

Crystal Structure of 1-Methyl-1,3,5,7-tetraazaadamantan-1-ium Ammonium Sulfate Hydrate, a Double Salt Containing Puckered Layers of Hydrogen-Bonded NH_4^+ and SO_4^{2-} Groups*

RICHARD K. McMULLAN

Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973, U.S.A.

FUSAO TAKUSAGAWA

Department of Chemistry, The University of Kansas, Lawrence, KA 66045, U.S.A.

and

THOMAS C. W. MAK**

Department of Chemistry, The Chinese University of Hong Kong, Shatin New Territories, Hong Kong

(Received: 10 November 1987)

Abstract. The double salt $[(\text{CH}_2)_6\text{N}_4\text{CH}_3](\text{NH}_4)\text{SO}_4 \cdot \text{H}_2\text{O}$ crystallizes in space group $P2_1/a$, with $a = 12.994(2)$, $b = 6.319(1)$, $c = 15.082(2)$ Å, $\beta = 93.78(2)^\circ$, and $Z = 4$. The structure was solved by the heavy-atom method and refined to $R_{F2} = 0.051$ for 2478 Mo $K\alpha$ data. The ammonium and sulfate ions are cross-linked by hydrogen bonds to form puckered layers disposed about the (001) family of planes. Each water molecule bridges a $[(\text{CH}_2)_6\text{N}_4\text{CH}_3]^+$ ion and a sulfate group, so that the organic cations lying on both sides of a puckered layer have their methyl groups pointing inward and fitting into depressions.

Key words. Hydrate, layer structure, hydrogen bonding, 1-methyl-1,3,5,7-tetraazaadamantan-1-ium, ammonium, sulfate.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82063 (18 pages).

I. Introduction

Hydrate inclusion compounds of quaternary ammonium salts generally possess host structures built of hydrogen-bonded anions and water molecules. The organic cations may fill cavities in a polyhedral cagework as in $(i\text{-C}_5\text{H}_{11})_4\text{NF} \cdot 38 \text{H}_2\text{O}$ [1] and $(n\text{-C}_4\text{H}_9)_4\text{NF} \cdot n \text{H}_2\text{O}$ ($n = 32.8$) [2], occupy two-dimensional channels as in $(\text{CH}_3)_4\text{NF} \cdot 4 \text{H}_2\text{O}$ [3] and $(\text{C}_2\text{H}_5)_4\text{NCl} \cdot 4 \text{H}_2\text{O}$ [4], or be sandwiched between puckered layers as in $(\text{C}_2\text{H}_5)_4\text{NCH}_3\text{COO} \cdot 4 \text{H}_2\text{O}$ [5]. Recent work has established the presence of urea–water–halide/pseudohalide puckered layers in the isomorphous series of ternary complexes $(\text{C}_2\text{H}_5)_4\text{NX} \cdot (\text{NH}_2)_2\text{CO} \cdot 2 \text{H}_2\text{O}$ ($X = \text{Cl}, \text{Br}, \text{CN}$) [6]. We now report the structure of the title compound featuring an unusual host lattice of the layer type, which is constructed with ammonium and sulfate ions as components and is anionic in character.

* Carried out, in part, under contract DE-AC02-76CH00016 with the U.S. Department of Energy, Office of Basic Energy Sciences.

** Author for correspondence.

2. Experimental

2.1. PREPARATION

Crystals of the double salt were obtained from aqueous solution, 2M in $(\text{CH}_2)_6\text{N}_4$ and 6M in H_2SO_4 , by slow evaporation. Among the crystals deposited, three distinct phases were identified by their X-ray diffraction patterns. Formation of the $[(\text{CH}_2)_6\text{N}_4\text{CH}_3]^+$ and NH_4^+ ions by acid hydrolysis suggests that the two phases not studied here differ in composition as well as structure from the title compound. Direct preparation of the double salt (methylation of $(\text{CH}_2)_6\text{N}_4$ with CH_3I , conversion to the sulfate with Ag_2SO_4 , and co-crystallizing $[(\text{CH}_2)_6\text{N}_4\text{CH}_3]_2\text{SO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ from aqueous solution) yielded crystals having diffraction patterns identical to that from the acid preparation used in the present study.

2.2. X-RAY CRYSTALLOGRAPHY

The selected crystal ($0.2 \times 0.2 \times 0.3$ mm) was attached to a glass fiber and positioned on a Enraf-Nonius CAD4 diffractometer (graphite-monochromatized Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å). Precise unit-cell parameters were determined by a least-squares fit of $\sin^2\theta$ values for 24 reflections. Crystal data: $[(\text{CH}_2)_6\text{N}_4\text{CH}_3](\text{NH}_4)\text{SO}_4 \cdot \text{H}_2\text{O}$, FW = 287.34, monoclinic, space group $P2_1/a$, $a = 12.994(2)$, $b = 6.319(1)$, $c = 15.082(2)$ Å, $\beta = 93.78(2)^\circ$, $V = 1235.7(2)$ Å³, $Z = 4$, $F(000) = 616$, $D_x = 1.544$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.881$ cm⁻¹. Intensities ($\pm h, k, \pm l$; 5684 data; $(\sin \theta/\lambda)_{\text{max}} = 0.65$ Å⁻¹) were collected using the $\omega/2\theta$ scan procedure. The data were corrected for Lp and absorption effects. The unique data set of $2478|F_o|^2$ values had an internal agreement index of 0.035. The structure was solved by the heavy-atom method. All hydrogen atoms were located in difference maps. Parameters were refined by a full-matrix least-squares procedure minimizing $\sum w(|F_o|^2 - |F_c|^2)^2$ with weights $w = [\sigma_c^2 + (0.01|F_o|^2)^2]^{-1}$, where the variances σ_c^2 were from counting statistics. The parameters varied in the final cycles of refinement included the coordinates of 39 independent atoms, anisotropic thermal parameters for non-hydrogen atoms, isotropic temperature factors for hydrogen atoms, one scale factor, an isotropic secondary extinction parameter (type 1 crystal, Becker & Coppens [7]; Lorentzian distribution of mosaicity, Thornley & Nelmes [8]). Indices of fit at convergence were $R_{F2} = 0.051$, $R_{wF2} = 0.061$, and $S = 1.23$. Residual peaks in the final difference map were in the range -0.38 to $+0.44$ eÅ⁻³.

Computations were performed on a CDC 7600 computer with modified versions of AGNOST [9] for absorption corrections, ORFLS [10] for least-squares refinement, FOR-DAP [11] for Fourier synthesis, and ORTEPII [12] for thermal ellipsoid plots. Neutral-atom scattering factors were taken from [13].

3. Results and Discussion

The final atomic coordinates are listed in Table I. Anisotropic thermal parameters and structure factors have been deposited as Supplementary Data.

3.1. PUCKERED LAYER OF AMMONIUM AND SULFATE IONS

As illustrated in Figure 1, the NH_4^+ and SO_4^{2-} ions are cross-linked by hydrogen bonds to form a puckered layer normal to the c axis. Atoms O(2), O(3) and O(4) of the sulfate group

Table I. Fractional atomic coordinates and thermal parameters^a (\AA^2) for $[(\text{CH}_2)_6\text{N}_4\text{CH}_3](\text{NH}_4)\text{SO}_4 \cdot \text{H}_2\text{O}$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U
(i) 1-Methyl-1,3,5,7-tetraazaadamantan-1-ium ion				
N(1)	0.3582(1)	0.6947(3)	0.2518(1)	0.026(1)
N(2)	0.4483(2)	0.9075(4)	0.3661(1)	0.037(1)
N(3)	0.4260(1)	0.5301(3)	0.3890(1)	0.032(1)
N(4)	0.2784(1)	0.7651(3)	0.3902(1)	0.033(1)
C(1)	0.4298(2)	0.8813(4)	0.2719(2)	0.034(1)
C(2)	0.4076(2)	0.4983(4)	0.2950(2)	0.033(1)
C(3)	0.2577(2)	0.7367(4)	0.2965(2)	0.032(1)
C(4)	0.4942(2)	0.7118(5)	0.4053(2)	0.040(1)
C(5)	0.3283(2)	0.5738(4)	0.4292(2)	0.033(1)
C(6)	0.3485(2)	0.9436(5)	0.4064(2)	0.042(2)
C(7)	0.3388(2)	0.6667(5)	0.1546(2)	0.041(1)
HC(1)A	0.493(2)	0.840(4)	0.245(1)	0.044(7)
HC(1)B	0.394(2)	1.000(4)	0.243(1)	0.048(7)
HC(2)A	0.470(2)	0.478(4)	0.269(1)	0.043(7)
HC(2)B	0.360(2)	0.394(4)	0.283(1)	0.037(6)
HC(3)A	0.215(2)	0.616(4)	0.282(1)	0.033(7)
HC(3)B	0.226(2)	0.856(4)	0.269(1)	0.042(7)
HC(4)A	0.511(2)	0.725(4)	0.472(1)	0.038(7)
HC(4)B	0.557(2)	0.696(4)	0.379(1)	0.046(7)
HC(5)A	0.343(1)	0.591(3)	0.495(1)	0.025(6)
HC(5)B	0.280(2)	0.459(4)	0.420(1)	0.045(8)
HC(6)A	0.364(1)	0.962(4)	0.476(1)	0.031(6)
HC(6)B	0.317(2)	1.061(4)	0.378(1)	0.055(7)
HC(7)A	0.306(2)	0.777(4)	0.132(1)	0.042(7)
HC(7)B	0.405(2)	0.647(4)	0.129(1)	0.032(6)
HC(7)C	0.293(2)	0.554(5)	0.144(2)	0.050(8)
(ii) Ammonium ion				
N(5)	0.3814(1)	0.1776(4)	0.0065(1)	0.038(1)
HN(5)A	0.436(2)	0.191(4)	0.057(2)	0.052(7)
HN(5)B	0.319(2)	0.190(5)	0.031(2)	0.073(8)
HN(5)C	0.380(2)	0.081(6)	-0.018(2)	0.07(1)
HN(5)D	0.392(2)	0.273(5)	-0.042(2)	0.082(9)
(iii) Sulfate ion				
S	0.12933(5)	0.1815(1)	0.13012(4)	0.0265(3)
O(1)	0.2066(1)	0.2110(3)	0.2037(1)	0.043(1)
O(2)	0.1738(2)	0.2282(4)	0.0462(1)	0.061(1)
O(3)	0.0426(1)	0.3250(4)	0.1406(1)	0.059(1)
O(4)	0.0915(1)	-0.0365(3)	0.1307(1)	0.052(1)
(iv) Water molecule				
O(5)	0.1245(1)	0.2764(4)	0.3662(1)	0.051(1)
HO(5)A	0.140(2)	0.263(5)	0.310(2)	0.071(8)
HO(5)B	0.066(2)	0.320(5)	0.353(2)	0.082(9)

^a For the non-hydrogen atoms the equivalent isotropic temperature factor U_{eq} is calculated as one-third of the trace of the orthogonalized U matrix. For the H atoms, the exponent of the isotropic temperature factor U takes the form $-8\pi^2 U \sin^2 \theta / \lambda^2$.

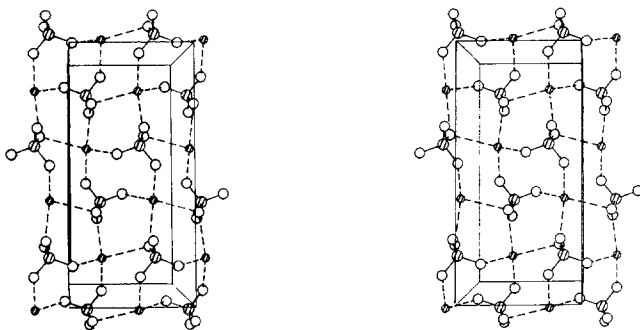


Fig. 1. Stereo drawing showing a layer composed of hydrogen-bonded NH_4^+ and SO_4^{2-} ions. The origin of the unit cell lies at the lower left corner, with a pointing from left to right, b upwards, and c towards the reader. Hydrogen atoms have been omitted for clarity, and atom types are distinguished by size and shading. Broken lines represent $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds.

are involved in bonding within each anionic layer, with O(2) linked by two acceptor hydrogen bonds, one long and one short, to neighboring N(5) atoms (Table II). The configuration about N(5) departs considerably from tetrahedral, as judged from the $\text{O}\cdots\text{N}(5)\cdots\text{O}$ angles in the range $87.1\text{--}121.7(3)^\circ$. The measured dimensions of the sulfate ion (Table II) are quite normal and in good accord with the corresponding values reported for $(\text{NH}_4)_2\text{SO}_4$ [14] and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ [15].

3.2. CRYSTAL STRUCTURE

Sulfate oxygen atoms of the type O(1), which take no part in the construction of the anionic lattice, protrude on both sides of each layer serving as fences around depressions. The water molecule plays a bridging role, forming donor hydrogen bonds with O(1) and a tertiary amino N atom of the $[(\text{CH}_2)_6\text{N}_4\text{CH}_3]^+$ ion, in such a way that the methyl group fits snugly into a depression in the layer. The resulting crystal structure thus comprises 'thick layers' consolidated by hydrogen bonding, the stacking of which is demarcated by van der Waals regions corresponding to the (002) plane (Figure 2).

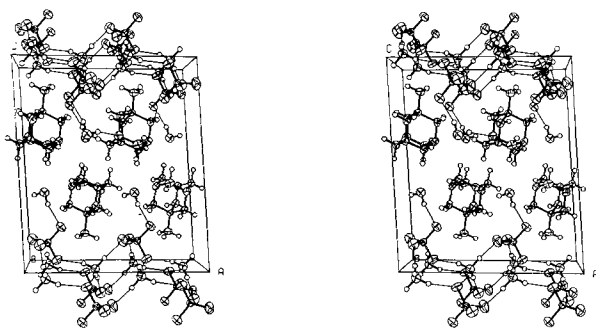


Fig. 2. Stereo drawing of the crystal structure of $[(\text{CH}_2)_6\text{N}_4\text{CH}_3](\text{NH}_4)\text{SO}_4\cdot\text{H}_2\text{O}$. The origin of the unit cell lies at the lower left corner, with a pointing from left to right, b away from the reader, and c upwards. Broken lines represent hydrogen bonds. The thermal ellipsoids are drawn at the 50% probability level.

Table II. Bond distances (Å) and angles (deg) in [(CH₂)₆N₄CH₃](NH₄)SO·H₂O.

(i) Molecular ions

S—O(1)	1.459(2)	O(1)—S—O(2)	110.1(1)
S—O(2)	1.456(2)	O(1)—S—O(3)	109.6(1)
S—O(3)	1.463(2)	O(1)—S—O(4)	109.3(1)
S—O(4)	1.463(2)	O(2)—S—O(3)	108.8(1)
		O(2)—S—O(4)	110.4(1)
N(1)—C(1)	1.521(3)	O(3)—S—O(4)	108.7(1)
N(1)—C(2)	1.524(3)		
N(1)—C(3)	1.532(3)	C(1)—N(1)—C(7)	110.6(2)
		C(2)—N(1)—C(7)	111.1(2)
N(2)—C(1)	1.434(3)	C(3)—N(1)—C(7)	111.5(2)
N(3)—C(2)	1.435(3)		
N(4)—C(3)	1.432(3)	C(1)—N(1)—C(2)	108.1(2)
		C(1)—N(1)—C(3)	107.8(2)
N(2)—C(4)	1.478(4)	C(2)—N(1)—C(3)	107.4(2)
N(2)—C(6)	1.486(4)		
N(3)—C(4)	1.461(3)	C(1)—N(2)—C(4)	109.6(2)
N(3)—C(5)	1.469(3)	C(1)—N(2)—C(6)	109.2(2)
N(4)—C(5)	1.475(3)	C(4)—N(2)—C(6)	107.7(2)
N(4)—C(6)	1.461(4)	C(2)—N(3)—C(4)	109.7(2)
		C(2)—N(3)—C(5)	109.9(2)
N(1)—C(7)	1.482(3)	C(4)—N(3)—C(5)	108.3(2)
		C(3)—N(4)—C(6)	109.6(2)
		C(3)—N(4)—C(5)	109.9(2)
		C(6)—N(4)—C(5)	108.3(2)
		N(1)—C(1)—N(2)	110.3(2)
		N(1)—C(2)—N(3)	110.2(2)
		N(1)—C(3)—N(4)	110.3(2)
		N(2)—C(4)—N(3)	111.3(2)
		N(3)—C(5)—N(4)	111.0(2)
		N(2)—C(6)—N(4)	111.5(2)

(ii) Hydrogen bonding

N(5)···O(2)	2.820(3)	O(2)···N(5)···O(2) ^a	87.1(3)
N(5)···O(3)	2.814(3)	O(2)···N(5)···O(3) ^b	121.7(3)
N(5)···O(4)	2.787(3)	O(2)···N(5)···O(4) ^c	104.7(3)
N(5)···O(2) ^a	3.022(3)	O(2) ^a ···N(5)···O(3) ^b	109.6(3)
O(5)···O(1)	2.768(3)	O(2) ^a ···N(5)···O(4) ^c	117.0(3)
O(5)···N(2) ^d	3.038(3)	O(2) ^a ···N(5)···O(4) ^c	114.4(3)
		O(1)···O(5)···O(2) ^d	115.6(4)

Symmetry transformations: ^a $\frac{1}{2} - x, -\frac{1}{2} + y, -z$; ^b $\frac{1}{2} + x, \frac{1}{2} - y, z$; ^c $\frac{1}{2} - x, \frac{1}{2} + y, -z$; ^d $-\frac{1}{2} + x, \frac{1}{2} - y, z$.

3.3. THE ORGANIC CATION

The 1-methyl-1,3,5,7-tetraazaadamantan-1-ium cage system (Figure 3) conforms closely to idealized *3m* molecular symmetry. Moving away from the quaternary N(1) atom, the three sets of endocyclic C—N bonds vary in the order 'long, short, and normal' relative to the standard bond length of 1.476(2) Å in crystalline (CH₂)₆N₄ [16]. The measured molecular dimensions (Table II), as well as the bond-angle pattern

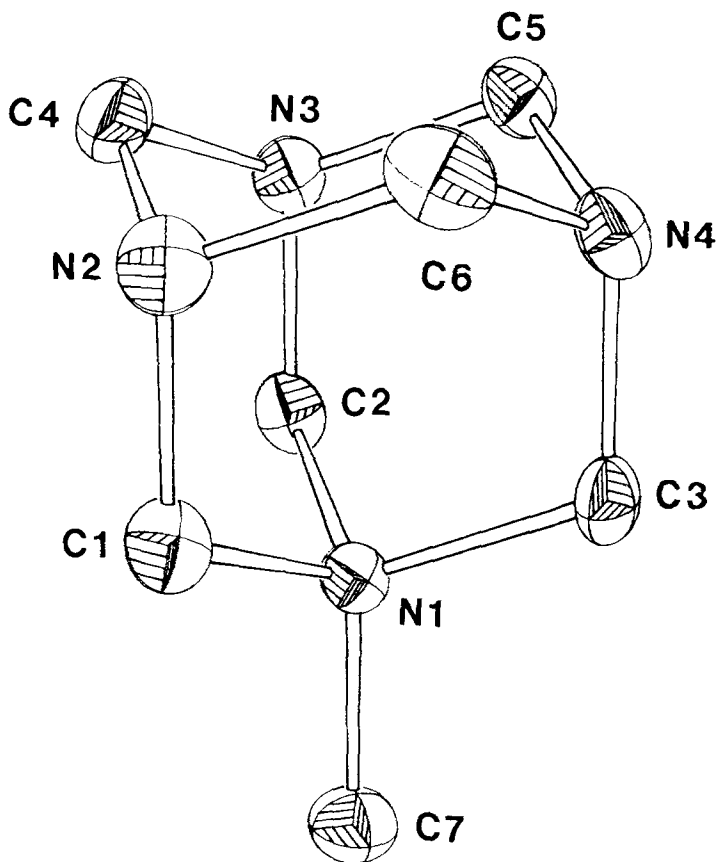


Fig. 3. Perspective view of the $[(\text{CH}_2)_6\text{N}_4\text{CH}_3]^+$ ion with atom numbering. The thermal ellipsoids are drawn at the 30% probability level.

$\text{N}_t-\text{C}-\text{N}_t > \text{N}_q-\text{C}-\text{N}_t \approx \text{C}-\text{N}_q-\text{C}(\text{methyl}) > \text{C}-\text{N}_t-\text{C} > \text{C}-\text{N}_q-\text{C}$ (where N_q and N_t stand for quaternary and tertiary nitrogen atoms, respectively), are in good agreement with the available structural data for compounds containing the $[(\text{CH}_2)_6\text{N}_4\text{CH}_3]^+$ [17, 18] and $[(\text{CH}_2)_6\text{N}_4\text{CH}_2\text{C}_6\text{H}_5]^+$ [19] ions.

References

1. D. Feil and G. A. Jeffrey: *J. Chem. Phys.* **35**, 1863 (1961).
2. R. K. McMullan, M. Bonamico, and G. A. Jeffrey: *J. Chem. Phys.* **39**, 3295 (1963).
3. W. J. McLean and G. A. Jeffrey: *J. Chem. Phys.* **47**, 414 (1967).
4. T. C. W. Mak, H. J. Bruins Slot, and P. T. Beurskens: *J. Incl. Phenom.* **4**, 295 (1986).
5. T. C. W. Mak: *J. Incl. Phenom.* **4**, 273 (1986).
6. T. C. W. Mak and R. K. McMullan: *J. Incl. Phenom.* **6**, 473-481 (1988).
7. P. Becker and P. Coppens: *Acta Crystallogr.* **A30**, 148 (1974).
8. F. R. Thornley and R. J. Nelmes: *Acta Crystallogr.* **A30**, 748 (1974).
9. L. Templeton and D. Templeton: *Amer. Cryst. Assoc. Abstr. Papers (Storrs, Connecticut Meeting)*, Abstract E10 (1973).
10. W. R. Busing, K. O. Martin, and H. A. Levy: ORFLS. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee (1962).
11. A. Zalkin: unpublished work.

12. C. K. Johnson: ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee (1976).
13. *International Tables for X-ray Crystallography*, Vol. IV, pp. 55, 99, 149. Kynoch Press, Birmingham (1974) (Distrib.: D. Reidel, Dordrecht).
14. E. O. Schlemper and W. C. Hamilton: *J. Chem. Phys.* **44**, 4498 (1966).
15. S. Suzuki and Y. Makita: *Acta Crystallogr.* **B34**, 732 (1978).
16. L. N. Becka and D. W. J. Cruickshank: *Proc. Roy. Soc. London* **A273**, 435 (1963).
17. P. K. Hon, T. C. W. Mak, and J. Trotter: *Inorg. Chem.* **18**, 2916 (1979).
18. T. C. W. Mak: *Inorg. Chem.* **23**, 620 (1984).
19. M.-C. Shao, L.-F. Wang, X.-M. Zheng, and Y.-Q. Tang: *Hua Hsueh Hsueh Pao* **40**, 223 (1982). [In Chinese].