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The Structures of Tutton's Salts. I. Diammonium Hexaaquamagnesium(II) Sulfate

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Abstract. The crystal structure of the title compound at 295 K was refined using both neutron and X-ray data. $[NH_4]_2[Mg(H_2O)_6](SO_4)_2$, $M_r = 359{\cdot}28$, monoclinic, $P2_1/a$, $a = 9{\cdot}316$ (3), $b = 12{\cdot}596$ (6), $c = 6{\cdot}198$ (2) Å, $\beta = 107{\cdot}09$ (3)°, $V = 695{\cdot}22$ Å^3 (X-ray results), $Z = 2$, $D_x = 1{\cdot}723$ Mg m^{-3}, $F(000) = 380$. X-ray data: Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}496$ mm^{-1}, $R = 0{\cdot}065$ for 7212 reflections. Neutron data: $\lambda = 0{\cdot}9891$ Å, $\mu = 0{\cdot}21$ mm^{-1}, $R = 0{\cdot}041$ for 1372 reflections. Covalent bond lengths in the structure are affected significantly by interactions between neighbouring groups. The differences between the neutron and X-ray structures also vary with the bonding environment, providing another measure of the strengths of these interactions.

Introduction. The title compound is a member of the isomorphous series $(NH_4)_2M^{II}(SO_4)_2(H_2O)_6$, known as Tutton's salts. M is a divalent metal. The structural characteristics of the series, including details of the hydrogen-bond network, are described by Montgomery & Lingafelter (1966). The magnesium member, with $M = \mathrm{Mg}$, is a convenient reference system, with which the complexes containing heavier metals may be compared. The X-ray scattering for magnesium is strong enough to yield reliable thermal parameters, but not so large as to preclude a study of the effect of hydrogen bonding on the electron density near the H nuclei. The bias in the X-ray positions, revealed by comparison with a neutron diffraction structure, indicates a local dipole component in the redistribution of electron density due to bonding. Neutron and X-ray data were collected, and the structures refined with these data to study these local dipole terms, as the first stage of the study of the electron density. Previous structural work on the magnesium complex is described by Montgomery & Lingafelter (1964).

Experimental. Crystals by evaporation of a solution containing stoichiometric quantities of ammonium and magnesium sulfates in water. Neutron measurements at 295 K with neutrons of wavelength $\lambda = 0{\cdot}9891$ Å on the 4-circle diffractometer at the HIFAR reactor at the Australian Atomic Energy Commission Research Establishment at Lucas Heights, New South Wales. Crystal volume 46·0 mm^3, 14 faces. Neutron cell dimensions determined by least-squares fit to the angular settings of 30 reflections fully centred in the counter aperture: $a = 9{\cdot}316$ (2), $b = 12{\cdot}580$ (4), $c = 6{\cdot}202$ (1) Å, $\beta = 107{\cdot}094$ (5)°.

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2865 intensities measured using an ω–2θ scan reduced by statistical averaging to 1447 unique reflections. $0 \le h \le 11$, $0 \le k \le 14$, $-7 \le l \le 7$; $0{\cdot}07 < (\sin\theta)/\lambda < 0{\cdot}66$ Å^{-1}. 75 with negative measured values classed as 'less-thans' during structure refinement. Standard $\bar{4}04$ reflection repeated after 26 other measurements, with 5% long-term variation. Data corrected for absorption using Gaussian integration with $\mu = 0{\cdot}21$ mm^{-1}, calculated from coefficients by Melkonian (1949) for H and those by Bacon (1975) for the remaining atoms. Transmission-factor range 0·37–0·63. $\sigma(I)$ estimated from counting statistics and probable error in the absorption correction, modified where necessary from a comparison of equivalent reflections. Data reduction programs by Elcombe, Cox, Pryor & Moore (1971). Neutron form factors from *International Tables for X-ray Crystallography* (1974). Parameters determined by full-matrix least-squares minimization of $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(|F_o|)$. Coordinates for atoms in general positions, anisotropic thermal parameters, a scale factor and an isotropic extinction coefficient refined until $S = 1{\cdot}35$, $R = 0{\cdot}041$, $wR = 0{\cdot}031$, largest shift $< 0{\cdot}1\sigma$, $r^* = 0{\cdot}0084$ (1) as in Larson (1970).

X-ray diffractometry: Nicolet $P\bar{1}$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Crystal volume 0·025 mm^3. Cell dimensions from 11 reflections with $11 < 2\theta < 37°$. 26 023 intensities measured using an ω–2θ scan reduced to 7212 unique reflections in the range $(\sin\theta)/\lambda < 1{\cdot}075$ Å^{-1}, $-19 \le h \le 19$, $0 \le k \le 27$, $0 \le l \le 13$. Three Friedel pairs of reflections (400, 080 and 004) measured as standards every 40 reflections. Variation of intensities for these standards during data collection of 7, 10 and 8% respectively, the major part being due to long-term drift in beam intensity. Absorption corrections evaluated using Gaussian integration with $\mu = 0{\cdot}496$ mm^{-1}. $R_{\rm int} = 0{\cdot}011$. Transmission-factor range 0·87–0·91. $\sigma(I)$ determined following the procedure for the neutron data.

Atomic scattering factors for H taken from Stewart, Davidson & Simpson (1965) and for C, Mg, N, O and S with dispersion corrections from *International Tables for X-ray Crystallography* (1974). Isotropic thermal parameters for H atoms and other parameters as in the neutron analysis refined by full-matrix least squares until $S = 2{\cdot}01$, $R = 0{\cdot}065$, $wR = 0{\cdot}029$, largest shift $< 0{\cdot}1\sigma$. $r^* = 0{\cdot}010$ (1) as in Larson (1970). Difference density range $-0{\cdot}59 < \Delta\rho < 0{\cdot}55$ e Å^{-3}. Absorption and structure refinement programs from the *XRAY76* system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).†

Discussion. Atomic positions are listed in Table 1, with bond lengths and angles in Table 2. Other distances and angles relevant to the hydrogen-bond network are given in Table 3. A description of the hydrogen-bond network is given by Montgomery & Lingafelter (1966).

Whereas the sulfate O(3), O(5) and O(6) atoms are each involved in three hydrogen bonds, O(4) is involved in two, one of which is the weaker member of a bifurcated hydrogen bond *via* H(13). The shorter length of the S(2)—O(4) bond, compared with S(2)—O(3), S(2)—O(5) and S(2)—O(6), is attributable to this weaker involvement of O(4) in hydrogen bonding.

The hydrogen-bond network around the ammonium group is also unsymmetrical, the hydrogen-bond lengths being unequal and H(13) being involved in the bifurcated hydrogen bond. Although the bond-length trend is analogous to that for the sulfate group, the differences in length have lower significance. A detailed discussion of the ammonium group geometry is deferred until more neutron structures are available.

The X-ray and neutron structures are compared in Table 4. The N-atom positions do not differ appreciably, as expected in view of the tetrahedral coordination of this atom. The larger differences for S(2) are attributable to the low scattering power for sulfur, which restricts the precision of the neutron diffraction position for this atom.

The largest differences involve the H atoms. The water H atoms have a greater range of displacements than the ammonium H atoms. These displacements have an inverse correlation with covalent-bond length, *i.e.* the longer the O—H bond, the smaller the difference between the neutron and X-ray positions. Thus the hydrogen-bond interaction, which lengthens the O—H bond, also reduces the magnitude of the dipole component of the density near the H nucleus.

The mean lengths of the displacements, 0·165 and 0·217 Å for the N—H and O—H bonds respectively, are virtually identical to the differences in N—H and O—H bond lengths, 0·162 and 0·216 Å, because the displacement vectors are almost antiparallel to the N—H and O—H vectors.

The displacements for the O atoms are much smaller, and of limited significance in the case of the sulfate O(3), O(5) and O(6) atoms. Those for the water O(7), O(8) and O(9) atoms have similar magnitudes and are larger than those for the sulfate O atoms. The displacement vectors are approximately parallel to the external bisector of the H—O—H angle.

The hexaaqua moiety departs more strongly from the ideal geometry than either the sulfate or the ammonium groups. This is partly due to the electropositive character of the Mg atom. With its high coordination and low electron density, the valence shell deforms more readily than those for the S and N atoms. The lengths of the bonds to the Mg atom are correspondingly more susceptible to change due to variation

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44485 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	Neutron (× 10^4)				X-ray (× 10^5 N, Mg, O, S; × 10^3 H)			
	x	*y*	*z*	B_{eq}(Å^2)	*x*	*y*	*z*	B_{eq}(Å^2)
Mg	0	0	0	1·26	0	0	0	1·46
S(2)	4046 (2)	1396 (2)	7430 (3)	1·53	40464 (2)	13948 (1)	74256 (3)	1·60
O(3)	4039 (2)	2295 (1)	5898 (2)	2·53	40411 (7)	22954 (4)	58976 (9)	2·83
O(4)	5463 (2)	825 (1)	7873 (3)	3·15	54670 (6)	8230 (5)	78785 (12)	3·42
O(5)	2807 (1)	674 (1)	6282 (2)	2·00	28066 (5)	6732 (4)	62795 (9)	2·10
O(6)	3821 (2)	1785 (1)	9546 (2)	2·27	38211 (6)	17874 (4)	95470 (9)	2·54
O(7)	1694 (1)	1045 (1)	1669 (2)	2·11	16848 (6)	10443 (5)	16657 (10)	2·26
O(8)	−1607 (1)	1096 (1)	303 (2)	1·94	−16000 (6)	10941 (4)	3128 (10)	2·27
O(9)	−20 (2)	−691 (1)	2982 (2)	1·91	−150 (6)	−6898 (4)	29781 (9)	2·13
N(10)	1316 (1)	3510 (1)	3611 (1)	2·45	13158 (9)	35085 (6)	36101 (13)	2·51
H(11)	584 (4)	3360 (3)	2086 (5)	4·95	69 (1)	337 (1)	229 (2)	4·26
H(12)	2201 (4)	3014 (3)	4046 (6)	4·43	205 (1)	306 (1)	395 (2)	3·47
H(13)	766 (5)	3421 (4)	4752 (6)	6·81	85 (1)	346 (1)	452 (2)	4·15
H(14)	1677 (4)	4263 (3)	3606 (5)	4·74	159 (1)	413 (1)	363 (2)	3·16
H(15)	2182 (3)	918 (2)	3257 (4)	3·14	205 (1)	93 (1)	288 (2)	2·73
H(16)	2450 (3)	1251 (2)	973 (4)	3·18	224 (1)	121 (1)	117 (2)	2·86
H(17)	−2652 (2)	973 (2)	−523 (4)	2·94	−239 (1)	100 (1)	−36 (2)	3·44
H(18)	−1419 (3)	1839 (2)	55 (4)	2·98	−146 (1)	171 (1)	10 (2)	3·28
H(19)	−942 (3)	−614 (2)	3389 (4)	3·50	−71 (1)	−65 (1)	329 (2)	3·67
H(20)	284 (3)	−1427 (2)	3290 (4)	2·86	21 (1)	−131 (1)	325 (2)	3·08

Table 2. *Bond lengths* (Å) *and angles* (°)

	X-ray	Neutron		X-ray	Neutron
Mg–O(7)	2·075 (1)	2·082 (1)	O(7)–Mg–O(8)	89·52 (4)	89·77 (6)
Mg–O(8)	2·080 (1)	2·085 (2)	O(7)–Mg–O(9)	91·44 (4)	91·56 (6)
Mg–O(9)	2·044 (1)	2·048 (2)	O(8)–Mg–O(9)	90·13 (3)	90·18 (6)
S(2)–O(3)	1·477 (1)	1·477 (3)	O(3)–S(2)–O(4)	109·54 (4)	109·41 (18)
S(2)–O(4)	1·460 (1)	1·457 (3)	O(3)–S(2)–O(5)	108·02 (4)	107·91 (14)
S(2)–O(5)	1·477 (1)	1·477 (3)	O(3)–S(2)–O(6)	109·83 (5)	110·03 (17)
S(2)–O(6)	1·476 (1)	1·472 (3)	O(4)–S(2)–O(5)	108·99 (4)	108·87 (18)
N(10)–H(11)	0·870 (12)	1·008 (3)	O(4)–S(2)–O(6)	110·62 (4)	110·75 (14)
N(10)–H(12)	0·867 (12)	1·005 (4)	O(5)–S(2)–O(6)	109·80 (4)	109·82 (17)
N(10)–H(13)	0·809 (15)	0·994 (5)	H(11)–N(10)–H(12)	111·2 (11)	114·2 (3)
N(10)–H(14)	0·820 (12)	1·007 (4)	H(11)–N(10)–H(13)	106·8 (13)	107·3 (3)
O(7)–H(15)	0·742 (12)	0·969 (3)	H(11)–N(10)–H(14)	109·3 (11)	108·0 (3)
O(7)–H(16)	0·708 (13)	0·963 (3)	H(12)–N(10)–H(13)	109·2 (12)	107·0 (4)
O(8)–H(17)	0·741 (10)	0·970 (2)	H(12)–N(10)–H(14)	113·2 (11)	109·7 (3)
O(8)–H(18)	0·810 (12)	0·973 (4)	H(13)–N(10)–H(14)	107·0 (13)	110·5 (4)
O(9)–H(19)	0·730 (14)	0·968 (4)	Mg–O(7)–H(15)	116·2 (8)	117·4 (2)
O(9)–H(20)	0·816 (11)	0·972 (3)	Mg–O(7)–H(16)	121·0 (9)	119·7 (2)
			H(15)–O(7)–O(16)	108·4 (12)	108·2 (2)
			Mg–O(8)–H(17)	117·2 (9)	118·8 (2)
			Mg–O(8)–H(18)	118·0 (8)	117·1 (2)
			H(17)–O(8)–H(18)	104·6 (10)	105·7 (2)
			Mg–O(9)–H(19)	117·1 (9)	115·9 (2)
			Mg–O(9)–H(20)	121·6 (9)	120·2 (2)
			H(19)–O(9)–H(20)	101·7 (12)	105·9 (3)

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°) *from the neutron structure*

Bond *A*–H···*B*	Distance *A*–*B*	Equivalent position*	Angle *A*–H···*B*
O(7)–H(15)···O(5)	2·780 (2)	x,y,z	171·1 (3)
O(7)–H(16)···O(6)	2·838 (2)	$x,y,z-1$	174·2 (3)
O(8)–H(17)···O(4)	2·724 (2)	$x-1,y,z-1$	176·1 (3)
O(8)–H(18)···O(6)	2·759 (2)	$x-\frac{1}{2},\frac{1}{2}-y,z-1$	177·0 (3)
O(9)–H(19)···O(5)	2·765 (2)	$-x,-y,1-z$	168·4 (3)
O(9)–H(20)···O(3)	2·716 (2)	$\frac{1}{2}-x,y-\frac{1}{2},1-z$	174·1 (2)
N(10)–H(11)···O(6)	2·906 (2)	$x-\frac{1}{2},\frac{1}{2}-y,z-1$	165·1 (3)
N(10)–H(12)···O(3)	2·945 (2)	x,y,z	160·3 (3)
N(10)–H(13)···O(3)	3·050 (2)	$x-\frac{1}{2},\frac{1}{2}-y,z$	151·5 (4)
N(10)–H(13)···O(4)	3·090 (2)	$x-\frac{1}{2},\frac{1}{2}-y,z$	141·9 (4)
N(10)–H(14)···O(5)	2·841 (2)	$\frac{1}{2}-x,\frac{1}{2}+y,1-z$	174·5 (4)

* Symmetry operation for the acceptor atom *B*.

in the strength of interactions with neighbouring groups. The reason for the variation, however, is not intuitively obvious.

Table 4. *Comparison of X-ray* (*X*) *and neutron* (*N*) *structures*

X *N*	Distance (Å)	*X* *N* *N*	Angle (°)
S(2)–S(2)	0·003 (2)	O(7)–O(7)–Mg	39 (10)
O(3)–O(3)	0·002 (2)	O(7)–O(7)–*B*7*	164 (10)
O(4)–O(4)	0·005 (2)	O(8)–O(8)–Mg	56 (12)
O(5)–O(5)	0·001 (1)	O(8)–O(8)–*B*8*	157 (12)
O(6)–O(6)	0·003 (2)	O(9)–O(9)–Mg	47 (11)
O(7)–O(7)	0·009 (1)	O(9)–O(9)–*B*9*	151 (15)
O(8)–O(8)	0·008 (1)	O(3)–O(3)–S(2)	107 (44)
O(9)–O(9)	0·006 (2)	O(4)–O(4)–S(2)	150 (23)
N(10)–N(10)	0·002 (1)	O(5)–O(5)–S(2)	135 (57)
H(11)–H(11)	0·138 (12)	O(6)–O(6)–S(2)	118 (28)
H(12)–H(12)	0·144 (12)	H(11)–H(11)–N(10)	6 (5)
H(13)–H(13)	0·189 (16)	H(12)–H(12)–N(10)	16 (5)
H(14)–H(14)	0·191 (13)	H(13)–H(13)–N(10)	10 (4)
H(15)–H(15)	0·231 (12)	H(14)–H(14)–N(10)	8 (4)
H(16)–H(16)	0·263 (14)	H(15)–H(15)–O(7)	6 (3)
H(17)–H(17)	0·238 (11)	H(16)–H(16)–O(7)	5 (2)
H(18)–H(18)	0·166 (12)	H(17)–H(17)–O(8)	7 (3)
H(19)–H(19)	0·246 (14)	H(18)–H(18)–O(8)	3 (4)
H(20)–H(20)	0·159 (12)	H(19)–H(19)–O(9)	5 (3)
		H(20)–H(20)–O(9)	9 (4)

* *B*7, *B*8 and *B*9 are the internal bisectors of the H—O—H angles centred on O(7), O(8) and O(9) respectively.

Of the three Mg—O bond lengths, those involving O(7) and O(8) are approximately equal, and about $0{\cdot}03_5$ Å longer than those involving O(9). This difference, which is virtually identical for both the neutron and the X-ray structures, is observed in the whole series of Tutton's salts. It has no obvious relationship to the hydrogen-bond system.

The lengths of the O—H bonds and the hydrogen-bond links for the water molecule containing O(9) are close to those involving O(8). The H—O—H angles are also quite similar. The corresponding quantities for O(7) are significantly different, but the Mg—O bonds to O(7) and O(8) are virtually identical.

Each of the water molecules in the hexaaqua moiety is hydrogen bonded to two sulfate O atoms. To a good approximation each symmetry-independent water molecule has the same orientation with respect to the other two. It is thus surprising, notwithstanding the susceptibility of the metal–oxygen bonds to deformation, that the geometry of the hexaaquametal group is less ideal than that of either the ammonium or the sulfate group.

The asymmetry in the hexaaquametal moiety does not relate directly to differences in X-ray and neutron structural geometry, nor to the hydrogen-bond network. It may be due to longer-range interactions – which are considered with the study of the electron density of Maslen, Ridout & Watson (1988).

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Abstract. The crystal structure of the title compound at 295 K was refined using both neutron and X-ray data. $[NH_4]_2[Ni(H_2O)_6](SO_4)_2$, $M_r = 395{\cdot}00$, $P2_1/a$, monoclinic, $a = 9{\cdot}179\ (3)$, $b = 12{\cdot}462\ (6)$, $c = 6{\cdot}241\ (2)$ Å, $\beta = 106{\cdot}95\ (3)°$, $V = 682{\cdot}90$ Å^3 (X-ray results), $Z = 2$, $D_x = 1{\cdot}921$ Mg m^{-3}, $F(000) = 412$. Neutron data: $\lambda = 0{\cdot}9840$ Å, $\mu = 0{\cdot}22$ mm^{-1}, $R = 0{\cdot}038$ and $wR = 0{\cdot}033$ for 1225 reflections. X-ray data: Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}772$ mm^{-1}, $R = 0{\cdot}047$ and $wR = 0{\cdot}033$ for 7025 reflections. Differences between the lengths of bonds which would be equal for isolated groups and small changes from the X-ray to the neutron structure are consistent with the effects of interactions between neighbouring groups.

Introduction. The title compound is a member of the isomorphous series $(NH_4)_2M^{II}(SO_4)_2(H_2O)_6$, known as Tutton's salts. *M* is a divalent metal. X-ray structures have previously been reported by Grimes, Kay & Webb (1963), by Montgomery & Lingafelter (1964) and by Treushnikov, Kuskov, Soboleva & Belov (1978). The last-named authors also made a study of the electron density distribution based on X-ray data only. The structural parameters from an X-ray refinement are biased by the redistribution of electron density due to bonding. The resulting bias, which potentially contains information on bonding, can be determined by comparison with a neutron diffraction experiment. Neutron diffraction data and more complete X-ray data were collected. The structure was refined with these data as the first stage of a charge density study.

Experimental. Crystals by evaporation of a solution containing stoichiometric quantities of ammonium and magnesium sulfates in water.

Neutron measurements on the 4-circle diffractometer at the HIFAR reactor at the Australian Atomic Energy Commission Research Establishment at Lucas Heights,

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