The Stereochemistry of Tutton's Salts $X_2[M(H_2O)_6](YO_4)_2$

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Neutron structure determinations have been made of Tutton's salts, $X_2[M(H_2O)_6]$ $(YO_4)_2$, where $Y = Se$, $X = K^+$, $M = Cu^{2+}$; $Y = S$, $X = K^+$, $M = Ni^{2+}$, Cu^{2+}, Zn^{2+}; $X = Rb^+$, Cs^+, $M = Cu^{2+}$. This work has shown that there are extensive hydrogen networks with almost linear hydrogen bonds from $[M(H_2O)_6]^{2+}$ to $(YO_4)^{2-}$. The (H . . .. O) distance increases in the Cu^{2+} series for $X = K^+$ to Cs^+ but there is no difference for the potassium copper salts when $Y = Se$ or S. Three different distorted $[M(H_2O)_6]^{2+}$ octahedra were found in the series (orthorhombic, tetragonal with two long and four short, or four long and two short bonds). The interatomic distances from X^+ to the neighboring O in a distorted XO_8^+ dodecahedron increases with increased cation size, implying that the X^+ polyhedron is maintaining its shape.

Current interest in the EPR (*1–3*), Raman, and infrared (*4*) spectra of Tutton's salts has prompted us to critically examine our neutron structure determinations of these compounds (*5–11*).

The interatomic distances and angles for relevant Tutton's salt compounds determined by this group are in Table I. The hydrogen bonding scheme used is based (*12*) on an arbitrary criterion, namely, that "a hydrogen bond is said to exist when the distance between the atoms H and O, $r(H \ldots . O)$, is shorter by at least 0.2 Å than the sum of the accepted van der Waal's contact radii r_H and r_O," with O a suitable hydrogen bond acceptor such as oxygen. Thus for a hydrogen bond to exist

$$r(H \cdots O)_{H-bond} < r_H + r_O - 0.2 \ (Å).$$

Using Pauling's values (*13*), an acceptable distance for a hydrogen-to-oxygen interaction is 2.4 Å. Also, the ideal geometry of the bond (O–H $\cdots$ O) is linear, although large deviations are possible.

There are extensive hydrogen networks in all Tutton's salts with almost linear hydrogen bonds from the $[M(H_2O)_6]^{2+}$ distorted octa-

hedral cation to the acceptor O atoms of the YO_4^{2-} tetrahedral anion. In all cases, the M–O(9) bond is the shortest distance. The (H $\cdots$ O) distance does increase in the Cu^{2+} series when comparing the K^+, Rb^+, and Cs^+ salts. However, there is no significant difference comparing the results of the potassium copper salts when the anion is either sulfate or selenate.

There is no significant difference for all the interatomic distances and angles between the nickel and zinc salts but a large difference when compared to the copper one. There is a tetragonally distorted octahedron around the metal with four long and two short bonds [M–O(9)]. This is accommodated in the packing with the [H $\cdots$ O] interactions being the longest for O(7) and shortest for O(8).

In all copper salts except $K_2[Cu(H_2O)_6](SeO_4)_2$ and $(NH_4)_2[Cu(H_2O)_6]$ $(SO_4)_2$, the Cu–O(8) bond is the longest distance. It should be noted when comparing the first compound with the corresponding sulfate, that the bonds appear to adjust so as to give an approximately tetrahedral environment around the water oxygen. The angle between

TABLE IA

GEOMETRICAL FEATURES OF THE HYDROGEN BONDS AROUND THE O(7)–H(15), H(16) WATER MOLECULE
BELONGING TO THE $M(OH_2)_6$ POLYHEDRA (DISTANCES IN Å, ANGLES IN DEGREES)

Compound	O–H	H····O	<O–H····O	M–O(7)	X–O(7)
		O(7)–H(15)····O(5)			
$K_2Cu(H_2O)_6(SeO_4)_2$	0.958 (4)	1.924 (4)	168 (1)	2.297 (2)	2.911 (4)
$K_2Cu(H_2O)_6(SO_4)_2$	0.976 (6)	1.775 (6)	171 (1)	2.069 (2)	3.096 (4)
$K_2Ni(H_2O)_6(SO_4)_2$	0.980 (3)	1.813 (3)	171 (1)	2.078 (2)	3.105 (4)
$K_2Cu(H_2O)_6(SO_4)_2$	0.976 (6)	1.775 (6)	171 (1)	2.069 (2)	3.096 (4)
$K_2Zn(H_2O)_6(SO_4)_2$	0.962 (9)	1.825 (9)	171 (1)	2.133 (4)	3.093 (5)
$K_2Cu(H_2O)_6(SO_4)_2$	0.976 (6)	1.775 (6)	171 (1)	2.069 (2)	3.096 (4)
$Rb_2Cu(H_2O)_6(SO_4)_2$	0.968 (6)	1.758 (6)	171 (1)	2.031 (3)	3.234 (6)
$Cs_2Cu(H_2O)_6(SO_4)_2$	1.01 (1)	1.70 (1)	171 (1)	2.004 (4)	3.424 (5)
		O(7)–H(16)····O(6)			
$K_2Cu(H_2O)_6(SeO_4)_2$	0.969 (5)	1.867 (5)	168 (1)	2.297 (2)	2.911 (4)
$K_2Cu(H_2O)_6(SO_4)_2$	0.974 (6)	1.812 (6)	172 (1)	2.069 (2)	3.096 (4)
$K_2Ni(H_2O)_6(SO_4)_2$	0.965 (4)	1.838 (4)	171 (1)	2.078 (2)	3.105 (4)
$K_2Cu(H_2O)_6(SO_4)_2$	0.974 (6)	1.812 (6)	172 (1)	2.069 (2)	3.096 (4)
$K_2Zn(H_2O)_6(SO_4)_2$	0.971 (11)	1.834 (11)	171 (1)	2.133 (4)	3.093 (5)
$K_2Cu(H_2O)_6(SO_4)_2$	0.974 (6)	1.812 (6)	172 (1)	2.069 (2)	3.096 (4)
$Rb_2Cu(H_2O)_6(SO_4)_2$	0.971 (7)	1.792 (7)	172 (1)	2.031 (3)	3.234 (4)
$Cs_2Cu(H_2O)_6(SO_4)_2$	0.97 (2)	1.75 (2)	173 (1)	2.004 (4)	3.424 (5)

TABLE IB

GEOMETRICAL FEATURES OF THE HYDROGEN BONDS AROUND THE O(8)–H(17), H(19) WATER MOLECULE
BELONGING TO THE $M(OH_2)_6$ POLYHEDRA. THE ACCEPTOR OXYGEN ATOMS ARE FROM THE YO_4^{2-}-TETRAHEDRA

Compound	O–H	H····O	<O–H····O	M–O (8)	X–O (8)
		O(8)–H(17)····O(4)			
$K_2Cu(H_2O)_6(SeO_4)_2$	0.976 (4)	1.680 (4)	179 (2)	2.044 (2)	3.020 (4)
$K_2Cu(H_2O)_6(SO_4)_2$	0.979 (6)	1.734 (6)	178 (2)	2.278 (2)	2.872 (4)
$K_2Ni(H_2O)_6(SO_4)_2$	0.974 (4)	1.684 (4)	178 (2)	2.087 (2)	2.952 (4)
$K_2Cu(H_2O)_6(SO_4)_2$	0.979 (6)	1.734 (6)	178 (2)	2.278 (2)	2.872 (4)
$K_2Zn(H_2O)_6(SO_4)_2$	0.98 (1)	1.70 (1)	179 (2)	2.126 (5)	2.940 (6)
$K_2Cu(H_2O)_6(SO_4)_2$	0.979 (6)	1.734 (6)	178 (2)	2.278 (2)	2.872 (4)
$Rb_2Cu(H_2O)_6(SO_4)_2$	0.971 (5)	1.773 (5)	175 (1)	2.307 (3)	3.034 (4)
$Cs_2Cu(H_2O)_6(SO_4)_2$	0.99 (2)	1.80 (2)	173 (1)	2.315 (5)	3.210 (5)
		O(8)–H(18)····O(6)			
$K_2Cu(H_2O)_6(SeO_4)_2$	1.001 (4)	1.719 (4)	175 (1)	2.044 (2)	3.020 (4)
$K_2Cu(H_2O)_6(SO_4)_2$	0.960 (6)	1.805 (6)	177 (1)	2.278 (3)	2.872 (4)
$K_2Ni(H_2O)_6(SO_4)_2$	0.987 (4)	1.755 (4)	173 (1)	2.087 (2)	2.952 (4)
$K_2Cu(H_2O)_6(SO_4)_2$	0.960 (6)	1.805 (6)	177 (1)	2.278 (2)	2.872 (4)
$K_2Zn(H_2O)_6(SO_4)_2$	1.002 (9)	1.746 (9)	175 (1)	2.126 (5)	2.940 (4)
$K_2Cu(H_2O)_6(SO_4)_2$	0.960 (6)	1.805 (6)	177 (1)	2.278 (2)	2.872 (4)
$Rb_2Cu(H_2O)_6(SO_4)_2$	0.976 (6)	1.786 (6)	175 (1)	2.307 (3)	3.034 (5)
$Cs_2Cu(H_2O)_6(SO_4)_2$	0.98 (2)	1.80 (2)	175 (1)	2.315 (5)	3.210 (5)

TABLE IC

GEOMETRICAL FEATURES OF THE HYDROGEN BONDS AROUND THE O(9)–H(19), H(20) WATER MOLECULE BELONGING TO THE $M(OH_2)_6$ POLYHEDRA. NO X–O(9) INTERACTION OCCURS

Compound	O–H	H····O	<O–H····O	M–O(9)
		O(9)–H(19)····O(5)		
$K_2Cu(H_2O)_6(SeO_4)_2$	0.980 (4)	1.700 (4)	174 (1)	1.936 (2)
$K_2Cu(H_2O)_6(SO_4)_2$	0.976 (6)	1.697 (6)	173 (1)	1.943 (2)
$K_2Ni(H_2O)_6(SO_4)_2$	0.959 (4)	1.767 (4)	169 (1)	2.021 (2)
$K_2Cu(H_2O)_6(SO_4)_2$	0.976 (6)	1.697 (6)	173 (1)	1.943 (2)
$K_2Zn(H_2O)_6(SO_4)_2$	0.998 (11)	1.736 (11)	171 (1)	2.032 (4)
$K_2Cu(H_2O)_6(SO_4)_2$	0.976 (6)	1.697 (6)	173 (1)	1.943 (2)
$Rb_2Cu(H_2O)_6(SO_4)_2$	0.972 (6)	1.724 (6)	172 (1)	1.957 (3)
$Cs_2Cu(H_2O)_6(SO_4)_2$	0.95 (2)	1.77 (2)	170 (1)	1.966 (5)
		O(9)–H(20)····O(3)		
$K_2Cu(H_2O)_6(SeO_4)_2$	1.003 (4)	1.658 (4)	172 (1)	1.936 (2)
$K_2Cu(H_2O)_6(SO_4)_2$	0.983 (5)	1.681 (5)	172 (1)	1.943 (2)
$K_2Ni(H_2O)_6(SO_4)_2$	0.984 (3)	1.681 (3)	170 (1)	2.021 (2)
$K_2Cu(H_2O)_6(SO_4)_2$	0.983 (5)	1.681 (5)	172 (1)	1.943 (2)
$K_2Zn(H_2O)_6(SO_4)_2$	0.96 (1)	1.69 (1)	171 (1)	2.032 (4)
$K_2Cu(H_2O)_6(SO_4)_2$	0.983 (5)	1.681 (5)	172 (1)	1.943 (2)
$Rb_2Cu(H_2O)_6(SO_4)_2$	0.986 (6)	1.698 (6)	170 (1)	1.957 (3)
$Cs_2Cu(H_2O)_6(SO_4)_2$	1.01 (1)	1.70 (1)	171 (1)	1.966 (5)

M–O bond and the plane of the water molecule remains approximately constant [SO_4, M–O(7), 129°; M–O(8), 128°; SeO_4, M–O(7),125°; M–O(8), 124°]. However, the expected angle between the bond and the plane in a tetrahedral system is 120°. Thus, even with a significant change in bond length, the distorted tetrahedral environment remains constant, and the O–H····O angle is almost linear. The approximately tetrahedral arrangement of water with the metal and hydrogen bond links indicate that sp^3 hybridization is likely to be important.

It has already been suggested (8) that probably a better way to explain the results is in terms of the packing of the three different polyhedra, $(YO_4)^{2-}$, $[M(H_2O)_6]^{2+}$, XO_8^+.

Although there are apparent distortions in $(SO_4)^{2-}$ tetrahedra, this is probably due to a technical difficulty involved in determining the exact location of the sulfur atom using neutron diffraction data. No distortion was found with the $(SeO_4)^{2-}$.

There are different types of $[M(H_2O)_6]^{2+}$ octahedra:

(a) orthorhombic distortion with three pairs of different bond lengths;

(b) tetragonal distortion with

(i) two long and two short bonds,

(ii) four long and two short bonds (nickel and zinc salts).

The first two cases occur with the copper salts. It has been recognized (14) that "... the ligand field near ... the Cu^{2+} ion ... is not dependent on the six neighbouring water dipoles alone but also upon how the more distant neighbours are situated ...." In the last case, the difference between M–O bond distances in the nickel salts is probably due to the increased transition metal radius.

Table II gives the eight closest univalent cation–oxygen distances. These distances are of the same order as those found (15) in organic complexes with alkali metal ions. Most of these may be considered as "lattice compounds" because they do not necessarily persist

TABLE II

THE CLOSEST NEIGHBORS AND DISTANCES TO THE X CATION[a]

$X \cdots O$ (Å)	$X = K^+$	$X = Rb^+$	$X = Cs^+$
	$X_2Cu(H_2O)_6(SO_4)_2$		
$X \cdots O(7)A$ (water)	3.097 (4)	3.234 (4)	3.424 (6)
$\cdots O(8)B$ (water)	2.871 (4)	3.034 (4)	3.210 (5)
$\cdots O(3)C$	2.900 (4)	2.990 (4)	3.110 (5)
$\cdots O(6)D2$	2.830 (4)	2.960 (4)	3.118 (5)
$\cdots O(3)D1$	2.976 (4)	3.052 (4)	3.170 (5)
$\cdots O(4)D1$	2.879 (5)	3.049 (4)	3.226 (5)
$\cdots O(5)E$	2.787 (4)	2.939 (4)	3.164 (5)
$\cdots O(4)E$	3.141 (5)	3.064 (4)	3.189 (5)
Crystal ion radii (12)	1.33	1.48	1.69

$K \cdots O$ (Å)	$M = Ni^{2+}$	$M = Cu^{2+}$	$M = Zn^{2+}$
	$K_2M(H_2O)_6(SO_4)_2$		
$K \cdots O(7)A$ (water)	3.105 (4)	3.097 (4)	3.093 (5)
$\cdots O(8)B$ (water)	2.952 (4)	2.871 (4)	2.940 (6)
$\cdots O(3)C$	2.876 (4)	2.900 (4)	2.891 (5)
$\cdots O(6)D2$	2.823 (4)	2.830 (4)	2.829 (5)
$\cdots O(3)D1$	2.909 (4)	2.976 (4)	2.931 (5)
$\cdots O(4)D1$	2.952 (4)	2.879 (5)	2.942 (5)
$\cdots O(5)E$	2.716 (4)	2.787 (4)	2.712 (5)
$\cdots O(4)E$	3.254 (4)	3.141 (4)	3.255 (5)
M ion radii	0.84	0.87	0.885

$K \cdots O$ (Å)	$YO_4^{2-} = SO_4^{2-}$	$YO_4^{2-} = SeO_4^{2-}$
	$K_2Cu(H_2O)_6(YO_4)_2$	
$K \cdots O(7)A$ (water)	3.097 (4)	2.911 (4)
$\cdots O(8)B$ (water)	2.871 (4)	3.020 (4)
$\cdots O(3)C$	2.900 (4)	2.833 (4)
$\cdots O(6)D2$	2.830 (4)	2.793 (4)
$\cdots O(3)D1$	2.976 (4)	2.992 (4)
$\cdots O(4)D1$	2.879 (5)	2.973 (4)
$\cdots O(5)E$	2.787 (4)	2.743 (4)
$\cdots O(4)E$	3.141 (4)	3.486 (4)

[a] Oxygens are labeled as in Ref. (8–10). Atoms with different letters belong to different polyhedra. The atoms labeled $D1$ and $D2$ belong to polyhedra related by a unit translation.

in solution." In the cases where the complexing molecule provides "all the ligating atoms for the cation," "the cation is often anhydrous ..." with "... the outside of the complex consisting of lipophilic groups." The complex may form or dissociate rapidly in solution, but the coordinated species may be observed spectroscopically.

The XO_8^+ unit is a distorted dodecahedron. In the alkali series, the interatomic distances from X^+ to the neighboring O increases with increased cation size, implying that the X^+ polyhedron or cage maintains its shape. The polyhedron is made up of oxygens from two different $[M(H_2O)_6]^{2+}$ octahedra, two monodentate from different $[YO_4]^{2-}$ tetrahedra, and

two bidentate from different tetrahedra. If the bonding about water uses sp^3 hybrid orbitals, the lone pair of electrons are directed towards X^+. The atom, O(9), with the consistently short M–O bond length is not involved in the X^+ cage.

Other similar systems have been studied (16, 17), where $(YO_4)^{2-} = (BeF_4)^{2-}$ and $(CrO_4)^{2-}$.

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