

Acta Cryst. (1975). B31, 613**Potassium Tetrakis(isothiocyanato)cobaltate(II) Trihydrate; a Redetermination**

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Abstract. $K_2Co(NCS)_4 \cdot 3H_2O$, $M=423.51$, orthorhombic, $a=11.116$ (5), $b=12.981$ (7), $c=5.354$ (5) Å, $U=771.2$ Å³, $Z=2$, $d_c=1.82$, $d_m=1.80$ (2) g cm⁻³, Mo $K\alpha$ radiation $\lambda=0.7107$ Å, $\mu=21.7$ cm⁻¹. Space group $P2_12_12$ from systematic absences $h00$, $h=2n+1$, $0k0$, $k=2n+1$. The discrete anion $[Co(NCS)_4]^{2-}$ has Co-N-C angles of 164.6 (7) and 166.8 (7)° and not 111 ° as reported earlier by Zhdanov & Zvonkova [*Zh. Fiz. Chim.* (1950). **24**, 1339–1344]. The cobalt atom has a distorted tetrahedral environment and the bond lengths are Co-N 1.967 (7), 1.949 (7); N-C 1.15 (1), 1.14 (1); C-S 1.627 (9), 1.657 (8) Å. 886 independent reflexions, measured by counter methods, have been refined to $R=0.054$.

Introduction. Deep-blue needles of $K_2Co(NCS)_4 \cdot 3H_2O$ were obtained by reacting excess potassium thiocyanate with cobalt nitrate. A crystal with dimensions $1.00 \times 0.25 \times 1.7$ mm was mounted with the c axis parallel to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions. It was equipped with a manual goniostat, scintillation counter and pulse-height discriminator. Zirconium-filtered molybdenum X-radiation was used. 1076 independent reflexions with $2\theta < 55^\circ$ were measured by the stationary-crystal stationary-counter method. Several standard reflexions were measured repeatedly during the course of the experiment but no significant change in intensity was detected. The standard deviation $\sigma(I)$ of the reflexions was taken to be $[I+2E+(0.03I^2)]^{1/2}$, where E is the estimated background of the reflexion. 886 reflexions with $I > \sigma(I)$ were used in subsequent calculations. No extinction or absorption corrections were applied. The positions of the cobalt atoms were determined from a Patterson function and Fourier syntheses were calculated to determine the positions of the remaining atoms. The anion has crystallographic C_2 symmetry with the cobalt atoms in special positions, $2(a)$, on the twofold axis. The structure was refined by full-matrix least-squares calculations, all atoms anisotropically to $R 0.054$. (Refinement with the opposite enantiomorph gave $R 0.059$.) The weighting scheme was chosen to give average values of $w\Delta^2$ for groups of reflexions independent of the values of F_o and $\sin \theta/\lambda$, and was $\sqrt{w}=1$ for $F_o < 15$ and $\sqrt{w}=15/F_o$ for $F_o > 15$. Calculations were made on a C.D.C. 7600 computer at the University of London Computer Centre using the X-RAY set of programs (Stewart,

1972). Atomic scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1962) as were the corrections for the real and imaginary parts of the anomalous dispersion for the cobalt, potassium and sulphur atoms. The anisotropic temperature factor is defined as $\exp[-0.25\pi^2 \sum_i \sum_j h_i h_j U_{ij} b_i b_j]$ ($i, j=1, 2, 3$), where b_i is the i th reciprocal cell dimension. The 190 zero reflexions showed no large discrepancies. A difference Fourier synthesis showed no extraneous peaks, and the hydrogen atoms of the water molecules were not discernible. In the final cycle of refinement all shifts were $< 0.05\sigma$. The final list of positions is given in Table 1, thermal parameters in Table 2 and bond lengths and angles in Table 3.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30766 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses

	x	y	z
Co	5000*	5000*	7718 (2)
K	3164 (2)	1230 (2)	2394 (5)
O(1)	0000*	5000*	-322 (26)
O(2)	3685 (7)	1980 (5)	7212 (15)
N(1)	5530 (6)	3904 (5)	5432 (12)
C(1)	5651 (6)	3362 (5)	3749 (14)
S(1)	5859 (2)	2596 (2)	1383 (4)
N(2)	6353 (6)	5385 (5)	9838 (12)
C(2)	6976 (6)	5651 (5)	11404 (14)
S(2)	7873 (2)	6056 (2)	13673 (4)

* Parameter fixed.

Table 2. Anisotropic thermal parameters ($\times 10^3$) with estimated standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	38 (1)	36 (1)	31 (1)	02 (1)	00*	00*
K	52 (1)	74 (1)	79 (2)	-11 (1)	4 (1)	-13 (1)
O(1)	85 (7)	59 (5)	108 (9)	-04 (5)	00*	00*
O(2)	77 (4)	70 (4)	83 (5)	-14 (4)	-19 (5)	-08 (5)
N(1)	57 (3)	47 (3)	43 (3)	05 (3)	02 (3)	-05 (3)
C(1)	32 (3)	38 (3)	38 (4)	01 (3)	-05 (3)	04 (3)
S(1)	62 (1)	47 (1)	44 (1)	05 (1)	-05 (1)	-13 (1)
N(2)	56 (3)	47 (3)	38 (3)	00 (3)	-05 (3)	-04 (3)
C(2)	41 (3)	35 (3)	37 (3)	02 (3)	05 (3)	03 (3)
S(2)	55 (1)	58 (1)	45 (1)	-13 (1)	-09 (1)	-07 (1)

* Parameter fixed.

Table 3. Bond lengths (Å) and angles (°)

Co—N(1)	1.967 (7)	Co—N(1)—C(1)	164.6 (7)
Co—N(2)	1.949 (7)	Co—N(2)—C(2)	166.8 (7)
N(1)—C(1)	1.151 (11)	N(1)—C(1)—S(1)	178.5 (7)
N(2)—C(2)	1.141 (11)	N(2)—C(2)—S(2)	179.1 (7)
C(1)—S(1)	1.627 (9)	N(1)—Co—N(2)	108.5 (3)
C(2)—S(2)	1.657 (8)	N(1)—Co—N(1)'	103.0 (3)
		N(1)—Co—N(2)'	114.1 (3)
		N(2)—Co—N(2)'	108.8 (3)

* Primed atoms are related to unprimed atoms by the two-fold axis.

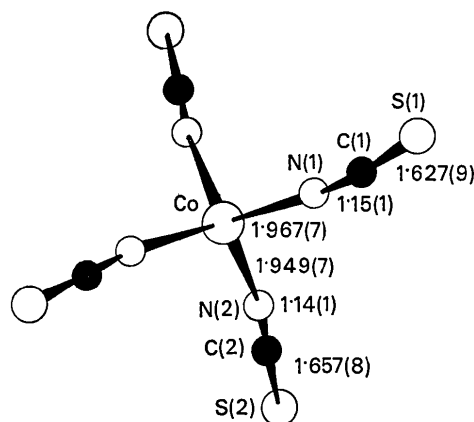
Discussion. In structures containing the thiocyanate ion bonded to a metal atom through nitrogen only, a wide variation of M—N—C angles has been found (Hazell, 1963; Knox & Eriks, 1968; Beck & Fehlhammer, 1972). In the majority of such examples the angles are in the range 150–180°. The most notable exception was the value of 111° found for the Co—N—C angles in $K_2Co(NCS)_4 \cdot 4H_2O$ by Zhdanov & Zvonkova (1950). As we could see no reason for this compound to be the odd one out, we redetermined its crystal structure. The structure of the anion $[Co(NCS)_4]^{2-}$ is shown in Fig. 1. Our structure determination establishes that the previous work is incorrect.*

Significant deviations from tetrahedral symmetry are observed in the anion as shown by the N—Co—N angles in Table 3. The Co—N distances are, as expected, slightly shorter than those observed in the five-coordinate bis(isothiocyanato)-[N,N-bis-(2-diethylaminoethyl)-2-methylthioethylamine-N,N,N]cobalt(II), which are 1.986 (12) and 1.971 (11) Å (Dapporto & Di Vaira, 1971) and much shorter than the 2.086 (7) Å found in the octahedral bis(isothiocyanato)tetrakis-(4-vinylpyridine)cobalt(II) by Andreotti & Sgarabotto (1972).

The Co—N—C angles are 164.6 (7) and 166.8 (7) and not 111° as previously found. The smallest M—N—C angles to be found in complexes of this type are now 129° in bis(isothiocyanato)bis-(N,N'-dimethylethylenediamine)copper(II) (Korvenranta & Pajunen, 1970) and 140° in bis(isothiocyanato)bis(ethylenediamine)-nickel(II) (Brown & Lingafelter, 1963).

It is often found (Knox & Eriks, 1968; Naik & Scheidt, 1973) that in a specific structure the large variations from linearity in M—N—C angles can be related to steric effects. These correlations are not always obvious but such effects are probably more important for thiocyanate groups than for nitrosyl groups

* Cell dimensions are 11.11, 12.98, 5.41 Å. Space group $P2_12_12$. The compound was stated to have the formula $K_2Co(NCS)_4 \cdot 4H_2O$, though no attempt was made to locate the water molecules. The structure was determined from $0kl$ and $hk0$ data but not refined. No R value was given. The wrong structure was obtained because, although the correct absolute values for the coordinates were found, the authors chose the wrong combinations of sign.

Fig. 1. The $[Co(NCS)_4]^{2-}$ anion in the c projection.

where the type of bonding with an M—N—O angle of 120° is well established (Frenz & Ibers, 1972). It has been shown that for a number of compounds (Hazell, 1963; Knox & Eriks, 1968) C—S distances decrease and to a lesser extent N—C distances increase with variations in M—N—C angles from 180°. Our values are consistent with these results.

The closest contact involving K^+ and the anion is 3.14 Å for $K \cdots N$.

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