Bis(tetra-*n*-butylammonium) Hexa-μ_3-sulfido-hexakis(nitrosoiron)

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Abstract

The title compound, $[N(C_4H_9)_4]_2[Fe_6S_6(NO)_6]$, is the second salt of the unusual cyclic anion $[Fe_6S_6(NO)_6]^{2-}$. The anion consists of two fused Fe_3S_3 rings, with terminal nitrosyl groups bound to the Fe atoms.

Comment

The substitution of tetra-*n*-butylammonium hydroxide for ammonium hydroxide in the synthesis of the ammonium salt of 'Roussin's black anion', $[Fe_4S_3(NO)_7]^-$, led to the growth, upon slow cooling in H_2O, of black crystals of the title compound, (I), imbedded in a mixture of other uncharacterized precipitates. The tetraethylammonium salt of $[Fe_6S_6(NO)_6]^{2-}$ has been reported previously (Scott & Holm, 1993). The average bond lengths and angles agree well with those reported by Scott & Holm (1993), and all Fe atoms have essentially identical geometries (thus valence states). The anion is located on an inversion center.

(I)
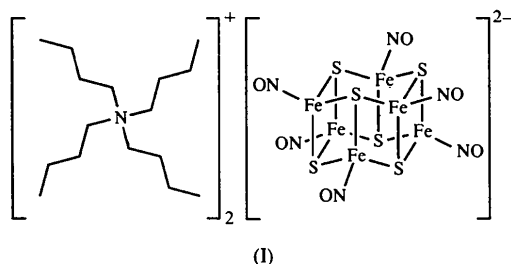
Various hexanuclear prismatic iron–sulfide clusters of the type $[Fe_6S_6L_6]^{n-}$, with L = halide, phosphine, alkoxide, have been prepared previously, the first ones by Saak *et al.* (1984) and Kanatzidis *et al.* (1984). The structural chemistry of hexanuclear iron–sulfur clusters has been reviewed by Snyder & Holm (1988).

The geometry of the tetra-*n*-butylammonium (TBA) cation is normal. Large displacement parameters of the atoms furthest from the N atom and various difference electron-density peaks of 0.5–1.3 e Å^{-3} (largest near C43 and C44) in the vicinity of the outer ends of the butyl chains indicate slight residual conformational disorder.
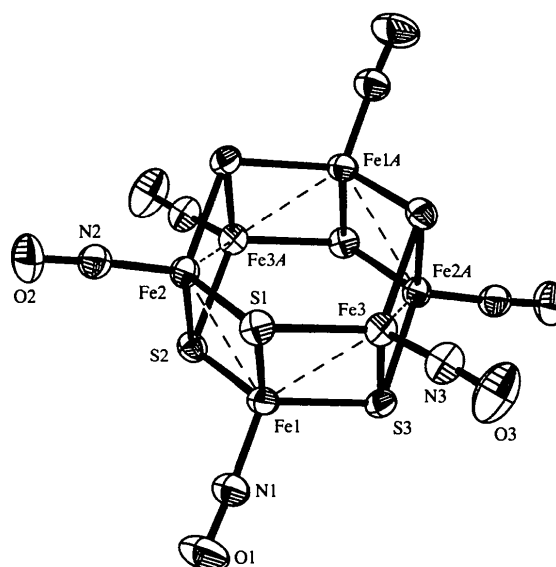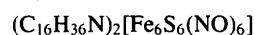

Fig. 1. The anion in $(TBA)_2[Fe_6S_6(NO)_6]$ with atomic labels. Selected inversion-symmetry-generated Fe atoms are indicated with a suffix *A* in the atomic label. The atomic displacement ellipsoids are drawn at the 50% probability level. Short Fe···Fe contacts of *ca* 2.6 Å are drawn as dashed lines.

Experimental

Crystal data

$(C_{16}H_{36}N)_2[Fe_6S_6(NO)_6]$	Mo $K\alpha$ radiation
$M_r = 1192.43$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 8192
$P2_1/n$	reflections
$a = 12.6451\,(6)$ Å	$\theta = 2$–$26°$
$b = 11.5793\,(6)$ Å	$\mu = 1.94$ mm^{-1}
$c = 17.7855\,(9)$ Å	$T = 153\,(2)$ K
$\beta = 99.4440\,(10)°$	Slanted block
$V = 2568.9\,(2)$ Å^3	$0.25 \times 0.20 \times 0.18$ mm
$Z = 2$	Black
$D_x = 1.542$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens SMART diffractometer	4912 reflections with
eter	$I > 2\sigma(I)$
Area-detector ω scans	$R_{int} = 0.045$
Absorption correction:	$\theta_{max} = 28.28°$
by integration	$h = -16 \rightarrow 16$
$T_{min} = 0.58$, $T_{max} = 0.75$	$k = -14 \rightarrow 14$
16 370 measured reflections	$l = -16 \rightarrow 23$
5937 independent reflections	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = -0.029$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$\Delta\rho_{max} = 1.3$ e Å^{-3}
$wR(F^2) = 0.114$	$\Delta\rho_{min} = -0.6$ e Å^{-3}
$S = 1.019$	Extinction correction:
5937 reflections	*SHELXTL*
263 parameters	Extinction coefficient:
H atoms constrained	0.0013 (2)

$$w = 1/[\sigma^2(F_o^2) + (0.051P)^2 + 4.29P]$$
$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Fe1—N1	1.664 (3)	Fe2—S1	2.2245 (9)
Fe1—S1	2.2114 (9)	Fe2—Fe3^i	2.6488 (6)
Fe1—S3	2.2235 (9)	Fe3—N3	1.666 (3)
Fe1—S2	2.2256 (9)	Fe3—S3	2.2163 (9)
Fe1—Fe2	2.6384 (6)	Fe3—S2^i	2.2184 (9)
Fe1—Fe3	2.6398 (6)	Fe3—S1	2.2214 (9)
Fe2—N2	1.664 (3)	N1—O1	1.186 (4)
Fe2—S2	2.2125 (9)	N2—O2	1.180 (4)
Fe2—S3^i	2.2218 (9)	N3—O3	1.187 (4)
N1—Fe1—S1	110.76 (10)	N3—Fe3—S1	109.95 (10)
N1—Fe1—S3	111.03 (11)	S3—Fe3—S1	106.91 (3)
S1—Fe1—S3	107.01 (3)	S2^i—Fe3—S1	113.68 (3)
N1—Fe1—S2	108.68 (11)	Fe1—S1—Fe3	73.10 (3)
S1—Fe1—S2	107.01 (3)	Fe1—S1—Fe2	72.99 (3)
S3—Fe1—S2	112.28 (3)	Fe3—S1—Fe2	110.31 (3)
N2—Fe2—S2	112.84 (10)	Fe2—S2—Fe3^i	73.42 (3)
N2—Fe2—S3^i	108.97 (10)	Fe2—S2—Fe1	72.95 (3)
S2—Fe2—S3^i	106.64 (3)	Fe3^i—S2—Fe1	111.80 (3)
N2—Fe2—S1	107.66 (10)	Fe3—S3—Fe2^i	73.28 (3)
S2—Fe2—S1	107.02 (3)	Fe3—S3—Fe1	72.96 (3)
S3^i—Fe2—S1	113.81 (3)	Fe2^i—S3—Fe1	111.50 (3)
N3—Fe3—S3	111.81 (10)	O1—N1—Fe1	172.9 (3)
N3—Fe3—S2^i	107.89 (11)	O2—N2—Fe2	175.6 (3)
S3—Fe3—S2^i	106.62 (3)	O3—N3—Fe3	173.9 (3)

Symmetry code: (i) $1 - x, 1 - y, -z$.

Crystal decay was monitored by repeating the initial 50 frames at the end of data collection and analyzing the duplicate reflections. No decay was observed. H atoms were placed geometrically and refined with a riding model (with 60° torsion angles for methyl groups) and with U_{iso} constrained to be $1.2U_{eq}$ of the carrier atom.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *XPREP* in *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1352). Services for accessing these data are described at the back of the journal. A hard-copy ellipsoid plot has also been archived.

References

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Bis(1,4,7-trithiacyclononane-S,S',S'')-cobalt(II) Bis(triiodide)

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Abstract

In the title compound, $[Co(C_6H_{12}S_3)_2](I_3)_2$, the cations and anions are linked into infinite sheets through inter-ion S$\cdots$I contacts of 3.800 (2)–3.989 (2) Å.

Comment

We have been studying the interactions of diiodine with both free homoleptic S-donor macrocyclic ligands (Blake, Cristiani *et al.*, 1997; Blake, Devillanova *et al.*, 1998; Blake, Li *et al.*, 1997) and their metal complexes (Blake *et al.*, 1995, 1996). In the former, a range of adduct stoichiometries is observed and for those with lower iodine–macrocycle ratios, we have established relationships between iodine content and observed structural features. With metal complexes, various polyiodide counter-anions such as I_3^-, I_5^-, I_7^- and I_9^- are observed, the anions producing extended polyiodide arrays containing features such as spirals, belts, ribbons, chains, sheets and cages (Blake *et al.*, 1998*a,b*). The metal complexes act as templates for the polyiodide lattices, as shown by the excellent matching of their size and shape with the surrounding polyiodide environments. In some cases, the polyiodide units are more isolated from each other and there are no I$\cdots$I contacts below *ca* 4.3 Å. However, there is still the possibility of S$\cdots$I interactions as described below.

There are two previously published examples of cobalt complexes of 1,4,7-trithiacyclononane ([9]-aneS$_3$), namely $[Co^{III}([9]aneS_3)_2](ClO_4)_3$, (2) (Kuppers *et al.*, 1986), and $[Co^{II}([9]aneS_3)_2](BF_4)_2.2CH_3NO_2$, (3) (Setzer *et al.*, 1983). Comparison of the geometries of the cations in the title complex, (1) (Fig. 1), and (3)