

(2,2'-Dithiodibenzoato)(*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(II)

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Abstract. $[\text{Co}(\text{C}_{16}\text{H}_{36}\text{N}_4)(\text{C}_{14}\text{H}_8\text{O}_4\text{S}_2)]$, $\text{C}_{30}\text{H}_{44}\text{CoN}_4\text{O}_4\text{S}_2$, monoclinic, $P2_1/a$, $a = 14.755$ (4), $b = 24.143$ (7), $c = 8.833$ (4) Å, $\beta = 100.91$ (2)°, $Z = 4$, $D_o = 1.38$ (1), $D_c = 1.392$ Mg m⁻³; final $R_F = 0.073$ for 2619 reflections with $F^2 \geq 3\sigma(F^2)$. The structure consists of discrete $\text{C}_{30}\text{H}_{44}\text{CoN}_4\text{O}_4\text{S}_2$ molecules. Each Co atom is ligated in a *cis* distorted octahedral fashion by four N atoms from the folded macrocyclic tetramine and two O atoms from one carboxylate group of the dithiodibenzoate. The Co–N bond lengths are 2.104 (6), 2.122 (6), 2.150 (7) and 2.159 (6) Å; the Co–O bond lengths are 2.208 (6) and 2.231 (6) Å. A dihedral angle of 83.2 (4)° and an S–S bond length of 2.063 (3) Å were observed for the disulfide unit. The carboxylate groups are twisted 29.5 (4) and 25.4 (4)° out of coplanarity with the benzene rings to which they are directly attached.

Introduction. To extend our studies of metal(II)–mercaptide complexes (Hughey, Fawcett, Rudich, Lalancette, Potenza & Schugar, 1979), we chose to prepare the Co^{II} and Zn^{II} analogs of (*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)(*o*-mercaptobenzoato)copper(II) monohydrate, $[\text{Cu}(\text{tet-b})(\text{o-SC}_6\text{H}_4\text{CO}_2)] \cdot \text{H}_2\text{O}$. A compositionally identical Co^{II} analog precipitated as pink microcrystals when an excess of deoxygenated aqueous $\text{o}^- \text{SC}_6\text{H}_4\text{CO}_2^- \cdot 2\text{Na}^+$ was reacted with deoxygenated 0.01 *M* aqueous $[\text{Co}(\text{tet-b})]^{2+}$. The rate of precipitation could be slowed by dilution of the above solutions. During the several-week period required to grow diffraction-quality crystals, air apparently leaked through a faulty serum cap seal and oxidized the mercaptide ligand to a disulfide. A crystallographically determined molecular weight along with subsequent elemental analysis (calculated $\text{C}_{30}\text{H}_{44}\text{CoN}_4\text{O}_4\text{S}_2$: C, 55.63; H, 6.85; N, 8.65; Co, 9.10%; found: C, 55.17; H, 7.07; N, 8.75; Co, 8.91%) revealed that the pink crystals obtained *via* slow precipitation were those of the title complex, $[\text{Co}(\text{tet-b})(\text{o-O}_2\text{CC}_6\text{H}_4\text{S}_2)]$. To determine if the Co atom was ligated by the disulfide group, a structural study was initiated.

A single pink prism of dimensions 0.17 × 0.19 × 0.44 mm was mounted on a glass fiber along the *c* axis

(long dimension). Examination of the reciprocal lattice using Weissenberg photographs and an Enraf–Nonius CAD-3 automated diffractometer revealed systematic absences consistent with space group $P2_1/a$. For four molecules per unit cell, the observed (flotation, cyclohexane/ethylene dibromide) and calculated densities agreed well. Data were collected at 295 ± 2 K with the CAD-3 diffractometer (θ – 2θ scan) using graphite-monochromated Mo *K* α radiation ($\lambda = 0.71069$ Å). Of the 5338 reflections recorded ($8^\circ < 2\theta < 45^\circ$), 2619 with $F^2 \geq 3\sigma(F^2)$ were corrected for Lp, decay (random, ±3%), and absorption effects ($\mu = 0.751$ mm⁻¹ for Mo *K* α radiation), and used in the refinement.

The structure was solved by direct methods using the program *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined using full-matrix least-squares techniques described previously (Hughey *et al.*, 1979). Neutral-atom scattering factors for all atoms and anomalous-dispersion corrections for Co and S were obtained from *International Tables for X-ray Crystallography* (1974). An *E* map, calculated using 264 phases from the starting set having the highest combined figure of merit, revealed 28 non-hydrogen atoms; the remaining non-hydrogen atoms were located on a difference electron density map. After several cycles each of isotropic and anisotropic refinement using weights taken as $\sigma^{-2}(F)$, another difference map was calculated and H atoms were added to the model. Amine, aromatic, and methylene H coordinates were calculated assuming either tetrahedral or trigonal-planar geometry, as appropriate, and N–H and C–H distances of 0.87 and 0.95 Å, respectively (Churchill, 1973). Methyl-group H atoms were located by placing three tetrahedrally oriented H atoms 0.95 Å from the appropriate C atom and rotating the set at 5° increments. The orientation yielding the highest combined electron density on the difference map was selected. All H atoms were located in positive regions of the difference map. Temperature factors for the H atoms were then set according to $B_H = B_{\text{eq}} + 1$, where B_{eq} is the equivalent isotropic temperature factor of the atom bonded to H. H-atom parameters were not refined.

Several additional cycles of anisotropic refinement

led to convergence with $R_F = \sum |F_o| - |F_c| / \sum |F_o| = 0.073$ and $R_{wF} = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2} = 0.079$. For the final cycle, all parameter changes were less than 0.1σ , where σ is the e.s.d. obtained from the inverse matrix. The two highest peaks on a final difference map were residuals of Co ($0.9 \text{ e } \text{Å}^{-3}$) and S ($0.6 \text{ e } \text{Å}^{-3}$). Atomic coordinates for the non-hydrogen atoms are given in Table 1.* Selected bond distances

* Lists of anisotropic thermal parameters, H-atom coordinates, and observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36058 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters, with estimated standard deviations in parentheses

$$B_{eq} = 8\pi^2/3 (U_{11}a^*a^2 + U_{22}a^*b^*ab \cos \gamma + \dots).$$

	x	y	z	$B_{eq} (\text{Å}^2)$
Co	7879.1 (8)	5885.0 (4)	1307.6 (13)	3.00 (3)
S(1)	7752 (2)	3975 (1)	2112 (3)	3.89 (6)
S(2)	7572 (2)	3190 (1)	2922 (3)	3.96 (6)
O(1)	7164 (4)	5412 (2)	-745 (7)	4.6 (2)
O(2)	8191 (4)	5000 (2)	1038 (8)	4.3 (2)
O(3)	6517 (4)	2073 (3)	5958 (7)	5.0 (2)
O(4)	7386 (5)	2187 (3)	4184 (8)	6.2 (2)
N(1)	7146 (4)	6634 (3)	1434 (8)	3.2 (2)
N(2)	7250 (5)	5537 (3)	3097 (8)	3.5 (2)
N(3)	9053 (4)	5992 (3)	3050 (7)	3.1 (2)
N(4)	8526 (4)	6345 (3)	-295 (7)	3.0 (2)
C(1)	6168 (6)	6611 (4)	1673 (11)	4.0 (3)
C(2)	5810 (8)	7198 (5)	1850 (15)	7.4 (4)
C(3)	6092 (6)	6281 (4)	3082 (11)	3.9 (3)
C(4)	6259 (6)	5653 (4)	3096 (11)	3.7 (2)
C(5)	5701 (6)	5376 (4)	1712 (13)	5.5 (3)
C(6)	5953 (7)	5414 (4)	4538 (12)	5.4 (3)
C(7)	7914 (6)	5680 (4)	4563 (10)	4.1 (3)
C(8)	8896 (6)	5610 (4)	4282 (10)	4.1 (2)
C(9)	9966 (6)	5917 (4)	2605 (9)	3.4 (2)
C(10)	10757 (7)	5993 (5)	3967 (12)	6.0 (3)
C(11)	10091 (6)	6313 (4)	1301 (11)	3.8 (2)
C(12)	9529 (6)	6251 (4)	-300 (10)	3.6 (3)
C(13)	9610 (6)	5665 (4)	-924 (11)	4.8 (3)
C(14)	9878 (7)	6653 (4)	-1419 (11)	4.8 (3)
C(15)	8259 (6)	6930 (3)	-121 (11)	3.9 (2)
C(16)	7263 (6)	6957 (3)	62 (11)	4.0 (3)
C(17)	7339 (6)	3945 (3)	67 (10)	3.3 (2)
C(18)	7277 (5)	4425 (3)	-802 (10)	3.2 (2)
C(19)	7569 (7)	4975 (4)	-137 (12)	3.7 (3)
C(20)	6933 (6)	4385 (4)	-2377 (10)	3.9 (3)
C(21)	6665 (7)	3895 (4)	-3100 (10)	4.5 (3)
C(22)	6726 (7)	3425 (4)	-2204 (11)	4.3 (3)
C(23)	7038 (6)	3443 (4)	-646 (11)	3.9 (2)
C(24)	6386 (5)	3174 (3)	3145 (9)	3.0 (2)
C(25)	6087 (6)	2755 (3)	4042 (9)	3.1 (2)
C(26)	6717 (7)	2296 (4)	4786 (11)	3.8 (3)
C(27)	5171 (7)	2753 (4)	4219 (10)	4.1 (3)
C(28)	4557 (6)	3153 (4)	3526 (11)	4.6 (3)
C(29)	4843 (7)	3575 (4)	2671 (11)	4.2 (3)
C(30)	5755 (7)	3585 (4)	2494 (10)	4.1 (3)

Table 2. Selected bond distances (Å) and angles ($^\circ$)

Co—N(1)	2.122 (6)	N(1)—Co—N(2)	90.0 (2)
Co—N(2)	2.150 (7)	N(1)—Co—N(3)	102.4 (2)
Co—N(3)	2.104 (6)	N(1)—Co—N(4)	83.7 (2)
Co—N(4)	2.159 (6)	N(1)—Co—O(1)	108.2 (2)
Co—O(1)	2.231 (6)	N(1)—Co—O(2)	161.7 (2)
Co—O(2)	2.208 (6)	N(2)—Co—N(3)	85.5 (3)
S(1)—S(2)	2.063 (3)	N(2)—Co—N(4)	171.7 (2)
S(1)—C(17)	1.795 (9)	N(2)—Co—O(1)	101.2 (2)
S(2)—C(24)	1.798 (8)	N(2)—Co—O(2)	80.1 (2)
O(1)—C(19)	1.279 (10)	N(3)—Co—N(4)	90.7 (2)
O(2)—C(19)	1.250 (10)	N(3)—Co—O(1)	148.7 (2)
O(3)—C(26)	1.250 (10)	N(3)—Co—O(2)	92.2 (2)
O(4)—C(26)	1.236 (10)	N(4)—Co—O(1)	86.0 (2)
C(18)—C(19)	1.483 (11)	N(4)—Co—O(2)	107.4 (2)
C(25)—C(26)	1.514 (12)	O(1)—Co—O(2)	59.6 (2)
O(3)···H(N1')*	2.07	S(1)—S(2)—C(24)	104.5 (3)
C(3)···H(N3')*	2.08	S(2)—S(1)—C(17)	105.7 (3)
C(17)—S(1)—S(2)/S(1)—S(2)—C(24)			83.2 (4)
O(1)—C(19)—O(2)/C(17)—C(18)—C(20)			29.5 (4)
O(3)—C(26)—O(4)/C(24)—C(25)—C(27)			25.4 (4)

* Primed atoms are related to unprimed atoms by the symmetry transformation $\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$.

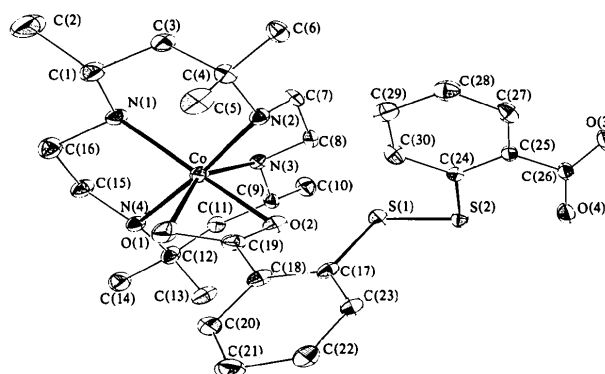


Fig. 1. View of the title complex showing the atom-numbering scheme.

and angles are presented in Table 2, while a view of the structure, showing the atom-numbering scheme, is given in Fig. 1.

Discussion. The structure consists of discrete $C_{30}H_{44}CoN_4O_4S_2$ molecules. Four N atoms from the folded tet-b ligand and two O atoms from a carboxylate group of the dithiodibenzoate constitute the *cis* distorted octahedral coordination polyhedron of the Co atom. Neither the disulfide group nor the second carboxylate group have any ligand role. The geometric parameters of the CoN_4O_2 unit (Table 2) are similar to those reported for the NiN_4O_2 unit of $[Ni(\text{tet-b})(\text{acetato})]ClO_4 \cdot \frac{1}{2}H_2O$ (Whimp, Bailey & Curtis, 1970), although there are significant differences. For example, the $M-N$ bond distances span similar ranges [Ni complex, 2.094 (11)–2.156 (10) Å; Co complex, 2.104 (6)–2.159 (6) Å] while the $Co-O$

distances [2.208 (6), 2.231 (6) Å] are substantially longer than the corresponding Ni—O bond lengths [2.103 (9), 2.116 (9) Å]. Distortion of the Ni and Co coordination polyhedra is caused in part by the limited bites of the bidentate carboxylate groups; the O—Co—O and O—Ni—O angles are 59.6 (2) and 62.4 (3)°, respectively.

In both the Co^{II} and Ni^{II} structures, the tet-b ligand is folded about the N(2)—M—N(4) axis. For reasons unknown to us, the tet-b ligand is folded about the N(1)—Cu—N(3) axis in the [Cu(tet-b)(*o*-SC₆H₄-CO₂)]·H₂O complex which contains an approximately trigonal-bipyramidal CuN₄S unit (Hughey *et al.*, 1979). Significant differences between the bound and free carboxylate groups of the title complex were not detected. As indicated by the dihedral angles of 29.5 (4) and 25.4 (4)°, neither carboxylate group is coplanar with its attached benzene ring. A somewhat larger carboxylate/phenyl dihedral angle (79.0°) was observed for the *o*-SC₆H₄CO₂ anion bound to Cu(tet-b) and attributed in part to intramolecular S···H—N bonding. Only intermolecular hydrogen bonding was observed in the title complex [between O(3) and H(N1), H(N3) of adjacent molecules, Table 2]. The remaining structural features for both the tet-b and dithiodibenzoate units are typical. The observed C—N, C—C, and C···C bond distances span the ranges 1.48 (1)–1.51 (1), 1.50 (1)–1.54 (1), and 1.36 (1)–1.41 (1) Å, respectively. The CSSC dihedral angle [83.2 (4)°] lies between

those reported for perfluorodiphenyl disulfide (76.5°, Woodward, Brown, Lee & Massey, 1976) and diphenyl disulfide (96.2°, Lee & Bryant, 1969), while the S—S bond length [2.063 (3) Å] is comparable to those in (C₆F₅)₂S₂ [2.059 (4) Å] and (C₆H₅)₂S₂ [2.03 (0.5) Å].

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Structure of 1,4,7,10,13-Pentaoxa-16-thiacyclooctadecane at 101 K

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Abstract. C₁₂H₂₄O₅S, *M_r* = 280.38, orthorhombic, *Pbca*, *a* = 8.295 (3), *b* = 20.372 (7), *c* = 8.476 (3) Å, *V* = 1432.3 Å³, *Z* = 4, *D_x* = 1.30 Mg m⁻³, *F*(000) = 608, *μ*(Mo *Kα*) = 0.226 mm⁻¹, colorless crystals, m.p. 303 K. The structure was determined from three-dimensional X-ray diffraction data collected at 101 K, solved by direct methods, and refined to *R* = 0.092 (*R_w* = 0.071) for a total of 834 unique intensities

[*I* > *σ*(*I*)]. The title compound is isomorphous with the hexaether 1,4,7,10,13,16-hexaoxacyclooctadecane [Dunitz & Seiler (1974). *Acta Cryst.* **B30**, 2739–2741]. The structure is disordered in that the S-atom position has an occupancy of 0.5 S and 0.5 O.

Introduction. The title compound was synthesized according to the procedure by Hui (Hui, 1972; Bradshaw, Hui, Chan, Haymore, Izatt & Christensen, 1974) and recrystallized from hexane. Systematic

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