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References

- ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
- BURLEY, G. (1963). *J. Chem. Phys.* **38**, 2807–2812.
- CHAN, L. Y. Y. & GELLER, S. (1977). *J. Solid State Chem.* **21**, 331–347.
- DANIELSSON, S., GRENTHE, I. & OSKARSSON, Å. (1976). *J. Appl. Cryst.* **9**, 14–17.
- ELDING, I. (1976). *Acta Chem. Scand. Ser. A*, **30**, 649–656.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HOLMBERG, B. & PERSSON, K. (1975). *Acta Cryst.* **A31**, S65.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JEFFREY, G. A. & VLASSE, M. (1967). *Inorg. Chem.* **6**, 396–399.
- JOHNSON, C. K. (1971). *ORTEP II*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
- KÖHLER, K., BREITINGER, D. & THIELE, G. (1974). *Angew. Chem. Int. Ed. Engl.* **13**, 821.
- MAHON, C. & BRITTON, D. (1971a). *Inorg. Chem.* **10**, 586–589.
- MAHON, C. & BRITTON, D. (1971b). *Inorg. Chem.* **10**, 2331–2333.
- MORSE, H. (1902). *Z. Phys. Chem.* **41**, 709–734.
- PERSSON, K. & HOLMBERG, B. (1982). *Acta Cryst.* **B38**, 900–903.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

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Preparation and Structure Refinement of the 2H Polytype of β -Copper(I) Thiocyanate

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Abstract. β -CuNCS, space group $P6_3mc$, $a = 3.850$ (3), $c = 10.937$ (3) Å, $Z = 2$, $V = 140.4$ (3) Å³, $D_x = 2.877$ Mg m⁻³. The structure was refined to $R = 0.059$ and $R_w = 0.065$ for a subset of the data (87 reflections). The crystals of β -CuNCS, which normally grow as trigonal or hexagonal pyramids, were obtained as pyramidal-capped hexagonal prisms. These crystals are predominantly the 2H polytype but also contain some 3R polytype in syntactic coalescence, along with disorder and twinning.

Introduction. Copper(I) thiocyanate [*poly- μ* -(thiocyanato-*N,S*)-copper(I)] is polymorphic (Kruger, Bussem & Tschirch, 1936; Kruger & Tschirch, 1941; Garaj & Gazo, 1965). The single-crystal structure of α -CuNCS, which is orthorhombic, was determined by Kabesova, Dunaj-Jurco, Serator, Gazo & Garaj (1976). Recently, we (Smith & Saunders, 1981) determined the structure of β -CuNCS and showed that this form is polytypic. Our β -CuNCS preparations usually produced pyramidal crystals which contained mostly 3R polytype with some 2H polytype in syntactic coalescence. We report here the preparation of hexagonal prisms of β -CuNCS which are predominantly the 2H polytype with some 3R form in syntactic coalescence.

Crystals were grown by vapor dilution of an aqueous solution of CuNCS in NaNCS. To 50 ml of 2.5 M NaNCS solution was added 0.40 g of finely divided CuNCS. After 30 min, the mixture was filtered and brought to 2.0 M NaNCS by the addition of 12 ml of H₂O. Diatomite filter aid (0.5 g) was stirred in and after 5 min the mixture was filtered into an evaporating dish which was then placed on a perforated disk above a supply of water in a closed desiccator. After 46 days, crystals of undecided habit could be seen. In 66 days the peculiar crystals shown in Fig. 1 were harvested. Further growth on crystals that remained in the solution was at the prismatic end of the crystals, indicating that crystal growth had been away from the apex.

Several crystals were examined with a precession camera and each was found to contain primarily the 2H polytype of β -CuNCS together with various small amounts of both *obverse* and *reverse* orientations of the 3R polytype and some disordering. The crystals were of poor quality, especially the larger ones, which gave *Ok*l precession pictures in which the spots were usually split laterally into three nearly equal components. Smaller rhomboid crystals seemed to be of better quality. The crystal chosen for data collection was an irregular hexagon approximately 0.06 mm on an edge and 0.13

mm long; much of the pyramidal portion had been broken off to minimize the $3R$ component which we assumed was located there. The cell orientation was chosen to put $+c$ at the apex.

The crystal was mounted on an Enraf-Nonius CAD-4 diffractometer which utilized graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Cell dimensions were calculated by a least-squares refinement of 23 carefully centered reflections ($7.5^\circ \leq 2\theta \leq 45.8^\circ$). Intensities were measured at $296 \pm 1 \text{ K}$ for $h \geq 0, k \geq h, l \geq 0$ by the ω - 2θ scan technique ($2\theta < 70^\circ$) from $2\theta(\text{Mo } K\alpha_1) - 1.0^\circ$ to $2\theta(\text{Mo } K\alpha_2) + 1.0^\circ$. Scan speeds varied between 3 and $20^\circ \text{ min}^{-1}$ (2θ). Backgrounds were measured by extending the scan range 25% at each end. The intensities of three standard reflections changed by about 5% and were used to scale the data. An empirical absorption correction [$\mu(\text{Mo } K\alpha) = 8.4 \text{ mm}^{-1}$] based on ψ scans (North, Phillips & Mathews, 1968) was made for which the normalized correction factor for I_o ranged from 0.87 to 1.00. Standard deviations $\sigma(I_o)$ were calculated from counting statistics and reduced to $\sigma(F_o)$ according to $\sigma(F_o) = \{[I_o + \sigma(I_o)]/\text{Lp}\}^{1/2} - F_o$.

The number of independent reflections measured was 139, of which 126 had $I_o > \sigma(I_o)$. This TOTAL data set was divided into two subsets: the ALL subset containing the 40 reflections [$39 > \sigma(I_o)$] with $h - k =$

$3n$ to which *all* polytypes, including disordered regions, contribute equivalently according to their relative volumes, and the AB subset containing 99 reflections [$87 > \sigma(I_o)$] with $h - k \neq 3n$ to which the $2H$ polytype contributes but not the $3R$.

In our original study of β -CuNCS (Smith & Saunders, 1981), we reported the structural parameters relative to six-layered ($6R$ and $6H$) cells. These structural parameters were transformed to the two-layered ($2H$) cell chosen here and were used as the starting point for full-matrix least-squares refinement. The function minimized was $\sum w\Delta^2$, where $\Delta = |F_o| - K|F_c|$ and $w^{-1} = \sigma^2(F_o) + (0.03F_o)^2$. Neutral-atom scattering factors were obtained from *International Tables for X-ray Crystallography* (1974). Corrections for anomalous scattering were applied to all atoms. The computer programs used were part of the Enraf-Nonius *Structure Determination Package* (1980) with local modifications.

The structure was fully refined for all three data sets, and the polarity was verified by refinement with the signs of the z parameters reversed for both the AB and ALL subsets. Agreement factors are given in Table 1. A comparison among the atomic parameters of the starting set and the three refined sets showed agreement within 2.6σ for all except B_{22} for Cu (5.1σ) and B_{33} for S (5.3σ) and Cu (17σ). Standard deviations were factors of 2 to 4 greater for the refinements than for the starting set. Although the ALL subset gave the lowest agreement indices, this refinement was judged unsatisfactory for several reasons. The averages of $w\Delta^2$ were not uniform with magnitude of F_o because of relatively poor agreement for some large F_o 's, especially 002 and 110, the B_{33} thermal parameters were too irregular, and the ratio of observations to parameters was only 3.3. The refinement with the AB subset had more uniform averages of $w\Delta^2$, more uniform B_{33} , and an observation-to-parameter ratio of 7.3, and therefore the parameters reported in Table 2 are from this refinement.* The large uncertainties in the scale factors pre-

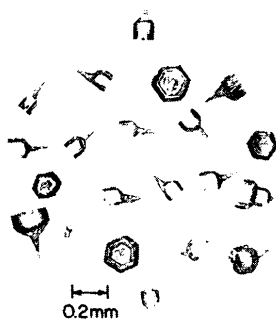


Fig. 1. Micrograph of β -CuNCS crystals which are primarily $2H$ polytype.

Table 1. Agreement factors

Data set	Reflections	R	R_w	Goodness	
				of fit	K
TOTAL	126	0.055	0.062	1.51	3.46 (7)
	139	0.065			
AB	87	0.059	0.065	1.55	3.43 (9)
	99	0.074			
ALL	39	0.033	0.033	1.02	3.64 (8)
	40	0.036			

$$R = \frac{\sum |F_o| - K|F_c|}{\sum |F_o|}; R_w = \left[\frac{\sum w(|F_o| - K|F_c|)^2}{\sum wF_o^2} \right]^{1/2}.$$

Table 2. Atomic parameters obtained from refinement of the AB data

	x	y	z	B_{22}	B_{33}
Cu	0	0	0	2.30 (7) \AA^2	1.56 (6) \AA^2
N	0	0	0.1764 (22)	3.7 (8)	1.7 (6)
C	0	0	0.2770 (23)	1.5 (6)	2.4 (8)
S	0	0	0.4328 (5)	1.9 (2)	1.8 (2)

The origin for $P6_3mc$ was moved from the conventional location on 6_3 to one of the other threefold axes. Equivalent positions are $00z; \frac{2}{3}, \frac{1}{3}, \frac{1}{2} + z$. The form of the anisotropic thermal parameter is $\exp\{-0.25[(h^2 + hk + k^2)a^{*2}B_{22} + l^2c^{*2}B_{33}]\}$.

* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36428 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

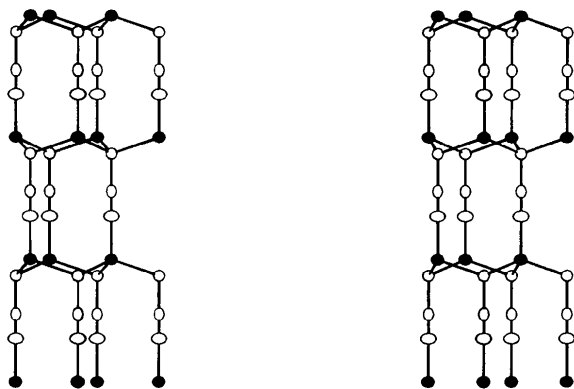


Fig. 2. Stereoscopic view of the 2H polytype. The filled atoms are Cu. The vertical axis is c and $[3\bar{1}0]$ is horizontal, left to right. The atoms are drawn as 50% probability thermal ellipsoids.

Table 3. Comparison of lattice constants (\AA), bond lengths (\AA) and angles ($^\circ$)

	3R*	2H†	Δ
a	3.856 (1)	3.850 (3)	0.006 (3)
c	10.968 (1)	10.937 (3)	0.031 (3)
S—C	1.683 (9)	1.704 (27)	-0.021 (28)
C—N	1.149 (15)	1.100 (29)	0.049 (33)
Cu—N	1.923 (11)	1.930 (23)	-0.007 (25)
Cu—S	2.343 (1)	2.341 (2)	0.002 (2)
N—Cu—S	108.13 (5)	108.28 (12)	-0.15 (13)
S—Cu—S	110.78 (5)	110.63 (11)	0.15 (12)

* Smith & Saunders (1981). The c dimension is the two-layer equivalent of the actual lattice constant.

† This study.

cluded any quantitative assignment of the polytypic content of the crystal.

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Structure de la Phase α du Dihydroxysulfate de Dicalcium*

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Abstract. α - $\text{Cd}_2(\text{OH})_2\text{SO}_4$, monoclinic, $a = 10.020$ (2), $b = 4.858$ (1), $c = 10.019$ (2) \AA , $\beta = 90.07$ (6) $^\circ$, $Z = 4$, $D_m = 4.81$, $D_x = 4.84$ g cm^{-3} ; final $R = 0.069$ for 549 independent reflexions. The space group is $P2_1/n$; however, the symmetry of the cell content, except for two sulphate groups, is very close to $P4/n$. These

Discussion. A stereoscopic view (Johnson, 1971) of a portion of the 2H structure is shown in Fig. 2. The structure and polytypism of β -CuNCS were described earlier (Smith & Saunders, 1981); the refinement of the 2H polytype presented here is a confirmation of the former work. Because the 2H crystals and consequently the data are of somewhat poorer quality, the standard deviations are considerably greater for the present work.

Comparisons of the cell constants and the bond lengths and angles for the 3R and 2H polytypes are given in Table 3. The only significant difference in these quantities is that the two-layer spacing (c) is less by 0.031 (3) \AA for the 2H polytype.

References

- GARAJ, J. & GAZO, J. (1965). *Chem. Zvesti*, **19**, 593–603.
International Tables for X-ray Crystallography (1974). Vol. IV, Ch. 2. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1971). *ORTEP II*. Report ORNL-3794, second revision. Oak Ridge National Laboratory, Tennessee.
 KABESOVA, M., DUNAJ-JURCO, M., SERATOR, M., GAZO, J. & GARAJ, J. (1976). *Inorg. Chim. Acta*, **17**, 161–165.
 KRUGER, D., BUSSEM, W. & TSCHIRCH, E. (1936). *Chem. Ber.* **B69**, 1601–1610.
 KRUGER, D. & TSCHIRCH, E. (1941). *Chem. Ber.* **B74**, 1378–1386.
 NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 SMITH, D. L. & SAUNDERS, V. I. (1981). *Acta Cryst.* **B37**, 1807–1812.
Structure Determination Package (1980). Revision 3B. Delft: Enraf-Nonius.

* Etude Structurale des Hydroxysulfates de Cadmium. III.

sulphate groups are disordered, six positions being statistically occupied by three O atoms. The crystal structure can be described in terms of highly distorted CdO_6 octahedra sharing edges and corners. The SO_4 tetrahedra share corners with the octahedra.

Introduction. L'hydroxysulfate de cadmium $\text{Cd}_2(\text{OH})_2\text{SO}_4$ présente à la température ambiante trois