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Bis(thioacetato-*S*)[tris(2-aminoethyl)amine]cobalt(III) Perchlorate

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Abstract. $[Co(C_2H_3OS)_2(C_6H_{18}N_4)]ClO_4$, $M_r = 454{\cdot}84$, monoclinic, $P2_1/c$, $a = 14{\cdot}894\,(8)$, $b = 7{\cdot}607\,(2)$, $c = 19{\cdot}596\,(11)$ Å, $\beta = 124{\cdot}57\,(3)°$, $V = 1828\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}653$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 12{\cdot}65$ cm^{-1}, $F(000) = 944$, room temperature, $R = 0{\cdot}058$ for 3921 independent reflections [$|F_o| > 3\sigma(|F_o|)$]. The Co atom is surrounded octahedrally by four N atoms of the $N(CH_2CH_2N_2)_3$ (tren) ligand and two S atoms of the thioacetates, which act as unidentate-*S* ligands. There are three intramolecular hydrogen bonds between the thioacetate O atoms and two N atoms of the tren ligand.

Introduction. In the course of investigations on the stereochemical and spectrochemical properties of cobalt(III) complexes with sulfur-containing ligands, we have newly prepared the title complex. The thioacetate ligand coordinates to several metals in a bidentate mode (Borel & Ledesert, 1978, and references therein; Hall & Sowerby, 1980), although it has three possible coordination modes, unidentate-*O*, unidentate-*S*, and bidentate. Tris(2-aminoethyl)amine (tren) is a tripod-like quadridentate ligand. Thus the (tren)cobalt(III) complex is convenient for investigation of the stereochemical preference of the thioacetate ligand for the remaining two *cis* coordination sites. In order to establish the geometry adopted by the title complex, we have determined its structure and report it here.

Experimental. The title complex was prepared as follows: to a solution containing 1·43 g of $[CoCl_2(tren)]Cl$ (Kimura, Young & Collman, 1970) in 30 cm^3 of water was added a solution containing 0·76 g of thioacetic acid in a mixture of 1 mol dm^{-3} NaOH aqueous solution (10 cm^3) and methanol (10 cm^3). The mixture was stirred for 10 min in an icebath. After removing insoluble material, 2 cm^3 of a saturated $NaClO_4$ solution was added dropwise to the filtrate. The solution was kept in a refrigerator overnight. The red crystals, which contained a small amount of black precipitate as an impurity, were collected by filtration and recrystallized from water.

Systematic absences $h0l$ for l odd and $0k0$ for k odd, space group $P2_1/c$; crystal $0{\cdot}23 \times 0{\cdot}45 \times 0{\cdot}45$ mm; Rigaku AFC-5 automated four-cirlce diffractometer, 50 kV and 160 mA; unit-cell dimensions by least-squares refinement from 25 reflections with $20 < 2\theta < 25°$; 2θ–ω scan, scan rate 3° min^{-1}, $\Delta\omega = (1{\cdot}0 + 0{\cdot}4\tan\theta)°$; three standard reflections every 50 measured, intensities constant within experimental error; 5359 unique reflections, $2\theta \le 60°$ ($-20 \le h \le 17$, $0 \le k \le 10$, $0 \le l \le 27$); 3921 reflections with $|F_o| > 3\sigma(|F_o|)$ used for structure determination; intensities corrected for Lorentz and polarization, not for absorption. The structure was solved by standard Patterson method and successive difference Fourier maps. All the H atoms were fixed by geometrical constraints (C—H = 0·97 and N—H = 0·87 Å). The structure was refined by full-matrix least squares using anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms; $R = 0{\cdot}058$ and $wR = 0{\cdot}066$, $w = 0{\cdot}8426/[\sigma^2(F_o) + 0{\cdot}005461|F_o|^2]$, $S = 0{\cdot}778$; $(\Delta/\sigma)_{\max} = 0{\cdot}13$, $|\Delta\rho|_{\max}$ in final difference Fourier map = 0·76 e Å^{-3}. All calculations were performed with *SHELX76* (Sheldrick, 1976) and the molecular illustration was drawn using *ORTEP* (Johnson, 1976) on a Facom M-780/20 computer. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The final atomic parameters are listed in Table 1.† The molecular structure and numbering scheme are illustrated in the *ORTEP* plot given in Fig. 1. Bond distances and angles are listed in Table 2. Both thioacetates act as unidentate ligands and coordinate to the Co atom through the S atom. The Co—S distances in the complex are significantly different [2·255 (1) and 2·283 (1) Å], and they are somewhat longer than those in other cobalt(III) complexes with sulfur-containing ligands, *e.g.*

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† Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and bond distances and angles for the perchlorate ion have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52271 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters* ($Å^2 \times 10^2$) *for the non*-H *atoms*

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

	x	y	z	U_{eq}
Co	0·24196 (4)	0·07228 (6)	0·28093 (3)	2·18 (2)
S(1)	0·28814 (8)	−0·07655 (15)	0·39780 (6)	3·13 (4)
S(2)	0·15493 (9)	−0·17343 (13)	0·20904 (6)	2·83 (4)
O(1)	0·0838 (3)	−0·0853 (5)	0·3523 (2)	4·12 (15)
O(2)	0·0049 (3)	0·0305 (5)	0·0900 (2)	3·57 (14)
N(1)	0·3219 (3)	0·2886 (4)	0·3401 (2)	2·51 (11)
N(2)	0·3842 (3)	−0·0121 (5)	0·3091 (2)	2·92 (13)
N(3)	0·2117 (3)	0·1917 (5)	0·1814 (2)	2·86 (13)
N(4)	0·1161 (3)	0·1844 (5)	0·2693 (2)	2·79 (12)
C(1)	0·4373 (3)	0·2369 (6)	0·4039 (3)	2·95 (15)
C(2)	0·4737 (3)	0·1146 (6)	0·3634 (3)	3·28 (16)
C(3)	0·3187 (4)	0·4163 (5)	0·2814 (3)	3·12 (16)
C(4)	0·2218 (4)	0·3829 (6)	0·1940 (3)	3·22 (16)
C(5)	0·2675 (4)	0·3593 (7)	0·3789 (3)	3·70 (18)
C(6)	0·1452 (4)	0·3527 (7)	0·3155 (3)	3·83 (19)
C(7)	0·1796 (4)	−0·1224 (6)	0·4048 (3)	3·31 (17)
C(8)	0·2116 (5)	−0·2118 (10)	0·4833 (3)	4·82 (25)
C(9)	0·0398 (1)	−0·1189 (6)	0·1117 (3)	3·00 (15)
C(10)	−0·0162 (4)	−0·2726 (7)	0·0550 (3)	3·91 (20)
Cl	0·39662 (9)	0·16435 (16)	0·11872 (7)	3·73 (4)
O(11)	0·4644 (3)	0·1667 (6)	0·0885 (2)	4·87 (16)
O(12)	0·2938 (5)	0·2297 (12)	0·0586 (4)	11·52 (44)
O(13)	0·3874 (6)	−0·0041 (7)	0·1438 (4)	9·50 (37)
O(14)	0·4424 (6)	0·2730 (9)	0·1888 (4)	11·40 (41)

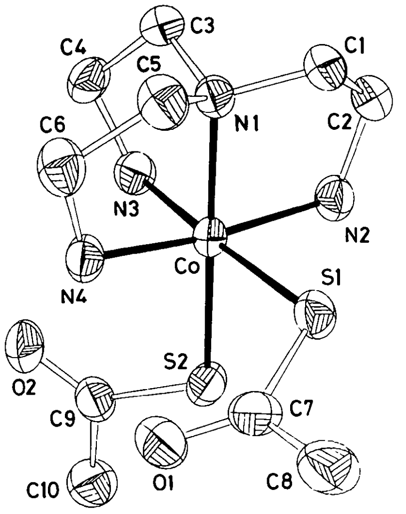

Fig. 1. *ORTEP* drawing (Johnson, 1976) of the $[Co(CH_3COS)_2(tren)]^+$ cation (50% probability thermal ellipsoids) with the atom-numbering scheme. H atoms are omitted for clarity.

$[Co\{CH_3SCH(CH_3)COO\}(tren)]^{2+}$ [2·239 (1) Å] (Ohba & Saito, 1984) and $[Co(en)_2\{S(O)_nCH_2CH_2NH_2\}]^{2+}$ [$n = 0$, 2·226 (2); $n = 1$, 2·253 (1); $n = 2$, 2·191 (2) Å; and en = ethylenediamine] (Adzamli, Libson, Lydon, Elder & Deutsch, 1979). Similar differences between the two coordination sites were also observed for the Co—O distances in the (tren)cobalt(III) complexes with 2,4-pentanedionate derivatives (Nakano & Sato, 1982, and references therein).

Table 2. *Bond distances* (Å) *and angles* (°)

Co—S(1)	2·283 (1)	N(1)—C(1)	1·494 (5)
Co—S(2)	2·255 (1)	N(1)—C(3)	1·486 (5)
Co—N(1)	1·976 (3)	N(1)—C(5)	1·491 (5)
Co—N(2)	1·969 (3)	N(2)—C(2)	1·494 (6)
Co—N(3)	1·959 (3)	N(3)—C(4)	1·469 (6)
Co—N(4)	1·952 (3)	N(4)—C(6)	1·484 (6)
S(1)—C(7)	1·734 (5)	C(1)—C(2)	1·509 (6)
S(2)—C(9)	1·744 (4)	C(3)—C(4)	1·508 (6)
O(1)—C(7)	1·228 (6)	C(5)—C(6)	1·516 (6)
O(2)—C(9)	1·221 (6)	C(7)—C(8)	1·491 (7)
		C(9)—C(10)	1·498 (7)

S(1)—Co—S(2)	87·39 (4)	Co—N(1)—C(5)	106·2 (3)
S(1)—Co—N(1)	94·9 (1)	Co—N(2)—C(2)	111·9 (3)
S(1)—Co—N(2)	83·9 (1)	Co—N(3)—C(4)	110·3 (3)
S(1)—Co—N(3)	175·7 (1)	Co—N(4)—C(6)	112·2 (3)
S(1)—Co—N(4)	93·2 (1)	C(1)—N(1)—C(3)	109·7 (3)
S(2)—Co—N(1)	176·6 (1)	C(1)—N(1)—C(5)	111·6 (3)
S(2)—Co—N(2)	92·9 (1)	C(3)—N(1)—C(5)	111·7 (3)
S(2)—Co—N(3)	92·1 (1)	N(1)—C(1)—C(2)	107·9 (3)
S(2)—Co—N(4)	96·6 (1)	N(1)—C(3)—C(4)	111·0 (3)
N(1)—Co—N(2)	85·0 (1)	N(1)—C(5)—C(6)	108·6 (4)
N(1)—Co—N(3)	85·4 (1)	N(2)—C(2)—C(1)	109·3 (3)
N(1)—Co—N(4)	85·6 (1)	N(3)—C(4)—C(3)	107·4 (3)
N(2)—Co—N(3)	91·9 (2)	N(4)—C(6)—C(5)	109·1 (4)
N(2)—Co—N(4)	169·9 (2)	S(1)—C(7)—O(1)	125·4 (4)
N(3)—Co—N(4)	91·1 (1)	S(2)—C(9)—O(2)	124·2 (4)
Co—S(1)—C(7)	114·5 (2)	S(1)—C(7)—C(8)	114·0 (4)
Co—S(2)—C(9)	110·2 (2)	S(2)—C(9)—C(10)	114·4 (3)
Co—N(1)—C(1)	107·2 (2)	O(1)—C(7)—C(8)	120·6 (4)
Co—N(1)—C(3)	110·3 (2)	O(2)—C(9)—C(10)	121·4 (4)

The tren ligand acts in the expected quadridentate mode. All of the three chelate rings in tren adopt envelope conformations, which are quite similar to those of the other (tren)cobalt(III) complexes (Nakano & Sato, 1982, and references therein). The average Co—N distance is 1·964 (3) Å, and the Co—N(1) and Co—N(3) distances bonded *trans* to the S atoms are 1·976 (3) and 1·959 (3) Å respectively. This indicates that the structural *trans* effect due to the coordinated S atom in thioacetate is not observed in the present complex, in contrast with other cobalt(III) complexes with thiolate-type ligands (Okamoto, Umehara, Nomoto, Einaga & Hidaka, 1987, and references therein).

Three intramolecular hydrogen bonds are observed between the O atoms in the thioacetate ligands and two of the N atoms in tren, N(4)—H···O(1) [2·823 (6) Å], N(3)—H···O(2) [2·818 (5) Å], and N(4)—H···O(2) [3·140 (5) Å].

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Structure of Tetramethylammonium Tetraiodozincate in the Monoclinic Phase

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Abstract. $[N(CH_3)_4]_2ZnI_4$, $M_r = 721{\cdot}2$, monoclinic, $P12_1/c1$, $a = 9{\cdot}612\,(9)$, $b = 16{\cdot}656\,(15)$, $c = 13{\cdot}222\,(18)$ Å, $\beta = 90{\cdot}15\,(4)^\circ$, $V = 2117\,(4)$ Å^3, $Z = 4$, $D_x = 2{\cdot}263$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 70{\cdot}74$ cm^{-1}, $F(000) = 1312$, $T = 250$ K, final $R = 0{\cdot}051$ for 1704 unique reflections with $F > 3\sigma(F)$. The structure is characterized by the counterclockwise rotations on axes along [010] of all ions from the basic room-temperature structure.

Introduction. $[N(CH_3)_4]_2ZnI_4$ is one of the members of $[N(CH_3)_4]_2MX_4$-type compounds. The highest-temperature phases are of the β-K_2SO_4-type structure with space group *Pmcn* in common (Wiesner, Srivastava, Kennard, DiVaira & Lingafelter, 1967). The setting of the crystal axes chosen by Sawada, Shiroishi, Yamamoto, Takashige & Matsuo (1978) is adopted in this paper. The crystal undergoes successive phase transitions at about 260 and 220 K (Werk, Chapuis & Schmid, 1987). These phases are denoted as I, II (monoclinic, $b = b_0$) and III (ferroelectric, $Pbc2_1$, $b = 2b_0$) in the order of decreasing temperature, where b_0 is the cell dimension in phase I. Crystal structures of phases I and III have been reported: in phase III the distortion with respect to the basic room-temperature structure is mainly due to rotations of the ZnI_4 tetrahedra (Werk, Chapuis & Perret, 1987). Most of the isomorphous compounds, $[N(CH_3)_4]_2MCl_4$ with M = Zn, Co, Ni, Fe, Mn and Cu, exhibit many modulated phases with modulation along [001] (Gesi, 1986). The title compound is especially of interest because of the modulation along [010]. This type of modulation has been reported only in two other compounds $[N(CH_3)_4]_2CuBr_4$ (Hasebe, Mashiyama, Tanisaki & Gesi, 1982) and $[N(CH_3)_4]_2CdI_4$ (Werk & Chapuis, 1988). The present paper reports the structure in phase II.

Experimental. Single crystals of $[N(CH_3)_4]_2ZnI_4$ were grown by the slow evaporation method from an aqueous solution containing an excess of ZnI_2 without acidification (Gesi & Perret, 1988). D_m was not determined. A spherical specimen with radius 0·112 mm was mounted on an automatic four-circle diffractometer (Rigaku AFC-5), graphite-monochromated Mo $K\alpha$ radiation. Temperature of the sample kept at 250 ± 0·3 K by controlled nitrogen gas flow. Cell dimensions from 24 reflections, $8{\cdot}9 < \theta < 11{\cdot}2^\circ$; the ω-mode up to $(\sin\theta)/\lambda < 0{\cdot}538$ Å^{-1} ($0 \le h \le 10$, $0 \le k \le 17$, $-14 \le l \le 14$), scan speed 10° min^{-1} in θ, scan width $1{\cdot}9^\circ + 0{\cdot}5^\circ \tan\theta$; three standard reflections (511, 163 and 136) monitored every 150 reflections, no significant variation detected. 3074 reflections measured, 2876 unique reflections; $R_{\text{int}} = 0{\cdot}02$ based on F. After absorption, Lorentz and polarization corrections, 1704 unique reflections with $F > 3\sigma(F)$ were used for the analysis. Min., max. transmission coefficients 0·325, 0·335.

When the single crystal was cooled down to phase II, a single peak of Bragg reflection split into two due to the formation of monoclinic domains with (001) in common. Because of the small deviation of angle β

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