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Structure of Barium Tetraisothiocyanatocobaltate(II) Heptahydrate

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Abstract. $Ba[Co(NCS)_4].7H_2O$, $M_r = 554.7$, tetragonal, $I\bar{4}$, $a = 18.950$ (4), $c = 10.361$ (3) Å, $V = 3721$ (2) Å^3, $Z = 8$, $D_x = 1.980$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 34.6$ cm^{-1}, $F(000) = 2152$, $T = 295$ K, final $R = 0.040$ for 1257 observed reflections. Isostructural with $Ba[Zn(NCS)_4].7H_2O$. Two independent tetrahedral $[Co(NCS)_4]^{2-}$ anions are packed in chains parallel to **c**, and are linked *via* O—H⋯S-type hydrogen bonds with chains of edge-sharing $BaS(H_2O)_9$ polyhedra.

Introduction. During an investigation of $Na_2[Co(NCS)_4].8H_2O$ (Mereiter & Preisinger, 1982) the title compound became of interest because symmetry, unit-cell dimensions and crystal habit indicated closely related structure-building principles. This was briefly mentioned in the cited work. Based on earlier work (Cuvelier, 1933; *Gmelins Handbuch der anorganischen Chemie*, 1961) the title compound was at that time considered as an octahydrate. The present investigation, however, showed it to be a heptahydrate which is isostructural with $Ba[Zn(NCS)_4].7H_2O$ (Brodersen, Hummel, Böhm & Procher, 1985).

Experimental. Deep-blue needles, elongated parallel to **c**, obtained by room-temperature evaporation of a filtered solution made from 6·1 g $Ba(SCN)_2.3H_2O$, 2·8 g $CoSO_4.7H_2O$ and 60 g H_2O. Preliminary information from precession photographs, further work on a Philips PW 1100 four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. Unit-cell dimensions from 32 reflections, $8 \le \theta \le 17°$. Data collection with a prism $0.04 \times 0.04 \times 0.36$ mm

mounted with its long axis **c** parallel to the φ axis, ω scans, scan width 1°, scan rate 0·6° min^{-1}; three standard reflections, $\pm 1\%$ variation. 1750 independent reflections measured, corrected for Lp, absorption effects small (transmission factors in the range 0·86–0·88) and therefore neglected; range θ: 2→25°; h, k: 0→22; l: 0→12. 1257 reflections with $F_o \ge 6\sigma(F_o)$ used. Structure determined by Patterson and Fourier methods in space group $I\bar{4}$; alternative space groups $I4$ and $I\bar{4}/m$ rejected by stereochemical considerations. Refinement on F with anisotropic temperature factors for Ba, Co, S and O, and isotropic ones for C and N; 147 parameters varied. Final $R = 0.040$, $wR = 0.039$, $w = [\sigma^2(F_o) + 0.0002F_o^2]^{-1}$, $(\Delta/\sigma)_{max} = 0.01$, $|\Delta\rho|_{max}$ -0.6 and 0.6 e Å^{-3}. Calculations with program *SHELX*76 (Sheldrick, 1976). Atomic scattering functions and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters are given in Table 1, bond lengths and angles in Table 2.* The structure contains two independent $[Co(NCS)_4]^{2-}$ anions of approximately tetrahedral configuration, both with symmetry 2, similar bond lengths but different degrees of distortion (Fig. 1). Both kinds of anions are packed rather efficiently in separate chains extending parallel to **c** (Fig. 2). Each chain is in contact with four others *via*

Table 1. *Atomic coordinates and isotropic or equivalent isotropic thermal parameters*

	x	y	z	$B_{eq}/B_{iso}(\text{Å}^2)$
Ba	0·23025 (4)	0·22662 (4)	0·48155 (8)	3·62 (2)*
Co(1)	0·5	0·5	0·24914 (23)	3·79 (4)*
Co(2)	0·0	0·5	0·00237 (26)	3·07 (4)*
S(1)	0·44673 (18)	0·31582 (19)	−0·0436 (4)	4·3 (1)*
S(2)	0·18353 (20)	0·50165 (21)	0·3111 (4)	4·0 (1)*
S(3)	0·31471 (20)	0·51580 (21)	0·5507 (4)	4·9 (1)*
S(4)	0·01161 (20)	0·31924 (20)	−0·3113 (4)	3·9 (1)*
C(1)	0·4654 (6)	0·3777 (6)	0·0652 (13)	3·3 (3)
C(2)	0·1248 (7)	0·4999 (7)	0·1973 (14)	3·3 (3)
C(3)	0·3749 (7)	0·5135 (7)	0·4385 (14)	3·9 (3)
C(4)	0·0048 (7)	0·3771 (7)	−0·1945 (13)	2·7 (3)
N(1)	0·4806 (6)	0·4195 (6)	0·1378 (11)	4·2 (3)
N(2)	0·0830 (5)	0·4998 (5)	0·1149 (10)	3·3 (3)
N(3)	0·4167 (6)	0·5121 (6)	0·3596 (11)	4·5 (3)
N(4)	0·0016 (5)	0·4173 (6)	−0·1132 (11)	3·4 (3)
O(1)	0·3500 (5)	0·1427 (5)	0·4791 (12)	5·6 (3)*
O(2)	0·2054 (6)	0·1115 (6)	0·6520 (10)	5·3 (3)*
O(3)	0·1975 (7)	0·1134 (6)	0·3099 (10)	5·4 (3)*
O(4)	0·3259 (7)	0·2488 (8)	0·2453 (11)	6·0 (4)*
O(5)	0·3157 (5)	0·3440 (5)	0·4843 (19)	9·3 (4)*
O(6)	0·1559 (5)	0·3536 (5)	0·4914 (18)	8·2 (4)*
O(7)	0·1693 (8)	0·2588 (9)	0·2223 (14)	8·9 (5)*

$$* B_{eq} = \tfrac{8}{3}\pi^2(U_{11} + U_{22} + U_{33}).$$

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

BaS(H₂O)₉ polyhedron

Ba—S(1ⁱᵛ)	3·459 (4)	Ba—O(4ⁱᵛ)	2·969 (13)
Ba—O(1)	2·771 (9)	Ba—O(5)	2·751 (10)
Ba—O(2)	2·846 (12)	Ba—O(6)	2·790 (10)
Ba—O(3)	2·855 (12)	Ba—O(7)	2·987 (15)
Ba—O(4)	3·075 (13)	Ba—O(7ⁱᵛ)	3·150 (15)

CoN₄ tetrahedra

Co(1)—N(1ⁱ·ⁱⁱ)	1·948 (12)	N(1ⁱ)—Co(1)—N(1ⁱⁱ)	107·4 (5)
Co(1)—N(3ⁱ·ⁱⁱ)	1·963 (12)	N(1ⁱ)—Co(1)—N(3ⁱ)	106·6 (5)
		N(1ⁱ)—Co(1)—N(3ⁱⁱ)	113·9 (5)
		N(3ⁱ)—Co(1)—N(3ⁱⁱ)	108·7 (5)
Co(2)—N(2ⁱ·ⁱⁱⁱ)	1·958 (12)	N(2ⁱ)—Co(2)—N(2ⁱⁱⁱ)	106·9 (5)
Co(2)—N(4ⁱ·ⁱⁱⁱ)	1·972 (12)	N(2ⁱ)—Co(2)—N(4ⁱ)	110·3 (5)
		N(2ⁱ)—Co(2)—N(4ⁱⁱⁱ)	112·0 (5)
		N(4ⁱ)—Co(2)—N(4ⁱⁱⁱ)	105·2 (5)

Thiocyanate groups

	N—C	C—S	N—S	N—C—S	Co—N—C
NCS(1)	1·130 (16)	1·665 (15)	2·794 (12)	177·5 (13)	172·6 (11)
NCS(2)	1·165 (16)	1·622 (15)	2·786 (12)	178·8 (13)	169·4 (11)
NCS(3)	1·139 (16)	1·629 (15)	2·768 (12)	179·6 (13)	168·8 (11)
NCS(4)	1·137 (16)	1·638 (15)	2·775 (12)	178·5 (13)	169·3 (11)
Mean	1·143 (15)	1·639 (19)	2·781 (12)	178·6 (9)	170·0 (17)

Hydrogen bonds

A1 D A2	D—A1	D—A2	A1—D—A2
S(2ᵛ)···O(1)···S(4ᵛⁱ)	3·64 (2)	3·45 (2)	127·7 (3)
S(1ᵛⁱⁱ)···O(2)···S(2ⁱᵛ)	3·34 (2)	3·43 (2)	69·6 (2)
S(3ᵛⁱⁱⁱ)···O(3)···S(4ⁱˣ)	3·64 (2)	3·31 (2)	64·3 (2)
S(3ˣ)···O(4)···S(4ⁱᵛ)	3·88 (2)	3·39 (2)	60·9 (2)
S(3)···O(5)···S(3ˣ)	3·33 (2)	3·26 (2)	101·2 (3)
S(2)···O(6)···S(4ˣⁱ)	3·41 (2)	3·48 (2)	126·6 (4)
S(2ˣⁱⁱ)···O(7)	3·38 (2)		

Symmetry code: none or (i) x, y, z; (ii) $1-x, 1-y, z$; (iii) $-x, 1-y, z$; (iv) $\tfrac{1}{2}-x, \tfrac{1}{2}-y, \tfrac{1}{2}+z$; (v) $1-y, x, 1-z$; (vi) $y, -x, -z$; (vii) $\tfrac{1}{2}-y, x-\tfrac{1}{2}, \tfrac{1}{2}-z$; (viii) $\tfrac{1}{2}-x, \tfrac{1}{2}-y, z-\tfrac{1}{2}$; (ix) $y, -x, -z$; (x) $1-y, x, 1-z$; (xi) $x, y, 1+z$; (xii) $y-\tfrac{1}{2}, \tfrac{1}{2}-x, \tfrac{1}{2}-z$.

the terminal S atoms which show interchain S—S distances of 3·524–3·863 (5) Å, about twice the van der Waals radius of S (intrachain S—S distances ≥ 5·02 Å). Large channels result from this arrangement and are occupied by BaS(H₂O)₉ polyhedra which are linked *via* shared O(4)—O(7) edges to form continuous BaS(H₂O)₇ chains. Lateral interconnections between the three kinds of chains are established by Ba—S(1) and O—H···S bonds. The basic building principle of the title compound agrees essentially with that of K₂[Co(NCS)₄].3H₂O (Drew & Hamid bin Othman, 1975), Na₂[Co(NCS)₄].8H₂O (Mereiter & Preisinger, 1982), and to a less pronounced degree with K₂[Co(NCS)₄].H₂O.2CH₃NO₂ (Wood & McMullan, 1984), all based on tetrahedral cobaltate anions which are packed in chains. While the [Co(NCS)₄] chains in
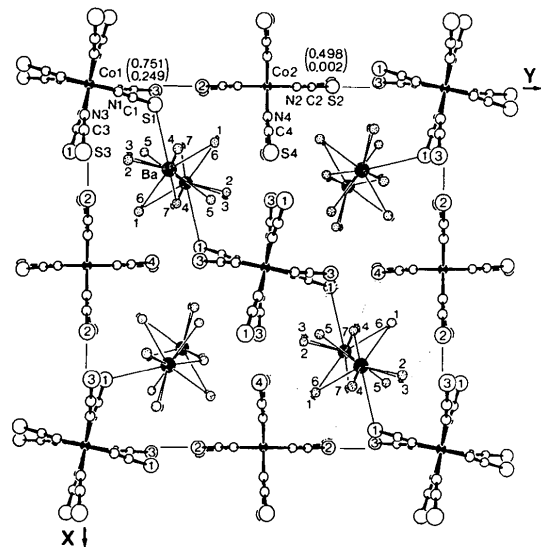

Fig. 1. View of the structure down the *c* axis. *z* coordinates of Co atoms are given in parentheses. Water molecules and hydrogen bonds (lower right quarter only) are dotted.
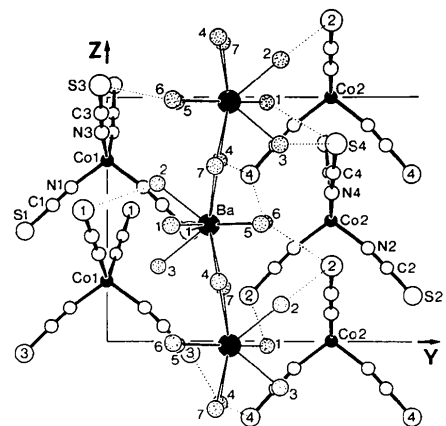

Fig. 2. View of the structure down the *a* axis. Co at $x=0$, Ba at $x \sim \tfrac{1}{4}$.

both potassium compounds are held together pre-dominantly by interactions between K and SCN and subordinately by O—H⋯S bonds, they are cross-linked in the Na compound exclusively via hydrogen bonds donated by Na(H₂O)₄ octahedral chains. $K_2[Co(NCS)_4].3H_2O$ and in particular $Na_2[Co(NCS)_4].8H_2O$ appear to be pseudotetragonal and similar to the title compound when viewed along the cobaltate chains. In fact they are orthorhombic and monoclinic, respectively [cf. Fig. 1 of Mereiter & Preisinger (1982)]. For the K compound deviations from tetragonal symmetry are attributable to the space requirements of K and H_2O, while the arrangement of $[Co(NCS)_4]$ chains is a distorted version of that in the title compound. In order to imagine the Na compound, the two $[Co(NCS)_4]$ chains on the left side of Fig. 1 must be thought of as being rotated by 90° around the chain directions, while the $Na(H_2O)_4$ chains, viewed in this direction, are of similar appearance to the $BaS(H_2O)_7$ chains. By contrast with all mentioned cobaltates, the repeat period of the $[Co(NCS)_4]$ chains is doubled in the title compound, a feature that stems mainly from the periodicity of the $BaS(H_2O)_7$ chains and the distortions imposed on the $[Co(1)(NCS)_4]$ chains by the Ba—S(1) bonds (Fig. 1). The pseudo-repeat period of $c/2 = 5.180$ Å [equivalent to the average Co—Co separation along the chains; individual Co—Co distances vary between 5.131 and 5.230 (3) Å] is similar to the corresponding unit-cell edges of the two K compounds (5.354 and 5.227 Å) and the Na compound (5.460 Å), but notably larger than in $Hg[Co(NCS)_4]$ (4.38 Å; Jeffery & Rose, 1968), a structure also based on $[Co(NCS)_4]$ chains.

Bond lengths and angles of the two CoN_4 tetrahedra and the four SCN groups (Table 2) agree reasonably with those observed in related compounds. Previously found Co—N mean bond lengths were 1.958 (12), 1.964 (1) and 1.967 (4) Å (Drew & Hamid bin Othman, 1975; Wood & McMullan, 1984; Mereiter & Preisinger, 1982). The bending of the SCN groups towards the $[Co(NCS)_4]$ chain axes, which is visible in Fig. 2 and causes Co—N—C angles to measure about 170°, is a common feature of the tetraisothiocyanato-cobaltates.

All water molecules of the structure are Ba-bonded, five of them at terminal positions and two of them bridging two Ba [O(4) and O(7)]. Based on experience with hydrated thiocyanates like NaSCN.2H₂O and related salts (Mereiter, Preisinger & Mikenda, 1984), a hydrogen-bond scheme was worked out for the title compound and is included in Table 2. There is no evidence for the presence of O—H⋯O-type bonds because all O—O distances below 3.5 Å represent edges of the $BaS(H_2O)_9$ polyhedra. Since the walls of the channels in which the polyhedra reside are mainly defined by the voluminous S atoms while the smaller N and C atoms are more covered up, it is not surprising to

find a considerable number of distances which doubt-less represent O—H⋯S-type hydrogen bonds. The ten shortest of these are in the range O—S = 3.2 – 3.5 Å. Their mean value of 3.38 (8) Å compares well with the O—S distance of 3.33 Å for the 'average' O—H⋯S bond (Mereiter, Preisinger & Guth, 1979) or the 3.377 (2) Å O—H⋯S bond known from neutron diffraction of $K_2[Co(NCS)_4].H_2O.2CH_3NO_2$ (Wood & McMullan, 1984). While three of the water molecules in the title compound show relatively weak interactions (O—S = 3.5–3.9 Å), there is no suitable second H-bond acceptor available for O(7). The nearest neighbour in an appropriate direction is C(2) at a distance of 3.98 (2) Å. A comparable situation is known, however, from a neutron diffraction study of $Na_3AsS_4.8D_2O$ (Mereiter, Preisinger, Baumgartner, Heger, Mikenda & Steidl, 1982).

The title compound is isostructural with $Ba[Zn(NCS)_4].7H_2O$ (Brodersen et al., 1985) and shows only small bond-length differences from it, all less than 0.1 Å.* A prerequisite of this property is the closely similar ionic radii of Co^{2+} (high-spin state) and Zn^{2+}, 0.82 and 0.83 Å, respectively, according to Shannon (1976). With the cell dimensions of the Zn compound as a basis for comparison [a = 18.947 (6), c = 10.324 (3) Å], corresponding atomic positions of both compounds coincide on the average within 0.03 (2) Å. The largest differences occur for N(4), 0.08, O(5), 0.06, and N(2), 0.05 Å. While the mean bond distances Co—N = 1.960 (10) and Zn—N = 1.950 (29) Å agree well and the $Co(1)N_4$ and $Zn(1)N_4$ tetrahedra are quite similar, there is a distinct difference in the dimensions of the $Co(2)N_4$ and $Zn(2)N_4$ tetrahedra. Closer comparison of the Co and the Zn compound indicates, however, that the N positions around Zn(2) may exhibit larger errors. Zn(2)—N(2) = 1.98 (2), Zn(2)—N(4) = 1.91 (2) and N(4)—C(4) = 1.22 (3) Å are evidently outliers.

* Atom designation and setting of the $Ba[Co(NCS)_4].7H_2O$ structure have been adopted from the Zn compound. Some atoms were moved to symmetry-equivalent positions in order to assemble them in functional groups.

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$Mo_4P_6Si_2O_{25}$, an Mo^{III} Phosphosilicate Closely Related to $V_3P_5SiO_{19}$: Oxygen Non-stoichiometry in Silicophosphates

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Abstract. $Mo_4P_6Si_2O_{25}$, $M_r = 1025 \cdot 76$, trigonal, $P\bar{3}$, $a = 14 \cdot 705$ (4), $c = 7 \cdot 3986$ (5) Å, $V = 1385 \cdot 5$ (8) Å^3, $Z = 3$, $D_x = 3 \cdot 69$ Mg m^{-3}, $\lambda(Mo\,K\bar{\alpha}) = 0 \cdot 71069$ Å, $\mu = 3 \cdot 38$ mm^{-1}, $T = 294$ K, $F(000) = 1458$, $R = 0 \cdot 065$ for 4016 observed reflections. The Mo has the valence III rarely observed in its oxides. The three-dimensional framework is built up from $P_6Si_2O_{25}$ units and Mo_2O_9 face-sharing clusters. The framework is very similar to that of $V_3P_5SiO_{19}$; both correspond to the general formulation $M_{12}P_{18+x}Si_{6-x}O_{75+x/2}$ $(0 \le x \le 6)$. The structure shows also '$M_2P_6Si_2O_{25}$' layers similar to those observed in other silicophosphates, but the stacking of these layers is different.

Introduction. Recent studies of oxides characterized by a mixed framework built up from octahedra and PO_4 and SiO_4 tetrahedra have shown the great ability of Mo to participate in the construction of such structures. Moreover, Mo offers a great diversity of oxidation states in those oxides, ranging from Mo^{VI} for MoP_2O_8 (Kierkegaard, 1962a), $(MoO_2)_2P_2O_7$ (Kierkegaard, 1962b), *via* Mo^V for $K_4Mo_8P_{12}O_{52}$ (Leclaire, Monier & Raveau, 1983) and Mo^{IV} for $AMo_2P_3O_{12}$ (A = K, Rb, Tl) (Leclaire, Monier & Raveau, 1985a; Leclaire & Raveau, 1988), to mixed-valence Mo^{IV-III} for AMo_3-$P_6Si_2O_{25}$ (A = K, Rb, Tl, Cs) (Leclaire, Borel, Grandin & Raveau, 1985; Leclaire, Monier & Raveau, 1984; Leclaire, Monier & Raveau, 1985b) and finally to Mo^{III} for MoP_3SiO_{11} (Leclaire & Raveau, 1987). Moreover, it appears that Mo^{III}, which is rather rarely observed in oxides, seems to be stabilized in those compounds, in the form of isolated MoO_6 octahedra. For this reason the investigation of the system Mo_2O_3–P_2O_5–SiO_2 was carried on further. The present work deals with the crystal structure of a new Mo^{III} oxide, $Mo_4P_6Si_2O_{25}$.

Experimental. The synthesis of the molybdenosilicophosphate $Mo_4P_6Si_2O_{25}$ in the form of a microcrystalline powder was carried out in two steps: First the oxides MoO_3, SiO_2 and the phosphate $(NH_4)_2$-HPO_4 were mixed in adequate proportions for P, Si and O ($\rightarrow Mo_2P_6Si_2O_{25}$) and heated at 870 K in air in order to eliminate ammonia and water. Then, in the second step, metallic molybdenum was added to the resulting products to obtain adequate proportions. The mixture was homogenized by crushing, introduced into an evacuated silica ampoule and heated at 1470 K for several days. The samples were quenched at room temperature. Single crystals were grown in the following way: mixtures of MoO_3 and $(NH_4)_2HPO_4$ were first heated at 870 K in air as above, and the resulting mixture was then mixed with metallic molybdenum and heated directly in an evacuated silica ampoule without adding SiO_2, at about 1470 K. The crystals grew on the walls of the silica tube in the form of yellowish plates.

A yellow crystal with dimensions $0 \cdot 41 \times 0 \cdot 24 \times 0 \cdot 10$ mm was selected for the structure determination. Cell parameters were initially measured on precession films and later refined by diffractometric techniques at 294 K with a least-squares refinement based upon 25 reflections. The structure refinement could only be performed in the space group $P\bar{3}$. The data were collected on an Enraf–Nonius CAD-4 diffractometer with Mo $K\bar{\alpha}$ radiation ($\lambda = 0 \cdot 71069$ Å). The intensities were measured up to $\theta = 41°$ with an ω–$\frac{4}{3}\theta$ scan of $(1 \cdot 0 + 0 \cdot 35 \tan\theta)°$ and a counter-slit aperture of $(1 \cdot 0 + \tan\theta)$ mm, all determined after a study of some reflections in the $\omega\theta$ plane (h −27→0, k 0→27, l 0→9). The background intensity was measured on both sides of each reflection. A periodic control of three reflections verified the stability of the sample. Of the 8063