

Neutron refinements of $\text{NaCu}_2(\text{H}_3\text{O}_2)(\text{SO}_4)_2$ and $\text{RbCu}_2(\text{H}_3\text{O}_2)(\text{SeO}_4)_2$: Variation of the hydrogen bond system in the natrochalcite-type series

G. Chevrier

Laboratoire Léon Brillouin (CEA-CNRS), CEN Saclay, F-91191 Gif-sur-Yvette, France

G. Giester and J. Zemann

Institut für Mineralogie und Kristallographie, Universität Wien,
Dr. Karl Lueger-Ring 1, A-1010 Wien, Austria

Received: January 30, 1992; in final form: July 13, 1992

$\text{NaCu}_2(\text{H}_3\text{O}_2)(\text{SO}_4)_2$ / $\text{RbCu}_2(\text{H}_3\text{O}_2)(\text{SeO}_4)_2$ /
Natrochalcite-type compounds / Hydrogen bonds in H_3O_2 configuration

Abstract. In the natrochalcite-type compounds $\text{NaCu}_2(\text{H}_3\text{O}_2)(\text{SO}_4)_2$ and $\text{RbCu}_2(\text{H}_3\text{O}_2)(\text{SeO}_4)_2$ the lengths of the two different hydrogen bridges vary widely: 2.44 Å and 2.70 Å in the Na-S member, and 2.60 Å and 3.03 Å in the Rb-Se member. Both structures were refined by single-crystal neutron diffraction methods. Least-squares refinements (harmonic vibrations for all atoms) resulted in a splitting of the H atom positions of the short bridges by 0.265(13) Å in the Na-S member, and by 0.472(6) Å in the Rb-Se member. In the two compounds no clear evidence for an ordering of the split position of the H atom was found.

Introduction

The representatives of the natrochalcite-type structures, Me^{1+} - $\text{Me}_2^{2+}(\text{H}_3\text{O}_2)(z\text{O}_4)_2$ [Me^{1+} = Na, K, Rb, Ag, Tl, NH_4 ; Me^{2+} = Cu, Mn, Ni, Co, Zn; z = S, Se, Mo, Cr; further $\text{KCu}_2(\text{H}_3\text{O}_2)(\text{PO}_3\text{F})_2$], form a large class of isotypic monoclinic compounds (cf. Giester and Zemann, 1987), and Giester, 1989, with references to the older literature; further Clearfield et al., 1985; Moïni et al., 1986; Möwius et al., 1987; Chevrier et al., 1990).

Table 1. Details of data collection and structure refinements. 4-circle diffractometer P110 at Orphée reactor (CEN-Saclay), wavelength $\lambda = 0.8307(5)$ Å; program system PROMETHEUS (Zucker et al., 1983); computer CONVEX C1-XP. Data collection up to $\sin\theta/\lambda = 0.974$ Å⁻¹ with ω -step scans for $3^\circ \leq 2\theta \leq 75^\circ$ and $\omega/2\theta$ -step scans for $75^\circ \leq 2\theta \leq 108^\circ$ (35 steps, 2 to 4 s per step as a function of $I/\sigma(I)$, of widths according to the instrumental resolution $40 - 136 \tan\theta + 223 \tan^2\theta$). Neutron scattering lengths: $b_{\text{Na}} = 3.62$, $b_{\text{Rb}} = 7.08$, $b_{\text{Cu}} = 7.689$, $b_{\text{S}} = 2.85$, $b_{\text{Se}} = 7.97$, $b_{\text{O}} = 5.805$ and $b_{\text{H}} = -3.741$ fm (Delapalme, 1985). Number of variables 55 (nonsplit models), 57 (split models).

		Na-S member	Rb-Se member
Number of measured reflections		3124	2467
Miller index range		$-16 \leq h \leq 16$ $-11 \leq k \leq 8$ $-13 \leq l \leq 13$	$-16 \leq h \leq 15$ $-9 \leq k \leq 11$ $0 \leq l \leq 14$
Unique reflections		1297	1525
R_{int}		0.023	0.023
$ F \geq 3\sigma(F)$ [considered as observed]		1003	1060
linear absorption coefficient μ		0.69 cm^{-1}	0.36 cm^{-1}
G^*		$0.37(9) \cdot 10^{-4}$	$0.99(2) \cdot 10^{-4}$
R (R_w) for obs. reflections	nonsplit	0.033 (0.030)	0.029 (0.017)
	split	0.036 (0.024)	0.027 (0.016)
Goodness of fit	nonsplit	0.77	3.69
	split	12.00	3.29

* Secondary isotropic extinction correction by the Becker and Coppens formalism Type I (Becker and Coppens, 1974).

The atomic arrangement is conveniently described as being built from $[\text{Me}^{2+}(\text{H}_3\text{O}_2)(\text{zO}_4)_2]^{1-}$ sheets interconnected by the Me^{1+} ions and further by normal to long hydrogen bridges. Of special interest is the centrosymmetric H_3O_2 configuration with a spread of the O-O distance from 2.44 Å in the Na-Cu-S member to 2.61 Å in the Tl-Cu-Se member; their O atoms are bonded to two Cu atoms with Cu-O ~ 2.0 Å.

The present investigation aimed at the careful location of all atoms in two members of this structure type which differ greatly in the hydrogen bond lengths. Single-crystal neutron diffraction was, of course, the method of choice, as in our work on $\text{KCu}_2(\text{H}_3\text{O}_2)(\text{SO}_4)_2$ (Chevrier et al., 1990).

Experimental and structure refinement

After overcoming technical difficulties, crystals of $\text{NaCu}_2(\text{H}_3\text{O}_2)(\text{SO}_4)_2$ and of $\text{RbCu}_2(\text{H}_3\text{O}_2)(\text{SeO}_4)_2$ were grown of a size (i.e. ca. 10 mm^3) and of a quality as required for the purpose by low-hydrothermal synthesis in a Teflon-lined autoclave and run times of 2 to 3 months.

Table 2. Atomic coordinates. First line $\text{NaCu}_2(\text{H}_3\text{O}_2)(\text{SO}_4)_2$, second line $\text{RbCu}_2(\text{H}_3\text{O}_2)(\text{SeO}_4)_2$. Space group: $C2/m - C_{2h}^3$ (No. 12). H(1): a) unsplit model, b) split model (position $4i$ half occupied).

Atom	Position	x	y	z
Me^{1+}	$2d$	0	1/2	1/2
		0	1/2	1/2
Cu	$4e$	1/4	1/4	0
		1/4	1/4	0
z	$4i$	0.0909(2)	0	0.3013(3)
		0.0720(1)	0	0.2789(1)
O(1)	$4i$	0.1931(1)	0	0.1919(2)
		0.1874(1)	0	0.1697(1)
O(2)	$4i$	0.2091(1)	0	0.5177(1)
		0.1801(1)	0	0.5029(1)
O(3)	$8j$	-0.0201(1)	0.1967(1)	0.2440(1)
		-0.0413(1)	0.2093(1)	0.2161(1)
O(H)	$4i$	0.1576(1)	1/2	0.0754(1)
		0.1565(1)	1/2	0.0727(1)
H(1) a)	$2b$	0	1/2	0
		0	1/2	0
b)	$4i$	0.0169(16)	1/2	0.0069(42)
		0.0277(3)	1/2	0.0210(9)
H(2)	$4i$	0.2070(2)	1/2	0.2239(3)
		0.1972(2)	1/2	0.2089(2)

A number of technical details of the neutron measurements and of the least-squares refinements are compiled in Table 1. During the measurements, two standard reflections 040 and $80\bar{3}$ (Na-S member) and 040 and 004 (Rb-Se member) were stable over 8 days within 1.3% and 0.9%, respectively. The integrated intensities were determined from resolution adapted profile measurement of the peaks: the background was calculated with an average of the first and the last 6 steps of each side, and in the Na-S member an ignorance factor $E = 0.01$ was introduced in the standard deviations (Busing et al., 1957). Due to the small linear absorption coefficients no absorption correction was performed.

The least-squares refinements were carried out in space group $C2/m - C_{2h}^3$ (no. 12), starting with the atomic parameters obtained in the single-crystal neutron work on the isotopic K-S member (Chevrier et al., 1990).

H(1), the “central” atom of the H_3O_2 configuration was put either on position $2b$ $0, 1/2, 0$ etc. (nonsplit model), or with half occupancy on position $4i$ $x, 0, z$ etc. (split model). The atomic coordinates and the parameters of the anisotropic harmonic vibration refined for all the atoms smoothly. The results are presented in Tables 2 and 3; because the results for the nonsplit and the split model mostly agree within 1σ , only the values for the latter are listed.

Table 3. Anisotropic displacement parameters. First line NaCu₂(H₃O₂)(SO₄)₂, second line RbCu₂(H₃O₂)(SeO₄)₂. U_{ij} in pm², B_{eq} in Å². ATF = $\exp[-2\pi^2 \sum_i \sum_j U_{ij} h_i h_j a_i^* a_j^*]$. H(1): a) and b) as in Table 2.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
Me ¹⁺	152(11)	389(16)	170(11)	0	37(9)	0	2.00
	128(3)	179(4)	99(3)	0	30(3)	0	1.12
Cu	53(2)	52(2)	72(2)	3(2)	21(2)	-11(2)	0.49
	70(2)	81(2)	108(2)	-2(2)	28(2)	-6(2)	0.71
z	48(6)	59(6)	35(6)	0	12(5)	0	0.40
	66(2)	77(2)	74(2)	0	25(2)	0	0.59
O(1)	131(4)	118(4)	145(4)	0	109(3)	0	0.89
	124(3)	132(3)	151(3)	0	83(2)	0	1.00
O(2)	137(4)	163(4)	48(4)	0	-4(3)	0	1.08
	157(3)	272(4)	85(3)	0	17(2)	0	1.46
O(3)	73(2)	77(2)	107(2)	14(2)	20(2)	-2(2)	0.75
	113(2)	91(2)	139(2)	19(2)	23(2)	-14(2)	1.00
O(H)	56(3)	69(3)	76(3)	0	33(3)	0	0.52
	107(3)	107(3)	151(3)	0	58(2)	0	0.96
H(1) a)	295(11)	168(8)	245(10)	0	165(9)	0	1.75
	951(25)	243(11)	627(20)	0	644(20)	0	3.94
	72(46)	169(10)	231(33)	0	102(50)	0	1.15
H(1) b)	221(21)	258(10)	324(27)	0	165(22)	0	1.99
	222(8)	248(9)	148(7)	0	87(6)	0	1.63
H(2)	339(7)	327(7)	224(7)	0	135(6)	0	2.31

The atomic coordinates of the non-hydrogen atoms agree very well with the earlier X-ray results (Giester and Zemann, 1987). Also for the displacement parameters the agreement seems to be satisfactory taking into account that they are much more sensitive to errors in the scattering curves (scattering lengths), in the absorption correction and in the extinction correction than the atomic coordinates. It is further considered to be comforting that the orientations of the displacement ellipsoids do not differ much between the X-ray and the neutron results. The values of the neutron refinements are, of course, definitely more reliable.

Because anharmonic refinements would enlarge the number of variables considerably and because in a trial to refine the Na-S member with anharmonic terms of 3rd and 4th order only 9 of the 73 additional terms were defined better than 1.5σ , we restricted ourselves to the harmonic refinement.

It is to be noted that we did not obtain indications for a splitting of the H(1) atoms on position 4g, 0, y, 0 etc., i.e. perpendicular to the plane of symmetry, as published for the Na-Mn-Mo member by Clearfield et al. (1985) on the basis of X-ray work, and for the Na-Ni-Mo member by Moini et al. (1986) on the basis of neutron powder work.¹

Table 4. Some important interatomic distances (Å) in $\text{NaCu}_2(\text{H}_3\text{O}_2)(\text{SO}_4)_2$ and $\text{RbCu}_2(\text{H}_3\text{O}_2)(\text{SeO}_4)_2$. Atomic coordinates from Table 2; Lattice parameters $a = 8.809(1)$, $b = 6.187(1)$, $c = 7.509(1)$ Å, $\beta = 118.74(1)^\circ$ (Na-S member), $a = 9.246(1)$, $b = 6.483(1)$, $c = 7.940(1)$ Å, $\beta = 116.11(1)^\circ$ (Rb-Se member) from Giester and Zemann (1987). Hydrogen bond systems are given for split models only.

	Multiplicity	Na-S	Rb-Se
$\text{Me}^{1+}\text{-O}(1)$	2 ×	2.578(1) Å	2.926(1) Å
$\text{Me}^{1+}\text{-O}(2)$	2 ×	2.629(1) Å	2.968(1) Å
$\text{Me}^{1+}\text{-O}(3)$	4 ×	2.631(1) Å	2.832(1) Å
$\text{Cu-O}(1)$	2 ×	2.327(1) Å	2.338(1) Å
$\text{Cu-O}(3)$	2 ×	1.999(1) Å	1.956(1) Å
Cu-O(H)	2 ×	1.955(1) Å	2.036(1) Å
$z\text{-O}(1)$	1 ×	1.481(2) Å	1.645(1) Å
$z\text{-O}(2)$	1 ×	1.450(2) Å	1.612(1) Å
$z\text{-O}(3)$	2 ×	1.489(1) Å	1.651(1) Å
$\text{O(H)-H}(1)$		1.089(12) Å	1.076(5) Å
$\text{H}(1)\cdots\text{O(H)}$		1.353(11) Å	1.529(5) Å
$\text{O(H)}\cdots\text{O(H)}$		2.443(1) Å	2.602(1) Å
$\text{H}(1)\cdots\text{H}(1)$		0.265(13) Å	0.472(8) Å
$\text{O(H)-H}(1)\cdots\text{O(H)}$		179.1(24)°	174.1(5)°
$\text{O(H)-H}(2)$		0.983(2) Å	0.976(2) Å
$\text{H}(2)\cdots\text{O}(2)$		1.712(2) Å	2.059(2) Å
$\text{O(H)}\cdots\text{O}(2)$		2.695(1) Å	3.026(1) Å
$\text{O(H)-H}(2)\cdots\text{O}(2)$		179.4(1)°	170.5(1)°

Discussion

For the general stereochemical features of the natrochalcite-type structures the reader is referred to Giester and Zemann (1987), Giester (1989) and to earlier papers on this group of structures. Selected bond lengths and angles are listed in Table 4; as the coordinates of the nonhydrogen atoms agree very well with the earlier X-ray results, only some few selected values of such interatomic distances are presented in the table.

Our discussion will concentrate on the hydrogen bond system (Fig. 1) which was not determined experimentally in either of the two compounds previously. The coordinates for the split models agree in principle with those found by neutron work in $\text{KCu}_2(\text{H}_3\text{O}_2)(\text{SO}_4)_2$ (Chevrier et al., 1990), but they differ distinctly from them, as well as from each other. As we deal here with extreme members of a large isotopic series, the details are of considerable interest.

¹ Additional material to this paper can be ordered referring to the no. CSD 55770, name(s) of the author(s) and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, FRG.

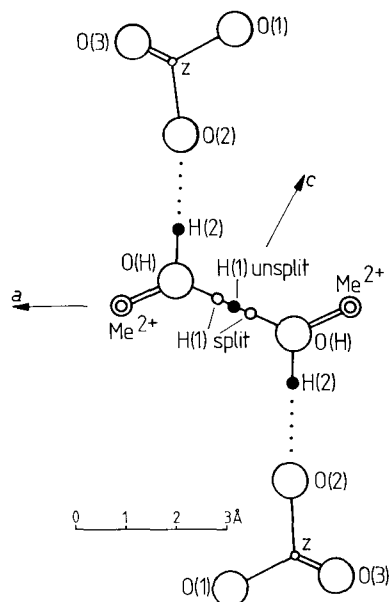


Fig. 1. Schematic detail of the natrochalcite-type structures parallel [010] showing the hydrogen bond system. With the exception of Me^{2+} and O(3) all atoms are in the mirror plane of drawing. Each two Me^{2+} and O(3) atoms coincide in the figure; they have equal distances from the plane of drawing, respectively.

Of primary importance is the stereochemical role of H(1). This atom is situated on the short, “intramolecular” hydrogen bridge of the H_3O_2 configuration. The corresponding O(H)-O(H) distances (Table 4) indicate in the Na-S member a low and in the Rb-Se member a considerably higher energy barrier between two potential minima (e.g. Schuster et al., 1976).

The nonsplit refinements resulted for H(1) in the Na-S member in a somewhat large $B_{\text{eq.}}$, i.e. 1.75 \AA^2 vs. an average of 1.01 \AA^2 for the other atoms and $B_{\text{eq.}}$ (Na) larger than that of H(1). In the Rb-Se member $B_{\text{eq.}}$ (H1) is 3.94 \AA^2 , a value considerably larger than for any other atom. The ellipticity of the displacement ellipsoid² for H(1) in the Na-S compound was found to be 1.34 vs. an average of 1.51 for the other atoms, while in the Rb-Se member it was considerably larger, i.e. 2.18 vs. 1.38 for the average of the other atoms.

In the split refinements the (H1)-(H1) distance was in the Rb-Se member approximately twice as large as in the Na-S member (Table 4), and the direction of the connecting line deviated in this case by only 5° from the

² Defined as (longest axis)/(shortest axis) of the ellipsoid derived from the U_{ij} of Table 3.

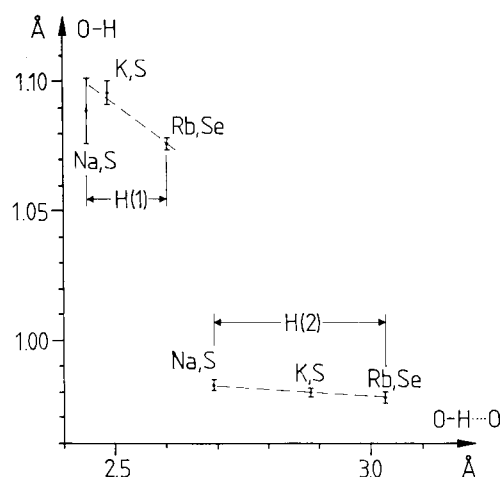


Fig. 2. Plot of bond lengths O—H vs. lengths of the hydrogen bridge in the Na-S, K-S and Rb-Se members of the natrochalcite-type structures, with Cu as Me^{2+} . The three hydrogen bridges on the left are statistically centered.

direction of the longest axis of the displacement ellipsoid of the nonsplit refinement. The splitting is extremely well established in the Rb-Se member, but the standard deviation of H(1)-(H1) indicates that also in the Na-5 member the splitting is well proven within the assumptions of the refinement. An ordering of H(1) could lower the space symmetry to Cm , but our displacement parameters (Table 3) give no conclusive evidence for that.

The well ordered hydrogen bonds of H(2) do not bear special problems. As expected, O(H)-H(2) is slightly shorter in the member where the hydrogen bridge O(H)-O(H) is longer (Table 4).

Together with our results on $\text{KCu}_2(\text{H}_3\text{O}_2)(\text{SO}_4)_2$ (Chevrier et al., 1990), three single-crystal neutron refinements of natrochalcite-type compounds are now available. Notable common results are: (a) the distance H(1)-H(1) in the split models is, within the limits of accuracy, a linear function of the length of the hydrogen bridge O(H)-O(H), (b) in the plot O-H vs. O-H...O the trend shown for the well ordered hydrogen bridge involving H(2) does not extend to the values for H(1) in the split refinements (Fig. 2).

References

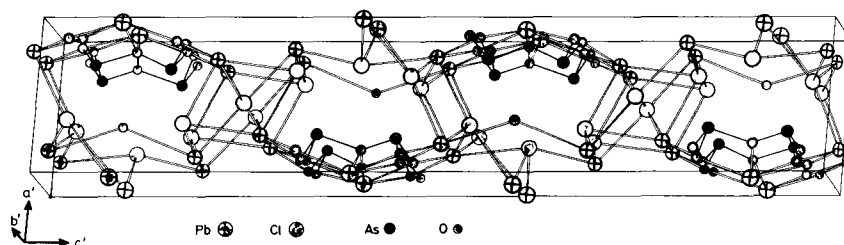
- Becker, P. J., Coppens, P.: Extinction within the limit of validity of the Darwin transfer equations. I. General formalisms for primary and secondary extinction and their application to spherical crystals. *Acta Crystallogr.* **A30** (1974) 129–147.
- Busing, W. R., Levy, H. A.: Neutron diffraction study of calcium hydroxide. *J. Chem. Phys.* **26** (1957) 563–568.

- Chevrier, G., Giester, G., Jarosch, D., Zemann, J.: Neutron diffraction study of the hydrogen-bond system in $\text{Cu}_2\text{K}(\text{H}_3\text{O}_2)(\text{SO}_4)_2$. *Acta Crystallogr.* **C46** (1990) 175–177.
- Clearfield, A., Moini, A., Rudolf, P. R.: Preparation and structure of manganese molybdates. *Inorg. Chem.* **24** (1985) 4606–4609.
- Delapalme, A.: International Report, DPhGr.SDN/85/59, LLB-CEN-Saclay, France (1985).
- Giester, G.: The crystal structures of $\text{Ag}^+\text{Cu}_2(\text{OH})(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{Me}^+\text{Cu}_2(\text{OH})(\text{SeO}_4)_2 \cdot \text{H}_2\text{O}$ [$\text{Me}^+ = \text{Ag}, \text{Tl}, \text{NH}_4$], four new representatives of the natrochalcite type, with a note on natural natrochalcite. *Z. Kristallogr.* **187** (1989) 239–247.
- Giester, G., Zemann, J.: The crystal structure of the natrochalcite-type compounds $\text{Me}^+\text{Cu}_2(\text{OH})(z\text{O}_4)_2 \cdot \text{H}_2\text{O}$ [$\text{Me}^+ = \text{Na}, \text{K}, \text{Rb}$; $z = \text{S}, \text{Se}$], with special reference to the hydrogen bonds. *Z. Kristallogr.* **179** (1987) 431–442.
- Moini, A., Rudolf, P. R., Clearfield, A.: Neutron powder time-of-flight Rietveld refinement and H-atom location in $\text{NaNi}_2(\text{OH})(\text{H}_2\text{O})(\text{MoO}_4)_2$. *Acta Crystallogr.* **C42** (1986) 1667–1669.
- Möwius, F., Ziemer, B., Reck, G., Meisel, M., Grunze, H.: Darstellung und Kristallstruktur von Kalium-dikupfer-hydroxid-bis(monofluorophosphat)-Monohydrat $\text{Cu}_2\text{K}(\text{OH})(\text{PO}_3\text{F})_2 \cdot \text{H}_2\text{O}$. *Z. Anorg. Allg. Chem.* **547** (1987) 75–82.
- Schuster, P., Zundel, G., Sandorfy, C. (Editors): *The Hydrogen Bond. Vol. I–III*. North-Holland Publishing Company: Amsterdam – New York – Oxford (1976).
- Zucker, U. R., Perenthaler, E., Kuhs, W. F., Bachmann, R., Schulz, H.: PROMETHEUS. A program system for investigation of anharmonic thermal vibrations in crystals. *J. Appl. Crystallogr.* **16** (1983) 358.

R. Klaska und W. Gebert (Inst. f. Min. der Ruhr-Universität, Bochum).
Polytypie und Struktur von Gebhardit-Pb₈OCl₆(As₂O₅)₂.

Gebhardit ist ein Mineral aus den tieferen Oxidationszonen der Tsumeb-Mine. Für die Bestimmung der Kristallstruktur von Pb₈OCl₆(As₂O₅)₂ wurde ein Bruchstück mit durchschnittlichen Abmessungen für die Richtungen [100], [010], [001] von 0,027 mm, 0,1 mm und 0,02 mm für die Vermessung mit MoK α am Einkristall-Diffraktometer (Syntex R3) präpariert. Als Symmetrie wurde $P2_1/c$ beobachtet, die aber als Folge des polytypen Charakters (s. u.) gewertet werden muß. Die Gitterkonstanten wurden mit 25 hkl zu $a = 6,724(6) \text{ \AA}$, $b = 11,20(1) \text{ \AA}$ und $c = 34,19(4) \text{ \AA}$ bei einem monoklinen Winkel $\beta = 85,2(1)^\circ$ verfeinert. Nach Absorptionskorrektur und monokliner Datenreduktion ($R = 4,8\%$) blieben 6529 hkl bei einem Signifikanzkriterium von $I_{\text{netto}} > 2,56$ übrig. Eine nur geringfügige Anhebung der Signmagrenze auf 3,0 führt zu einer starken Reduzierung der beobachteten Reflexe (2874) und der Feststellung, daß $h2nl$ mit $k/2 + l = 2n + 1$ an der Beobachtungsgrenze liegen. Wird zusätzlich die zweifache Überstruktur in Richtung b berücksichtigt, so beobachtet man für die Subzelle $a, b/2, c$ ein A -Gitter. Dies bedeutet, daß weder c noch 2_1 für die angegebene Zelle real beobachtet sind. Für die kleine Zelle gilt die maximale Symmetrie $A2/m, 2_1/c$. Diese symmetriedichte Subzelle erklärt die Schwierigkeiten bei der Aufklärung der Kristallstruktur über die Patterson-Synthese als auch über die direkten Methoden. Im Patterson-Diagramm spiegeln die einzig interpretierbaren Peaks $0, \frac{1}{2}, 0$ und $0, \frac{1}{4}(\frac{3}{4}), \frac{1}{2}$ obige Beobachtungen wieder, während die Phasenbestimmung über die direkten Methoden an einer Fixierung des Ursprungs scheitert. Doch eine Reduzierung auf die Subzelle oder eine zusätzliche Renormalisierung, welche Überstruktur und A -Gitter berücksichtigt, helfen, einen Lösungsansatz der Struktur über 3 Pb und 2 As-Atome zu finden. — Die Pb-Atome koordinieren sich mit Cl und O zu Polyedern, die von 6 bis 8 Atomen gebildet werden. Hierbei binden sich die Cl-Atome in Abständen von 2,96 bis 3,49 \AA , und die O-Atome von 2,1 bis 2,8 \AA . Das dreiwertige As koordiniert sich mit drei Sauerstoffatomen zu einer tetraederförmigen Pyramide, dessen Spitze As belegt. Zwei dieser „Tetraeder“ bilden jeweils eine Gruppe $[\text{As}_2\text{O}_5]^{-4}$. Die mittleren Abstände lauten $\langle \text{As}-\text{O} \rangle = 1,78 \text{ \AA}$, die Winkel $\langle \text{O}-\text{As}-\text{O} \rangle = 97^\circ$. Ein Sauerstoffatom ist nur an Pb gebunden mit einem dichtesten Abstand von 2,7 \AA .

Das Beugungsbild von Gebhardit zeigt mit der zweifachen Überstruktur in b und dem A -Gitter für die Subzelle das Muster einer aus translativ äquivalenten Schichten aufgebauten polytypen Struktur. Hierbei sind die möglichen Schichtsymmetrien als Untergruppen der Maximalsymmetrie $A2/m, 2_1/c$ zu suchen. Aus der Beobachtung, daß starke Reflexe in das Gesetz $k + 2l = 4n$ einzuordnen sind und entsprechend $k + 2l \neq 4n$ schwache Maxima aufweisen, leitet sich als mögliche Schichtsymmetrie $p12/m(1)$ oder $p12_1/m(1)$ mit $b/2$ als Pseudotranslation ab. Für alle Schweratome sollte es

Abb. 1. Gebhardtit $\text{Pb}_8\text{OCl}_6(\text{As}_2\text{O}_5)_2$

Koordinaten von Gebhardtit

Atom	x	y	z	Atom	x	y	z
Pb1	0,7435	0,6283	0,2193	Cl4	0,3375	-0,1334	0,6817
Pb2	0,7970	0,6294	-0,0122	Cl5	0,7453	-0,3763	0,8953
Pb3	0,1468	0,3750	0,1914	Cl6	0,3600	0,6164	0,0366
Pb4	0,7443	0,1236	0,2197	O1	0,7928	0,3695	0,1016
Pb5	0,8045	0,1234	-0,0093	O2	0,8345	0,8545	0,1144
Pb6	0,8427	0,3742	0,3059	O3	0,1011	0,7411	0,9551
Pb7	0,9794	0,8998	0,5960	O4	0,0907	0,2544	0,4566
Pb8	0,9901	0,1521	0,1037	O5	0,8784	0,2362	0,6715
As1	0,7503	0,8718	0,0604	O6	0,8454	0	0,6658
As2	0,7227	0,3729	0,0552	O7	0,8710	0,7386	0,6750
As3	0,6983	0,1235	0,6552	O8	0,8514	0,5002	0,6638
As4	0,7230	0,8759	0,1551	O9	0,8603	0,4991	0,5343
Cl1	0,6784	-0,1339	0,8215	O10	0,1401	0,9975	0,4629
Cl2	0,3623	0,1159	0,0357	O11	0,7467	0,1174	0,8851
Cl3	0,4937	0,3682	0,2509				

ein Untergitter mit $a, b/2, c$ und der Symmetrie $A1 2/m, 2_1/m (1)$ geben. Als reale Symmetrie sollte dann $P 1 2/c 1$ oder $P 1 2_1/c 1$ resultieren. Der polytype Charakter der Struktur von Gebhardtit, der sich für die meisten Atome durch den Verschiebungsvektor $x, \pm \frac{1}{4} + y, \frac{1}{2} + z$ beschreiben läßt, muß zum Schluß führen, daß sowohl 2_1 als auch c unbeobachtet sind, da sie durch die obige Translation erzeugt werden, trotzdem wird $P 2_1/c$ als Realsymmetrie angenommen. Darüberhinaus wird aber auch die Symmetrie $P 2_1$ mit den Punktlagen $x, y, z; -x, \frac{1}{2} + y, \frac{1}{2} - z; x, \frac{1}{4} + y, \frac{1}{2} + z; -x, \frac{3}{4} + y, -z$ diskutiert.

Crystal structure of synthetic makatite $\text{Na}_2\text{Si}_4\text{O}_8(\text{OH})_2 \cdot 4\text{H}_2\text{O}$

H. Annehed, L. Fälth, and F. J. Lincoln*

Inorganic Chemistry 2, Chemical Center, University of Lund,
P.O. Box 740, S-22007 Lund 7, Sweden

Received: July 6, 1981

Makatite / Crystal structure

Abstract. The crystal structure of synthetic makatite, $\text{Na}_2\text{Si}_4\text{O}_8(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, [monoclinic, $a = 7.3881(5) \text{ \AA}$, $b = 18.094(3) \text{ \AA}$, $c = 9.5234(5) \text{ \AA}$, $\beta = 90.64(1)^\circ$, $P2_1/c$, $z = 4$] was solved by direct methods, (MULTAN), and Fourier syntheses and refined to $R = 0.051$ for 834 independent reflexions. The makatite structure is built up of corrugated $[\text{Si}_2\text{O}_4(\text{OH})]_n^-$ layers containing rings of six tetrahedra. The layers are connected by octahedral $[\text{Na}(\text{H}_2\text{O})_4]_n^+$ rods and sodium atoms coordinating five oxygens which form distorted trigonal bipyramids. Hydrogen atoms positions have not been determined.

Introduction

As a part of a general study of zeolites with ion exchange properties for the treatment of nuclear power station wastes we have synthesized a large number of different zeolites. Exclusion of the aluminium component from the $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ system led to the preparation of a number of hydrous layer silicates, of which some are known as minerals, e.g. magadiite ($\text{Na}_2\text{O} \cdot 14\text{SiO}_2 \cdot 9\text{H}_2\text{O}$) (McAtee, House, and Eugster, 1968), kenyaite ($\text{Na}_2\text{O} \cdot 22\text{SiO}_2 \cdot 10\text{H}_2\text{O}$) (Eugster, 1967) and makatite (Hay, 1968), and some as purely synthetic products, e.g. sodium polysilicate ($\text{Na}_2\text{O} \cdot 8\text{SiO}_2 \cdot 9\text{H}_2\text{O}$) previously reported by McCulloh (1952) and Iler (1964). Many of these layer silicates have interesting ion exchange properties and this present structure determination was undertaken in order to understand the mechanism of the ion exchange. The details of the syntheses will be published elsewhere but in general most of the preparations yielded crystals too small for single crystal X-ray work. However, in the case of makatite, the introduction

* Permanent address: School of Chemistry, University of Western Australia, Nedlands, 6009, W. Australia

of the complexing agent triethanolamine (Charnell, 1971) resulted in the growth of larger, more suitable crystals.

Recently Dent Glasser et al. (1980) have proposed by help of electron microscopy methods a new chain type structure for makatite with a repeat distance of 3.4 Å in the fibre direction which by our investigation is shown not to be the case.

Experimental

The cell dimensions, shown in Table 1, were refined by least squares methods from 45 single indexed lines of a powder pattern obtained in a Guinier-Hägg focusing camera with $\text{CuK}\alpha_1$ radiation. A thin platy crystal ($0.090 \times 0.052 \times 0.006 \text{ mm}^3$), selected with the Weissenberg technique, was mounted on a CAD-4 four circle diffractometer. Table 1 gives information on the data collection, reduction of the intensities and subsequent refinement. Systematic absences were $h0l: l = 2n + 1$ and $0k0: k = 2n + 1$, which is consistent with

Table 1. Experimental details

Cell data	$a = 7.3881(5) \text{ \AA}$ $b = 18.094(3) \text{ \AA}$ $c = 9.5234(5) \text{ \AA}$ $\beta = 90.64(1)^\circ$ $z = 4$ Space group $P2_1/c$ $\rho_c = 2.04 \text{ g cm}^{-3}$ $\rho_m^a = 2.03 \text{ g cm}^{-3}$
Radiation	$\text{CuK}\alpha$
θ interval ($^\circ$)	5–70
$w-2\theta$ scan width w ($^\circ$)	$0.5 + 0.9 \tan \theta$
Maximum recording time (min)	4
Measured reflexions	(5, 70 $^\circ$) all
μ (mm^{-1})	5.71
Range of transmission factors	0.73–0.97
Number of reflexions measured ^b	2386
Number of reflexions with zero weight	1552 [$I < 2\sigma_c(I)$]
Number of reflexions used in the final refinement, m	834
Number of parameters refined, n	185
$R = \Sigma (F_o - F_c) / \Sigma F_o $	0.051
$R_w = [\Sigma w (F_o - F_c)^2 / \Sigma w F_o ^2]^{1/2}$	0.055
$S = [\Sigma w (F_o - F_c)^2 / (m - n)]^{1/2}$	1.52
g ($\times 10^{-4}$) extinction ^c	0.22

^a Measured by flotation

^b One set of independent reflexions was measured

^c Zachariasen, 1968

