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Neutron refinements of $NaCu_2(H_3O_2)(SO_4)_2$ and $RbCu_2(H_3O_2)(SeO_4)_2$: Variation of the hydrogen bond system in the natrochalcite-type series

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$NaCu_2(H_3O_2)(SO_4)_2$ / $RbCu_2(H_3O_2)(SeO_4)_2$ /
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Abstract. In the natrochalcite-type compounds $NaCu_2(H_3O_2)(SO_4)_2$ and $RbCu_2(H_3O_2)(SeO_4)_2$ 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+}-$Me_2^{2+}(H_3O_2)(zO_4)_2$ [Me^{1+} = Na, K, Rb, Ag, Tl, NH_4; Me^{2+} = Cu, Mn, Ni, Co, Zn; z = S, Se, Mo, Cr; further $KCu_2(H_3O_2)(PO_3F)_2$], 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; Moini 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 $3° \leq 2\Theta \leq 75°$ and $\omega/2\Theta$ -step scans for $75° \leq 2\Theta \leq 108°$ (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: $b_{Na} = 3.62$, $b_{Rb} = 7.08$, $b_{Cu} = 7.689$, $b_s = 2.85$, $b_{Se} = 7.97$, $b_O = 5.805$ and $b_H = -3.741$ 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			
		$-16 \leq h \leq 16$	$-16 \leq h \leq 15$
		$-11 \leq k \leq 8$	$-9 \leq k \leq 11$
		$-13 \leq l \leq 13$	$0 \leq l \leq 14$
Unique reflections		1297	1525
R_{int}		0.023	0.023
$\lvert F\rvert \geq 3\sigma(F)$ [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 $[Me^{2+}(H_3O_2)(zO_4)_2]^{1-}$ 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 $KCu_2(H_3O_2)(SO_4)_2$ (Chevrier et al., 1990).

Experimental and structure refinement

After overcoming technical difficulties, crystals of $NaCu_2(H_3O_2)(SO_4)_2$ and of $RbCu_2(H_3O_2)(SeO_4)_2$ 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 $NaCu_2(H_3O_2)(SO_4)_2$, second line $RbCu_2(H_3O_2)(SeO_4)_2$. Space group: $C2/m - C_{2h}^3$ (No. 12). H(1): a) unsplit model, b) split model (position 4*i* half occupied).

Atom	Position	*x*	*y*	*z*
Me^{1+}	2*d*	0	1/2	1/2
		0	1/2	1/2
Cu	4*e*	1/4	1/4	0
		1/4	1/4	0
z	4*i*	0.0909(2)	0	0.3013(3)
		0.0720(1)	0	0.2789(1)
O(1)	4*i*	0.1931(1)	0	0.1919(2)
		0.1874(1)	0	0.1697(1)
O(2)	4*i*	0.2091(1)	0	0.5177(1)
		0.1801(1)	0	0.5029(1)
O(3)	8*j*	−0.0201(1)	0.1967(1)	0.2440(1)
		−0.0413(1)	0.2093(1)	0.2161(1)
O(H)	4*i*	0.1576(1)	1/2	0.0754(1)
		0.1565(1)	1/2	0.0727(1)
H(1) a)	2*b*	0	1/2	0
		0	1/2	0
b)	4*i*	0.0169(16)	1/2	0.0069(42)
		0.0277(3)	1/2	0.0210(9)
H(2)	4*i*	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 $0\bar{4}0$ and $80\bar{3}$ (Na-S member) and $0\bar{4}0$ 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 isotypic K-S member (Chevrier et al., 1990).

H(1), the "central" atom of the H_3O_2 configuration was put either on position 2*b* 0, 1/2, 0 etc. (nonsplit model), or with half occupancy on position 4*i* *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 $NaCu_2(H_3O_2)(SO_4)_2$, second line $RbCu_2(H_3O_2)(SeO_4)_2$. U_{ij} in pm^2, B_{eq} in $Å^2$. ATF = $\exp[-2\pi^2\Sigma_i\Sigma_jU_{ij}h_ih_ja^*_ia^*_j]$. 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
b)	72(46)	169(10)	231(33)	0	102(50)	0	1.15
	221(21)	258(10)	324(27)	0	165(22)	0	1.99
H(2)	222(8)	248(9)	148(7)	0	87(6)	0	1.63
	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 considerabely 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 then 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 4*g*, $0, y, 0$ 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 $NaCu_2(H_3O_2)(SO_4)_2$ and $RbCu_2(H_3O_2)(SeO_4)_2$. 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
Me^{1+}-O(1)	2×	2.578(1) Å	2.926(1) Å
Me^{1+}-O(2)	2×	2.629(1) Å	2.968(1) Å
Me^{1+}-O(3)	4×	2.631(1) Å	2.832(1) Å
Cu-O(1)	2×	2.327(1) Å	2.338(1) Å
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-O(1)	1×	1.481(2) Å	1.645(1) Å
z-O(2)	1×	1.450(2) Å	1.612(1) Å
z-O(3)	2×	1.489(1) Å	1.651(1) Å
O(H)-H(1)		1.089(12) Å	1.076(5) Å
H(1)···O(H)		1.353(11) Å	1.529(5) Å
O(H)--O(H)		2.443(1) Å	2.602(1) Å
H(1)···H(1)		0.265(13) Å	0.472(8) Å
O(H)-H(1)···O(H)		179.1(24)°	174.1(5)°
O(H)-H(2)		0.983(2) Å	0.976(2) Å
H(2)···O(2)		1.712(2) Å	2.059(2) Å
O(H)--O(2)		2.695(1) Å	3.026(1) Å
O(H)-H(2)···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 $KCu_2(H_3O_2)(SO_4)_2$ (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 isotypic series, the details are of considerable interest.

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[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.

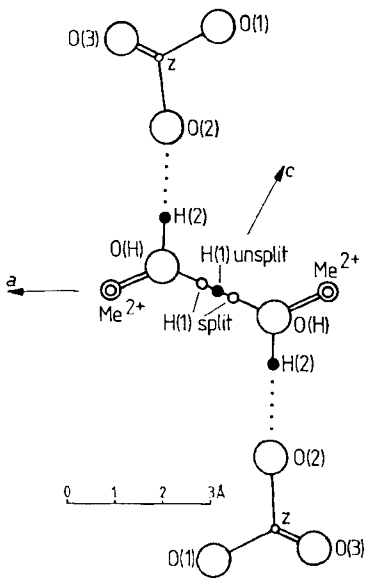

Fig. 1. Schematic detail of the natrochalcite-type structures parallel [010] showing the hydrogen bond system. With the exception of Me^{2+} and O(3) all atoms are in the mirror plane of drawing. Each two Me^{2+} and O(3) atoms coincide in the figure; they have equal distances from the plane of drawing, 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 $B_{eq.}$, i.e. 1.75 $Å^2$ vs. an average of 1.01 $Å^2$ for the other atoms and $B_{eq.}$ (Na) larger than that of H(1). In the Rb-Se member $B_{eq.}$ (H1) is 3.94 $Å^2$, a value considerably larger than for any other atom. The ellipticity of the displacement ellipsoid[2] 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

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

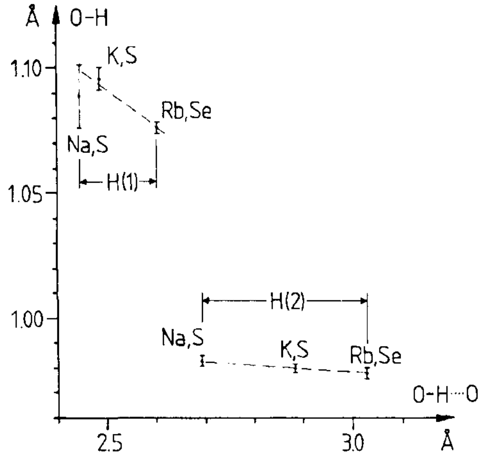

Fig. 2. Plot of bond lengths O–H vs. lengths of the hydrogen bridge in the Na-S, K-S and Rb-Se members of the natrochalcite-type structures, with Cu as Me^{2+}. The three hydrogen bridges on the left are statistically centered.

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(2) is longer (Table 4).

Together with our results on $KCu_2(H_3O_2)(SO_4)_2$ (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).

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