Bis(1,4,7-trithiacyclononane-$\kappa^3 S,S',S''$)-iron(II) bis(perchlorate)

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Key indicators

Single-crystal X-ray study
T = 175 K
Mean σ(C–C) = 0.003 Å
R factor = 0.026
wR factor = 0.065
Data-to-parameter ratio = 20.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, [Fe([9]aneS$_2$)$_2$](ClO$_4$)$_2$ or [Fe(C$_4$H$_8$S$_2$)$_3$](ClO$_4$)$_2$, contains an octahedral Fe^{II}S$_6$ core, with the Fe atom located on an inversion center. The asymmetric unit comprises two independent half cations and two anions.

Comment

Intrigued by the possibility of using eight octahedral metal complexes as the vertices of a molecular crate (Hsu *et al.*, 2003), we are investigating the iron(II) chemistry of facially coordinating ligands, such as 1,4,7-trithiacyclononane, [9]-aneS$_3$. This tripodal ligand can conceivably act as a capping group that protects three of the coordination sites of an octahedral metal complex. In the course of these studies, we found that this ligand has a strong tendency to form [Fe([9]-aneS$_3$)$_2$]$^{2+}$, as previously noted by Fukui *et al.* (1990).

(I)
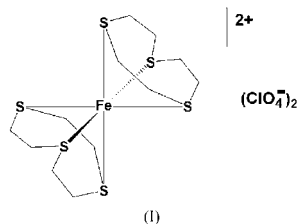
The title compound, (I), crystallizes with the Fe atoms of two independent cations on inversion centers, the asymmetric unit also containing two anions (Fig. 1). The packing of the complex in the *bc* plane is depicted in Fig. 2. Compound (I) contains an octahedral Fe^{II}S$_6$ core, with S—Fe—S angles in the range 89.42 (2)–89.92 (2)°. The Fe—S bond distances are in the range 2.2508 (4)–2.2568 (4) Å for Fe1 and a slightly larger variation is observed for distances about Fe2 [2.2523 (4)–2.2613 (4) Å]. Similar bond variation, 2.243 (1)–2.249 (1) Å, is observed for [Fe([9]aneS$_3$)$_2$]FeCl$_4$ (Grillo *et al.*, 1996). The related complexes [Fe([9]aneS$_3$)$_2$](PF$_6$)$_2$ (Wieghardt *et al.*, 1985), [Fe([9]aneS$_3$)$_2$](BF$_4$)$_2$ (Sowrey *et al.*, 2002) and [Fe([9]aneS$_3$)$_2$]Sb$_2$Cl$_8$ (Willey *et al.*, 1994) show somewhat larger variations in the Fe—S distances [2.241 (1)– 2.259 (1), 2.2437 (7)–2.2581 (7) and 2.243 (2)–2.266 (2) Å, respectively]. In contrast, the Fe—S distances in [Fe([9]-aneS$_3$)$_2$](ClO$_4$)$_3$ (Blake *et al.*, 1989) show the expected lengthening [2.276 (3)–2.285 (3) Å], related to reduction of π-backbonding ability.

Experimental

Compound (I) was prepared in a manner similar to that described by Wieghardt *et al.* (1985).
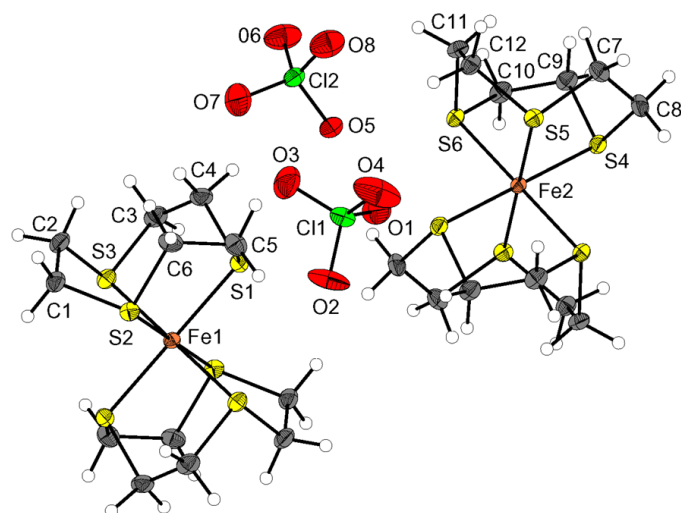
Figure 1
The structure of (I), showing the atomic labeling and 50% probability ellipsoids. The unlabeled half of each cation is generated by inversion centers at atoms Fe1 and Fe2.
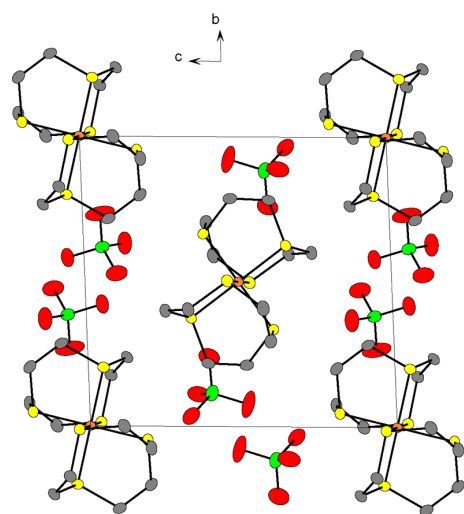

Figure 2
Packing diagram of (I) in the *bc* plane.

Crystal data

$[Fe(C_4H_8S_2)_3](ClO_4)_2$	$Z = 2$
$M_r = 615.42$	$D_x = 1.856$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.7854$ (2) Å	Cell parameters from 7696
$b = 11.3729$ (1) Å	reflections
$c = 11.5862$ (3) Å	$\theta = 2.4–28.2°$
$\alpha = 85.828$ (1)°	$\mu = 1.54$ mm^{-1}
$\beta = 84.276$ (1)°	$T = 175$ (2) K
$\gamma = 73.129$ (1)°	Rod, purple
$V = 1101.13$ (4) Å^3	$0.40 \times 0.16 \times 0.16$ mm

Data collection

Bruker SMART 1K platform CCD	5333 independent reflections
diffractometer	4592 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.021$
Absorption correction: multi-scan	$\theta_{max} = 28.2°$
(*SADABS*; Sheldrick, 1996)	$h = -11 \rightarrow 11$
$T_{min} = 0.602$, $T_{max} = 0.782$	$k = -15 \rightarrow 15$
11 893 measured reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.026$	$+ 0.7215P]$
$wR(F^2) = 0.065$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
5333 reflections	$\Delta\rho_{max} = 0.49$ e Å^{-3}
265 parameters	$\Delta\rho_{min} = -0.39$ e Å^{-3}
H-atom parameters constrained	

H atoms were either located directly from a difference map or calculated based on geometric criteria (C—H = 0.99 Å) and treated with a riding model in subsequent refinement cycles. The isotropic displacement parameters for the H atoms were defined as $1.2U_{eq}$ of the carrier atom.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *DIAMOND* (Crystal Impact, 1997); software used to prepare material for publication: *SHELXTL*.

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