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**Bis(μ -ethylthio-S)-bis[carbonyl(η^5 -cyclopentadienyl)iron](Fe–Fe) Chlorate,
C₁₆H₂₀Fe₂O₂S₂⁺·ClO₃⁻**

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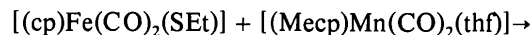
(Received 17 October 1983; accepted 30 May 1984)

Abstract. $M_r = 503.6$, tetragonal, $P4_32_12$, $a = 9.180(5)$, $c = 24.156(5)$ Å, $V = 2036(6)$ Å³, $Z = 4$, $D_m = 1.70(5)$, $D_x = 1.643(5)$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 1.056$ mm⁻¹, $F(000) = 1028$, $T = 295$ K, final $R = 0.078$ for 862 observed reflections. The Fe–Fe distance of 2.957(4) Å corresponds to an overall one-electron interaction; S–Fe = 2.240(4) Å. Both the cation and the chlorate anion exhibit crystallographic twofold symmetry; this symmetry imposes disorder on the latter.

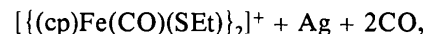
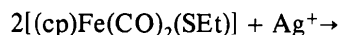
Introduction. We are currently attempting to synthesize the mixed-metal complex [(cp)Fe(CO)₂(μ -SEt)(CO)₂Mn(Mecp)]⁺ (cp = η^5 -cyclopentadienyl, Mecp = η^5 -methylcyclopentadienyl). This complex is a hybrid of the known cations [(cp)Fe(CO)₂]₂(μ -SEt)]⁺ (English, Nassimbeni & Haines, 1978) and [(Mecp)Mn(CO)₂]₂(μ -SEt)]⁺ (Burckett-St. Laurent, Caira, English, Haines & Nassimbeni, 1977); the latter compound has an Mn–Mn bond while there is no Fe–Fe interaction in the former. The degree of interaction between Fe and Mn in the hybrid would therefore be of interest. However, in the course of an attempt to prepare this compound by reacting [(cp)Fe(CO)₂(SEt)] (Ahmad, Bruce & Knox, 1966) with [(Mecp)Mn(CO)₂(thf)] (thf = tetrahydrofuran) (Strohmeier, von Hobe, Schönauer & Laporte, 1962), the title complex was obtained when AgClO₄ was added to the reaction mixture. The complex was initially characterized as the perchlorate salt; however, as a referee has pointed out, the model used for the anion in the X-ray structure analysis was incompatible with ClO₄⁻ and closer investigation of difference maps of the electron density round Cl confirmed the presence of ClO₃⁻. The

mechanism whereby ClO₄⁻ is reduced to ClO₃⁻ in this particular reaction is not clear: however, thf is susceptible to oxidation at the α -carbon position (Robertson, 1948) and perchloric acid is of course a powerful oxidizing agent. As the thf was not dried before use, it seems likely that this oxidation, with corresponding reduction of ClO₄⁻ to ClO₃⁻, was the source of ClO₃⁻. ¹H NMR spectra of thf solutions of AgClO₄ support this hypothesis.

With hindsight it would seem that the reaction



is in fact in equilibrium and in the presence of Ag⁺ and excess thf the competing reaction



which has not been hitherto reported, results in the formation of the title compound. While the structure of the methylthio analogue of this compound as the tetrafluoroborate salt has been communicated (Connelly & Dahl, 1970), a subsequent full report on the crystallographic analysis has not appeared. An X-ray analysis was therefore carried out on [(cp)Fe(CO)(SEt)]₂ClO₃, which could be obtained in suitable crystalline form.

Experimental. When an excess of AgClO₄ (1.0 g, 4.8 mmol) was added to a thf solution of [(cp)Fe(CO)₂(SEt)] (0.3 g, 1.3 mmol) and [(Mecp)Mn(CO)₂(thf)] formed *in situ* by UV irradiation of a thf solution of [(Mecp)Mn(CO)₃] (0.3 g, 1.4 mmol), the

Table 1. Fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$) for non-H atoms with *e.s.d.*'s in parentheses

	$U_{eq} = \frac{1}{3} \sum_i U_{ii}$			
	x	y	z	$U_{eq}(\text{Å}^2)$
Fe	1890 (2)	126 (2)	2785 (1)	37 (1)
S	84 (4)	-1278 (4)	3107 (1)	41 (2)
C(1)	938 (16)	1705 (16)	2888 (7)	42 (9)
O(1)	356 (14)	2816 (14)	2959 (5)	70 (8)
C(2)	3719 (19)	1141 (21)	3171 (8)	62 (12)
C(3)	3237 (17)	-110 (23)	3483 (6)	58 (10)
C(4)	3387 (19)	-1331 (20)	3154 (8)	55 (11)
C(5)	3898 (19)	-907 (20)	2642 (9)	61 (12)
C(6)	4113 (17)	633 (24)	2626 (9)	68 (13)
C(7)	-1429 (16)	-219 (22)	3357 (6)	58 (11)
C(8)	-2657 (22)	-1210 (26)	3571 (8)	82 (15)
Cl	42 (5)	42 (5)	0	58 (2)
O(10)	-37 (26)	-913 (20)	405 (7)	174 (18)
O(11)	1064 (17)	1064 (17)	0	151 (19)

Table 2. Selected bond lengths (Å) and angles (°)

S—Fe	2.240 (4)	C(3)—C(2)	1.44 (2)
C(1)—Fe	1.71 (1)	C(6)—C(2)	1.44 (3)
C(2)—Fe	2.14 (2)	C(4)—C(3)	1.38 (2)
C(3)—Fe	2.10 (2)	C(5)—C(4)	1.38 (2)
C(4)—Fe	2.12 (2)	C(6)—C(5)	1.43 (2)
C(5)—Fe	2.10 (2)	C(8)—C(7)	1.54 (2)
C(6)—Fe	2.13 (2)	O(10)—Cl	1.32 (1)
C(7)—S	1.80 (2)	O(11)—Cl	1.33 (2)
O(1)—C(1)	1.16 (2)		
Fe—S—Fe'	82.8 (2)	O(1)—C(1)—Fe	177 (2)
S—Fe—S'	95.7 (2)	C(6)—C(2)—C(3)	107 (2)
C(1)—Fe—S	93.4 (5)	C(4)—C(3)—C(2)	108 (1)
C(2)—Fe—C(6)	39.6 (7)	C(5)—C(4)—C(3)	109 (2)
C(3)—Fe—C(2)	39.8 (7)	C(6)—C(5)—C(4)	110 (2)
C(4)—Fe—C(3)	38.2 (7)	C(5)—C(6)—C(2)	105 (2)
C(5)—Fe—C(4)	38.2 (7)	O(11)—Cl—O(10)	120.7 (8)
C(6)—Fe—C(5)	39.5 (7)	O(10)—Cl—O(10')	119 (2)
C(7)—S—Fe	112.2 (6)		

Symmetry code: (') $-y, -x, 0.5 - z$; (") $y, x, -z$.

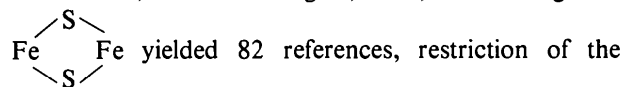
solution turned from brown to dark green with precipitation of Ag. Solvent was removed under vacuum and the solid residue was washed with benzene. Extraction of the residue with CH₂Cl₂ followed by recrystallization at 258 K from CH₂Cl₂/ether (1:1 v/v) yielded large glossy black prisms of the title complex in approximately 60% yield. Chemical analysis (C, H, S, Cl, Fe) was consistent with the title formula.

Crystal fragment 0.2 \times 0.1 \times 0.07 mm. D_m by flotation in C₂H₅I/*n*-hexane. Phillips PW 1100 diffractometer, graphite-monochromated Mo $K\alpha$, ω -2 θ scan, width 1.1° (θ), speed 0.03° (θ)s⁻¹. Lattice parameters from 25 high-angle reflections. Three standard reflections varied <3%. 6° < 2 θ < 46°; index range h, k 0/10, l 0/26. 921 independent reflections; 862 observed with $I > \sigma(I)$, $\sigma(I)$ defined previously (Gafner & Kruger, 1974). Lp correction, no absorption correction. Structure solution by Patterson synthesis; refined by least squares based on F_o ; unit weights; all non-H atoms refined anisotropically, H atoms refined with common isotropic temperature factors and coordinates based on

idealized geometries; final R 0.078. $P4_32_12$ established to be the correct space group ($R_G = 0.0788$) by refining the enantiomeric structure (reflected in the plane $z = 0.25$) in $P4_12_12$ [$R_G = 0.0822$, significantly (Hamilton, 1965) higher than R_G for $P4_32_12$]. Several models tried for refining the anion, first thought to be ClO₄⁻, within the restriction of the local twofold symmetry; anion finally recognized as ClO₃⁻ with one O in general position and the other O and the Cl on the twofold axis; this symmetry forces planarity and therefore disorder on the non-planar ClO₃⁻ ion: the disorder was not resolvable and the O atoms show considerable thermal motion. (Δ/σ)_{max} in final cycle 0.9. $\Delta\rho$ in final difference map within ± 0.55 e Å⁻³; highest peak in vicinity of ClO₃⁻ at 0.46 e Å⁻³, no peak > 0.35 e Å⁻³ within bonding distance of Cl. $f_j f' f''$ from *International Tables for X-ray Crystallography* (1974). Program SHELX76 (Sheldrick, 1976).

Discussion. Atomic coordinates and derived parameters are listed in Tables 1 and 2.* The structure of the cation is shown in Fig. 1, while Fig. 2 depicts the packing in the unit cell. Fig. 3 shows the thermal ellipsoids of the ClO₃⁻ ion.

The Fe—Fe distance in the title compound is 2.957 (4) Å, slightly longer than that [2.925 (4) Å] reported by Connelly & Dahl (1970) in [$\{(\text{cp})(\text{CO})\text{Fe}(\mu\text{-SMe})\}_2$]₂BF₄. While a search on the current (1983) Cambridge Data File (see Kennard, Watson, Allen, Motherwell, Town & Rodgers, 1975) for the fragment



Fe—Fe distance to the range 2.8–3.2 Å reduced this figure to two. Bonnet, Mathieu, Poilblanc & Ibers (1979) describe the structure of the methylene-bridged compound [$\{(\text{CO})_3\text{Fe}(\mu\text{-SMe})\}_2(\mu\text{-FCCF}_3)$] with Fe—Fe 2.963 (6) Å, and Trinh-toan, Teo, Ferguson, Meyer & Dahl (1977) report an investigation into the structures exhibited by the clusters [$(\text{cp})_4\text{Fe}_4(\mu_3\text{-S})_4$]^{*n*} ($n = -1$ to $+3$), in which an Fe—Fe distance of 2.834 (3) Å was found. Among those references in which no atomic coordinates were given and the above restriction could not be applied, only Henkel, Tremel & Krebs (1981) quote an Fe—Fe distance of 2.799 Å and remark that Fe—Fe bonding interactions in multinuclear Fe—S clusters lie in the upper ranges of Fe—Fe bond lengths. The hiatus between Fe—Fe distances of 2.5–2.8 Å, representing two-electron bonds, and the range 2.92–2.96 Å is well defined, and it seems reasonable to differentiate sharply between the two interactions,

* Lists of structure amplitudes, anisotropic thermal parameters and calculated H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39519 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

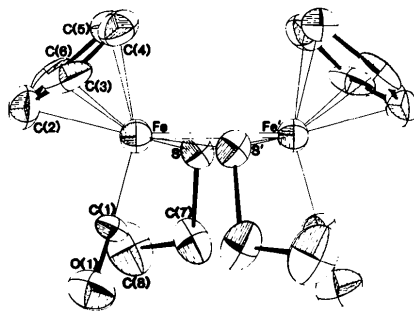


Fig. 1. Structure of the cation with atomic nomenclature.

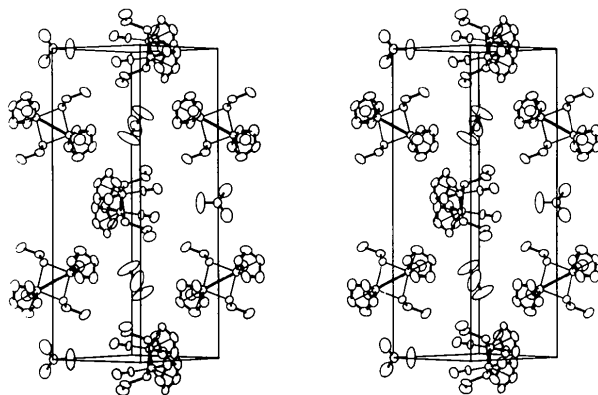


Fig. 2. Stereoscopic diagram of the unit cell.

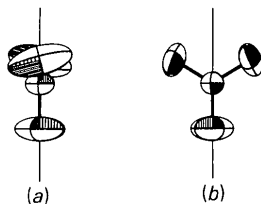


Fig. 3. Anisotropic thermal ellipsoids of the ClO_3^- ion viewed (a) parallel to and (b) perpendicular to the ClO_3^- plane; both views perpendicular to the twofold axis (thin line).

terming the second a *one-electron metal-metal bond*. Other bond lengths and angles are unremarkable. Both the cation and anion exhibit site symmetry C_2 (2) and in this the title compound resembles its methylthio analogue. Unfortunately no comparisons may be made between packing in the two compounds since no atomic coordinates are available for the latter. The neutral phenylthio analogue [$\{(\text{cp})\text{Fe}(\text{CO})(\text{SPh})\}_2$] (Ferguson, Hannaway & Islam, 1968) does not exhibit crystallographic twofold symmetry, although it approximates to it.

It is remarkable that to date only four structural analyses (including the present study) on organic or organometallic chlorates have been reported [Mitchell

& Boeyens (MB), 1970; Hlavatá (H), 1971; Gentile & Ocampo (GO), 1978]. Considerable thermal motion of the O atoms and corresponding spread in bond lengths and angles of the ClO_3^- ions are common to all four studies. The best resolved ($R = 0.055$) structure was that reported by MB, who gave Cl—O as 1.45 (2) Å and O—Cl—O 107 (1)° (mean values). In the analysis by GO ($R = 0.11$) Cl—O ranges from 1.275 (18) to 1.412 (11) Å and O—Cl—O from 106.3 (9) to 108.1 (9)°. Disorder was observed by H ($R = 0.098$), the O atoms partially occupying four tetrahedral sites round the Cl: the mean Cl—O length was 1.43 Å and O—Cl—O ranged from 92 (1) to 107.5 (5)°. The overall pattern is that of a pyramidal ClO_3^- ion with Cl—O between 1.40 and 1.45 Å, the Cl—O bonds directed to three corners of a tetrahedron with Cl at the centroid, and the O—Cl—O angles slightly compressed. The structure of the chlorate ion reported here may be interpreted in terms of an average between two such pyramidal configurations; the disorder may be due to rapid inversion of the ClO_3^- ions in the crystal lattice, or to a statistical distribution of the two orientations. The average structure corresponds to a projection of the Cl—O vectors onto a plane through the Cl atom equidistant from the two sets of O positions, and the averaged Cl—O bond lengths of 1.32 (1) and 1.34 (2) Å correspond to real tetrahedrally directed bond lengths of 1.40 (1) and 1.42 (2) Å (dividing by $\cos 19.47^\circ$) which agree well with the previous results.

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2,5,8,11,14,17,20-Heptaoxahenicosane–Barium Isothiocyanate, $C_{14}H_{30}O_7 \cdot Ba(NCS)_2^*$

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Abstract. $M_r = 563.89$, triclinic, $P\bar{1}$, $a = 7.859$ (3), $b = 11.010$ (4), $c = 14.299$ (4) Å, $\alpha = 89.65$ (2), $\beta = 78.39$ (3), $\gamma = 78.50$ (3)°, $V = 1186.9$ (7) Å³, $Z = 2$, $D_x = 1.578$ (1) Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 1.87$ mm⁻¹, $F(000) = 568$, $T = 291$ K, final $R = 0.025$ for 3979 observed reflections. The open-chain oligoether approximates to one turn of a helix, thus facilitating a sevenfold coordination of the cation to all the ether O atoms (mean 2.91 Å) and additional interactions with the two anions (mean $Ba^{2+} \cdots N^-$ distance = 2.83 Å). No linkages between the complex units were observed.

Introduction. Linear oligoethers containing $(-CH_2-CH_2-O-)_n$ units are well established ligands for alkali and alkaline-earth metal ions (Vögtle & Weber, 1979; Hilgenfeld & Saenger, 1982). Terminal donor groups such as aromatic bases (e.g. Vögtle & Sieger, 1977; Saenger, Suh & Weber, 1979), $-OH$ or $-CO_2H$ (capable of additional hydrogen bonding) (e.g. Hughes & Wingfield, 1978; Hughes, Mortimer & Truter, 1978; Yamaguchi, Miki, Yasuoka & Kasai, 1982) or, at least, terminal aromatic nuclei (e.g. Sieger & Vögtle, 1978; Hilgenfeld *et al.*, 1984) seemed essential for the stability of the complexes formed (e.g. Tümmler, Maass, Vögtle, Sieger, Heimann & Weber, 1979; Parsons, Truter & Wingfield, 1981). Complexes with unsubstituted oligoglymes could be obtained (Sieger & Vögtle, 1978) but X-ray investigations have been reported only for complexes with mercuric salts (Iwamoto, 1973), $CdCl_2$

(Iwamoto & Wakano, 1976) and for a compound in which potassium accepts additional π -interactions (Hodgson & Raymond, 1972). We report here the first structure determination of a complex between an alkaline-earth metal cation and an unsubstituted oligoglyme.

Experimental. Sample kindly provided by Professor F. Vögtle, University of D-5300 Bonn (FRG), crystal ca $0.7 \times 0.3 \times 0.1$ mm, grown from ethyl acetate/petroleum ether; Stoe-Siemens four-circle diffractometer, cell dimensions from 2θ angles for 24 reflections ($20 \leq 2\theta \leq 25^\circ$); 5261 profile-fitted (Clegg, 1981) data up to $2\theta = 50^\circ$, $-9 \leq h \leq 1$, $-13 \leq k \leq -13$, $-17 \leq l \leq 17$; no significant decline in intensities of three standard reflections; empirical absorption correction based on ψ scans, max./min. transmission 0.63/0.53; 4169 reflections unique ($R_{int} = 0.012$), 3982 with $F > 3\sigma(F)$, three suppressed (machine fault); Ba^{2+} position from an $E \times F$ Patterson map, positions of remaining non-H atoms from a subsequent difference Fourier synthesis; structure refined anisotropically by blocked-cascade least squares on F , $C(3)-C(4)$ restrained to 1.4800 ± 0.0003 Å because of slight conformational (irresolvable) disorder; H atoms included in idealized positions [$C-H = 0.96$ Å; $U(H_i) = 1.2U_{eq}(C_i)$], methylene H atoms treated as 'riding atoms', methyl groups as 'rigid groups'; 259 LS parameters, $R = 0.025$, $wR = 0.027$, $w^{-1} = \sigma^2(F) + 0.0004F^2$, $S = 1.25$, slope of normal probability plot 1.15, max. $\Delta/\sigma = 0.06$ [rotation of methyl group C(1)], mean 0.004, largest peak 0.66 e Å⁻³ (close to Ba^{2+}), largest hole 0.35 e Å⁻³ in

* Structures of Polyether Complexes. XXI. Part XX: Suh, Namgung, Ku Yoon, Saenger & Vögtle (1984).