SHORT-FORMAT PAPERS

Redetermination of Decacarbonyl Di-μ_4-sulfido-tetracobalt

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Abstract. Di-μ-carbonyl-1:2κ^2C-octacarbonyl-1κ^2C,-2κ^2C,3κ^2C,4κ^2C-di-μ_4-thio-tetracobalt(4 Co—Co), [Co$_4$(CO)$_{10}$S$_2$], $M_r = 579.96$, monoclinic, $P2_1/n$, $a = 9.962$ (4), $b = 6.711$ (2), $c = 12.339$ (5) Å, $\beta = 96.76$ (3)°, $V = 819.1$ (5) Å^3, $Z = 2$, $D_x = 2.35$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 41$ cm^{-1}, $F(000) = 560$, $T = 173$ K, $R = 0.0212$ for 1312 unique reflections [$I > 3\sigma(I)$]. The structure lies on a crystallographic inversion centre and consists of two S atoms bridging the faces of a rectangular array of four Co atoms. Two terminally bonded CO ligands are attached to each Co atom, with Co—C distances 1.811 (3)–1.814 (3) Å, and the two remaining CO groups bridge two opposite Co—Co edges. The S—Co distances are in the range 2.270 (1)–2.283 (1) Å and the Co—Co bond lengths are 2.488 (1) (CO-bridged) and 2.605 (1) Å (nonbridged). This redetermination gives e.s.d.'s an order of magnitude lower than for the original study [Wei & Dahl (1975). *Cryst. Struct. Commun.* 4, 583–588].

Experimental. The title compound was isolated from the reaction of H$_3$SiSSiH$_3$ with Co$_2$(CO)$_8$ in hexane; a more direct synthesis is available (Marko, Bor & Almasy, 1961). A black diamond-shaped crystal from CH$_2$Cl$_2$, of dimensions 0.74 × 0.3 × 0.08 mm, was used for data collection on a Nicolet $P3$ diffractometer, with monochromated Mo $K\alpha$ X-radiation. Cell parameters were determined from 16 reflections (2θ = 16–33°). Data were collected using fixed-speed ω scans for 4 < 2θ < 52° and h 0→13, k 0→9, l −16 →16. No significant crystal movement or decay was detected. An empirical absorption correction was applied using φ scans (transmission factors: 0.800 maximum, 0.681 minimum). 1919 reflections were collected, of which 1617 were unique (R_{merge} = 0.0069) giving 1312 with $I > 3\sigma(I)$ for all calculations. The previously reported structure was used as a starting point for the refinement (full-matrix least squares based on F^2; 118 parameters refined). All

Table 1. *Final positional and equivalent isotropic thermal parameters* (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Co(1)	0.51502 (4)	0.45743 (6)	0.35796 (3)	0.013
Co(2)	0.32490 (4)	0.42902 (6)	0.47093 (3)	0.013
S(1)	0.46465 (7)	0.6972 (1)	0.47649 (6)	0.017
C(1)	0.3276 (3)	0.3774 (4)	0.3159 (2)	0.019
O(1)	0.2564 (2)	0.3306 (4)	0.2396 (2)	0.028
C(2)	0.5225 (3)	0.6370 (5)	0.2493 (2)	0.019
O(2)	0.5280 (2)	0.7456 (3)	0.1791 (2)	0.029
C(3)	0.6012 (3)	0.2550 (5)	0.2974 (2)	0.019
O(3)	0.6577 (2)	0.1339 (4)	0.2585 (2)	0.031
C(4)	0.1735 (3)	0.5826 (4)	0.4549 (2)	0.016
O(4)	0.0763 (2)	0.6722 (3)	0.4439 (2)	0.024
C(5)	0.2454 (3)	0.2006 (5)	0.5093 (2)	0.019
O(5)	0.1934 (2)	0.0621 (3)	0.5362 (2)	0.033

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Co(1)—Co(2)	2.488 (1)		Co(1)—Co(2')	2.605 (1)
Co(1)—S(1)	2.270 (1)		Co(1')—S(1)	2.279 (1)
Co(2')—S(1)	2.283 (1)		Co(2)—S(1)	2.271 (1)
Co(2)—C(5)	1.814 (3)		Co(1)—C(1)	1.953 (3)
C(1)—O(1)	1.154 (4)		Co(1)—C(2)	1.811 (3)
C(2)—O(2)	1.137 (4)		Co(1)—C(3)	1.814 (3)
C(3)—O(3)	1.128 (4)		Co(2)—C(4)	1.818 (3)
C(4)—O(4)	1.134 (3)		Co(2)—C(1)	1.947 (3)
C(5)—O(5)	1.133 (4)		S(1)···S(1')	2.783 (1)

Co(2)—Co(1)—S(1)	56.8 (1)		C(4)—Co(2)—C(5)	97.2 (1)
Co(1)—S(1)—Co(2)	66.4 (1)		Co(1)—C(1)—Co(2)	79.3 (1)
C(2)—Co(1)—C(3)	97.5 (1)		Co(1)—Co(2)—S(1)	56.8 (1)
Co(1)—Co(2)—Co(1')	89.9 (1)		Co(2)—Co(1')—Co(2')	90.1 (1)
Co(1')—S(1)—Co(2')	66.1 (1)		Co(1)—S(1)—Co(2')	69.8 (1)
Co(2)—S(1)—Co(1')	69.9 (1)		Co(1)—S(1)—Co(1')	104.6 (1)
S(1)—Co(1)—S(1')	75.4 (1)		S(1)—Co(2)—S(1')	75.3 (1)
S(1)—Co(1')—Co(2')	57.1 (1)		S(1)—Co(2')—Co(1')	56.9 (1)
S(1)—Co(2)—Co(1')	55.2 (1)		S(1)—Co(1')—Co(2)	54.9 (1)
S(1)—Co(2')—Co(1)	54.8 (1)		S(1)—Co(1)—Co(2')	55.3 (1)

atoms were assigned anisotropic thermal parameters and refined without constraint. At convergence $R = 0.0212$, $wR = 0.0216$. The weighting scheme $w = [\sigma(F)^2 + 0.000207F^2]^{-1}$ gave satisfactory agreement analyses. Final maximum $\Delta/\sigma = 0.01$; residual peak $= 0.36$ e Å^{-3} adjacent to Co. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations used the *SHELX* programs (Sheldrick, 1976, 1986). Atomic coordinates and equivalent isotropic thermal parameters
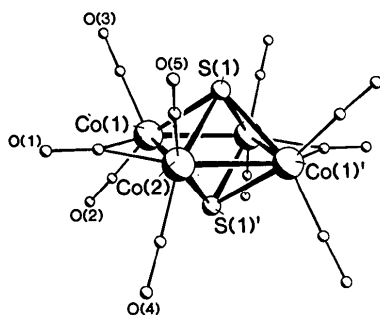
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Fig. 1. A *PLUTO* (Motherwell & Clegg, 1978) diagram of the structure of [Co₄(CO)₁₀(μ₄-S)₂]. The molecule lies about a crystallographic inversion centre.

are given in Table 1, and selected structural parameters in Table 2. The structure is illustrated in Fig. 1.*

Related literature. This determination gives parameters an order of magnitude more precise than those previously determined using visually estimated photographic data ($R = 0.092$) (Wei & Dahl, 1975).

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* Lists of structure factors, full bond parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55307 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1006]

Some significant changes have been found in the present determination. Compounds with a square-bipyramidal core μ_4-E_2M_4 are of structural [see Albright, Yee, Saillard, Kahlal, Halet, Leigh & Whitmire (1991) for a recent list] and of theoretical interest (Halet, Hoffmann & Saillard, 1985; Halet & Saillard, 1987).

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Structure of Monosodium N¹-(4,6-Dimethyl-2-pyrimidyl)sulfanilamidate Dihydrate

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Abstract. Na⁺.C₁₂H₁₃N₄O₂S⁻.2H₂O, $M_r = 336.34$, triclinic, $P\bar{1}$, $a = 11.570$ (3), $b = 12.725$ (3), $c = 5.790$ (4) Å, $\alpha = 101.28$ (3), $\beta = 102.35$ (4), $\gamma = 70.01$ (3)°, $V = 775.6$ Å³, $Z = 2$, $D_m = 1.46$, $D_x = 1.44$ g cm⁻³, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 23.06$ cm⁻¹, $F(000) = 352$, $T = 298$ K, $R = 0.074$ for 1538 reflections with $F > 5\sigma(F)$. The Na⁺ ion is directly coordinated to the sulfonyl O atoms, one water molecule and the amide N atom. The molecules are held together by a three-dimensional network of hydrogen bonds of type N—H⋯O, O—H⋯O and O—H⋯N. Molecular packing shows the presence of alternate layers of hydrophilic and hydrophobic regions along the **a** direction.

Experimental. Colourless needle-shaped crystals were obtained from aqueous solution; crystal size 0.22 × 0.12 × 0.40 mm. Symmetry $P\bar{1}$ was determined from oscillation and Weissenberg photographs. Density was measured by flotation in benzene–bromoform. Data were collected on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation. Cell parameters were refined by least-squares method on the basis of 25 independent 2θ values ($37 < 2\theta < 62°$). Intensities of 2052 independent reflections with $I > 3\sigma(I)$ ($-11 \le h \le 12$, $-13 \le k \le 13$, $0 \le l \le 6$, $3 \le 2\theta \le 126°$) were measured by $\omega/2\theta$-scan technique with scan speed 4° min⁻¹. Three standard reflections monitored every 200 reflections