Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	Occupancy	*x*	*y*	*z*	B_{eq}
Cu	1.0	0.67671 (11)	0.24621 (9)	0.23119 (4)	2.65 (3)
O(1)	1.0	0.6742 (10)	0.5579 (4)	0.3253 (4)	3.9 (3)
O(2)	1.0	0.7507 (8)	−0.0618 (4)	0.3243 (4)	3.3 (2)
O(*W*1)	1.0	0.9884 (7)	0.2475 (6)	0.1890 (3)	4.5 (3)
O(*W*2)	1.0	0.6861 (12)	−0.1365 (5)	0.4856 (4)	4.6 (3)
O(*W*3)	0.6	0.632 (3)	−0.3737 (11)	0.4831 (11)	6.4 (8)
O(*W*3′)	0.4	0.784 (3)	−0.3511 (15)	0.4749 (14)	5.5 (10)
N(1)	1.0	0.6105 (15)	0.3684 (6)	0.1511 (5)	4.8 (4)
N(2)	1.0	0.6924 (11)	0.3675 (5)	0.3119 (5)	2.6 (3)
N(3)	1.0	0.6955 (12)	0.1264 (5)	0.3130 (5)	2.8 (3)
N(4)	1.0	0.6439 (13)	0.1170 (5)	0.1521 (4)	3.1 (3)
C(1)	1.0	0.7304 (17)	0.5584 (8)	0.1434 (7)	5.4 (5)
C(2)	1.0	0.6182 (10)	0.4781 (6)	0.1896 (5)	2.9 (3)
C(3)	1.0	0.6653 (11)	0.4686 (6)	0.2830 (5)	2.7 (3)
C(4)	1.0	0.7244 (17)	0.3542 (8)	0.4016 (6)	3.7 (4)
C(5)	0.6	0.8080 (18)	0.2530 (14)	0.4253 (6)	3.7 (5)
C(5′)	0.4	0.626 (2)	0.254 (2)	0.4347 (9)	3.3 (7)
C(6)	1.0	0.6953 (19)	0.1395 (7)	0.4058 (6)	3.8 (4)
C(7)	1.0	0.7248 (11)	0.0271 (6)	0.2834 (5)	2.6 (3)
C(8)	1.0	0.7423 (10)	0.0225 (5)	0.1871 (4)	2.6 (3)
C(9)	1.0	0.6847 (16)	−0.0883 (6)	0.1496 (5)	3.7 (3)

Table 2. *Selected geometric parameters* (Å, °)

Cu—O(*W*1)	2.479 (5)	N(3)—C(7)	1.303 (9)
Cu—N(1)	2.008 (8)	N(4)—C(8)	1.47 (1)
Cu—N(2)	1.946 (7)	C(1)—C(2)	1.49 (1)
Cu—N(3)	1.945 (7)	C(2)—C(3)	1.53 (1)
Cu—N(4)	2.014 (7)	C(4)—C(5)	1.43 (2)
O(1)—C(3)	1.269 (9)	C(4)—C(5′)	1.51 (3)
O(2)—C(7)	1.267 (9)	C(5)—C(6)	1.64 (2)
N(1)—C(2)	1.46 (1)	C(5′)—C(6)	1.55 (3)
N(2)—C(3)	1.315 (9)	C(7)—C(8)	1.54 (1)
N(2)—C(4)	1.46 (1)	C(8)—C(9)	1.52 (1)
N(3)—C(6)	1.48 (1)		
O(*W*1)—Cu—N(1)	93.8 (4)	N(1)—C(2)—C(1)	113.9 (7)
O(*W*1)—Cu—N(2)	96.6 (3)	N(1)—C(2)—C(3)	110.4 (6)
O(*W*1)—Cu—N(3)	96.6 (3)	C(1)—C(2)—C(3)	113.0 (7)
O(*W*1)—Cu—N(4)	87.5 (3)	O(1)—C(3)—N(2)	126.0 (8)
N(1)—Cu—N(2)	83.4 (3)	O(1)—C(3)—C(2)	117.6 (6)
N(1)—Cu—N(3)	169.6 (4)	N(2)—C(3)—C(2)	116.4 (7)
N(1)—Cu—N(4)	97.9 (3)	N(2)—C(4)—C(5)	115.4 (8)
N(2)—Cu—N(3)	96.3 (3)	N(2)—C(4)—C(5′)	110.2 (9)
N(2)—Cu—N(4)	175.7 (4)	C(4)—C(5)—C(6)	115 (1)
N(3)—Cu—N(4)	81.7 (3)	C(4)—C(5′)—C(6)	116 (1)
Cu—N(1)—C(2)	112.7 (5)	N(3)—C(6)—C(5)	106.0 (8)
Cu—N(2)—C(3)	116.9 (6)	N(3)—C(6)—C(5′)	113.0 (8)
Cu—N(2)—C(4)	125.0 (5)	O(2)—C(7)—N(3)	127.9 (7)
C(3)—N(2)—C(4)	118.1 (7)	O(2)—C(7)—C(8)	117.9 (6)
Cu—N(3)—C(6)	125.9 (5)	N(3)—C(7)—C(8)	114.0 (6)
Cu—N(3)—C(7)	116.7 (6)	N(4)—C(8)—C(7)	107.7 (6)
C(6)—N(3)—C(7)	117.2 (7)	N(4)—C(8)—C(9)	112.2 (7)
Cu—N(4)—C(8)	107.2 (5)	C(7)—C(8)—C(9)	113.3 (6)

The structure was solved by direct and Fourier methods and refined by full-matrix least-squares techniques. H atoms were located by difference Fourier methods. Eight H atoms attached to C(4), C(5), C(5′), C(6), O(*W*3) and O(*W*3′) could not be located because of disorder. *NRCVAX* (Gabe, Le Page, White & Lee, 1987) was used for all calculations.

The authors thank the National Science Council for support under grants NSC82-0208-M007-119 and NSC82-0208-M007-032. They are also indebted to Ms Shu-Fang Tung for collecting the X-ray diffraction data.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71694 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1062]

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Trichloro(1,4,7-trithiacyclononane-*S*,*S*′,*S*″)iron(III), $[FeCl_3(C_6H_{12}S_3)]$

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(*Received* 10 *May* 1993; *accepted* 2 *November* 1993)

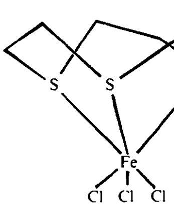
Abstract

The crystal structure of red trichloro(1,4,7-trithiacyclononane-*S*,*S*′,*S*″)iron(III), $[FeCl_3(C_6H_{12}S_3)]$, containing a distorted octahedral high-spin $[Fe^{III}Cl_3S_3]$ core, is reported. The structure of $[FeCl_3(C_6H_{12}S_3)]$ consists of discrete molecules containing six-coordinate Fe atoms. The three chlorides range in distance from the Fe atom from

2.252 (2) to 2.276 (2) Å forming the three legs of a table with the $C_6H_{12}S_3$ ring forming the table top. The three S atoms in the puckered ring coordinate to the Fe atom at distances ranging from 2.538 (3) to 2.585 (3) Å.

Comment

The coordination chemistry of crown thioether ligands has received considerable attention recently from several laboratories (Wieghardt, Küppers & Weiss, 1985; Küppers, Wieghardt, Nuber, Weiss, Bill & Trautwein, 1987; Wilson, Swanson & Glass, 1986; Rawle, Timothy & Cooper, 1987). The small cyclic trithia crown ether 1,4,7-trithiacyclononane has been shown to be ideally suited for binding as a facially coordinated tridentate ligand to several different metal centers. This ligand is reported to exert a slightly stronger ligand field than the nitrogen analog, 1,4,7-triazacyclononane. Most of the previous studies have involved homoleptic complexes; heteroleptic 1,4,7-trithiacyclononane complexes constitute a newly emerging class of compounds (Kim, Do, Lee, Jeong & Sohn, 1991; Elias, Schmidt, Küppers, Saher, Wieghardt, Bernhard & Weiss, 1989). Previous crystal structures have been determined for iron(III) in the low-spin state. We report here the crystal structure of a heteroleptic high-spin iron(III) complex, (I).



(I)

The structure is shown in Fig. 1, and the packing of the complex in the unit cell is shown as a stereoscopic plot in Fig. 2. The Fe^{III}—Cl bond lengths of 2.252 (2)-2.276 (2) Å are in the normal range for octahedrally coordinated iron(III). In the compound [Fe^{III}Cl(sal$_2$en)] [sal$_2$en = bis(salicylaldehyde)ethylenediimine], the Fe^{III}—Cl distance was found to be 2.238 (4) Å (Gerloch & Mabbs, 1967). [FeCl$_3$([9]aneS$_3$)] has been reported by Wieghardt, Küppers & Weiss (1985) to be a high-spin d^5 complex that is paramagnetic with a temperature-independent magnetic moment of 5.92 μ_B. The Fe^{III}—S bond lengths of 2.538 (3), 2.579 (2) and 2.585 (3) Å are very long in this complex when compared to the expected bond lengths. A comparison of low-spin six-coordinate iron(II) with high-spin six-coordinate iron(III) shows an expected increase in the bond length by 0.035 Å (Huheey, 1993). The average Fe^{III}—S bond length is 2.567 Å. This compares with 2.250 Å in [Fe([9]aneS$_3$)$_2$]$^{2+}$, which is a low-spin diamagnetic complex (Wieghardt, Küppers & Weiss, 1985). Beissel, Bürger, Voight & Wieghardt (1993) have determined the crystal structure of [1,4,7-tris(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane]iron(III), in which the three Fe^{III}—S bonds lengths average 2.28 Å. These authors have evidence that the solid is predominantly low spin at ambient temperature. The increased Fe^{III}—S bond lengths in the high-spin [FeCl$_3$([9]aneS$_3$)] complex may be a result of a decrease in the π-acid bonding character between Fe and the 1,4,7-trithiacyclononane ligand.

The cation [Fe([9]aneS$_3$)$_2$]$^{2+}$ has bond angles that are very close to those expected for an octahedral complex (Wieghardt, Küppers & Weiss, 1985). In contrast, [FeCl$_3$([9]aneS$_3$)] has S—Fe—S bond angles which are reduced to an average of 81° and Cl—Fe—Cl bond angles that increase to an average of 103°. The origin of this distortion remains unexplained.

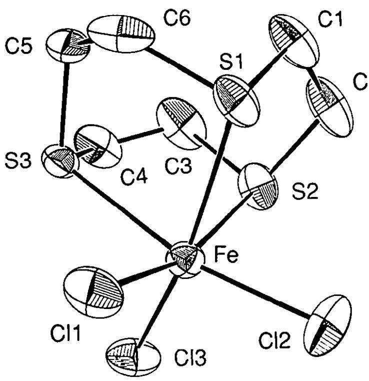


Fig. 1. An *ORTEP* (Johnson, 1965) plot of [FeCl$_3$(C$_6$H$_{12}$S$_3$)] showing the atom-numbering scheme. H atoms have been omitted. Displacement ellipsoids are shown at the 50% probability level.

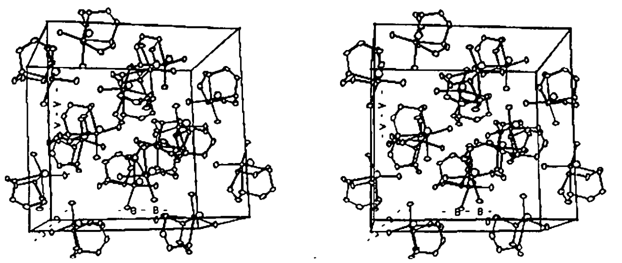


Fig. 2. Stereoscopic plot of the unit cell of [FeCl$_3$(C$_6$H$_{12}$S$_3$)].

Experimental

The title compound was prepared by the method of Wieghardt, Küppers & Weiss (1985). The red crystals were recrystallized from nitromethane by solvent evaporation.

Crystal data

[FeCl$_3$(C$_6$H$_{12}$S$_3$)]
M_r = 342.55
Tetragonal
$I4_1cd$

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 24 reflections

a = 17.352 (2) Å
c = 16.522 (3) Å
V = 4975 (1) Å^3
Z = 16
D_x = 1.91 Mg m^{-3}

θ = 10.1-20.2°
μ = 2.304 mm^{-1}
T = 294 K
Flat hexagonal prism
0.35 × 0.12 × 0.05 mm
Red

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan
$T_{\min}$ = 0.65, $T_{\max}$ = 1.00
2265 measured reflections
1214 independent reflections
790 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int}$ = 0.033
$\theta_{\max}$ = 25.0°
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 19$
1 standard reflection
frequency: 60 min
intensity variation: 0.57%

Refinement

Refinement on F
R = 0.030
wR = 0.033
S = 0.91
790 reflections
165 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.0004F^2]$

$(\Delta/\sigma)_{\max}$ = 0.26
$\Delta\rho_{\max}$ = 0.53 e Å^{-3}
$\Delta\rho_{\min}$ = −0.46 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) and Cromer & Mann (1968)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Fe	0.98043 (5)	0.22072 (6)	0.257†	2.37 (2)
Cl1	1.0192 (1)	0.0977 (1)	0.2774 (1)	3.82 (4)
Cl2	0.9797 (2)	0.2273 (2)	0.1209 (1)	5.26 (6)
Cl3	0.8525 (1)	0.2185 (1)	0.2874 (1)	4.13 (5)
S1	1.1258 (1)	0.2518 (1)	0.2550 (1)	3.16 (4)
S2	0.9738 (1)	0.3695 (1)	0.2582 (1)	3.71 (4)
S3	1.0027 (1)	0.2426 (1)	0.4071 (1)	2.60 (3)
C1	1.1362 (5)	0.3556 (5)	0.2538 (6)	4.3 (2)
C2	1.0674 (6)	0.3959 (5)	0.2170 (6)	5.3 (2)
C3	0.9836 (6)	0.3982 (5)	0.3634 (6)	4.7 (2)
C4	0.9614 (5)	0.3381 (5)	0.4223 (5)	4.3 (2)
C5	1.1046 (4)	0.2578 (5)	0.4233 (5)	3.7 (2)
C6	1.1545 (5)	0.2285 (5)	0.3577 (6)	4.2 (2)

† Coordinate fixed to define origin

Table 2. *Selected geometric parameters* (Å, °)

Fe—Cl1	2.264 (3)	S2—C2	1.82 (1)
Fe—Cl2	2.252 (2)	S2—C3	1.82 (1)
Fe—Cl3	2.276 (2)	S3—C4	1.82 (1)
Fe—S1	2.579 (2)	S3—C5	1.81 (1)
Fe—S2	2.585 (3)	C1—C2	1.51 (2)
Fe—S3	2.538 (3)	C3—C4	1.48 (2)
S1—C1	1.810 (9)	C5—C6	1.48 (2)
S1—C6	1.82 (1)		
Cl1—Fe—Cl2	101.5 (1)	Fe—S1—C1	107.8 (3)
Cl1—Fe—Cl3	104.0 (1)	Fe—S1—C6	102.1 (4)
Cl1—Fe—S1	84.72 (8)	C1—S1—C6	101.8 (6)
Cl1—Fe—S2	162.58 (9)	Fe—S2—C2	102.0 (4)
Cl1—Fe—S3	87.13 (9)	Fe—S2—C3	106.1 (4)
Cl2—Fe—Cl3	102.5 (1)	C2—S2—C3	101.8 (7)
Cl2—Fe—S1	89.0 (1)	Fe—S3—C4	102.2 (4)
Cl2—Fe—S2	87.5 (1)	Fe—S3—C5	108.4 (4)
Cl2—Fe—S3	165.7 (1)	C4—S3—C5	103.4 (6)
Cl3—Fe—S1	163.7 (1)	S1—C1—C2	112.7 (8)
Cl3—Fe—S2	88.36 (9)	S2—C2—C1	116.0 (8)
Cl3—Fe—S3	86.27 (9)	S2—C3—C4	114.4 (8)
S1—Fe—S2	80.50 (8)	S3—C4—C3	116.6 (7)
S1—Fe—S3	80.38 (8)	S3—C5—C6	114.4 (8)
S2—Fe—S3	81.37 (8)	S1—C6—C5	116.7 (8)

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement, data reduction, structure solution and refinement, molecular graphics and software used to prepare material for publication: *MolEN* (Fair, 1990).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71815 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1079]

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