

Fig. 1. Projection de la structure de $\text{Li}_3\text{In}_2\text{P}_3\text{O}_{12}$ suivant (010).

Ce type de structure est déjà observé dans $\text{Fe}_2(\text{SO}_4)_3$ (More & Araki, 1974); il en résulte de cet réarrangement structural la disparition du site 'mobile' (cavité de rayon $\approx 3 \text{ \AA}$) caractéristique des structures de type Nasicon.

On note aussi que le motif O—T—T—O constitue, d'après nos études structurales en cours des phases du moins riche au plus riche en indium, une constante structurale s'étendant sur tout le système $\text{Li}_{1+x}\text{Ti}_{2-x}\text{In}_x\text{P}_3\text{O}_{12}$.

Les ions de lithium dans $\text{Li}_3\text{In}_2\text{P}_3\text{O}_{12}$ occupent uniquement les sites tétraédriques déformés (Tableau 2) en partageant soit une arête commune avec l'octaèdre

$\text{In}(2)\text{O}_6$ [c'est le cas de $\text{Li}(1)\text{O}_4$ et de $\text{Li}(3)\text{O}_4$], soit deux avec les octaèdres $\text{In}(1)\text{—O}_6$ et $\text{In}(2)\text{—O}_6$ [c'est le cas de $\text{Li}(2)\text{O}_4$]. Le groupe $\text{Li}(3)\text{O}_4$ partage deux de leurs quatre sommets avec les tétraèdres $\text{Li}(1)\text{O}_4$ et $\text{Li}(2)\text{O}_4$ formant une chaîne finie de (LiO_4) . Les distances des sites de lithium appartenant à une même chaîne $\text{Li}_1\text{—Li}_3$ et $\text{Li}_2\text{—Li}_3$, sont respectivement 3,06 et 2,99 Å, tandis que les distances intersites [appartenant à deux chaînes différentes de (LiO_4)] varient de 3,36 à 3,84 Å.

Références

- FISCHER, R. X. (1985). *STRUPLO84*. Version modifiée pour la station graphique VS2. *J. Appl. Cryst.* **18**, 258–262.
- HAGMAN, L. O. & KERRKEGAARD, P. (1968). *Acta Chem. Scand.* **22**, 1822–1832.
- HAMDOUNE, S., GONDRAND, M. & TRAN QUI, D. (1986). *Mater. Res. Bull.* Sous presse.
- HAMDOUNE, S., TRAN QUI, D. & SCHOULER, E. J. L. (1986). *Solid State Ionics*, **18–19**, 587–591.
- International Tables for X-ray Crystallography* (1974). Tome IV. Birmingham: Kynoch Press. (Distributeur actuel D. Reidel, Dordrecht.)
- LARSON, A. C., LEE, F. L., LE PAGE, Y. & GABE, E. J. (1982). *NRC VAX Crystal Structure System*. Chemistry Division NRC, Ottawa.
- LI SHI-CHUN & LIN ZU-XIANG (1983). *Solid State Ionics*, **10**, 835–838.
- MAIN, P., FISKE, S., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. de York, Angleterre, et Louvain, Belgique.
- MORE, P. B. & ARAKI, T. (1974). *Neues Jahrb. Mineral. Abh.* **121**, 208–228.

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The Structure of Pentasodium Tricopper(II) Hydrogentetraarsenate(V)

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Abstract. $\text{Na}_5\text{Cu}_3\text{H}(\text{AsO}_4)_4$, $M_r = 862.26$, triclinic, $P\bar{1}$, $a = 5.275$ (1), $b = 8.585$ (2), $c = 9.297$ (2) Å, $\alpha = 116.26$ (1), $\beta = 89.96$ (1), $\gamma = 105.33$ (1)°, $V = 360.8 \text{ \AA}^3$, $Z = 1$, $D_x = 3.97 \text{ Mg m}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$, $\mu = 13.3 \text{ mm}^{-1}$, $F(000) = 403$, room temperature, $R = 0.035$ for 2451 reflections up to $(\sin\theta)/\lambda = 0.81 \text{ \AA}^{-1}$. The title compound is isostructural with $\text{Na}_5\text{Cu}_3\text{H}(\text{PO}_4)_4$. In the arsenate compound the three Na atoms are [2+2+2] ([4+4] in the phosphate compound), [5+2] and [5+1] coordinated; the Cu

atoms are [4] and [4+1] coordinated (the fifth Cu—O bond is only 2.18 Å). Half of the arsenate groups are connected by an extremely short (symmetrically restricted) hydrogen bond with an O...O distance of 2.427 (4) Å.

Introduction. Recently the crystal structure of $\text{Na}_5\text{Cu}_3\text{H}(\text{PO}_4)_4$ was determined (Effenberger, 1985). In this compound two of the four phosphate groups are connected by a hydrogen bond *via* a centre of

symmetry (either symmetrically or only apparently symmetrically). The distance $O\cdots O = 2.388 \text{ \AA}$ is extremely short compared with general crystal chemical experience (Baur, 1972; Brown, 1976; Catti & Ferraris, 1976; Ferraris & Ivaldi, 1984). The replacement of phosphate groups by arsenate groups seemed to be of interest for a study of the $O\cdots O$ bond-length variation. Up to now only in a few cases with XO_4 tetrahedra ($X = P, As$) connected by short hydrogen bonds are the crystal structures of both phosphate and arsenate homologues known in detail [e.g. CaH_2XO_4 – monetite and weilite – Catti, Ferraris & Mason (1980), Ferraris & Chiari (1970); $PbHXO_4$ – schultenite-type structures – Effenberger & Pertlik (1986); $KMg_2H(XO_4)_2 \cdot 15H_2O$ – Takagi, Mathew & Brown (1982); and $Ca(H_2XO_4)_2$ – Ferraris, Jones & Yerkess (1972), Dickens, Prince, Schroeder & Brown (1973)].

All data concerning the crystal structure of $Na_5Cu_3H(PO_4)_4$ were taken from Effenberger (1985). For a detailed discussion of the structure type, the coordination polyhedra and their connection as well as a projection of the crystal structure see Effenberger (1985). The present paper describes the arsenate compound and deals with the comparison of the two isomorphs.

Experimental. Synthesis. Crystals of $Na_5Cu_3H(AsO_4)_4$ were synthesized under hydrothermal conditions in a steel vessel lined with teflon (~6 ml capacity). 2 g of a 1M mixture of $Na_2HAsO_4 \cdot 7H_2O + NaNO_3$ and 1 g of native copper (wire) were put into the vessel. It was filled with H_2O to about 80 vol.% and was heated for 48 h at 493 (5) K. After cooling to room temperature (~12 h) crystals of $Na_5Cu_3H(AsO_4)_4$, $Na_4Cu(AsO_4)_2$ and Cu_2O (cuprite) were observed. The title compound forms light blue crystals, which are elongated parallel to [100]; their length is up to 1 mm, their diameter up to 0.2 mm.

Synthetic crystal, $0.06 \times 0.06 \times 0.12 \text{ mm}$; four-circle diffractometer AED2 (Stoe & Cie, Darmstadt), graphite-monochromatized $Mo K\alpha$ radiation; lattice parameters from 66 reflections up to $2\theta = 47^\circ$; $2\theta/\omega$ scan, minimum of 45 steps per reflection increased for ($\alpha_1 - \alpha_2$) dispersion, step width 0.03° , step time 0.5 to 1.5 s per step, data collection up to $2\theta = 70^\circ$, three standard reflections with no significant intensity variation, 5297 reflections measured ($h: -8 \rightarrow 8$, $k: -13 \rightarrow 13$, $l: -14 \rightarrow 7$), 3176 reflections in unique data set ($R_{int} = 0.043$), 2451 reflections used for refinement [$F_o > 3\sigma(F_o)$]; two ψ scans for absorption correction (transmission factors from 0.141 to 0.188), correction for Lorentz and polarization effects. Complex neutral atomic scattering factors (*International Tables for X-ray Crystallography*, 1974). All calculations were performed with program system STRUCSY (Stoe & Cie, Darmstadt) on an Eclipse S140 (Data General). The atomic coordinates of the isostructural phosphate

compound given by Effenberger (1985) were used in the starting set of structure refinement; several cycles of least-squares refinement on F with anisotropic temperature parameters for atoms As, Cu, Na and O gave $R = 0.035$ and $wR = 0.028$, $w = [\sigma(F_o)]^{-2}$ (131 variables); max. $\Delta/\sigma < 10^{-3}$. Max. and min. heights in final difference Fourier map 1.16 and $-1.58 e \text{ \AA}^{-3}$; the H atom could not be located. The value g for the isotropic secondary-extinction correction (Zachariasen, 1967) is $8.3 (6) \times 10^{-6}$. The atomic coordinates and the equivalent isotropic temperature parameters are given in Table 1.* Table 2 gives some important interatomic distances and bond angles.

Discussion. The crystal structures of the two compounds $Na_5Cu_3H(XO_4)_4$ with $X = P$ and As are very similar. The replacement of the smaller PO_4 tetrahedron by the larger AsO_4 tetrahedron predominantly causes changes in the coordination polyhedron of the Na(1) atoms (site symmetry $\bar{1}$). As can be seen from Fig. 1 the Na(1) atom in the phosphate compound is [4+4] coordinated. Two O(12) and two O(21) atoms have $Na(1)-O < 2.50 \text{ \AA}$; between each two of the four additional O atoms with $Na(1)-O(24) \sim 2.80 \text{ \AA}$ one has to postulate the extremely short hydrogen bond [simultaneously an edge between two different Na(1) polyhedra!]. In the arsenate compound, however, the coordination number of the Na(1) atom is [2+2+2]: There are only two 'short' $Na(1)-O(12)$ bonds below 2.50 \AA ; two of the $Na(1)-O(24)$ bonds are shortened to 2.57 \AA ; the two $Na(1)-O(21)$ bonds are elongated to 2.73 \AA . Two other $Na(1)-O(24)$ distances are 3.20 \AA and therefore they are excluded from the discussion of the coordination.

The coordination polyhedra of the Na(2) and Na(3) atoms in the two compounds show only slight differences. The Na(2) atoms are [5+2] coordinated and the Na(3) atoms are [5+1] coordinated. In the arsenate compound the 'short' $Na-O$ bonds vary from 2.32 to 2.44 \AA , the 'longer' ones vary from 2.76 to 2.99 \AA . The gap between 'shorter' and 'longer' $Na-O$ bonds is somewhat increased as compared with the phosphate compound. Up to 3.40 \AA there is no further O-atom ligand.

The Cu atoms are [4] and [4+1] coordinated by O atoms. The four nearest O atoms are 'square planar' arranged with the same average $Cu-O$ bond lengths of 1.98 \AA in both compounds. The $O-Cu-O$ angles of neighbouring O atoms deviate up to 5° from the ideal value of 90° . For opposite O atoms the $O-Cu-O$ angles are symmetrically restricted to exactly 180° for

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43485 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the Cu(1) atoms (site symmetry $\bar{1}$); for the Cu(2) atoms distortions up to 15° have been observed. The fifth O atom in the coordination polyhedra of the Cu(2) atoms has $\text{Cu}(2)\text{—O}(23) = 2.183 \text{ \AA}$ in the phosphate compound and 2.189 \AA in the arsenate compound. In both

Table 1. Atomic fractional coordinates and equivalent isotropic temperature parameters (\AA^2) with e.s.d.'s in parentheses for $\text{Na}_5\text{Cu}_3(\text{AsO}_4)_2(\text{AsO}_4\text{HAsO}_4)$

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Na(1)	$\frac{1}{2}$	0	$\frac{1}{2}$	0.0330
Na(2)	0.2035 (3)	0.4525 (2)	0.2340 (2)	0.0154
Na(3)	0.8393 (3)	0.6424 (2)	0.1359 (2)	0.0161
Cu(1)	0	0	0	0.0117
Cu(2)	0.67001 (8)	0.25193 (5)	0.29423 (5)	0.0102
As(1)	0.43331 (6)	-0.17760 (4)	0.07498 (4)	0.0085
As(2)	0.24118 (6)	0.31179 (4)	0.52361 (4)	0.0094
O(11)	0.2387 (5)	-0.1619 (3)	-0.0633 (3)	0.0105
O(12)	0.4737 (5)	0.0062 (3)	0.2532 (3)	0.0129
O(13)	0.7247 (5)	-0.1999 (3)	0.0027 (3)	0.0125
O(14)	0.2883 (5)	-0.3629 (3)	0.0951 (3)	0.0138
O(21)	0.5677 (5)	0.3325 (3)	0.5121 (3)	0.0132
O(22)	0.2237 (5)	0.5014 (3)	0.6886 (3)	0.0141
O(23)	0.0765 (5)	0.2570 (3)	0.3487 (3)	0.0137
O(24)	0.1317 (6)	0.1536 (3)	0.5917 (3)	0.0190

Table 2. Interatomic distances (\AA) and bond angles ($^\circ$) for $\text{Na}_5\text{Cu}_3(\text{AsO}_4)_2(\text{AsO}_4\text{HAsO}_4)$

The e.s.d.'s are 0.003 \AA for Na—O, 0.002 \AA for Cu—O and As—O, 0.004 \AA for O—O, and 0.2° for the bond angles. Na—O $< 3.40 \text{ \AA}$ and Cu—O $< 3.00 \text{ \AA}$ are given.

Na(1)—O(12)	2.324 2x	Na(1)—O(21)	2.732 2x	
Na(1)—O(24)	2.568 2x	Na(1)—O(24')	3.204 2x	
Na(2)—O(23)	2.321	Na(2)—O(22)	2.442	
Na(2)—O(21)	2.327	Na(2)—O(11)	2.760	
Na(2)—O(14)	2.411	Na(2)—O(22')	2.988	
Na(2)—O(13)	2.428			
Na(3)—O(14)	2.327	Na(3)—O(14')	2.407	
Na(3)—O(24)	2.332	Na(3)—O(22)	2.420	
Na(3)—O(13)	2.377	Na(3)—O(14'')	2.918	
Cu(1)—O(13)	1.956 2x	O(13) O(11) 2x	87.8	2.745 a*
Cu(1)—O(11)	2.015 2x	O(13) O(11) 2x	92.2	2.853
Cu(1)—O(23)	2.957 2x			
Cu(2)—O(12)	1.950	O(12) O(21)	86.7	2.682 a
Cu(2)—O(21)	1.956	O(12) O(22)	164.6	3.889
Cu(2)—O(22)	1.975	O(12) O(11)	91.8	2.865
Cu(2)—O(11)	2.040	O(12) O(23)	101.1	3.199
Cu(2)—O(23)	2.189	O(21) O(22)	93.8	2.871
		O(21) O(11)	177.7	3.995
		O(21) O(23)	99.0	3.156
		O(22) O(11)	87.2	2.768 a
		O(22) O(23)	94.1	3.051 a
		O(11) O(23)	82.9	2.803 a
As(1)—O(14)	1.665	O(14) O(12)	109.4	2.721
As(1)—O(12)	1.671	O(14) O(13)	107.4	2.711 b
As(1)—O(13)	1.699	O(14) O(11)	110.2	2.776
As(1)—O(11)	1.720	O(12) O(13)	112.9	2.808
		O(12) O(11)	108.7	2.756
		O(13) O(11)	108.3	2.772
		O(23) O(21)	112.1	2.775
		O(23) O(22)	118.3	2.877
		O(23) O(24)	113.3	2.809
		O(21) O(22)	106.3	2.713 b
		O(21) O(24)	105.4	2.707 b
		O(22) O(24)	100.1	2.611 b

* Common O—O edges are between the coordination polyhedra around (a) the Cu and Na atoms and (b) the As and Na atoms.

cases the Cu(2) atoms are slightly shifted out of the $\text{Cu}(2)\text{O}_4$ 'squares' towards this fifth O atom. Oxygen-coordinated Cu^{II} atoms with five Cu—O bonds $\leq 2.20 \text{ \AA}$ in a 'tetragonal pyramidal' arrangement have seldom been found in inorganic crystal structures; such distances are the rule for the rare 'trigonal bipyramidal' coordination figure (cf. Zemann, 1961, 1972; Shannon & Calvo, 1973; Hathaway, 1984; Effenberger, 1987).

The arsenate groups form tetrahedra with average As—O bond lengths of 1.689 and 1.688 \AA . The distortion parameters of the XO_4 tetrahedra within the title compound and its phosphate analogue are compiled in Table 3. The bond-length distortions are smaller in both arsenate tetrahedra. The bond-angle distortions are large for the $\text{X}(2)\text{O}_4$ tetrahedra, especially for the $\text{As}(2)\text{O}_4$ tetrahedron. This might be because (a) the $\text{X}(2)\text{O}_4$ tetrahedron shares three common O—O edges with coordination polyhedra around the Na atoms, and (b) two $\text{X}(2)\text{O}_4$ tetrahedra are connected by the very short hydrogen bond to form dimers.

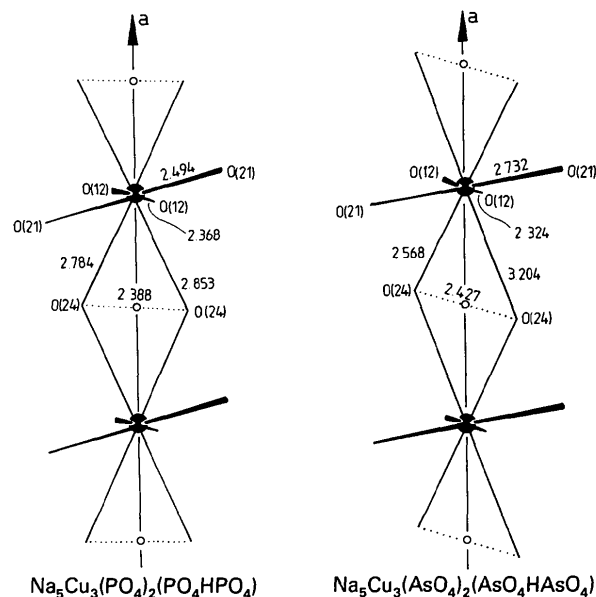


Fig. 1. The coordination of the Na(1) atoms and the positions of the hydrogen bonds in $\text{Na}_5\text{Cu}_3(\text{XO}_4)_2(\text{XO}_4\text{HXO}_4)$. Projections onto a plane defined by the atoms Na(1) and O(24). The postulated hydrogen bonds are dotted. Interatomic distances in \AA . The centre of symmetry is indicated by \circ .

Table 3. Distortion parameters of the XO_4 tetrahedra in $\text{Na}_5\text{Cu}_3(\text{XO}_4)_2(\text{XO}_4\text{HXO}_4)$, $\text{X} = \text{P, As}$

Bond-length distortion: $\Delta = \frac{1}{4} \sum_{i=1}^4 \{(R_i - \bar{R})/\bar{R}\}^2$; bond-angle distortion: $\sigma^2 = \frac{1}{6} \sum_{i=1}^6 (\theta_i - 109.47)^\circ$ (Robinson, Gibbs & Ribbe, 1971; Fleet, 1976).

$\text{Na}_5\text{Cu}_3(\text{PO}_4)_2(\text{PO}_4\text{HPO}_4)$		$\text{Na}_5\text{Cu}_3(\text{AsO}_4)_2(\text{AsO}_4\text{HAsO}_4)$	
1.89×10^{-4}	$\text{X}(1)\text{O}_4$	Δ	1.72×10^{-4}
1.93	$\text{X}(1)\text{O}_4$	σ^2	3.67
1.82×10^{-4}	$\text{X}(2)\text{O}_4$	Δ	1.49×10^{-4}
19.73	$\text{X}(2)\text{O}_4$	σ^2	42.81

Bond-valence calculations (Brown & Wu, 1976) gave only 1.54 v.u. (valence units) for the O(24) atom, but 1.87 to 2.04 v.u. for all the other O atoms in the title compound. The comparable values in the phosphate compound are 1.61 and 1.85 to 2.09 v.u. So one has to assume that the H atom is bonded to the O(24) atom. The short distance O(24)···O(24) indicates that between these two atoms there exists a symmetrically restricted hydrogen bond (either symmetrically linear with the H atom at $\bar{1}$ or only apparently symmetrical). Therefore the crystal chemical formula of the little compound is $\text{Na}_5\text{Cu}_3(\text{AsO}_4)_2(\text{AsO}_4\text{HAsO}_4)$. In the arsenate compound the distance O(24)···O(24) = 2.427 (4) Å is larger than the equivalent distance O(24)···O(24) = 2.388 (7) Å in the phosphate compound. Resulting from these short hydrogen bonds, the bond lengths P(2)—O(24) and As(2)—O(24) are 1.559 and 1.709 Å. These values are only 0.023 and 0.021 Å larger than the average X(2)—O distances. In particular, the X(2)—O(24) bonds are still comparatively short for an X—OH bond. Ferraris & Ivaldi (1984) gave average X—OH distances of 1.581 Å for X = P and 1.731 Å for X = As in $(\text{HXO}_4)^{2-}$ groups.

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Structure of Hydroxylammonium Nitrate (HAN) and the Deuterium Homolog

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Abstract. HAN, $[\text{NH}_3\text{OH}]\text{NO}_3$, $M_r = 96.04$, monoclinic, $P2_1/c$, $a = 4.816$ (1), $b = 6.800$ (1), $c = 10.728$ (1) Å, $\beta = 99.35$ (1)°, $V = 346.7$ (1) Å³, $Z = 4$, $D_x = 1.841$ g cm⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71073$ Å, $\mu = 1.86$ cm⁻¹, $F(000) = 200$, $T = 296$ K, $R_F = 0.032$ for 836 unique reflections. HAN- d_4 , $[\text{ND}_3\text{OD}]\text{NO}_3$, $M_r = 100.07$, monoclinic, $P2_1/c$, $a = 4.8165$ (8), $b = 6.8007$ (9), $c = 10.7298$ (13) Å, $\beta = 99.303$ (11)°, $V = 346.84$ (8) Å³, $Z = 4$, $D_x = 1.916$ g cm⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71073$ Å, $\mu = 1.86$ cm⁻¹, $F(000) = 200$, $T = 296$ K, $R_F = 0.0411$ for 1073 unique reflections. HAN

and HAN- d_4 are isostructural. All of the H atoms are involved in hydrogen bonding with one being bifurcated. The shortest heavy-atom interionic distance is O···O at 2.796 (1) Å.

Introduction. Hydroxylammonium nitrate (HAN) is an oxidizer and a chemical propellant when it is combined with an alkylammonium nitrate fuel in an aqueous solution (Klein, 1985). HAN dissolves in water in a stoichiometry up to about six HAN molecules to one H₂O molecule. The interionic distances are of interest in interpreting the IR spectra and as a starting point for modeling the solution (Fifer, 1984;

References

- BAUR, W. H. (1972). *Acta Cryst.* **B28**, 1456–1465.
 BROWN, I. D. (1976). *Acta Cryst.* **A32**, 24–31.
 BROWN, I. D. & WU, K. K. (1976). *Acta Cryst.* **B32**, 1957–1959.
 CATTI, M. & FERRARIS, G. (1976). *Acta Cryst.* **B32**, 2754–2756.
 CATTI, M., FERRARIS, G. & MASON, S. A. (1980). *Acta Cryst.* **B36**, 254–259.
 DICKENS, B., PRINCE, E., SCHROEDER, L. W. & BROWN, W. E. (1973). *Acta Cryst.* **B29**, 2057–2070.
 EFFENBERGER, H. (1985). *Z. Kristallogr.* **172**, 97–104.
 EFFENBERGER, H. (1987). *J. Solid State Chem.* In the press.
 EFFENBERGER, H. & PERTLIK, F. (1986). *Tschermaks Mineral. Petrogr. Mitt.* **35**, 157–166.
 FERRARIS, G. & CHIARI, G. (1970). *Acta Cryst.* **B26**, 403–410.
 FERRARIS, G. & IVALDI, G. (1984). *Acta Cryst.* **B40**, 1–6.
 FERRARIS, G., JONES, D. W. & YERKES, J. (1972). *Acta Cryst.* **B28**, 2430–2437.
 FLEET, M. E. (1976). *Mineral. Mag.* **40**, 531–533.
 HATHAWAY, B. J. (1984). *Struct. Bonding (Berlin)*, **57**, 55–118.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 ROBINSON, K., GIBBS, G. V. & RIBBE, P. H. (1971). *Science*, **172**, 567–570.
 SHANNON, R. D. & CALVO, C. (1973). *Acta Cryst.* **B29**, 1338–1345.
 TAKAGI, S., MATHEW, M. & BROWN, W. E. (1982). *Acta Cryst.* **B38**, 44–50.
 ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.
 ZEMANN, J. (1961). *Fortschr. Mineral.* **39**, 59–68.
 ZEMANN, J. (1972). In *Handbook of Geochemistry*, Vol. II-3, p. 29/A. Berlin, Heidelberg, New York: Springer Verlag.

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