210
4	$[Ph_4P]^+$	170.5	876 (vs)		460 (vw) 468 (vw)?		362 (b, s)	358	318 (m)	300	210	212
5	$[Ph_4As]^+$	170.9	876 (vs)		468 (m) 476 (m)	*b*	362 (s) 348 (ms)	*b*	318 (m)	*b*	215	*b*
	$[Hpy]^{+}$[c]	155.6	868 (vs)	870 (vw)		458	360 (ms)	357	311 (m)	311		203

[a] Abbreviations: bpy = 2,2′-bipyridine; Bz = benzyl; Et = ethyl; py = pyridine; IR = infrared; Ra = Raman; s = strong; vs = very strong; ms = medium strong; m = medium; b = broad; sh = shoulder. [b] Not measurable due to strong fluorescence. [c] IR data in refs 1 and 2; Raman data in ref 2.

plane. This places the oxygen atom perpendicular to this plane; it is located behind the iron atom Fe(1), which masks it. For structures where the Fe–Cl distances are inequivalent (**1** and **5**) we have designated the chlorine atom belonging to the longest Fe–Cl bond and have positioned it in a "northern" direction. The position of the second half-dimer is then determined by the Fe–O–Fe bond angle and conformational twist angles. Again the longest Fe–Cl bond is marked.

Interestingly, it appears that the longest Fe–Cl bond in the second half-dimer in **1** and **5** is directed toward the most "southern" and in **3** to the most "northern" direction. This implies that a structural trans influence of the oxo bridge produces the anti and syn conformers A and B since the Cl–Fe–O–Fe–Cl atoms are



then arranged in a nearly planar fashion. Orientational disorder of these conformers is probably the main reason why these conformers are not detected in the other crystal structures. It should be noted that crystallographically (even in **1** and **3**) the Fe–Cl bond lengths are barely significantly different but the infrared spectra corroborate this interpretation because three ν(Fe–Cl) stretching modes are observed which are compatible with C_s but not C_{3v} symmetry of the Cl_3FeO half-dimers (see below).

Vibrational Spectroscopy. Table V summarizes infrared and Raman spectroscopic data of five salts containing the $[Fe_2Cl_6O]^{2-}$ anion which we chose to study in detail because (i) the crystal structures show no or only small disorder problems, (ii) they do not contain solvent molecules of crystallization, and (iii) they cover the widest range of available (Fe–O–Fe) angles (148–170°). At the outset it was hoped to find a dependence of a characteristic vibrational mode (e.g. the ν_{as}(Fe–O–Fe) stretching frequency) on the (Fe–O–Fe) angle α as has been found and interpreted for other oxo-bridged complexes.[29] This would allow us to determine—or at least estimate—the magnitude of this angle in other easily prepared salts where the crystal structures have not been determined.

Infrared spectra of **1**[13] and **4**[5] have been reported previously; agreement between our and reported data is excellent (±2 cm^{-1}). This is not the case for **2** and **3** where the literature data and ours differ by 6–10 cm^{-1} and also in the number of observed $\nu(FeCl)$ bands in the 300–400-cm^{-1} region. Solbrig, Duff, Shriver, and Klotz have reported the only Raman spectrum of an [Fe₂-

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(29) (a) Cotton, F. A.; Wing, R. M. *Inorg. Chem.* **1965**, *4*, 867. (b) Callahan, K. P.; Wing, R. M. *Inorg. Chem.* **1969**, *8*, 871.

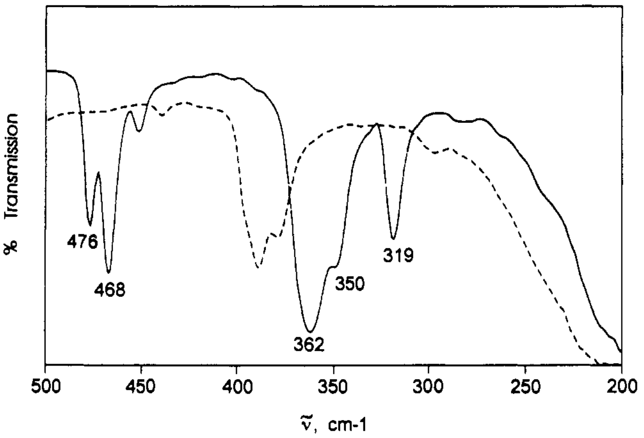

Figure 3. Infrared spectra of $[BzPh_3P]_2[Fe_2Cl_6O]$ (solid line) and $[BzPh_3P]\ FeCl_4$ (broken line) in the region 200–500 cm^{-1} (KBr disks).

$Cl_6O]^{2-}$-containing species, namely $[Hpy]_2[Fe_2Cl_6O]py$, where they have proven the assignment of two ν(Fe–O–Fe) stretching modes by an ^{18}O-labeling experiment.[2] In many other instances authors have reported the—in the infrared spectrum—readily detectable ν_{as}(Fe–O–Fe) stretching frequency only.

We have recorded the Raman spectra of salts **1**–**5**. In order to ascertain the assignment of a given band as originating from a vibration of the $[Fe_2Cl_6O]^{2-}$ anion, we have also recorded infrared and Raman spectra of $[BzEt_3N]FeCl_4$, $[BzPh_3P]FeCl_4$, $[Ph_4P]FeCl_4$, and $[Ph_4As]FeCl_4$. For each of these salts we have observed a strong band at 335–337 cm^{-1} (ν_1) of $FeCl_4^-$ [30] in Raman spectrum and at 380–390 cm^{-1} (ν_3) in the infrared in agreement with literature data.[30] Bands due to the respective cation are very similar—but not always identical—in the two series [cation]$FeCl_4$ and $[cation]_2[Fe_2Cl_6O]$.

Most authors have analyzed the vibrational spectra of $[Fe_2Cl_6O]^{2-}$ species by assuming local C_{3v} symmetry about each iron(III), which predicts two IR-active Fe–Cl stretching vibrations (E and A_1, $\nu_{as}(FeCl_3)$ and $\nu_s(FeCl_3)$). They have treated the bent Fe–O–Fe unit as an independent moiety giving rise to an antisymmetric and a symmetric ν(Fe–O–Fe) stretching mode. Dehnicke et al.[5] pointed out that this might be an oversimplification and analyzed the infrared spectrum of $[Ph_4P]_2[Fe_2Cl_6O]$ (solvate-free species!) in the point group D_{3d} assuming a linear Fe–O–Fe unit, which is clearly not supported by the crystallographic data.

From the above discussion of the crystal structures, it is clear that the actual symmetry of the $[Fe_2Cl_6O]^{2-}$ anion in the solid state is quite low—C_s at most.[1] We found evidence in the infrared spectra of compounds **1**–**5** that local C_s symmetry appropriately describes the symmetry about the iron ions in agreement with the structure determinations. In contrast to previous reports we found *two* bands in the 350–370-cm^{-1} region in the infrared. Only for **4** a single—but broad—band is observed at 362 cm^{-1} in accord with Dehnicke's report.[5] These bands are assigned to ν(Fe–Cl) stretching modes. In C_s symmetry three ν(Fe–Cl) modes are IR-active: $\nu_{as}(FeCl_2)$, $\nu_s(FeCl_2)$, and one ν(Fe–Cl) vibration. These three bands are observed for **1**, **2**, **3**, and **5**: $\nu_{as}(FeCl_2)$ at ≈362 and $\nu_s(FeCl_2)$ at ≈318 cm^{-1} and (Fe–Cl) at ≈350 cm^{-1} (Figure 3).

This assignment is corroborated by the fact that the high-quality crystal structures with no disorder problems clearly show the presence of two shorter Fe–Cl and one longer Fe–Cl distance. It is also significant that in the Raman spectra of **1**–**4** the ν(Fe–Cl) vibration corresponding to the long Fe–Cl distance (≈350 cm^{-1}) is not observed—only the $\nu_{as}(FeCl_2)$ and $\nu_s(FeCl_2)$ modes are detected.

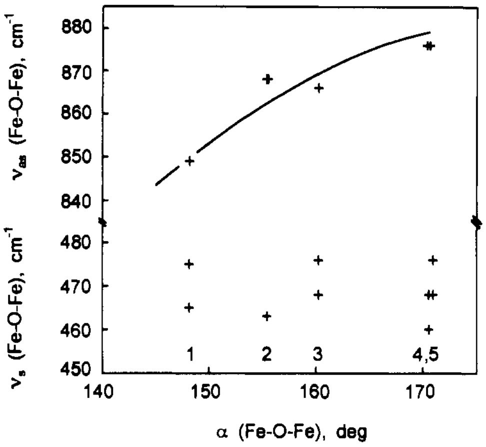

Figure 4. Plot of the ν_{as}(Fe–O–Fe) and ν_s(Fe–O–Fe) stretching frequencies versus the (Fe–O–Fe) bond angle α (labeling of complexes as in Figure 2 and Table V).

Table VI. Magnetic Properties of Complexes Containing the $[Fe_2Cl_6O]^{2-}$ Anion[a]

compd	α(Fe–O–Fe), deg	$-J$, cm^{-1} [b]	P, %[d]	$-J$, cm^{-1} [c]	P, %[d]
1	148.1	107 (134)[e]	0.6 nr	113	0.5
2	155.3	116 (146)[e]	2.3 nr	110, 112	0.8
3	160.2	117	1.2	113, 108	0.6
4	170.4	112, 117	2.6	108	0.7
5	170.8	117	1.5	114	0.1
$[Hpy]_2[Fe_2Cl_6O]\cdot py$	155.6	(127)[e]	nr	92[f]	0.0
$[\{Ph_3P\}_2CSe]_2[Fe_2Cl_6O]$	180?	(190)[e]	nr		
$[Et_4N]_2[Fe_2Cl_6O]$	155.5(+/−5)			109	0.6
$[PhMe_3N]_2[Fe_2Cl_6O]$	170(+/−5)			113	0.4
$[BzMe_3N]_2[Fe_2Cl_6O]$	170(+/−5)			107	0.4
$[MePh_3P]_2[Fe_2Cl_6O]$	170(+/−5)			113, 108	0.5
$[EtPh_3P]_2[Fe_2Cl_6O]$	170(+/−5)			107	0.7

[a] Abbreviations: nr = not reported; py = pyridine; Ph = phenyl; Et = ethyl; Me = methyl; Bz = benzy; Hpy = pyridinium cation. [b] Susceptibility data 2.7–295 K. [c] Susceptibility data 77–295 K. [d] Monomeric paramagnetic impurity ($S = {}^5/_2$). [e] Value from ref 3. [f] Value from ref 1; temperature range 130–293 K.

Three frequencies of the bent Fe–O–Fe unit are generally observed: ν_{as}(Fe–O–Fe) at 860–880 cm^{-1}, ν_s(Fe–O–Fe) at 450–475 cm^{-1}, and—possibly—a δ(Fe–O–Fe) deformation band at ≈210 cm^{-1}. In contrast to Shriver's[2] Raman spectrum of $[Hpy]_2[Fe_2Cl_6O]py$ we have not been able to observe the ν_{as}(Fe–O–Fe) vibration in the Raman spectra of compounds **1**–**4**; only the ν_s(Fe–O–Fe) vibration has been detected as very weak band(s) both in the Raman and the infrared spectra. Figure 4 shows a plot of the two ν(Fe–O–Fe) frequencies versus the Fe–O–Fe bond angle α. Clearly the ν_{as}(Fe–O–Fe) frequency shifts to higher wavenumbers with increasing bond angle α. A dependence of ν_s(Fe–O–Fe) on α is, in contrast, not detected within experimental error limits; a shift to lower frequencies with increasing α is expected as has been reported by Sanders-Loehr et al.[31] for other oxo-bridged diiron(III) complexes. The significant dependence of ν_{as}(Fe–O–Fe) on α allows one to determine the magnitude of α from infrared data with an estimated accuracy of ≈±5°. The assignment of the band(s) at ≈210 cm^{-1} to a δ(Fe–O–Fe) deformation band is tentative.

Magnetochemistry. We have measured the molar magnetic susceptibility of compounds **1**–**4** in the temperature range 2.7–295 K by using a SQUID magnetometer. Table VI summarizes the magnetochemical data, and Figure 5 shows a representative plot of χ_M vs T for $[BzEt_3N]_2[Fe_2Cl_6O]$. Corrections for

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(30) Avery, J. J.; Burbridge, L. D.; Goodgame, D. L. *Spectrochim. Acta* **1968**, *24A*, 1721.

(31) Sanders-Loehr, J.; Wheeler, W. D.; Shiemke, A. K.; Averill, B. A.; Loehr, T. M. *J. Am. Chem. Soc.* **1989**, *111*, 8084.

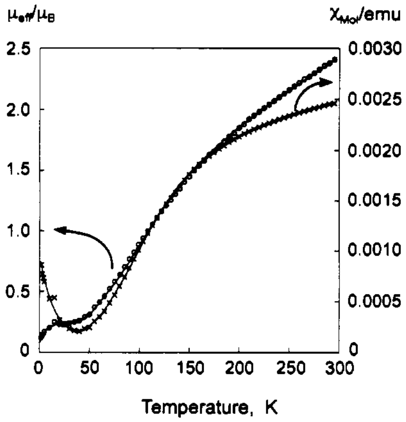

Figure 5. Plot of the molar susceptibility and effective magnetic moments vs temperature for $[BzEt_3N]_2[Fe_2Cl_6O]$. Solid lines represent least-squares best fits to data (see text).

diamagnetic contributions were applied by using Pascal's tabulated constants.[32] The antiferromagnetism of the $[Fe_2Cl_6O]^{2-}$ anion is well established[1,3] and is usually described by eq 1, which has

$$\chi_M = Ng^2\beta^2/kT\left[\frac{2e^{2x} + 10e^{6x} + 28e^{12x} + 60e^{20x} + 110e^{30x}}{1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x} + 11e^{30x}}\right](1 - p) + 35\beta^2N/3k(T - \Theta)p \quad (1)$$

$$x = J/kT$$

been developed under the usual spin Hamiltonian $H = -2JS_1 \cdot S_2$ ($S_1 = {}^5/_2$, $S_2 = {}^5/_2$).[32] The fraction of paramagnetic impurity p was treated as high-spin Fe(III); other symbols have their usual meaning. The g value was fixed at 2.00 in all cases. Least-squares fit parameters were only J and p and the constant Θ. The presence of a paramagnetic impurity is experimentally clearly verified by a sharp increase of χ_M at temperatures <10 K. We have used the following function as the criterion of best fit:

$$R = \sum[\chi^M{}_{exptl} - \chi^M{}_{calcd}]^2/\sum[\chi^M{}_{exptl}]^2$$

R indices in the range $(1-8) \times 10^{-5}$ were considered to represent satisfactory fits; data reported in Table VI fall in this range.

We have carried out a check for internal consistency of data by measuring χ_M as a function of the temperature of the same sample **4** (from the same preparation) twice. Both data sets were treated in exactly the same fashion, but the obtained J values differ by 5 cm^{-1}. Therefore, we estimate that the accuracy of J values as obtained from these SQUID measurements is not better than $J \pm 5$ cm^{-1}.

We have also measured χ_M of many other compounds in the temperature range 77–295 K by using the Faraday method. Data were treated in exactly the same manner as described above. The fits were excellent ($R < 3 \times 10^{-5}$), and the J values for **1**–**4** obtained agree generally within ±5 cm^{-1} with those obtained from the full temperature range. In addition to measurements on compounds **1**–**4** we have studied a series of $[Fe_2Cl_6O]^{2-}$ compounds with the cations $[Et_4N]^+$, $[PhMe_3N]^+$, $[BzMe_3N]^+$, $[PhMe_3P]^+$, and $[Ph_3EtP]^+$. Since $[Et_4N]_2[Fe_2Cl_6O]$ displays a strong ν_{as}(Fe–O–Fe) stretching mode at 857 cm^{-1} in the infrared, we estimate the (Fe–O–Fe) bond angle to be 155 ± 5°; all other salts show this band at 883–887 cm^{-1} indicating an (Fe–O–Fe) angle of 170 ± 5°. $|J|$ values for this series fall in the narrow range 107–113 cm^{-1} as do all values in Table VI. Thus internal consistency is very good.

J values reported by Adler et al.[3] for $[Fe(bpy)_3][Fe_2Cl_6O]$ (–133.8 cm^{-1}), $[Hpy]_2[Fe_2Cl_6O]py$ (–126.8 cm^{-1}), $[BzEt_3N]_2[Fe_2Cl_6O]$ (–146.1 cm^{-1}), and $[\{Ph_3P\}_2CSe]_2[Fe_2Cl_6O]\cdot 4CH_2Cl_2$ (–190.3 cm^{-1}) are systematically too large. The value for the last compound is unrealistic. Sample decomposition is most probably the problem.[33] The J value for $[Hpy]_2[Fe_2Cl_6O]py$ reported by Drew et al.[1] of –92 cm^{-1} has been evaluated from susceptibility measurements in the rather small temperature range 130–293 K without taking into account any paramagnetic impurity. Therefore, we consider this value less reliable.

The most important result of this study is the fact that all experimentally determined J values fall in the narrow range –107 to –117 cm^{-1} (average –112 ± 5 cm^{-1}). We do not detect a systematic trend of J on the Fe–O–Fe bond angle α. Mukherjee, Stack, and Holm[22] report such an angle dependence for two five-coordinate complexes $[Fe(3\text{-}t\text{-}Busaltmen)]_2O$ (α = 173.4° and J = –100 cm^{-1}) and $[Fe(salen)]_2O$ (α = 145°; J = –91.5). Thus an increase of 9% in J arises by enlarging the Fe–O–Fe angle by 29°. If we assume an angle dependence of similar magnitude in our series, we must conclude that given the smaller range of α available to us of only 22.8° a variation of only ≈7% in J is within our experimental uncertainty and, therefore, escapes detection. We can rule out a larger effect.

Interestingly, these conclusions are supported by an ab initio calculation of the magnetic exchange interactions in $Na_2[Fe_2OCl_6]$, where the magnetic interaction was found to be sensitive to the Fe–O distance but rather insensitive to the Fe–O–Fe angle.[34]

Acknowledgment. We thank Dipl. Phys. C. Butzlaff (Medizinische Universität Lübeck) for measuring the magnetic susceptibility of complexes **1**–**5** in the range 2.7–295 K. We also gratefully acknowledge financial support of this work by the Fonds der Chemischen Industrie. Dr. S. M. Gorun (Science Laboratories, Exxon Research, Annandale, NJ) is thanked for communicating his results[34] prior to publication.

Supplementary Material Available: Tables giving crystal data and details of the structure determination, atom coordinates, bond distances and angles, anisotropic displacement parameters, and H-atom coordinates and figures showing plots of the temperature-dependent magnetic susceptibility of complexes **1**–**5** (16 pages). Ordering information is given on any current masthead page.

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(32) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203.

(33) Gütlich, P. Private communication.

(34) Hart, J. R.; Rappé, A. K.; Gorun, S. M.; Upton, T. H. *Inorg. Chem.* **1992**, *31*, 5254.