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(I)

Tetrakis(ethylenediamine)yttrium(III) Hydrosulfide Iodide

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Abstract

An yttrium hydrosulfide complex, $[Y(H_2NCH_2CH_2-NH_2)_4](SH)_{2.72}I_{0.28}$, was synthesized by solvothermal methods. The $Y(en)_4^{3+}$ and SH^- ions are well separated, and the Y atom is coordinated in a distorted square antiprism by the eight N atoms and lies on a twofold axis. The Y—N distances are in the range 2.488 (4)–2.520 (4) Å. There are two hydrosulfide sites, the one on the twofold axis being partially occupied by an iodide ion.

Comment

Attempts at solvothermal crystallization of Y_2S_3 in liquid anhydrous ammonia with an NH_4I mineralizer at temperatures of 473–573 K produced colorless crystals which rapidly lost solvent and crumbled when removed from the tube. In order to gain a better understanding of the identity of this product, ethylenediamine (en) was used as a high-boiling substitute for ammonia. From Y_2S_3 and NH_4I at 568 K, monoclinic crystals of the title compound $Y(en)_4(SH)_{2.72}I_{0.28}$, (I), were isolated. Each $Y(en)_4^{3+}$ ion in the lattice is surrounded by a total of nine SH^- or I^- ions. There are two sites for the SH^- ions, one of which lies on a twofold axis. This site is also partially occupied by an iodide ion.
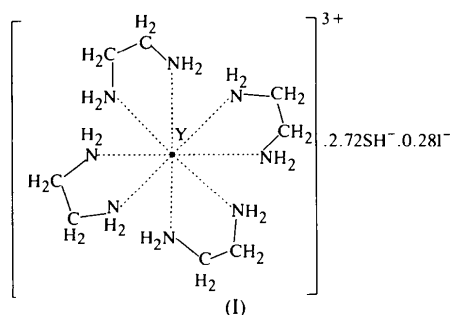
The YN_8 coordination polyhedron (Fig. 2) is a distorted square antiprism (Porai-Koshits & Aslanov, 1972), where (N1, N2, N1' and N2') and (N1A, N1'A, N2A and N2'A) form the rectangular faces where the mean deviation from a least-squares plane is 0.167 Å. The two planes deviate from being parallel by 0.2°. A square antiprism of approximate D_2 symmetry is what one would usually expect from coordination to four bidentate ligands with a normalized bite (N···N distance/Y—N distance) between 1.07 and 1.3 (Kepert, 1978). The normalized bite of the en ligands in $Y(en)_4(SH)_{2.72}I_{0.28}$ averages 1.11, and the bite angles are 67.3 (1) and 68.1 (1)°. Despite extensive use of ethylenediamine and its tetramethyl derivative as ligands, only one structurally characterized example of a metal ion surrounded by four ethylenediamine ligands, $[La(en)_4SO_3CF_3]^{2+}(SO_3CF_3^-)_2$, has been reported (Smith & Raymond, 1985). An IR spectral study showed that the lanthanide ion in tetrakis-(ethylenediamine) complexes of lanthanide salts can be either eight-coordinate $\{[Ln(en)]_4^{3+}(X^-)_3\}$ or nine-coordinate $\{[Ln(en)_4X]^{2+}(X^-)_2\}$ depending on ion size and the coordinating power of the anion (Forsberg & Moeller, 1969). The Y—N distances of 2.488 (4)–
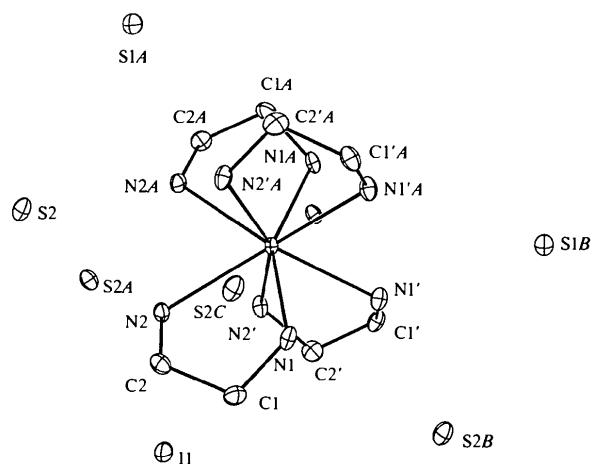

Fig. 1. Displacement ellipsoid drawing (20% probability) of the title compound. H atoms have been omitted for clarity and the nine nearest symmetry-related S or I atoms are shown. Sites labeled as I1, S1A and S1B are partially occupied by both I and S.

2.520 (4) Å are normal for eight-coordinate yttrium complexes (Reger, Lindeman & Lebioda, 1988; Folyakova, Starlkova, Parusnikov & Krasavin, 1982). Each S atom is well isolated from all other non-H atoms, as the nearest Y—S distances range from 4.965 (2) to 5.138 (1) Å, the nearest S—S distances are 4.146 (2) and 4.957 (3) Å, and the closest S—N distance is 3.434 (5) Å, which exceeds the sum of the van der Waals radii of N and S (3.35 Å; Huheey, 1978). The hydrosulfide H-atom positions were chosen from among the largest difference-map peaks but were not well defined and were constrained to an S—H distance of 1.05 Å. An S—H stretching peak in the IR spectrum (2556 cm^{-1}) confirms the presence of SH groups in Y(en)4(SH)2.72I0.28.
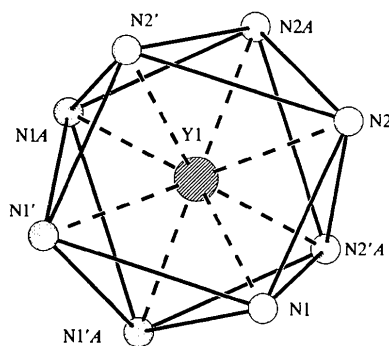

Fig. 2. Coordination polyhedron around yttrium in the title compound.

Experimental

A thick-walled Pyrex tube (Wilmad 502-PP) was charged with Y2S3 (50 mg, 0.18 mmol) and NH4I (24 mg, 0.17 mmol), partially filled with dry ethylenediamine (en), then frozen at 77 K and sealed under vacuum. The tube was 17 cm high and was 56% full at 298 K. The tube was subjected to an external hydrostatic pressure of 25 000 psi and heated to 513 K for 1 d in a LECO HR-1B hydrothermal system, which produced a few very small crystals upon cooling to 298 K. Repeated heat treatment at 513 K for 1 d caused larger crystals to grow, which were removed from the tube in the Dri-lab. The data crystal was mounted in a sealed glass capillary containing a small amount of ethylenediamine to prevent solvent loss. The presence of iodine was verified by a qualitative chemical test.

Crystal data

[Y(C2H8N2)4](SH)2.72I0.28
M_r = 451.99
Monoclinic
$C2/c$
a = 9.029 (2) Å
b = 15.416 (3) Å
c = 14.695 (3) Å
β = 107.80 (3)°
V = 1947.5 (7) Å^3
Z = 4
D_x = 1.542 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 40 reflections
θ = 3.00–12.25°
μ = 3.690 mm^{-1}
T = 293 (2) K
Irregular
0.38 × 0.32 × 0.26 mm
Clear colorless

Data collection

Siemens $P4$ diffractometer
$\theta/2\theta$ scans
Absorption correction:
   empirical ψ scans
   (*SHELXTL-Plus*;
   Sheldrick, 1994)
   T_{min} = 0.30, T_{max} = 0.38
2288 measured reflections
1701 independent reflections

1327 reflections with
   $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 25°
h = -1 → 10
k = -1 → 18
l = -17 → 17
3 standard reflections
   every 97 reflections
   intensity decay: 4.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.105
S = 1.055
1701 reflections
99 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 6.0039P]$
   where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.090
$\Delta\rho_{max}$ = 0.735 e Å^{-3}
$\Delta\rho_{min}$ = -0.573 e Å^{-3}
Extinction correction: none
Scattering factors from
   International Tables for Crystallography (Vol. C)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Y1	1/2	0.63441 (4)	1/4	0.0205 (2)
N1	0.7025 (5)	0.6724 (3)	0.4022 (3)	0.0325 (10)
C1	0.8290 (6)	0.6084 (4)	0.4302 (4)	0.0415 (15)
C2	0.7592 (7)	0.5185 (4)	0.4258 (4)	0.0400 (14)
N2	0.6513 (5)	0.5031 (3)	0.3293 (3)	0.0305 (10)
N1'	0.6267 (5)	0.7649 (3)	0.2023 (3)	0.0350 (11)
C1'	0.6862 (7)	0.7528 (3)	0.1212 (4)	0.0373 (13)
C2'	0.7609 (7)	0.6652 (4)	0.1284 (4)	0.0440 (15)
N2'	0.6495 (5)	0.5975 (3)	0.1363 (3)	0.0356 (11)
S1†	1	0.47525 (8)	1/4	0.0497 (5)
I1‡	1	0.47525 (8)	1/4	0.0497 (5)
S2	0.4160 (2)	0.35534 (9)	0.39556 (9)	0.0370 (4)

† Site occupancy = 0.722 (3).   ‡ Site occupancy = 0.278 (3).

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

Y1—N1	2.488 (4)	Y1—N1'	2.517 (4)
Y1—N2'	2.513 (4)	Y1—N2	2.520 (4)
N1—Y1—N1'	152.8 (2)	N1'—Y1—N2'	68.13 (13)
N1—Y1—N1'	77.93 (14)	N1''—Y1—N2	137.85 (13)
N1'—Y1—N1'	80.40 (14)	N2'—Y1—N2	73.1 (2)
N1—Y1—N2'	138.63 (13)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

The common site for S1 and I1 was refined with constraints requiring equivalent coordinates and anisotropic thermal parameters for both S1 and I1. The site occupation parameters were constrained to sum to 1. The population of H1S is then 0.36.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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(2S)-(+)-Dicarbonyl(η^4-2,6,6-trimethylcyclohepta-2,4-dienone)(triphenylphosphine-P)iron

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Abstract

The title compound, [Fe(C$_{10}$H$_{14}$O)(C$_{18}$H$_{15}$P)(CO)$_2$], is the first crystalline and enantiomerically pure iron complex with eucarvone as an organic ligand. The absolute configuration could be determined as 2*S*.

Comment

Chiral carbonyl iron complexes of prochiral 1,3-dienes are valuable tools in stereoselective organic synthesis (Grée, 1989). It is necessary therefore to determine the absolute configuration of these complexes. Various methods are used to obtain optically pure or enantiomerically enriched complexes (Grée, 1989; Knölker & Hermann, 1996; Kane-Maguire, Pyne, Siu, Skelton & White, 1996; Maywald & Eilbracht, 1996). For the eucarvone (2,6,6-trimethyl-2,4-cycloheptadien-1-one) complex, the best preparative method, with up to 64% e.e., is kinetic resolution of the tricarbonyliron complex with various sparteine *N*-oxides as a chiral auxiliary (Petrowitsch & Eilbracht, 1997). The phosphine complex can be separated to its pure enantiomers by chiral HPLC. Correlation of the CD spectra of these samples with those of tricarbonyl(cycloheptadienone)iron (Sotokawa *et al.*, 1987) leads to the absolute configuration of the title compound, (I), as shown in Fig. 1 (Petrowitsch & Eilbracht, 1997).

(I)
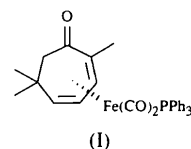
This absolute configuration is confirmed by X-ray anomalous diffraction. The geometry of the organic ligand in the title compound, (I), is similar to the corresponding unsubstituted fragment in the crystal structure of tricarbonyl(2,3-dihydrotropone)iron (Sotokawa *et al.*, 1987). The replacement of the H atoms at C7 by bulkier methyl groups does not significantly influence the geometry of the seven-membered ring as a visual comparison [fractional coordinates or torsion angles are not given by Sotokawa *et al.* (1987)] of the two
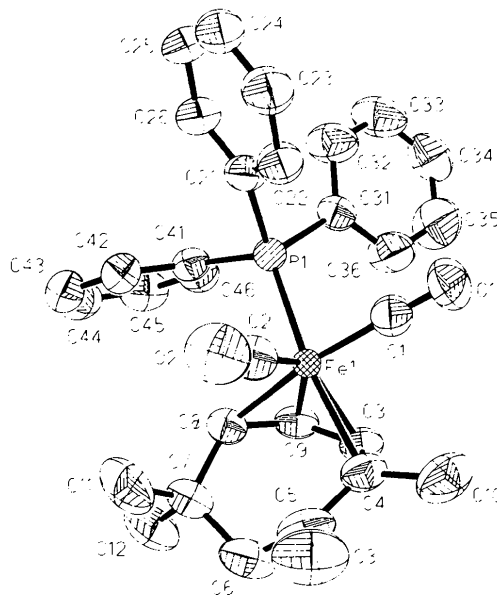

Fig. 1. View of the title compound showing the labelling of all non-H atoms. Displacement ellipsoids are shown at 50% probability levels.

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