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Diammonium μ-oxobis[trichloroferrate(III)] salts. Crystal and molecular structure of bis(benzyldimethylphenylammonium) μ-oxobis(trichloroferrate)

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Abstract

Several alkyl-, aralkyl-, and aryl-substituted diammonium μ-oxobis[trichloroferrate(III)] salts, of potential interest as model compounds for the study of certain electrophysical and biological processes, are synthesized via the corresponding tetrachloroferrate(III) salts and are characterized by IR and Raman spectroscopy. A structure analysis is performed on the representative bis(benzyldimethylphenylammonium) μ-oxobis(trichloroferrate). The (tetracoordinate) iron atoms in the oxo-bridged dinuclear anion of the salt each possess an ever so slightly distorted tetrahedral ligand environment; the bridge geometry [Fe–O distances 1.757(5) and 1.775(5) Å, Fe–O–Fe angle 147.7(3)°] compares well with that of other salts containing the $[Cl_3Fe{-}O{-}FeCl_3]^{2-}$ anion. Crystallographic Data: $a = 26.392(5)$ Å, $b = 14.015(3)$ Å, $c = 9.638(2)$ Å, $\beta = 92.65(2)°$, and $Z = 4$; space group $P2_1/n$. $R(F) = 0.070$, $R_w(F) = 0.078$ for 4447 observed reflections.

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Introduction

Dinuclear oxygen-bridged iron(III) complexes have been extensively studied in recent years because of their crucial role in certain oxygen carrier and iron transport proteins. An excellent earlier review of the subject is available (Murray, 1974), and a comprehensive list of later references can be found in a recent article in the field (Armstrong and Lippard, 1983). The complexes discussed generally were μ-oxodiferrates possessing penta- or hexacoordinate ligand environments around the two iron centers, and little is known about oxo-bridged diferrates with tetracoordinated iron. Of the latter type, in fact, only one representative, the μ-oxobis [trichloroferrate(III)] dianion, has been quoted in the more recent literature (Solbrig *et al.*, 1982; Neuse and Meirim, 1984). X-ray structure analyses show that in some salts this anion has a bent oxo bridge (Drew *et al.*, 1978; Weiss and Strähle, 1984; Reiff *et al.*, 1983) and in others a linear oxo bridge (Dehnicke *et al.*, 1983; Schmidbauer *et al.*, 1983). In the following, we describe a general synthesis, previously utilized for the preparation of **2a** and **2c** (Neuse and Meirim, 1984), of various alkyl-, aralkyl-, and aryl-substituted ammonium μ-oxobis[trichloroferrate(III)] salts **2** including a polymeric representative. We also present the results of a structure determination of the representative **2d,** bis(benzyldimethylphenylammonium) μ-oxobis(trichloroferrate). These oxodiferrates should be of interest as simple model compounds for the study of spectroscopic features and magnetic interaction (Murray, 1974; Armstrong and Lippard, 1983; Drew *et al.*, 1978; O'Keeffe *et al.*, 1975) in Fe–O–Fe systems with tetrahedral ligand coordination about the iron centers.

Experimental

Synthesis

Reagents. The commercially available (Fluka AG) salts, tetramethylammonium chloride, benzyltrimethylammonium chloride, and benzyltriethylammonium chloride, were used as received. Benzyldimethylphenylammonium chloride was prepared as described (Cowell *et al.*, 1970). Cetyltrimethylammonium chloride was prepared from the bromide (Fluka AG) by repeated dissolution in 1 M aqueous HCl and solvent removal under reduced pressure. The salt was dried at 100°C/0.1 torr. Poly(diallyldimethylammonium chloride), received as a commercial product (Kayafloc C-570H, Kouyoh Trading Co. Ltd., Tokyo), was purified as described below (procedure for **1f**).

Ammonium tetrachloroferrate(III) (1)

A. General procedure for ***1a–e.*** The predried, appropriately substituted ammonium chloride (20 mmol) is dissolved, together with anhydrous iron(III) chloride (21 mmol; 25 mmol for **1e**), in boiling methanol (30–40 ml). The solution, filtered while hot, is reduced in volume in a rotating evaporator to approximately one-half, rewarmed for redissolution of crystallized material, and allowed to stand overnight at −10°C. After removal of a major crystalline portion of **1** by filtration, the mother liquor is further concentrated to near dryness, and a second, slightly less pure portion of the salt is collected. The fractions are washed with cold methanol and dried at 70–80°C/0.2 torr. Yield, 68–92%. A single recrystallization from methanol (in the presence of 0.1 molar equivalent of anhydrous $FeCl_3$ for **1e**) gives analytically pure **1** as fine yellow (**1a–d**) or orange-yellow (**1e**) needles or platelets very soluble in water and soluble in acetonitrile, carbinols, and other polar organic solvents. No further compositional changes, yet slightly higher melting points (where applicable), result from one or more additional recrystallization steps. Spectroscopic and microanalytical data are found in Table 1.

B. Procedure for 1f. Commercial poly(diallyldimethylammonium chloride) is purified by dialysis (12 h; cut-off molecular mass 10,000) of its aqueous solution (ca. 15%) against deionized water, followed by partial (ca. 50%) solvent removal (rotatory evaporation, 50°C) and precipitation with acetone (double volume) of the polymer as a gummy, colorless solid. After repeated, thorough masticating with acetone for water removal, the product is dried for 48 h at 65°C/0.1 torr, ground to a powder, and redried in the same fashion. Anal. found: C, 58.89; H, 10.23; Cl, 22.25; N, 8.29%. Calcd. for recurring unit, $C_8H_{16}ClN$ (161.7): C, 59.43; H, 9.98; Cl, 21.93; N, 8.66%. Dissolved in aqueous 0.02 M sodium chloride solution (0.05 g dl^{-1}), it gives an inherent viscosity, η_{inh}, of 6.3 dl g^{-1}.

A portion of the polymeric chloride so purified, 1.62 g (10 mmol), is dissolved in absolute methanol (75 ml) at the boiling temperature. Anhydrous $FeCl_3$, 2.45 g (15 mmol), is dissolved in the rapidly stirred, warm solution, and the polymeric **1f** soon begins to flocculate out. Stirring is continued for 1 h, and the mixture is left to stand overnight at room temperature. The precipitated yellow polymer is filtered off, washed well with 1 : 1 methanol/ether and ether, and dried for 48 h at 70°C/0.1 torr. Yield, 2.95 g (91.0%; 85–94% in repeat runs). The light yellow polysalt is readily soluble in water. Dissolved in aqueous 0.02 M benzyltrimethylammonium tetrachloroferrate (**1b**) solution (0.05 g dl^{-1}), it gives $\eta_{inh} = 3.1$ dl g^{-1}. Spectroscopic and analytical results are in Table 1.

Bisammonium μ-oxobis[trichloroferrates(III)] (2)

A. General procedure for 2a–e. To the rapidly stirred solution of the appropriately substituted ammonium tetrachloroferrate **1** (20 mmol) in 1 : 1 acetonitrile/methanol (10–20 ml) is added dropwise, by means of a syringe, a solution of KOH (30 mmol) in 1 : 2 aqueous methanol (4 ml). The syringe is rinsed with 1 : 2 aqueous methanol (1.2 ml), which is added to the main solution. Some

Table 1. Analytical and spectroscopic data for ammonium tetrachloroferrates **1**

Compound	Composition	Crude yield (%)	mp (°C)	Anal. found (calcd.) (%) C	H	Cl	N	IR (cm^{-1})[a] ν_{as} (Fe–Cl)	Rama (cm^{-1})[b] ν_{sym} (Fe–Cl)
1a	$[Me_4N][FeCl_4]$	68–74	>300	17.95 (17.68)	4.48 (4.45)	52.34 52.17	5.01 (5.15)	379s (379s)	335s
1b	$[C_6H_5CH_2(Me)_3N][FeCl_4]$	85–92	79–81	34.39 (34.52)	4.55 (4.64)	40.94 (40.76)	3.74 (4.03)	371s[c]	333s
1c	$[C_6H_5CH_2(Et)_3N][FeCl_4]$	70–85	82–83	40.12 (40.04)	5.59 (5.69)	36.10 36.36	3.44 (3.59)	379s (379s)	335s
1d	$[C_6H_5CH_2(Me)_2(C_6H_5)N][FeCl_4]$	75–85	78–79	43.57 (43.94)	4.41 (4.43)	34.64 (34.59)	3.21 (3.42)	378s	336s
1e	$[C_{16}H_{33}(Me)_3N][FeCl_4]$[d]	75–83	64–65	47.68 (47.32)	8.90 (8.78)	28.80 (29.41)	3.01 (2.90)	380s	335m
1f	$[C_8H_{16}N]_x[FeCl_4]_x$[e]	85–94	>300	30.01 (29.67)	5.11 (4.98)	43.14 (43.78)	4.55 (4.32)	377s	331, 335 (d)s

[a] KBr matrix. In parentheses, frequencies cited by Neuse and Meirim (1984).

[b] Powder, packed in rotating glass capillary; laser excitation, $\nu_0 = 676.4$ nm.

[c] Strong shoulder at 390 cm^{-1}.

[d] Cetyltrimethylammonium cation.

[e] Poly(diallyldimethylammonium) polycation.

inorganic matter is removed from the hot mixture by filtration through a medium-porosity frit and is washed with a few milliliters of hot 1 : 1 acetonitrile/methanol. Solvent removal from the combined filtrate and washings under reduced pressure leaves crude **2** as a brownish solid, which is dried at 65°C/0.2 torr. Yield, 70–95%. The crude salt is recrystallized from methanol (typically 10 ml/g) in the presence of pyridine (0.2–0.5 molar equivalents), added as a 20% solution in ether, to give analytically pure **2** as yellow-brown or orange-brown needles possessing similar solubility properties as shown by the precursors **1**. A minor melting point increase is achieved by further recrystallization from methanol. Spectroscopic and microanalytical data are compiled in Table 2.

B. Procedure for 2f. To the solution of polymeric tetrachloroferrate **1f**, 3.24 g (10 mmol), in water (5 ml) is added methanol (30 ml), and the mixture is stirred for complete dissolution. Pyridine, 791 mg (10 mmol), dissolved in methanol (10 ml), is added to the vigorously stirred polymer solution, whereupon **2f** precipitates as a yellow-brown resinous mass. The material is thoroughly masticated with methanol (4 ml) and then ether (2 × 10 ml), and is dried for 48 h at 65°C/0.1 torr. Yield, 2.57 g (86.7%; 85–89% in repeat experiments). The analytically pure polymer **2f** so obtained is a light yellow-tan solid that dissolves readily in water but is insoluble in carbinols; $\eta_{\text{inh}} = 3.2$ dl g^{-1} [0.05 g dl^{-1}, in aqueous 0.01 M bis(benzyltrimethylammonium) μ-oxobis (trichloroferrate) **2b**]. Spectroscopic and analytical data are found in Table 2.

Occasionally, the precipitated polymer has been found to contain small proportions (up to 10%, assessed by IR) of unchanged tetrachloroferrate recurring units. Such material may be converted to pure **2f** by stirring, for 12 h at room temperature, its suspension (0.5 mmol) in methanol (2 ml) containing pyridine (0.25 mmol) and water (2 mmol). Polymer **2f** is filtered off, washed, and dried as before; recovery 95–97%.

Crystallography

A crystal with dimensions 0.24 × 0.34 × 0.62 mm was selected for the X-ray experiments. All data were taken at room temperature on a Philips PW-1100 single-crystal diffractometer (graphite monochromator, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å). Crystal data are as follows: $C_{30}Cl_6Fe_2H_{36}N_2O$, $M = 765.04$, monoclinic, $P2_1/n$, $a = 26.392(5)$, $b = 14.015(3)$, $c = 9.638(2)$ Å, $\beta = 92.65(2)°$ (from the setting angles of 25 reflections); $d_{\text{obsd}} = 1.40$ g/cm^3 (by flotation in chloroform/pentane), $d_{\text{calcd}} = 1.427$ g/cm^3, $Z = 4$.

Intensity data were collected ($\theta/2\theta$ technique) at 2°/min with background counted at each end of the scan for half the scan time; scan width, 1°. A total of 4959 independent reflections with $4 < 2\theta < 46°$ was obtained. Data reduction: intensity $I = C - RB$, $\sigma(I) = (C + R^2B)^{1/2}$ (scan counts, S; total back-

Table 2. Analytical and spectroscopic data for diammonium μ-oxo-bis(trichloroferrates) **2**

		Crude yield (%)		Anal. found (calcd.) (%)				
Compound	Composition		mp (°C)	C	H	Cl	N	O
2a	$[Me_4N]_2[Cl_3Fe\text{–}O\text{–}FeCl_3]$	75–88	255–256	19.50	4.98	43.34	5.58	3.10
				(19.66)	(4.95)	(43.52)	(5.53)	(3.27)
2b	$[C_6H_5CH_2(Me)_3N]_2$	86–95	142–144	37.56	5.19	33.26	4.29	2.66
	$\cdot\ [Cl_3Fe\text{–}O\text{–}FeCl_3]$			(37.48)	(5.03)	(33.19)	(4.37)	(2.50)
2c	$[C_6H_5CH_2(Et)_3N]_2$	70–75	107–108	43.25	6.18	29.38	3.75	2.32
	$\cdot\ [Cl_3Fe\text{–}O\text{–}FeCl_3]$			(43.07)	(6.12)	(29.34)	(3.86)	(2.21)
2d	$[C_6H_5CH_2(Me)_2(C_6H_5)N]_2$	85–92	142–143	47.22	4.87	27.70	3.61	2.20
	$\cdot\ [Cl_3Fe\text{–}O\text{–}FeCl_3]$			(47.10)	(4.74)	(27.80)	(3.66)	(2.09)
2e	$[C_{16}H_{33}(Me)_3N]_2$	88–94	97–98[f]	50.32	9.53	23.33	3.02	1.09
	$\cdot\ [Cl_3Fe\text{–}O\text{–}FeCl_3]$[e]			(50.18)	(9.31)	(23.39)	(3.08)	(1.76)
2f	$[C_8H_{16}N]_{2x}$	85–89	>300	32.33	5.39	35.62	4.50	2.89
	$\cdot\ [Cl_3Fe\text{–}O\text{–}FeCl_3]_x$[h]			(32.41)	(5.44)	(35.88)	(4.72)	(2.70)

[a] KBr matrix. In parentheses, frequencies cited by Neuse and Meirim (1984).
[b] Powder, packed in rotating glass capillary; laser excitation, $\nu_0 = 676.4$ nm.
[c] Merging with cation band at 885 cm^{-1}(ms).
[d] In addition to cation bands at 882 and 821 cm^{-1}(ms).
[e] Cetyltrimethylammonium cation.
[f] Sintering at 74–76°C.
[g] Partially merging with cation band at 905 cm^{-1}(m).
[h] Poly(diallyldimethylammonium) polycation.

ground counts, B; time ratio of scan to total background, R). The set of 4447 reflections with $I > 0.5\sigma(I)$ was used in the subsequent calculations; $F_o = (I/\mathrm{Lp})^{1/2}$ and $\sigma(F_o) = \sigma(I)/(2F_o\mathrm{Lp})$ (Lorentz and polarization factor, Lp). An empirical absorption correction (method of Walker and Stuart, 1983; $\mu = 12.2$ cm^{-1}) was applied in a later stage.

The structure was solved with Debaerdemaeker's XMY program (a program for solving structures by a random phase approach: T. Debaerdemaeker, University of Ulm). The nonhydrogen atoms were refined with anisotropic temperature factors. Most hydrogen atoms could be located in ΔF maps; the remaining ones were assigned positions on stereochemical grounds. H atoms were held at fixed positions in the following refinement cycles. Scattering factors for neutral atoms were taken from the literature (Cromer and Mann, 1968). Anomalous dispersion corrections were applied (Cromer and Liberman, 1970). $R = 0.070$, $R_w(F) = 0.078$. The highest peak in a final difference Fourier map was 0.46 e/Å^3. The SHELX-76 program package (SHELX-76 Program system; G. M. Sheldrick, University of Göttingen, unpublished) was used in this structure analysis.[1]

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[1] Further details on the structure investigation can be obtained from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen, Federal Republic of Germany, by quoting the deposition number CSD-51690, the name of the authors, and complete citation of the journal.

IR (cm^{-1})[a]			Raman (cm^{-1})[b]	
ν_{as} (Fe-O-Fe)	ν_{as} (Fe-Cl)	ν_{sym} (Fe-Cl)	ν_{sym} (Fe-O-Fe)	ν_{sym} (Fe-Cl)
879s	365, 353s(d)	318ms	454 w	300s
(897s)	(365, 353s(d)	(318ms)		
883, 873s(d)[c]	361s	318ms	457 w	304 m, 320s
845ms				
869s	365, 349s(d)	316ms	463w	307s
(869s)	366, 351s(d)	(316ms)		
848, 835s(d)[d]	370, 361s(d)	320ms		301m, 320s
878s(d)[g]	362, 355s(d)	316ms	452, 460w	305s
846s,br	364, 352s(d)	315ms	463w	315-320 ms

Results and Discussion

Synthesis

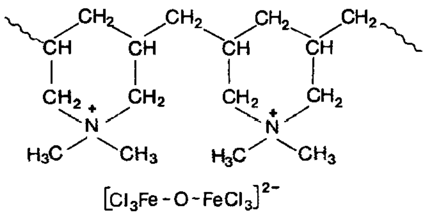
The synthesis of the nonpolymeric oxodiferrates **2a–e** is carried out by treatment of the corresponding ammonium tetrachloroferrate(III) salts **1a–e** in acetonitrile/methanol solution with carefully controlled quantities of water and base. The tetrachloroferrates **1,** in turn, are readily accessible by anion complexation of the respective chloride salts with $FeCl_3$ [eq. (1)], as first demonstrated (Meek and Drago, 1961) for **1a.** By scavenging liberated HCl, the base used in the **1** → **2** conversion shifts the equilibrium sufficiently far to the right to enforce anion dimerization through oxygen bridging [eq. (2)]. However, excessive base addition, so as to raise the pH of the system beyond ~4, must be avoided as this would destroy the Fe–O–Fe linkage with generation of (mononuclear) chlorohydroxyferrates; 1.2–1.5 molar equivalents of alkali provide optimal results.

The crude oxodiferrates **2** collected from the solutions in 70–95% yield after separation of inorganic matter are purified by recrystallization from acetonitrile or methanol in the presence of 0.2–0.5 molar equivalents of pyridine. The crystalline salts **2a–e** so obtained are nonhygroscopic (contrasting in this respect with some of the chloride precursors) and possess well-defined melting points. They are stable in alcoholic solution; in the presence of HCl, however, they are reconverted to the precursors **1** in a reversal of Eq. (2).

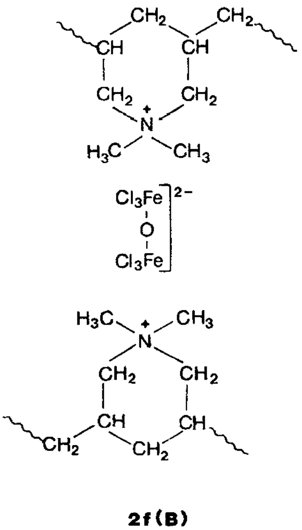
$$Cl^- + FeCl_3 \rightleftharpoons FeCl_4^- \tag{1}$$

$$2FeCl_4^- + H_2O \rightleftharpoons |Cl_3Fe\text{–}O\text{–}FeCl_3|^{2-} + 2HCl \tag{2}$$

With slight modification, the synthetic approach to **2** can be utilized also for the preparation of polymeric oxodiferrates from suitable poly(ammonium tetrachloroferrate) precursor salts. The preparation of **2f** from the poly(diallyldimethylammonium tetrachloroferrate) **1f**, for example, is conveniently accomplished in aqueous methanol, with one molar equivalent (per recurring unit) of pyridine added as the base. The poly(oxodiferrate) precipitates from the solution in 90–100% purity; impure material is converted to analytically pure **2f** by treatment of its suspension in moist methanol with 0.5 molar equivalents of pyridine. The polysalt dissolves readily and rapidly in water and can be recovered unchanged from its aqueous solution by immediate precipitation with THF. On the basis of this behavior we prefer the assignment of the linear segment structure **2f(A)**, with two adjacent monocationic recurring units connected by a mutual dianion, over that of **2f(B)**, in which the dianion functions as an electrostatic crosslink between different polycationic chains. The latter alternative would require hydrolytic cleavage of the oxo bridge to precede dissolution, and on recovery of the polymer the greater part, if not all, of the recurring units would be expected to appear as mononuclear $FeCl_4^-$.



2f (A)



2f (B)

The described synthesis is not applicable as such to the preparation of dipyridinium μ-oxobis(trichloroferrate) from a pyridinium tetrachloroferrate precursor. Although the tetrachloroferrate is readily formed from pyridinium chloride and excess[2] $FeCl_3$, we found its subsequent treatment with alkali or pyridine to cause substantial anion degradation, and the soluble product salts invariably proved to be mixtures of oxodiferrate and tetrachloroferrate [spectroscopically similar to the recently reported (Drew *et al.*, 1978; Solbrig *et al.*, 1982) oxodiferrate pyridine solvate that could not be clearly separated by recrystallization.

Spectroscopic features

Some physical, spectroscopic, and microanalytical data for the products **2** and their precursors **1** are listed in Tables 1 and 2. The tetrachloroferrates **1** give vibrational spectra characterized in the low-frequency region by the strong IR-allowed anion band near 379 cm^{-1} (antisymmetric Fe–Cl stretching, ν_3, of tetrahedral $FeCl_4$) and the prominent Raman shift at 335 cm^{-1} (corresponding symmetric mode, ν_1) (Table 1). The electronic absorption spectra (in N_2-saturated acetonitrile; not tabulated) show the typical tetrachloroferrate anion absorptions at the positions, and in the intensities, earlier reported (Neuse and Meirim, 1984) for **1a** (slightly perturbed by phenyl absorption in cases **1b–d**). The vibrational spectra of **2** feature the characteristic (Hewkin and Griffith, 1966) antisymmetric Fe–O–Fe stretching IR band near 880–850 cm^{-1} in high intensity; in addition, local C_{3v} symmetry of the pseudotetrahedral Cl_3FeO part in the anion of **2** leads to the emergence of two IR-allowed Fe–Cl stretching bands in the vicinity of 365(s) and 320(m) cm^{-1}. Raman shifts appear at 460–450 and 320–300 cm^{-1}, which, following Solbrig *et al.* (1982), are assigned, respectively, to the symmetric Fe–O–Fe and Fe–Cl stretching modes (Table 2). The electronic absorption spectra (in N_2-saturated acetonitrile; not tabulated) are in accord with the pattern of **2a** previously discussed in some detail (Neuse and Meirim, 1984), superimposed phenyl absorption again being indicated in the spectra of **2b–d.**

Structure analysis

The fundamental unit of the structure, consisting of two benzyldimethylphenylammonium cations and one μ-oxobis(trichloroferrate) anion, is shown in Fig. 1. Bond distances and angles are listed in Table 3. The bond distances of the $[Cl_3Fe–O–FeCl_3]^{2-}$ anion for the present salt agree within narrow limits

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[2] Use of stoichiometric quantities of $FeCl_3$ gives a salt predominantly composed of $(pyH)_3Fe_2Cl_9$. The nonachlorodiferrate has been previously reported (Weinland and Kissling, 1922; Ginsberg and Robin, 1963).

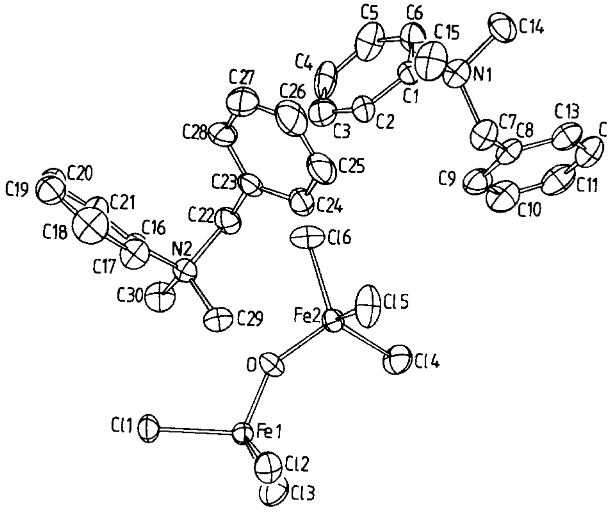

Fig. 1. Fundamental unit of $C_{30}Cl_6Fe_2H_{36}N_2O$.

Table 3. Interatomic Distances (Å) and Selected Angles (deg)

Fe(1) · · · Fe(2)	3.393(1)	N(1)-C(1)	1.521(8)
Fe(1)-Cl(1)	2.217(2)	-C(7)	1.543(9)
-Cl(2)	2.205(2)	-C(14)	1.524(11)
-Cl(3)	2.202(2)	-C(15)	1.508(10)
Fe(2)-Cl(4)	2.216(2)	N(2)-C(16)	1.498(8)
-Cl(5)	2.223(2)	-C(22)	1.559(9)
-Cl(6)	2.196(2)	-C(29)	1.516(9)
O-Fe(1)	1.757(5)	-C(30)	1.527(9)
-Fe(2)	1.775(5)		
Fe(1)-O-Fe(2)	147.7(3)	C(1)-N(1)-C(7)	108.4(5)
O-Fe(1)-Cl(1)	109.0(2)	-C(14)	112.4(6)
-Cl(2)	109.0(2)	-C(15)	109.9(6)
-Cl(3)	110.3(2)	C(7)-N(1)-C(14)	110.5(6)
Cl(1)-Fe(1)-Cl(2)	110.4(1)	-C(15)	108.5(6)
-Cl(3)	108.1(1)	C(14)-N(1)-C(15)	107.0(6)
Cl(2)-Fe(1)-Cl(3)	110.1(1)	N(1)-C(7)-C(8)	113.2(6)
O-Fe(2)-Cl(4)	110.7(2)	C(16)-N(2)-C(22)	109.5(5)
-Cl(5)	109.7(2)	-C(29)	113.2(5)
-Cl(6)	107.9(2)	-C(30)	109.8(5)
Cl(4)-Fe(2)-Cl(5)	110.5(1)	C(22)-N(2)-C(29)	110.1(5)
-Cl(6)	110.3(1)	-C(30)	107.7(5)
Cl(5)-Fe(2)-Cl(6)	107.7(1)	C(29)-N(2)-C(30)	106.4(5)
		N(2)-C(22)-C(23)	112.9(5)

with those of the other salts investigated so far. The Fe–O–Fe angle of 147.7(3)° is relatively small. Angles of 180° (Schmidbaur *et al.*, 1983; Dehnicke *et al.*, 1983), 161.6(9)° (Reiff *et al.*, 1983), 155.6(7)° (Drew *et al.*, 1978), and 148.1(2)° (Weiss and Strähle, 1984) have been reported. As discussed by Dehnicke *et al.*, the linear Fe–O–Fe arrangement found in two cases (with O residing on a crystallographic center of symmetry) might be interpreted as resulting from orientation-disordered, slightly bent anions. The two cations show the expected geometry. There are no significant nonbonded contacts between neighboring ions.

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