

La Fig. 5 représente un schéma comparatif de l'empilement des couches dans  $\text{Cd}(\text{OH})_2\text{-}\beta$  de structure brucite, dans les composés  $\text{Cd}_2(\text{OH})_2\text{SO}_4\text{-}\beta$  et  $\text{-}\gamma$  et dans  $\text{Cd}_8(\text{OH})_{12}(\text{SO}_4)_2\cdot\text{H}_2\text{O}$ . L'écartement des feuillettes qui est noté  $d$  est de 5,16 et 5,12 Å dans  $\text{Cd}_2(\text{OH})_2\text{SO}_4\text{-}\beta$  et  $\text{-}\gamma$ . Il est donc légèrement dilaté par rapport à l'hydroxyde  $\text{Cd}(\text{OH})_2\text{-}\beta$  (4,702 Å), du fait de l'intercalation des groupements  $\text{SO}_4$  qui participent à deux couches différentes. La dilatation est beaucoup plus importante dans  $\text{Cd}_8(\text{OH})_{12}(\text{SO}_4)_2\cdot\text{H}_2\text{O}$  ( $d = 6,54$  Å) car chaque groupement  $\text{SO}_4$  n'appartient qu'à un seul feuillet. De plus, la présence de Cd(4) entre chaque couche, conduit à la formation de 'tunnels' parallèles à [010], que l'on peut observer sur la Fig. 2.

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## The Structure of Sodium Tetraisothiocyanatocobaltate(II) Octahydrate $\text{Na}_2[\text{Co}(\text{NCS})_4]\cdot 8\text{H}_2\text{O}$

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#### Abstract

The structure of  $\text{Na}_2[\text{Co}(\text{NCS})_4]\cdot 8\text{H}_2\text{O}$ ,  $M_r = 481.36$ , has been redetermined from three-dimensional X-ray data by means of direct methods and has been refined to  $R = 0.063$  for 1022 observed reflections. The salt which was previously reported to be tetragonal, space group  $P4$ ,  $a = 19.00$  (5),  $c = 5.47$  (2) Å, is in fact monoclinic, space group  $P2_1/n$ ,  $a = 18.941$  (2),  $b = 19.209$  (2),  $c = 5.460$  (1) Å,  $\beta = 91.64$  (1)° and  $Z = 4$  [ $V = 1985.7$  Å<sup>3</sup>,  $D_c = 1.61$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 1.34$  mm<sup>-1</sup>]. The structure is built up from tetrahedral  $[\text{Co}(\text{NCS})_4]^{2-}$  anions which are packed in chains and

from  $\text{Na}(\text{H}_2\text{O})_6^+$  octahedra which are linked by edge-sharing to form two independent  $\text{Na}(\text{H}_2\text{O})_4$  zigzag chains. All chains extend along  $c$  and are interconnected by hydrogen bonds. Average bond lengths are:  $[\text{Co}(\text{NCS})_4]$  tetrahedron,  $\text{Co}-\text{N} = 1.967$  Å; thiocyanate groups,  $\text{N}-\text{C} = 1.152$  and  $\text{C}-\text{S} = 1.621$  Å;  $\text{NaO}_6$  octahedra,  $\text{Na}-\text{O} = 2.416$  Å.

#### Introduction

In the course of continuing studies on salt hydrates with hydrogen bonds between water and sulfur (Mereiter,

Preisinger, Guth, Heger, Hiebl & Mikenda, 1979)  $\text{Na}_2[\text{Co}(\text{NCS})_4] \cdot 8\text{H}_2\text{O}$ , a salt which is also known as the mineral julienite (Schoep & Billiet, 1935), was reinvestigated. A structural model for this salt based on a tetragonal unit cell with  $a = 19.00$ ,  $c = 5.47$  Å and  $Z = 4$  has been derived by Preisinger (1953) from a small number of  $hk0$  and  $hk1$  reflections, which were obtained from powder, rotation and Weissenberg photographs. For reinvestigation we prepared  $\text{Na}_2[\text{Co}(\text{NCS})_4] \cdot 8\text{H}_2\text{O}$  by slowly evaporating aqueous solutions of  $\text{NaSCN}$  and  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  at room temperature (*Gmelins Handbuch der anorganischen Chemie*, 1961). Weissenberg photographs showed the crystals to be monoclinic rather than tetragonal, although a pronounced tetragonal pseudosymmetry with respect to the unit cell and to the intensities of the  $hk0$  reflections was observed. Unfortunately all inspected crystals were unsuitable for X-ray data collection because of frequent subparallel intergrowth and of twinning according to two different twin laws, either normal twins with (110) as twin plane or plane twins with [001] as twin axis. Next we examined crystals from the investigation of Preisinger (1953) which had been stored in contact with some mother liquor for almost thirty years. These crystals, too, were found to be monoclinic but were of better quality than the freshly prepared ones. Several tiny, untwinned crystals could be found among them, which were used for further studies. A reinspection of X-ray photographs from the senior author's work showed that the monoclinic symmetry of the crystals had been overlooked because of twinning and because of the poor quality of the photographs.

### Experimental

$\text{Na}_2[\text{Co}(\text{NCS})_4] \cdot 8\text{H}_2\text{O}$  forms thin, deep-blue needles which are elongated parallel to  $c$ . A crystal,  $0.015 \times 0.015 \times 0.4$  mm, was mounted on a Philips PW 1100 four-circle diffractometer with  $c$  approximately parallel to the  $\varphi$  axis. Graphite-monochromatized  $\text{Mo } K\alpha$  radiation was used to determine accurate cell dimensions and the diffraction intensities. 3511 independent reflections with  $3 < \theta < 25^\circ$  were measured in the  $\omega$ -scan mode (scan speed  $0.8^\circ \text{ min}^{-1}$ , scan width  $1.2^\circ$ , background measuring times of 30 s on both sides of the scan). Three standard reflections monitored at 6 h intervals showed no significant change in intensity. Due to the small size of the crystal (the largest available), only 1022 of the measured reflections had  $I > 3\sigma(I)$  and these were used for the structure refinement. Systematic extinctions derived from the measured data and checked by Weissenberg photographs were consistent with the space group  $P2_1/n$ .

The positions of the Co and S atoms were determined by direct methods. The remaining atoms were

subsequently located from Fourier maps. Parameters were refined by full-matrix least squares. The final refinement with anisotropic temperature factors for Na, Co, S and isotropic ones for C, N and O converged to  $R = 0.063$ ,  $R_w = 0.061$  and  $S = [\sum w(\bar{F}_o - F_c)^2 / (1022 - 128)]^{1/2} = 1.49$ , where  $w = 1/[\sigma^2(F_o) + 0.0009F_o^2]$ . A final difference map showed no unusual features; H atoms could not be located from this map, probably because the X-ray data were too poor and thermal motion effects too large. Complex neutral-atom scattering functions were used (*International Tables for X-ray Crystallography*, 1974). Most calculations were performed with *SHELX 76* (Sheldrick, 1976). Final atomic parameters are given in Table 1, interatomic distances and angles in Table 2.\*

### Results and discussion

The structure of  $\text{Na}_2[\text{Co}(\text{NCS})_4] \cdot 8\text{H}_2\text{O}$  is shown in Figs. 1(a) and 2. It is built up from discrete tetrahedral  $[\text{Co}(\text{NCS})_4]^{2-}$  anions which are packed in chains and from  $\text{Na}(\text{H}_2\text{O})_6^+$  octahedra which are linked by edge-sharing to form two independent  $\text{Na}(\text{H}_2\text{O})_4$  zigzag chains. The chains extend parallel to  $c$  and are

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36484 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^4$ ) and isotropic temperature factors ( $\text{Å}^2$ )

The  $B_{\text{eq}}$ 's for Na, Co and S were calculated according to  $B_{\text{eq}} = \frac{2}{3}\pi^2(U_{11} + U_{22} + U_{33})$ .

	$x$	$y$	$z$	$B/B_{\text{eq}}$
Na(1)	5575 (3)	4986 (3)	2579 (10)	3.8 (1)
Na(2)	4947 (3)	553 (3)	2459 (10)	3.9 (1)
Co	2473 (1)	2532 (1)	4841 (4)	3.15 (6)
S(1)	4225 (3)	2717 (3)	-1131 (8)	4.1 (1)
S(2)	2345 (3)	4412 (3)	10364 (10)	6.4 (1)
S(3)	594 (3)	2287 (3)	-960 (8)	4.7 (1)
S(4)	2654 (3)	812 (3)	11001 (8)	4.7 (1)
C(1)	3671 (8)	2670 (8)	1065 (27)	3.4 (3)
C(2)	2344 (8)	3800 (8)	8366 (29)	3.4 (3)
C(3)	1208 (8)	2382 (8)	1150 (27)	3.1 (3)
C(4)	2598 (8)	1347 (8)	8668 (30)	3.5 (3)
N(1)	3278 (6)	2623 (6)	2657 (20)	3.2 (3)
N(2)	2358 (7)	3361 (7)	6914 (23)	3.9 (3)
N(3)	1631 (6)	2429 (7)	2683 (20)	3.7 (3)
N(4)	2565 (7)	1747 (6)	7126 (23)	3.4 (3)
O(1)	5409 (5)	4296 (5)	6164 (17)	3.4 (3)
O(2)	5442 (5)	5704 (5)	-1048 (18)	3.6 (3)
O(3)	6342 (7)	5727 (7)	4949 (22)	6.1 (3)
O(4)	6274 (7)	4192 (7)	404 (21)	5.8 (3)
O(5)	4353 (6)	-513 (6)	3872 (17)	3.7 (3)
O(6)	4206 (6)	347 (6)	-1192 (17)	3.6 (3)
O(7)	4135 (6)	1250 (6)	4634 (19)	4.5 (3)
O(8)	5495 (6)	1442 (6)	88 (19)	5.1 (3)

Table 2. *Interatomic distances (Å) and angles (°)*

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

(a)  $\text{NaO}_6$  octahedra

Na(1)—O(1)	2.392 (11)	Na(2)—O(5)	2.471 (13)
—O(1 <sup>h</sup> )	2.433 (11)	—O(5 <sup>hh</sup> )	2.372 (13)
—O(2)	2.421 (11)	—O(6)	2.437 (11)
—O(2 <sup>h</sup> )	2.464 (11)	—O(6 <sup>h</sup> )	2.471 (13)
—O(3)	2.388 (14)	—O(7)	2.382 (13)
—O(4)	2.362 (14)	—O(8)	2.397 (13)
Mean value	2.410	Mean value	2.422

(b)  $\text{CoN}_4$  tetrahedron

Co—N(1)	1.970 (12)	N(1)—Co—N(2)	112.1 (5)
—N(2)	1.969 (13)	—N(3)	106.0 (5)
—N(3)	1.966 (11)	—N(4)	113.4 (5)
—N(4)	1.962 (12)	N(2)—N(3)	108.9 (5)
Mean value	1.967	—N(4)	105.4 (5)
		N(3)—N(4)	111.1 (5)

## (c) Thiocyanate groups

	N—C	C—S	N—S	N—C—S	Co—N—C
N(1)—C(1)—S(1)	1.164 (19)	1.618 (16)	2.782 (13)	178.6 (14)	168.9 (12)
N(2)—C(2)—S(2)	1.158 (20)	1.604 (17)	2.762 (13)	178.6 (15)	170.8 (13)
N(3)—C(3)—S(3)	1.146 (19)	1.624 (16)	2.769 (12)	177.5 (15)	169.9 (12)
N(4)—C(4)—S(4)	1.140 (2)	1.638 (17)	2.777 (13)	176.5 (15)	171.7 (13)
Mean value	1.152	1.621	2.773	178.0	170.3

## (d) Water molecules bonded to two Na atoms

O(1)—Na(1)	2.392 (11)	Na(1)—O(1)—Na(1 <sup>h</sup> )	92.1 (4)
—Na(1 <sup>h</sup> )	2.433 (11)	—S(3 <sup>h</sup> )	101.9 (4)
—S(3 <sup>h</sup> )*	3.277 (11)	—O(4 <sup>h</sup> )	128.9 (5)
—O(4 <sup>h</sup> )*	2.805 (15)	Na(1 <sup>h</sup> )—S(3 <sup>h</sup> )	135.8 (4)
		—O(4 <sup>h</sup> )	104.0 (4)
		S(3 <sup>h</sup> )—O(4 <sup>h</sup> )	99.2 (4)
O(2)—Na(1)	2.421 (11)	Na(1)—O(2)—Na(1 <sup>h</sup> )	91.9 (4)
—Na(1 <sup>h</sup> )	2.464 (11)	—S(1 <sup>h</sup> )	102.3 (4)
—S(1 <sup>h</sup> )*	3.312 (11)	—O(3 <sup>h</sup> )	126.4 (5)
—O(3 <sup>h</sup> )*	2.810 (16)	Na(1 <sup>h</sup> )—S(1 <sup>h</sup> )	138.9 (4)
		—O(3 <sup>h</sup> )	103.3 (4)
		S(1 <sup>h</sup> )—O(3 <sup>h</sup> )	98.7 (4)
O(5)—Na(2)	2.471 (13)	Na(2)—O(6)—Na(2 <sup>h</sup> )	92.4 (4)
—Na(2 <sup>h</sup> )	2.372 (13)	—S(2 <sup>h</sup> )	122.5 (4)
—S(2 <sup>h</sup> )*	3.258 (13)	—O(8 <sup>h</sup> )	103.1 (5)
—O(8 <sup>h</sup> )*	2.825 (16)	Na(2 <sup>h</sup> )—S(2 <sup>h</sup> )	114.9 (5)
		—O(8 <sup>h</sup> )	124.0 (5)
		S(2 <sup>h</sup> )—O(8 <sup>h</sup> )	101.1 (4)
O(6)—Na(2)	2.437 (11)	Na(2)—O(6)—Na(2 <sup>h</sup> )	88.8 (4)
—Na(2 <sup>h</sup> )	2.471 (13)	—S(4 <sup>h</sup> )	99.0 (3)
—S(4 <sup>h</sup> )*	3.327 (13)	—O(7 <sup>h</sup> )	124.4 (5)
—O(7 <sup>h</sup> )*	2.864 (15)	Na(2 <sup>h</sup> )—S(4 <sup>h</sup> )	151.1 (5)
		—O(7 <sup>h</sup> )	102.5 (4)
		S(4 <sup>h</sup> )—O(7 <sup>h</sup> )	95.8 (4)

(e) Water molecules bonded to one Na atom: all distances with  $\text{O} \cdots \text{S} < 3.8 \text{ \AA}$  and  $\text{O} \cdots \text{N}, \text{C} < 3.4 \text{ \AA}$  are given.

O(3)—Na(1)	2.388 (14)	O(7)—Na(2)	2.382 (13)
—O(2 <sup>h</sup> )†	2.810 (16)	—O(6 <sup>h</sup> )†	2.864 (15)
—S(1 <sup>h</sup> )	3.782 (14)	—S(1 <sup>h</sup> )	3.646 (12)
—S(2 <sup>h</sup> )	3.527 (14)	—S(4 <sup>h</sup> )	3.492 (12)
—C(2 <sup>h</sup> )	3.249 (20)	—N(1)	3.264 (16)
—N(2 <sup>h</sup> )	3.211 (19)		
O(4)—Na(1)	2.362 (14)	O(8)—Na(2)	2.397 (13)
—O(1 <sup>h</sup> )†	2.805 (15)	—O(5 <sup>h</sup> )†	2.825 (16)
—S(2 <sup>h</sup> )	3.778 (15)	—S(1)	3.484 (13)
—S(3 <sup>h</sup> )	3.717 (14)	—S(3 <sup>h</sup> )	3.260 (12)
—S(4 <sup>h</sup> )	3.602 (14)	—N(3 <sup>h</sup> )	3.350 (17)
—C(4 <sup>h</sup> )	3.206 (20)		
—N(4 <sup>h</sup> )	3.160 (18)		

\* Hydrogen-bond acceptor.

† Hydrogen-bond donor.

interconnected only by hydrogen bonds. These structural features are in accordance with the needle-like habit of the crystals. The basic ideas on the building principle of the structure (Preisinger, 1953) turned out to be correct, although the space group,  $P\bar{4}$ , was wrong. The (001) projections of the previous and the present structures are very similar. Taking into account also the third dimension, the previous structural model differs significantly from the actual structure and cannot be transformed into the latter without considerable reconstruction. For example, the upper and lower right  $[\text{Co}(\text{NCS})_4]^{2-}$  tetrahedra of Fig. 1(a) have changed their orientation by inversion at the Co atom. Even after idealizing polyhedral shapes and arrange-

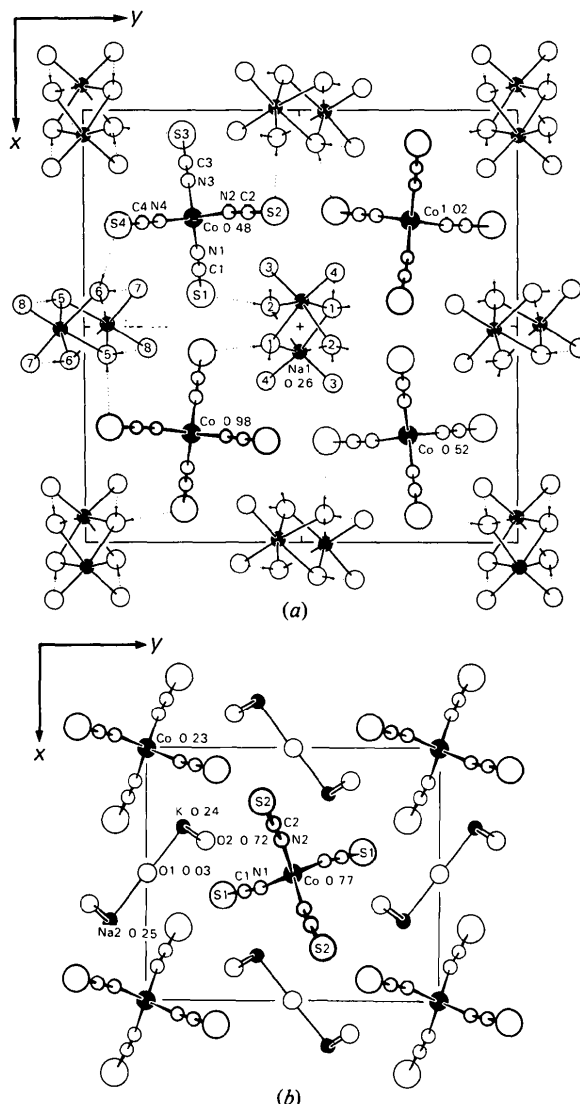


Fig. 1. The crystal structure of (a)  $\text{Na}_2[\text{Co}(\text{NCS})_4] \cdot 8\text{H}_2\text{O}$  and (b)  $\text{K}_2[\text{Co}(\text{NCS})_4] \cdot 3\text{H}_2\text{O}$  [space group  $P2_12_12_1$ ,  $a = 11.116 (5)$ ,  $b = 12.981 (7)$ ,  $c = 5.354 (5) \text{ \AA}$ ] (Drew & Hamid bin Othman, 1975) in (001) projections. Numbers with two decimal places are  $z$  coordinates. Hydrogen bonds are dotted.

ments, the actual structure would not comply with any type of fourfold axis, parallel to *c*. The pseudo-tetragonal appearance of the structure is, therefore, restricted to the (001) projection but lost in three-dimensional direct and reciprocal space. The only way in which to achieve, on average, tetragonal symmetry for the crystals is by twinning according to the law of normal twins with (110) as twin plane. This is, indeed, frequently observed.

In the  $[\text{Co}(\text{NCS})_4]^{2-}$  anion the Co atom is tetrahedrally coordinated by the N atoms of four independent thiocyanate groups. The Co–N bonds (Table 2b) do not differ significantly and average 1.967 Å. N–Co–N angles vary from 105.4 to 113.4° and indicate small, but significant, deviations from ideal tetrahedral symmetry. Bond lengths and angles within the thiocyanate groups are in the usual range with mean values N–C = 1.152, C–S = 1.621 Å, N–C–S = 178.0 and Co–N–C = 170.3°. These values are similar to those for the  $[\text{Co}(\text{NCS})_4]^{2-}$  anion in  $\text{K}_2[\text{Co}(\text{NCS})_4] \cdot 3\text{H}_2\text{O}$  (Drew & Hamid bin Othman, 1975) where mean bond lengths of 1.958 for Co–N, 1.146 for N–C and 1.638 Å for C–S were found. With N–Co–N angles of 103.0–114.1° and Co–N–C angles of 164.6–166.8° the  $[\text{Co}(\text{NCS})_4]^{2-}$  anion is more distorted than in the title compound. This may be explained by the presence of direct links between the anions and potassium in the potassium salt, which are replaced in the title compound by indirect links *via* hydrogen bonds.

Bond lengths within the two different  $\text{Na}(\text{H}_2\text{O})_6^+$  octahedra of the structure vary from 2.36 to 2.48 Å and average 2.410 Å for Na(1) and 2.422 Å for Na(2). Both octahedra are considerably distorted (Fig. 2); the O–Na–O angles deviate by up to 18° from 90 and 180°. The individual  $\text{Na}(\text{H}_2\text{O})_6^+$  octahedra are linked by sharing pairs of non-parallel edges to form Na-

$(\text{H}_2\text{O})_4$  zigzag chains. Thus, one half of the water molecules are at bridging positions linking two  $\text{Na}^+$  ions, while the remaining water molecules are at terminal positions bonded to one Na only. Na–O bonds involving bridging water molecules are on average larger by 0.05 Å than those of the terminal molecules.

For the water molecules bridging two  $\text{Na}^+$  ions, O(1), O(2), O(5) and O(6), hydrogen bonds are easy to assess by stereochemical considerations. Each of these molecules has a distorted tetrahedral coordination and acts as a donor in two hydrogen bonds, one to an S atom and one to a terminal water molecule (Table 2d). The O...S distances are 3.26–3.33 Å, which is close to the mean value of 66 O...S bonds, 3.324 Å (Mereiter, Preisinger & Guth, 1979). The O...O bonds, of length 2.81–2.86 Å, are remarkable because they involve the terminal  $\text{H}_2\text{O}$  molecules of the same NaO chain and, therefore, reinforce the chains. Moreover these bonds are considerably shorter than those in the edges of the  $\text{NaO}_6$  octahedra, although they would be as large as the latter if the  $\text{NaO}_6$  octahedra were regular. Very similar O...O bonds have been found in  $\text{NaClO}_2 \cdot 3\text{H}_2\text{O}$  (Tazzoli, Riganti, Giuseppetti & Coda, 1975), a structure which contains the same type of NaO zigzag chains as the title compound, but with a terminal water molecule being replaced by a chlorite O atom.

For the terminal water molecules, O(3), O(4), O(7) and O(8), the distances to possible hydrogen-bond acceptor atoms are in most cases appreciably larger than for the bridging molecules. Each of these molecules has three to five neighboring S, C and/or N atoms at distances (Table 2e) which could be suitable for weak hydrogen-bond interactions, if one applies the operational criterion of Hamilton & Ibers (1968), which requires  $\text{O} \cdots \text{S} < 3.8$  Å and  $\text{O} \cdots \text{C}, \text{N} < 3.4$  Å. Without precise knowledge of the hydrogen positions, however, no definite conclusions can be drawn on these interactions.

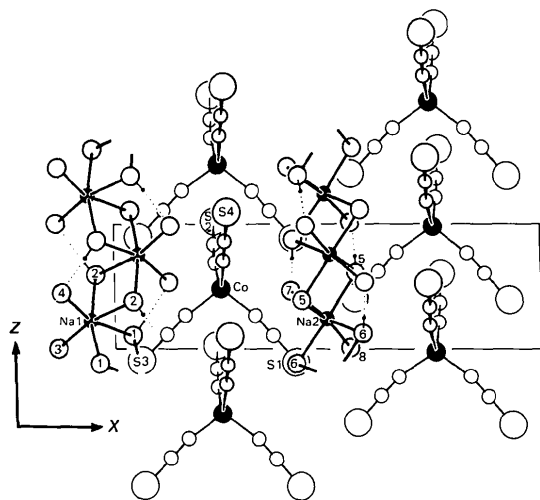


Fig. 2.  $\text{Na}_2[\text{Co}(\text{NCS})_4] \cdot 8\text{H}_2\text{O}$ ; a part of the structure viewed parallel to [010].

### Structural relationships

Close relationships between the structures of  $\text{Na}_2[\text{Co}(\text{NCS})_4] \cdot 8\text{H}_2\text{O}$  and  $\text{K}_2[\text{Co}(\text{NCS})_4] \cdot 3\text{H}_2\text{O}$  (Drew & Hamid bin Othman, 1975) are evident from Fig. 1. The chain-like arrangement of the  $[\text{Co}(\text{NCS})_4]^{2-}$  tetrahedra in the title compound is also present in the potassium salt and the chain repeat periods of both salts are similar, 5.460 and 5.354 Å respectively. Though the Co atoms in both salts define an almost *I*-centered lattice, the spatial arrangement and orientation of the  $[\text{Co}(\text{NCS})_4]^{2-}$  tetrahedra is not the same, because half of the tetrahedra in the potassium salt have a reverse orientation with respect to the sodium salt. Another difference arises from the replacement of the  $\text{Na}_2(\text{H}_2\text{O})_8$  chains by  $\text{K}_2(\text{H}_2\text{O})_3$  ribbons. These

ribbons are ladder-like and consist of two parallel  $K-H_2O-K-H_2O$  chains which are cross-linked by an additional water molecule. Due to the smaller size of the ribbons the structure of the potassium salt is more compressed in the (001) plane and appears like an imploded version of that of the sodium salt.

The chain-like arrangement of the  $[Co(NCS)_4]^{2-}$  groups occurs also in  $Hg[Co(NCS)_4]$  (space group  $I4$ ,  $a = 11.109$ ,  $c = 4.379$  Å,  $Z = 2$ ) (Jeffery & Rose, 1968) and, moreover, seems to be present in  $Ba[Co(NCS)_4] \cdot 8H_2O$  (Cuvelier, 1933; *Gmelins Handbuch der anorganischen Chemie*, 1961) which we recently found to crystallize with an  $I$ -centered tetragonal unit cell,  $a = 18.95$ ,  $c = 10.36$  Å and  $Z = 8$ . Reasons why the  $[Co(NCS)_4]^{2-}$  groups apparently prefer this chain-like arrangement could be that the bulky groups are packed very efficiently (see Fig. 2), and that this arrangement permits some weak interactions between consecutive  $[Co(NCS)_4]^{2-}$  groups of the chain.

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## Structure Cristalline de l'Oxynitrofluorure d'Indium $In_{32}ON_{17}F_{43}$

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### Abstract

$In_{32}ON_{17}F_{43}$  crystallizes in the cubic space group  $Ia\bar{3}$  with  $a = 10.536$  (4) Å,  $Z = 1$ ,  $d_{exp} = 6.80 \pm 0.10$ ,  $d_{calc} = 6.73$  g cm<sup>-3</sup>,  $\mu(Mo K\alpha) = 151$  cm<sup>-1</sup>. Its structure has been solved by single-crystal X-ray analysis and refined to a conventional  $R = 0.051$  for 327 independent reflexions. Time-of-flight neutron diffraction experiments on powdered samples ( $R_{profile} = 0.028$ ) confirmed these results and revealed an ordered distribution of N and (O,F) anions. This fluorite-related

structure is built with infinite strings of corner-sharing  $In(O,F)_6N_2$  distorted cubes, lying along all four  $\langle 111 \rangle$  directions. Its relationship to the  $In_2O_3$  bixbyite structure is discussed.

L'étude du système  $In-F_3-In_2O_3$  nous a permis d'isoler et de caractériser parmi d'autres phases solides, un composé cristallisé, apparemment nitrofluoré, puisque préparé par action en tube de nickel scellé du nitrure  $InN$  sur le fluorure  $InF_3$  dans les proportions 1,175  $InN, InF_3$ , mais contenant en fait une faible quantité d'oxygène et de composition probable  $In_{32}ON_{17}F_{43}$  (Abriat, Laval, Gaudreau & Frit, 1981).

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