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The crystal structure of the natrochalcite-type compounds $Me^{+}Cu_2(OH)(zO_4)_2 \cdot H_2O$ [Me^{+} = Na, K, Rb; z = S, Se], with special reference to the hydrogen bonds

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Dedicated to the memory of Martin J. Buerger

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$Me^{+}Cu_2(OH)(zO_4)_2 \cdot H_2O$ [Me^{+} = Na, K, Rb; z = S; Se] /
Natrochalcite-type structures / H_3O_2 configurations / Hydrogen bonds

Abstract. The structures of the six natrochalcite-type compounds $Me^{+}Cu_2(OH)(zO_4)_2 \cdot H_2O$ [Me^{+} = Na, K, Rb; z = S, Se] were determined (or only refined: Na–S and K–S members) by single crystal X-ray methods in space group $C2/m$ ($Z = 2$). The oxygens of the OH's and H_2O's occupy together the position 4(*i*) to form – at least statistically – H_3O_2 configurations with O–O distances as characteristic for short hydrogen bonds: these distances vary from 2.440(3) Å in the Na–S member to 2.588(5) Å in the Rb–Se member. The lengths of the two crystallographically equivalent hydrogen bonds of the H_3O_2 configuration to oxygens of the zO_4 tetrahedra vary greatly: from 2.695(2) Å in the Na–S member to 3.114(4) Å in the Rb–S member. This stereochemistry indicates that a formulation of the compounds as $Me^{+}Cu_2(H_3O_2)(zO_4)_2$ seems also to be justified.

Introduction

The crystal structure of the monoclinic mineral natrochalcite, $NaCu_2(OH)(SO_4)_2 \cdot H_2O$, was determined by Rumanova and Volodina (1958) from photographic X-ray data in space group $C2/m$, $Z = 2$. The

OH's and H_2O's were found to occupy together the position 4(*i*) in this space group to form pairs with $O-O = 2.42$ Å. This O—O distance was interpreted as a short hydrogen bond. Cord et al. (1970) determined the lattice constants of the analogous synthetic selenium salt, but did not determine its structure in detail.

Tardy and Brégeault (1974) investigated the potassium sulphate compound. They refined the structure in space groups $C2/m$ and Cc, but could not find conclusive evidence for the acentric space group. For the short hydrogen bond they obtained $O-O = 2.49(3)$ Å.

The (at least statistically) centrosymmetric hydrogen bonds postulated in the publications cited above are extremely reasonable both from their lengths and from their general stereochemical role. Unfortunately, the further hydrogen bonds were either not discussed at all (Rumanova and Volodina, 1958), or in a way that does not completely meet todays standards (Tardy and Brégeault, 1974, who list in their Table V distances 0—0 as possible hydrogen bonds part of which are edges in the coordination polyhedron around Cu).

In this context it should be mentioned that also $KCo_2\,(OH)(MoO_4)_2 \cdot H_2O$ (Pezerat, 1967) and $NaZn_2(OH)(MoO_4)_2 \cdot H_2O$ (Clearfield et al., 1976) belong to the natrochalcite-type compounds. In neither of them the hydrogen bonds from the O—H—O dumb-bell to oxygens of the MoO_4 groups were substantiated experimentally, but in $Na_2Zn(OH)(MoO_4)_2 \cdot H_2O$ they were postulated on very reasonable stereochemical arguments. As to further molybdates and chromates which were reported to belong to this structure type, the reader is referred to Pezerat (1967) and Tardy and Brégeault (1974), and to references therein.

It seemed interesting to us (a) to refine the crystal structures of natrochalcite and of the corresponding potassium salt, and (b) to extend the investigation to possible further representatives of the natrochalcite-type among alkali-copper sulphates and -selenates, with the aim to learn more of the dependence of the details of this structure type on the sizes of the alkali ions and of the zO_4 tetrahedra, especially so for the hydrogen bonds.

Syntheses

Of the ten theoretically possible non-radioactive alkali-copper-sulphates and selenates with the formula type of natrochalcite, the six members $Me^+Cu_2(OH)(zO_4)_2 \cdot H_2O$ [$Me^+ = Na, K, Rb$; $z = S, Se$] were synthesized as follows: Approximately 0.5 g copper oxide rods (Kupferoxid Drahtform, Art. 2767 Fa. E. Merck, Darmstadt, FRG) were heated in a closed "Teflon"-lined steel vessel of $\sim 6\ cm^3$ volume together with ~ 0.25 g of the corresponding neutral alkali sulphate or selenate, very little water and some few droplets of the pertinent acid to 180—240 °C for several days. Upon cooling a number of phases had formed, among them also light green crystals of the phases mentioned above; their size was usually some few tenths of a millimeter. The lithium and cesium members were not obtained by this procedure.

X-ray work and computations

Before quantitative data collection all six substances were examined by photographic Weissenberg methods (Cu radiation). As in the literature on the Na – S and K – S members (Rumanova and Volodina, 1958; Tardy and Brégeault, 1974) no weak reflections violating the diffraction aspect $C2/m$ were observed.

All quantitative work was done on a Stoe AED 2 four-circle diffractometer with Mo$K\alpha$ radiation (graphite monochromator), nearly all computations with the program system STRUCSY (Fa. Stoe and Cie., Darmstadt, FRG).

The lattice constants were determined by least-squares treatment of 46 – 72 carefully measured 2ϑ values in the range $29° < 2\vartheta < 49°$.

Diffraction intensities were collected up to $2\vartheta = 90°$ for all six compounds, $2\vartheta/\omega$ scans, minimum step number 35 – 48, step width 0.03°, step time 0.5 – 1.5 s, 5 – 8 steps on each side of the reflections for background correction; three standard reflections; no significant shift was observed. The intensities were measured in a half-sphere of the reciprocal space. The unified data sets comprised 1662 – 1870 possible reflections; 1490 – 1670 of them had $|F_o| > 3\,\vartheta(|F_o|)$ and were treated as observed. The intensities were corrected for absorption according to the shape and size of the crystals, as well as polarization and Lorentz effects. The origin of the unit cell and the labeling of the non-hydrogen atoms were chosen as by Rumanova and Volodina (1958), with the exception of their O4 which we call O(H).

In the least-squares refinements scattering curves for neutral atoms as given in the *International Tables for X-ray Crystallography* (1974) were used. The starting set for the non-hydrogen coordinates was that given by Rumanova and Volodina (1958).

In the first least-squares refinements the H atoms were neglected, and 45 parameters were allowed to vary: one overall scaling factor, 11 atomic coordinates, 32 parameters of the anisotropic thermal motion, and the g value of the isotropic secondary extinction (Zachariasen, 1967). Hydrogen atoms were then set on their probable positions in a fully ordered structure: two H(1)'s on 2(b) and four H(2)'s on 4(i) on the connection line O(H) – O(2) ca. 1.0 Å from O(H). In subsequent least-squares cycles the temperature factor of H(1) could not be refined for any of our six members. However, the coordinates plus the isotropic temperature factor of H(2) could be refined for the Na – Se member [result: $U_{\text{iso}} = 190(120)$ pm^2], and the coordinates of H(2) in the K – S and K – Se members when the isotropic temperature factor was fixed at $U_{iso} = 200\ pm^2$.

Lattice constants, final atomic coordinates, R-values and parameters g for the secondary extinction for the six compounds are compiled in Table 1, the parameters of the thermal motion in Table 2[1]. In view of the large data sets, the R-values are considered to be very satisfactory. For the Na – S and K – S members the agreement of our non-hydrogen coordinates with those published by Rumanova and Volodina (1958) and Tardy and Brégeault (1974) is good, but according to the standard deviations our values are more accurate.

The probable cause for our failure to locate the H(2)'s in the Na – S member is to be sought in the large extinction of our crystal of this substance; its g value as obtained by the least-squares refinement is larger than for any other of our substances (Table 1). While the number of the H(2)'s per unit cell is four, that of the H(1)'s is only two; in addition it seems well possible that they do not occupy a two-fold position fully, but rather position 4(*e*) with occupancy one half (see below). Therefore, it is not surprising that we could not locate the H(1)'s reliably by Fourier or least-squares methods in any of our compounds – also not in the Na – S, K – S and K – Se members where this was possible for the H(2)'s.

Discussion

Before discussing the atomic distances, it seems appropriate shortly to deal with the problem of the space group. As already mentioned, a preliminary photographic X-ray investigation showed no violations of the diffraction aspect $C2/m$. In addition, the refinements in this space group yielded very satisfactory reliability indices (Table 1). However, there arises a stereochemical problem if one considers $C2/m$ to be the true space group: In a fully ordered natrochalcite-type structure the two H(1) atoms per unit cell have then necessarily to occupy one of the positions 2(*a*) – 2(*d*) [all with point symmetry $2/m$], but for our choice of the cell only 2(*b*) needs further consideration – as also recognized by the earlier authors. Thereby, H(1) would have two exactly equal distances to two O(H) atoms, and the corresponding hydrogen bond would be strictly centrosymmetric. This does not seem to find support in the O(H) – O(H) distances which vary from 2.44 – 2.59 Å, especially not in the upper part of the range (cf. Joswig et al., 1982). Two solutions of the problem seem to be possible: (a) The H(1) atoms are located statistically on the connection line O(H) – O(H) near to

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[1] $(F_o - F_c)$ lists and lists with interatomic distances and bond angles can be ordered from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference No. CSD 52282, the names of the authors and the title of the paper.

Table 1. Lattice constants (Å), atomic coordinates, R-values and values g of the isotropic secondary extinction for six natrochalcite-type sulphates and selenates. Space group: $C2/m$; $Z = 2$. H(1) [if fully ordered] on 2(b), Me^+ on 2(d), Cu on 4(e), S, Se, O(1), O(2), O(H) and H(2) on 4(i), O(3) on 8(j). Standard deviations in parentheses. Weighting scheme for R_w: $[\sigma(F_o)]^{-2}$.

		Na–S	Na–Se	K–S	K–Se	Rb–S	Rb–Se
a		8.809(1)	9.063(2)	8.955(2)	9.186(1)	9.005(2)	9.246(1)
b		6.187(1)	6.303(2)	6.265(1)	6.423(1)	6.305(2)	6.483(1)
c		7.509(1)	7.678(2)	7.628(1)	7.830(1)	7.802(2)	7.940(1)
β		118.74(1)	118.45(1)	117.45(1)	117.26(1)	116.22(2)	116.11(1)
Me^{1+}	x	0	0	0	0	0	0
	y	1/2	1/2	1/2	1/2	1/2	1/2
	z	1/2	1/2	1/2	1/2	1/2	1/2
Cu	x	1/4	1/4	1/4	1/4	1/4	1/4
	y	1/4	1/4	1/4	1/4	1/4	1/4
	z	0	0	0	0	0	0
z	x	0.09107(7)	0.08666(3)	0.08019(9)	0.07820(3)	0.07277(9)	0.07206(4)
	y	0	0	0	0	0	0
	z	0.30151(8)	0.30139(3)	0.28786(11)	0.28821(3)	0.27646(10)	0.27885(4)
O(1)	x	0.1933(3)	0.1876(3)	0.1862(3)	0.1901(3)	0.1819(3)	0.1880(3)
	y	0	0	0	0	0	0
	z	0.1920(3)	0.1713(3)	0.1851(4)	0.1736(3)	0.1798(4)	0.1697(3)
O(2)	x	0.2088(3)	0.2254(3)	0.1847(3)	0.1954(3)	0.1695(3)	0.1797(3)
	y	0	0	0	0	0	0
	z	0.5181(3)	0.5313(3)	0.5000(4)	0.5171(3)	0.4819(4)	0.5031(3)
O(3)	x	−0.0201(2)	−0.0329(2)	−0.0283(2)	−0.0373(2)	−0.0344(2)	−0.0415(2)
	y	0.1969(2)	0.2143(2)	0.1946(3)	0.2113(2)	0.1931(3)	0.2094(3)
	z	0.2442(2)	0.2478(2)	0.2276(3)	0.2267(2)	0.2155(3)	0.2156(2)
O(H)	x	0.1574(2)	0.1559(2)	0.1560(3)	0.1561(2)	0.1548(3)	0.1557(3)
	y	1/2	1/2	1/2	1/2	1/2	1/2
	z	0.0750(3)	0.0714(3)	0.0746(4)	0.0722(3)	0.0732(4)	0.0719(3)
H(2)	x		0.211(6)	0.184(9)	0.173(7)		
	y		1/2	1/2	1/2		
	z		0.194(8)	0.194(11)	0.177(9)		
R		0.038	0.034	0.045	0.033	0.043	0.041
R_w		0.033	0.031	0.040	0.031	0.036	0.036
$g \cdot 10^4$		2.58	0.14	1.73	0.28	0.61	0.22

Table 2. Parameters of the anisotropic thermal motion for six natrochalcite-type sulphates and selenates. U_{ij} in pm^2; standard deviations in parentheses. ATF = exp $\left[-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} a_i^* a_j^* h_i h_j\right]$.

		Na–S	Na–Se	K–S	K–Se	Rb–S	Rb–Se
Me^{1+}	U_{11}	152(9)	197(8)	96(3)	131(3)	106(2)	147(2)
	U_{22}	364(12)	262(9)	203(5)	182(3)	228(2)	208(2)
	U_{33}	184(9)	251(9)	106(3)	121(3)	113(2)	117(1)
	U_{12}	0	0	0	0	0	0
	U_{13}	48(7)	97(7)	29(3)	41(2)	29(1)	28(1)
	U_{23}	0	0	0	0	0	0
Cu	U_{11}	60(1)	84(1)	57(2)	77(1)	71(1)	99(1)
	U_{22}	62(1)	105(1)	72(2)	85(1)	95(1)	111(2)
	U_{33}	83(1)	124(1)	110(2)	111(1)	148(2)	139(1)
	U_{12}	4(1)	3(1)	3(1)	−1(1)	4(1)	0(1)
	U_{13}	26(1)	36(1)	27(1)	29(1)	37(1)	31(1)
	U_{23}	−9(1)	−5(1)	−10(1)	−6(1)	−9(1)	−9(1)
z	U_{11}	55(2)	75(1)	53(2)	68(1)	70(2)	93(1)
	U_{22}	70(2)	106(1)	79(3)	81(1)	106(2)	105(1)
	U_{33}	51(2)	97(1)	69(2)	76(1)	99(3)	97(1)
	U_{12}	0	0	0	0	0	0
	U_{13}	22(1)	35(1)	24(2)	27(1)	31(2)	25(1)
	U_{23}	0	0	0	0	0	0
O(1)	U_{11}	142(8)	193(7)	99(9)	140(8)	116(8)	180(11)
	U_{22}	134(7)	155(7)	137(10)	134(7)	153(9)	173(11)
	U_{33}	145(7)	222(8)	124(9)	154(7)	144(9)	194(9)
	U_{12}	0	0	0	0	0	0
	U_{13}	109(6)	154(7)	74(7)	102(6)	70(8)	127(9)
	U_{23}	0	0	0	0	0	0
O(2)	U_{11}	140(8)	179(8)	106(9)	163(9)	130(9)	173(11)
	U_{22}	183(9)	251(9)	216(13)	251(10)	252(11)	314(15)
	U_{33}	56(6)	106(6)	68(8)	83(7)	112(9)	87(7)
	U_{12}	0	0	0	0	0	0
	U_{13}	7(6)	6(6)	16(7)	10(6)	27(8)	3(7)
	U_{23}	0	0	0	0	0	0
O(3)	U_{11}	80(4)	105(4)	80(6)	117(5)	98(5)	134(6)
	U_{22}	77(4)	129(4)	86(6)	90(4)	104(5)	117(7)
	U_{33}	120(5)	159(5)	133(6)	147(5)	178(7)	185(6)
	U_{12}	14(3)	20(4)	16(5)	21(4)	11(4)	17(6)
	U_{13}	27(4)	34(4)	25(5)	30(4)	33(5)	27(5)
	U_{23}	1(4)	−3(4)	−8(6)	−11(4)	−13(5)	−19(6)
O(H)	U_{11}	64(6)	97(5)	71(8)	94(6)	91(7)	156(10)
	U_{22}	76(6)	128(6)	90(9)	108(6)	105(7)	132(10)
	U_{33}	73(5)	121(6)	107(8)	123(7)	176(9)	176(9)
	U_{12}	0	0	0	0	0	0
	U_{13}	36(4)	55(5)	42(7)	49(6)	66(7)	75(8)
	U_{23}	0	0	0	0	0	0

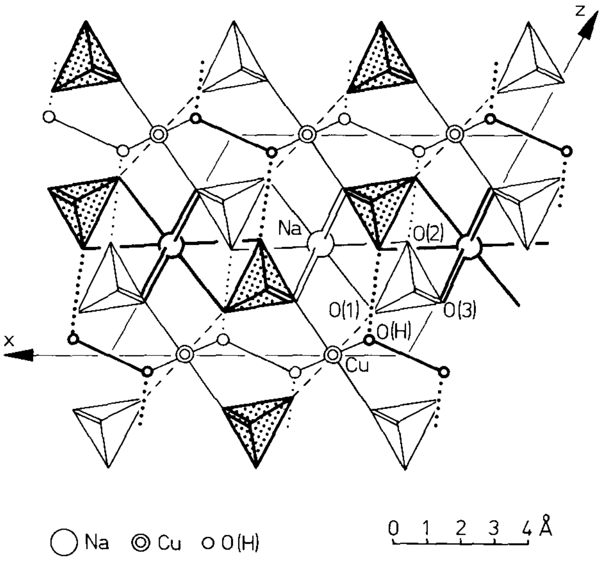

Fig. 1. Projection of the natrochalcite structure parallel [010]. Cu at $y = 1/4$ and $3/4$; Na, SO_4 and O(H): bold at $y = 1/2$, weak at $y = 0$. Na—O bonds, "short" Cu—O bonds and short hydrogen bonds: full lines; "long" Cu—O bonds: broken lines; long hydrogen bonds: dotted lines.

position 2(*b*), or (b) the true space group is *Cm* (cf. Tardy and Brègeault, 1974). In the latter case the refinements would have been made in a too highly symmetric space group. Such errors can become evident by a careful inspection of the parameters of the anisotropic thermal motion as obtained in the least-squares refinements. Table 2 shows that the U_{ii}'s have normal values, and also the axes of the thermal ellipsoids as derived from the U_{ij}'s show no conspicuous features. The maximum value of the quotient (longest axis)/(shortest axis) for any of the thermal ellipsoids is 2.0. It occurs for O(2) in the Rb—Se member; but it is very comforting that the largest axis is oriented approximately prependicular to the Se—O bond, while the shortest axis approximately coincides with this direction. In this connection it should be mentioned that for none of the O(1), O(2) and O(3) atoms the shortest axis of the thermal ellipsoid deviates greatly from the corresponding z—O direction. On this account, the parameters of the thermal motion do not give conclusive evidence for *Cm* being the true space group. We assume, therefore, that at least for the atoms Me^+, Cu, z, O and H(2) the structures should be described in space group *C*2/*m* within the errors of our determinations.

Figure 1 gives a projection of the natrochalcite structure parallel to [010]. It is clearly seen that the atomic arrangement is built from $[\mathrm{Cu}_2^{[4+2]}$

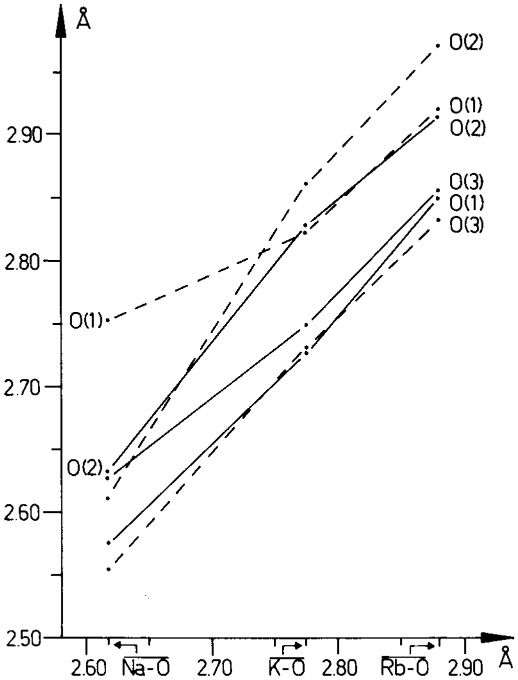

Fig. 2. Variation of the individual Me^+-O bond lengths with the average Me^+-O bond lengths. Full lines connect values of sulphates, broken lines of selenates. Weighted averages Me^+-O in the MeO_8 polyhedra are taken over the sulphate *and* the corresponding selenate. $\sigma(Me-O) \leq 0.003$ Å.

$(OH)(SO_4)_2 \cdot H_2O]^-$ sheets which are interconnected by Na^+ ions and $O(H)-O(2)$ hydrogen bonds. For further descriptions the reader is referred to Rumanova and Volodina (1958) and to Tardy and Brégeault (1974). We abstain here from presenting for the six compounds extensive lists with bond distances and bond angles, but rather concentrate the discussion on some changes of the structure type with the sizes of the Me^+ ions and of the zO_4 tetrahedra, as well as on the highly interesting hydrogen bond system.

The Me^+ ions are coordinated to each two O(1)'s and O(2)'s, and further to four O(3)'s. The MeO_8 polyhedra share two edges with two equivalent zO_4 tetrahedra. Figure 2 presents the individual $Me-O$ bond lengths as a function of the average $Me-O$ bond lengths. Especially conspicuous is that in the $Na-Se$ member $Na-O(1)$ is considerably longer than both $Na-O(2)$ and $Na-O(3)$; this means that we have here a transition to an octahedral six coordination. This is clearly correlated with a rotation of the zO_4 tetrahedron (see Fig. 3). An even more pronounced

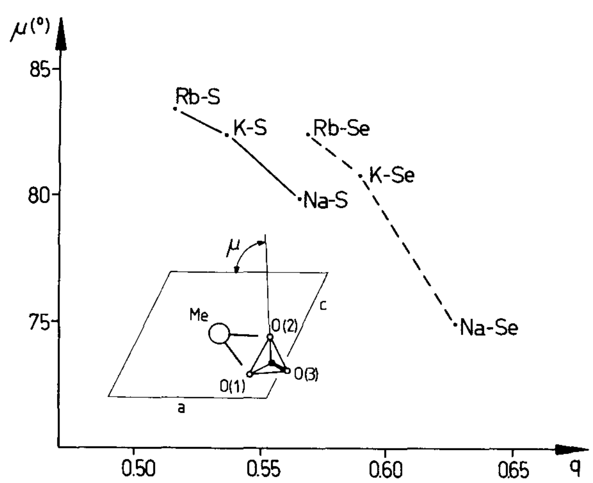

Fig. 3. Angle of rotation μ of the zO_4 tetrahedra as a function of q = (average z – O distance)/(average Me^+ – O distance for eight coordination). $\sigma(\mu) \leq 0.1°$.

example for this effect is offered by $NaZn_2(OH)(MoO_4)_2 \cdot H_2O$ with its large MoO_4 tetrahedron; the Na^+ ions adopt there a clear-cut six coordination (Clearfield et al., 1976).

Cu(II) has the usual [4 + 2] coordination. The variation of the Cu – O bond lengths with the sizes of the Me^+ ions and of the zO_4 tetrahedra is illustrated in Figure 4.

The bond lengths in the zO_4 tetrahedra are almost independent of the sizes of the Me^+ ions. The average values are (in Å): S – O(1) = 1.482(2), S – O(2) = 1.448(2), S – O(3) = 1.493(2); Se – O(1) = 1.646(2); Se – O(2) = 1.611(2), Se – O(3) = 1.654(2). The relatively short z – O(2)'s are correlated with the further coordination of O(2) to only one Me^+ (besides of being acceptor of a hydrogen bond), while O(1) is further coordinated to one Me^+ and two Cu's (with "long" Cu – O bonds), and O(3) to one Me^+ and one Cu (with a short Cu – O bond).

The change of the hydrogen bond lengths with the size of the Me^+ ions is shown in Figure 5. Both O(H) – H(1) – O(H) and O(H) – H(2)· · ·O(2) increase with increasing average Me^+ – O. The short hydrogen bond O(H) – H(1) – O(H) varies from 2.440(3) in the Na – S member to 2.588(5) Å in the Rb – Se member; it is always longer in the Se member than in the corresponding S member. The hydrogen bonds O(H) – H(2)· · ·O(2), the H atom of which was located in three members, vary greatly in length: from 2.695(2) Å in the Na – S member to 3.114(4) Å in the Rb – S member.

The very short hydrogen bonds O(H) – O(H) suggest that the formula of our compounds could also be written as $Me^+Cu_2(H_3O_2)(zO_4)_2$. This

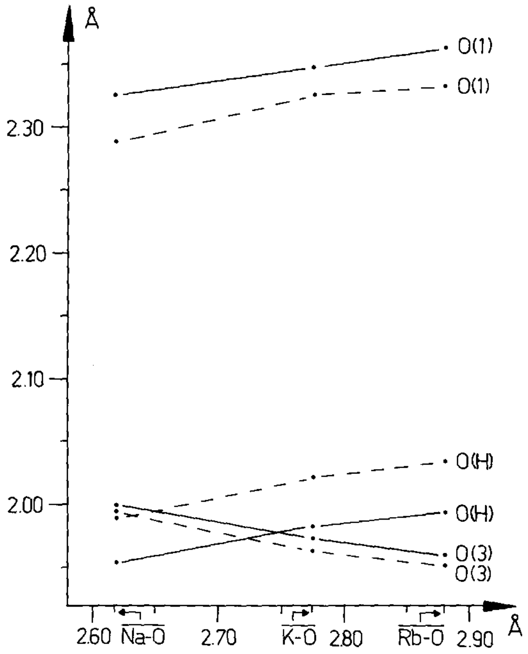

Fig. 4. Cu–O bond lengths as a function of average Me^+–O bond lengths. σ(Cu–O) ≤ 0.002 Å. For further explanations see Figure 2.

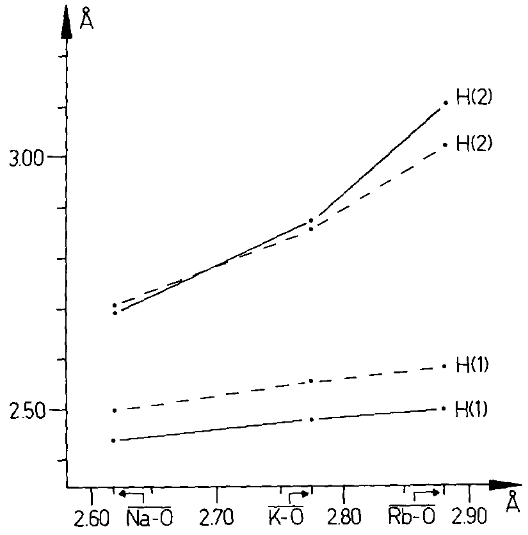

Fig. 5. Hydrogen bond lengths as a function of average Me^+–O. The ordinates give the O(H)–H(1)–O(H) and O(H)–H(2)···O(2) distances. σ(O–O) ≤ 0.005 Å. For further explanations see Figure 2.

formula would be in agreement with part of the chemical literature. Such hydrogen-oxygen configurations were described in crystallized complexes of transition metals with organic ligands, and they were found either isolated (bonded further by hydrogen bonds only) or – as in our compounds – via the oxygen atoms to metals. They were clearly formulated as (H_3O_2), or as ($H_3O_2^-$) anions (Abu-Dari et al., 1979; Ardon and Bino, 1983; Bino and Gibson, 1981, 1982 and 1984). The natrochalcite-type compounds seem to be the only purely inorganic representatives with H_3O_2 configurations known at present. For theoretical work on H_3O_2 groups see Newton and Ehrenson (1971), Kraemer and Diercksen (1972) and Hermansson (1985). – Neutron diffraction work would be promising for a further investigation of the hydrogen positions in our compounds, but it must await the growth of crystals of suitable size.

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