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Structure Refinement of Skutterudite-Type Cobalt Triantimonide, $CoSb_3$

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Abstract. $CoSb_3$, $M_r = 424{\cdot}2$, cubic, $Im\bar{3}$, $a = 9{\cdot}0385\,(3)$ Å [9·0775 (6) Å; two experiments with Cl_2 and I_2, respectively, as transport agents], $V = 738{\cdot}40\,(7)$ [748·0 (2)] Å^3, $Z = 8$, $D_x = 7{\cdot}63$ (7·53) Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 26{\cdot}04$ (25·71) mm^{-1}, $F(000) = 1440$, $T = 293$ K, $R = 0{\cdot}028$ (0·031) for 418 (408) reflections. The structure of skutterudites with trigonally distorted $CoSb_6$ octahedra {Co—Sb 2·5287 (3) [2·5382 (4)] Å} and rectangular arrangement of the Sb atoms {Sb—Sb 2·8540 (6) [2·8799 (8)] and 2·9760 (6) [2·9836 (9)] Å} is confirmed and refined.

Introduction. As part of the lattice dynamical and structural studies on skutterudites MY_3 (M = Co, Rh, Ir, Y = P, As, Sb) (Lutz & Kliche, 1981, 1982), we refined the crystal structure of $CoSb_3$ by single-crystal X-ray methods. Hitherto structure determinations of skutterudite-type compounds have been made by X-ray powder methods only, see, for example Kjekshus & Rakke (1974), with the exception of the natural mineral $CoAs_3$ (Mandel & Donohue, 1971).

Experimental. Single crystals of $CoSb_3$ were grown by both the chemical vapour transport technique with chlorine as transport agent (Ackermann & Wold, 1977) (specimen 1) and the recrystallization of powdery material in the presence of iodine at 1123 K (specimen 2). A spherical crystal (0·2 mm diameter) (specimen 1) and a cube-shaped crystal (0·18 mm diameter) (specimen 2), respectively, were transferred to an Enraf–Nonius CAD-4 diffractometer. Graphite-monochromatized Mo $K\alpha$ radiation was used. The intensities of 1310 (1315, specimen 2) reflections [$2\theta \le 80°$, ω–2θ scan, $(\sin\theta)/\lambda < 0{\cdot}905$ Å^{-1}, range of hkl $0 \le h \le 16$, $0 \le k \le 16$, $0 \le l \le 16$] were corrected for Lorentz and polarization effects (*SDP*; Enraf–Nonius, 1982). Of the 440 (441) unique reflections (intensities averaged) 22 (33) with $I \le 2\sigma_I$ (σ_I from counting statistics) were considered unobserved. An absorption correction assuming spherical crystal shape ($\mu R = 2{\cdot}6$) (specimen 1) and an empirical correction for absorption (North, Phillips & Mathews, 1968) by ψ scans (range of transmission from 0·96 to 0·80) (specimen 2), respectively, were made. To control the intensity decrease three standard reflections, *viz* 231, $23\bar{1}$, $04\bar{2}$ ($\bar{3}50$, 330, 422), were measured without decay. Full-matrix least-squares refinement of the positional and anisotropic thermal parameters, the extinction coefficient, and the scale factor ($N_p = 10$) using scattering factors for Co^0 and Sb^0 (*International Tables for X-ray Crystallography*, 1974) and the atomic coordinates given by Kjekshus & Rakke (1974) as starting parameters based on the F magnitudes of 418 (408) reflections with $I \ge 2\sigma_I$ gave a final $R = 0{\cdot}028$ (0·031), $wR = 0{\cdot}029$ (0·035) ($w = 1/\sigma_I$), $S = 2{\cdot}153$ (5·423), and an extinction coefficient of $7{\cdot}37\,(6) \times 10^{-7}$ [$7{\cdot}34\,(4) \times 10^{-7}$]. The ratios of the maximum least-squares shifts to the e.s.d.'s in the final cycle were $< 0{\cdot}002$ and the maximum heights in the final difference Fourier syntheses 4·17 (4·37) e Å^{-3}. The final atomic coordinates and thermal parameters are given in Table 1.*

Table 1. *Fractional coordinates and equivalent isotropic temperature factors* (*defined as* $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}$, $i = j$) *with e.s.d.'s in parentheses; figures in square brackets data for specimen 2, in curly brackets data from Kjekshus & Rakke* (1974)

		x	y	z	U_{eq} ($\times 10^{-2}$ Å^2)
Co	$8(c)(\bar{3})$	0·25	0·25	0·25	0·456 (4) [0·202 (4)]
Sb	$24(g)(m)$	0·0	0·33537 (4) [0·33566 (5)] {$0{\cdot}335_1$}	0·15788 (4) [0·15863 (5)] {$0{\cdot}160_2$}	0·637 (4) [0·555 (5)]

The cell parameters were obtained by least-squares methods from Guinier powder data of the ground single crystals (Huber FR 600 system, Cr $K\alpha_1$ radiation, 14 reflections, α-quartz as internal standard, $a = 4{\cdot}9136$, $c = 5{\cdot}4054$ Å). The systematic absences $h+k+l = 2n$ for hkl, $l = 2n$ for hhl confirm space group $Im\bar{3}$ (T_h^5) (No. 204) (*International Tables for Crystallography*, 1983).

Discussion. The structure of skutterudites, *i.e.* a cubic primitive lattice of trigonally distorted MX_6 octahedra with a rectangular arrangement of the nonmetal atoms

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44003 (13 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 2. *Interatomic distances* (Å) *and angles* (°) *for* $CoSb_3$; *figures in square brackets data for specimen* 2, *in curly brackets data from Kjekshus & Rakke* (1974)

Sb–Sb	2·8540 (6)		[2·8799 (8)]	{2·891}
	2·9760 (6)		[2·9836 (9)]	{2·982}
	3·4322 (5)	4×	[3·4396 (6)]	
	3·7146 (5)	4×	[3·7336 (7)]	
Co–Sb	2·5287 (3)	6×	[2·5382 (4)]	{2·520}
Co–Co	4·5192 (2)	6×	[4·5388 (3)]	{4·517} = *a*/2
Sb–Co–Sb	85·47 (1)	6×	[85·31 (1)]	{ 85·3}
Sb–Co–Sb	94·53 (1)	6×	[94·69 (1)]	{ 94·7}
Co–Sb–Sb	107·77 (1)	2×	[107·84 (1)]	{107·7}
Co–Sb–Sb	109·22 (1)	2×	[109·07 (1)]	{108·8}
Co–Sb–Co	126·65 (2)		[126·78 (1)]	{127·3}
Sb–Sb–Sb	90·00 (1)		[90·00 (1)]	{ 90·0}

[figure given among others in Lutz & Kliche (1981)], is confirmed. The Co–Sb, Sb–Sb and Co–Co distances are given in Table 2. The shortest intermolecular Sb–Sb distances, *i.e.* 3·4322 (5) [3·4396 (6)] Å, are even smaller than those calculated from the van der Waals radii of the smaller atoms As or P [3·70 and 3·60 Å, respectively (Bondi, 1964)]. The unit-cell dimensions of the crystals studied are somewhat larger than those of powdery material, *i.e.* 9·0385 (3) [9·0775 (6)] instead of 9·0356 (6) (this work) and 9·0347 (6) Å (Kjekshus & Rakke, 1974). These findings are possibly due to incorporation of the transport agents Cl and I, respectively.

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Structure of Di-μ-chloro-bis(dicarbonylpalladium)*

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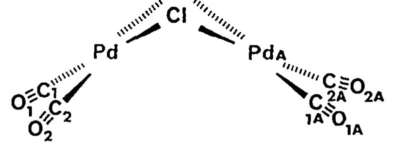
Abstract. $[Pd_2Cl_2(CO)_4]$, $M_r = 395·8$, tetragonal, $I\bar{4}2d$, $a = 14·279$ (9), $b = 14·279$ (9), $c = 9·280$ (5) Å, $V = 1892(2)$ Å^3, $Z = 8$, $D_x = 2·78$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·7071$ Å, $\mu = 4·297$ mm^{-1}, $F(000) = 1456$, $T = 293$ K, $R = 0·033$ for 535 observed reflections with $I > 2·5\sigma(I)$. The structure consists of discrete dimeric molecules formed by two deformed square-planar arrangements around the Pd atoms joined at a common edge, with bridging chlorines equally shared between the Pd atoms. The Pd–Cl distances are 2·387 (3) and 2·371 (2) Å; the Pd–Pd intramolecular distance is 3·114 (2) Å.

Introduction. As part of a study of metal carbonyl halides, the title compound (1) was synthesized from the reaction of $PdCl_2$ (420 mg, 2·36 mmol), $NaHCO_3$ (780 mg, 9·5 mmol) and anhydrous methanol (100 ml) in the presence of 2-(1,5-dimethyl-4-hexenyl)-3-hydroxy-5-methyl-1,4-benzoquinone (perezone) (460 mg, 196 mmol). The reaction vessel was purged with dry nitrogen and carbon monoxide was then passed through the stirred solution for 6 h at 343 K. The reaction product was isolated and recrystallized from degassed *n*-hexane to give air-stable crystals. IR (KBr pellets): 2103 *m*, 2082 *s*, 2024 *vs* and 1997 *w* cm^{-1}. The structure determination was undertaken to elucidate the stereochemistry of (1).



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