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Neutron Diffraction Study of the Hydrogen-Bond System in $Cu_2K(H_3O_2)(SO_4)_2$

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Abstract. $Cu_2K(H_3O_2)(SO_4)_2$, $M_r = 393{\cdot}34$, monoclinic, $C2/m$, $a = 8{\cdot}955\,(2)$, $b = 6{\cdot}265\,(1)$, $c = 7{\cdot}628\,(1)$ Å, $\beta = 117{\cdot}45\,(1)°$, $V = 379{\cdot}8$ Å^3, $Z = 2$, $D_x = 3{\cdot}440$ Mg m^{-3}, $\lambda = 0{\cdot}8307\,(5)$ Å, $\mu = 0{\cdot}08$ mm^{-1}, $F(000) = 141{\cdot}88$ for cell content, $T = 298$ K, $R = 0{\cdot}017$, $wR = 0{\cdot}011$ for 1285 single-crystal neutron reflections. The structure contains $H_3O_2^-$ groups with symmetry $2/m$, $O\cdots O = 2{\cdot}486\,(1)$ Å; the H atom at the center is split by 0·30 (1) Å. The two O atoms are each bonded to two Cu atoms and are further donors of a weak hydrogen bond of 2·878 (1) Å to an O atom of the sulfate group.

Introduction. The title compound was investigated previously with X-ray methods by Tardy & Brégeault (1974) and by Giester & Zemann (1987). They showed that it is isotypic with the Na member natrochalcite (Rumanova & Volodina, 1958) and – with the exception of the H atoms – located the atoms accurately; Giester & Zemann (1987) in addition determined approximate coordinates for some of the H atoms. The natrochalcite-type compounds are remarkable in that they can be considered to contain $H_3O_2^-$ groups (Zemann, 1986; Giester & Zemann, 1987, 1988; Giester, 1989). Such groups are well known from coordination compounds containing organic radicals (*cf.* Ardon & Bino, 1987) and were proposed by Ardon & Bino (1987) to occur also in a crystal species with formula previously written as $[(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(OH)]Br_3.2H_2O$ (Andersen, Nielsen & Petersen, 1984) on the basis of an O···O distance of only 2·45 Å in an OH—H_2O configuration. An isoelectronic $H_3F_2^+$ group with $F\cdots F = 2{\cdot}30\,(1)$ Å was recently reported to occur in $(H_3F_2)(As_2F_{11})$ by Mootz & Bartmann (1988). Only X-ray work seems to have been performed on such compounds until now. Therefore, it seemed interesting to investigate $Cu_2K(H_3O_2)(SO_4)_2$ by neutron diffraction to find the details of the hydrogen-bond system.

Experimental. Approximately 300 cm^3 of an unsaturated aqueous solution with K_2SO_4:$CuSO_4$ ~ 1:4 on a molecular basis were very slowly evaporated in a glass vessel at *ca* 330 K. Precipitation of green crystals of $Cu_2K(H_3O_2)(SO_4)_2$ began after two weeks, and in two months some of the crystals had grown to the required size.

The crystal used for the neutron measurements had dimensions ~1 × 3·5 × 3 mm. Data collection was performed on the four-circle diffractometer *P*110 at the Orphée reactor in Saclay, wavelength $\lambda = 0{\cdot}8307\,(5)$ Å. Lattice constants were taken from Giester & Zemann (1987). Data were collected up to $\sin\theta/\lambda = 0{\cdot}974$ Å^{-1}; $3 \leq 2\theta \leq 75°$, ω scans, and $75 \leq 2\theta \leq 108°$, $\omega/2\theta$ scans (35 steps, 2 s per step) of widths according to the instrumental resolution: $9–27\tan\theta + 40\tan^2\theta$; standard reflections ($0\bar{4}0$ and $\bar{8}03$) stable over 14 d within 1·3% (no decay or crystal movement); data-collection index range h: −17 to 17, k: −12 to 0, l: −14 to 14. Integrated intensities were determined from resolution adopted profile measurements of the peaks; background was determined by averaging the first and the last six steps on each side. $R_{int} = 0{\cdot}0135$. The 3444 measured reflections were averaged to give 1561 unique reflections; 1285 of them had $|F_o| \geq 3\sigma(|F_o|)$ and were used in the structure refinement.

The least-squares refinement (on F) with program *RFINE*4 (Finger & Prince, 1975) was started in space group $C2/m$ with the structural parameters of Giester & Zemann (1987) for the non-H atoms and H(2); H(1) was placed at position 2(*b*). Neutron scattering lengths: $b_K = 3{\cdot}7$, $b_{Cu} = 7{\cdot}6$, $b_S = 2{\cdot}85$, $b_O = 5{\cdot}75$, $b_H = -3{\cdot}72$ fm (*International Tables for X-ray Crystallography,* 1974). The refinement converged for 1285 reflections to $R = 0{\cdot}017$, $wR = 0{\cdot}011$, $w = 1/\sigma^2(F)$. The shifts of the non-H atoms as compared with the previous X-ray results were very minor. With the exception of H(1), the anisotropic displacement parameters did not show conspicuous features. For this H atom, the r.m.s. axes were 0·14, 0·14 and 0·22 Å, practically those of an elongated rotation

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Table 1. *Fractional atomic coordinates* (× 10^5, *e.s.d.'s in parentheses*) *and equivalent isotropic thermal parameters* (Å^2 × 8π^2)

$B_{eq} = (1/3)\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

		x	y	z	B_{eq}
K	2(*d*)	0	$\frac{1}{2}$	$\frac{1}{2}$	1·13
Cu	4(*f*)	$\frac{1}{4}$	$\frac{1}{4}$	0	0·63
S	4(*i*)	8005 (7)	0	28776 (8)	0·52
O(1)	4(*i*)	18600 (4)	0	18542 (5)	0·85
O(2)	4(*i*)	18462 (4)	0	49968 (5)	1·10
O(3)	8(*j*)	−2809 (3)	19442 (4)	22737 (3)	0·84
O(H)	4(*i*)	15621 (4)	$\frac{1}{2}$	7523 (5)	0·68
H(1)	4(*i*)†	1876 (38)	$\frac{1}{2}$	1207 (114)	1·63
H(2)	4(*i*)	20284 (10)	$\frac{1}{2}$	21942 (10)	1·93

† Occupancy: $\frac{1}{2}$.

ellipsoid [with the rotation axis inclined to the connection line O(H)···O(H) by ~25°]. Therefore, the structure was also refined with H(1) appropriately split at position 4(*i*) with occupancy one half. The least-squares refinement converged again smoothly, even when H(1) anisotropic displacement parameters were allowed to vary. Final R and wR were as before, and at the end of the refinement all parameter shifts were $< 10^{-3}$ of the e.s.d. Within the e.s.d.'s, all coordinates and anisotropic displacement parameters of the non-H atoms and of H(2) did not change. The connection line of the split H(1) atom deviated from the direction of the longest axis of the displacement ellipsoid in the preceeding refinement, *i.e.* with H(1) on position 2(*b*), by only 5°: in view of the relatively large error in the localization of the split H(1) a very good agreement. Positional and equivalent isotropic displacement parameters are listed in Table 1.*

Discussion. Table 2 presents interatomic distances and bond angles not involved in the hydrogen-bond system. These agree very well with the X-ray results of Tardy & Brégeault (1974) and of Giester & Zemann (1987). For a projection of the structure see, for example, Fig. 1 of Giester & Zemann (1987).

Table 2. *Bond distances* (Å) *and bond angles* (°) *not involved in the hydrogen-bond system*

E.s.d.'s are given in parentheses.

K—O(1)	2·7284 (3) 2 ×	O(1)—K—O(2)	51·26 (1) 2 ×	128·74 (1) 2 ×
—O(2)	2·8231 (3) 2 ×	—O(3)	68·73 (1) 4 ×	111·27 (1) 4 ×
—O(3)	2·7515 (2) 4 ×	O(2)—K—O(3)	75·14 (1) 4 ×	104·86 (1) 4 ×
		O(3)—K—O(3)	88·18 (1) 2 ×	91·82 (1) 2 ×
Cu—O(1)	2·3515 (2) 2 ×	O(1)—Cu—O(3)	90·85 (1) 2 ×	89·15 (1) 2 ×
—O(3)	1·9750 (2) 2 ×	—O(H)	95·67 (1) 2 ×	84·33 (1) 2 ×
—O(H)	1·9830 (2) 2 ×	O(3)—Cu—O(H)	89·74 (1) 2 ×	90·26 (1) 2 ×
S—O(1)	1·4807 (7) 1 ×	O(1)—S—O(2)	110·30 (4) 1 ×	
—O(2)	1·4472 (7) 1 ×	—O(3)	108·66 (2) 2 ×	
—O(3)	1·4908 (4) 2 ×	O(2)—S—O(3)	109·81 (2) 2 ×	
		O(3)—S—O(3)	109·58 (5) 1 ×	

Table 3. *Bond distances* (Å) *and bond angles* (°) *in the hydrogen-bond system*

E.s.d.'s are given in parentheses.

D—H···*A*	*D*···*A*	*D*—H	H···*A*	∠*D*—H···*A*
O(H)—H(1)···O(H)	2·487 (1)	1·096 (5)	1·392 (5)	178 (2)
O(H)—H(2)···O(2)	2·878 (1)	0·980 (1)	1·902 (1)	174·2 (3)
H(1)—O(H)—H(2)	107·7 (5) 1 ×	∠S—O(2)···H(2)		173·0 (3)
H(1)—O(H)—Cu	114·4 (2) 2 ×			
H(2)—O(H)—Cu	107·85 (4) 2 ×			
Cu—O(H)—Cu	104·34 (2) 1 ×			

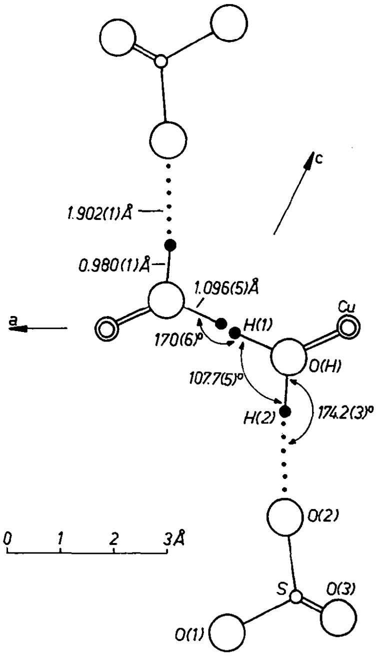

Fig. 1. Hydrogen-bonding system in projection parallel to [010].

Great progress was made, as expected, in finding the parameters of the H atoms. Table 3 and Fig. 1 give the geometry of the hydrogen-bond system for the model with H(1) split. The half-occupied H(1)'s are 0·023 (9) Å off the line connecting the two O(H) atoms; their mutual distance is 0·30 (1) Å. The main axes of the displacement ellipsoid are 0·11, 0·14 and 0·17 Å; it seems worth mentioning that the shortest axis is not approximately in the direction O(H)—H(1), but rather forms an angle of ~30° with this direction. For H(2) the r.m.s. axes of the displacement ellipsoid measure 0·13, 0·17 and 0·17 Å, *i.e.* we are dealing with a flattened rotation ellipsoid; its shortest axis almost coincides with the bond direction O(H)—H(2). The geometry of the hydrogen-bond system in $Cu_2K(H_3O_2)(SO_4)_2$ agrees with general expectations from the literature (*e.g.* Olovsson & Jönsson, 1976; Emsley, 1980; Emsley, Jones & Lucas, 1981; Chiari & Ferraris, 1982;

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* Lists of structure amplitudes and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52218 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Ferraris, Fuess & Joswig, 1986; Ardon & Bino, 1987).

From X-ray investigations it is well known that among the sulfates and selenates of natrochalcite type, the hydrogen-bond lengths vary considerably: O(H)···O(H) = 2·44 to 2·61 Å, O(H)···O(2) = 2·70 to 3·11 Å (Giester & Zemann, 1987, 1988; Giester, 1989). Neutron work on further members would provide information on the influence of the chemistry and stereochemistry of the compounds on the geometry of the hydrogen-bond system: a problem of considerable interest. Such investigations have, however, to await the growth of crystals of suitable size.

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Structure of the Trivanadate TlV_3O_8

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Abstract. Thallium trivanadate, $M_r = 485·2$, monoclinic, $P2_1/m$, $a = 7·780\,(2)$, $b = 8·423\,(3)$, $c = 4·993\,(1)$ Å, $\beta = 96·48\,(2)°$, $V = 325·2$ Å^3, $Z = 2$, $D_x = 4·957\ \mathrm{g\,cm^{-3}}$, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 2·90\ \mathrm{cm^{-1}}$, $F(000) = 428$, $T = 293$ K, $R = 0·049$ for 2032 unique observed reflections. Full isotypy with the known CsV_3O_8 structure is found, but e.s.d. values are about four times better. The structure is built from $V(2)O_5$ square-pyramidal units; these entities share a common edge in order to give condensed $V_2O_8^{6-}$ polyanions. Their corner sharing leads to infinite chains $(V_2O_7^{4-})_\infty$ lying along the *b* axis. The V(1) atoms occupy an octahedral coordination between these chains; the result is a packing of corrugated sheets $(V_3O_8^-)_\infty$ parallel to the (100) plane.

Introduction. The hydrothermal treatment of a mixture of $V_2O_5 + V_2O_3 + Tl_2CO_3 + H_2O$ (mole ratio 0·5/0·12/0·38/99) at 473 K during 24 h in a sealed glass tube leads to three phases: (*a*) microcrystalline tetragonal phase $Tl_2V^{IV}V_2^{V}O_8$ (Tudo & Jolibois, 1971; Théobald & Théobald, 1984); (*b*) colorless needles of the metavanadate $TlVO_3$ (Ganne, Piffard & Tournoux, 1974; Howard & Evans, 1960); (*c*) red-orange crystals. The crystallographic characterization of the last crystals allowed us to deduce first the composition TlV_3O_8 and second their full isotypy with the homologous K, Rb, Cs and NH_4 compounds (Kelmers, 1961; Howard, Evans & Block, 1966). This analogy was suggested on the grounds of powder data (Tudo & Jolibois, 1971); these last authors obtained TlV_2O_8 as a red-orange powder by reaction at 643 K of a mixture of Tl_2CO_3 and $3V_2O_5$ under inert atmosphere; we show that their published powder data are in accordance with the calculated intensities obtained from our single-crystal study.

Experimental. [001]-elongated prismatic crystal with ±(010), ±(410) lateral faces; 0·15 × 0·07 × 0·06 mm. Siemens AED2 four-circle diffractometer (graphite monochromator); 26 reflections used for measuring