The writer wishes to thank J.P. Remeika and E.G. Spencer for making this work possible by supplying the crystals of In_2O_3, S.C. Abrahams for suggesting the use of Mo $K\alpha$ radiation, Mrs V.B. Compton, R.D. Burbank and D.B. McWhan for their comments on this manuscript and Professor W.H. Zachariasen for many valuable discussions.

References

BURBANK, R. D. (1965). *Acta Cryst.* **18**, 88.
BUSING, W. R. & LEVY, H. A. (1959). ORNL Report 59-12-3. Oak Ridge National Laboratory, Tennessee.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORNL Report TM-305. Oak Ridge National Laboratory, Tennessee.
CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
DACHS, H. (1956). *Z. Kristallogr.* **107**, 370.
EYRING, L. & BAENZIGER, N. C. (1962). *J. Appl. Phys.* **33**, 428.
FERT, A. (1962). *Bull. Soc. franç. Miner. Crist.* **85**, 267.
HOEKSTRA, H. R. & GINGERICH, K. A. (1964). *Science*, **146**, 1163.
International Tables for X-ray Crystallography (1959). Vol.II. Birmingham: Kynoch Press.
PAULING, L. & SHAPPELL, M. D. (1930). *Z. Kristallogr.* **75**, 128.
REMEIKA, J. P. & SPENCER, E. G. (1964). *J. Appl. Phys.* **35**, 2803.
ROTH, R. S. (1957). *J. Res. Nat. Bur. Stand.*, **58**, 75.
ZACHARIASEN, W. H. (1927). *Norsk Geol. Tidssk.* **9**, 310.
ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139.

Acta Cryst. (1966). **20**, 728

The Crystal Structure of Tutton's Salts. IV. Cadmium Ammonium Sulfate Hexahydrate

BY H. MONTGOMERY,
Canadian Services College, Royal Roads, Victoria, B.C., Canada

AND E.C. LINGAFELTER,
Department of Chemistry, University of Washington, Seattle, Washington 98105, *U.S.A.*

(*Received* 27 *September* 1965)

The crystal structure of cadmium ammonium sulfate hexahydrate, $Cd(NH_4)_2(SO_4)_2 \cdot 6H_2O$, has been determined by a three-dimensional X-ray analysis with the use of Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). The crystals are monoclinic, space group $P2_1/a$, with 2 molecules per unit cell. The cell dimensions are $a = 9{\cdot}43$, $b = 12{\cdot}82$, $c = 6{\cdot}29$ Å; $\beta = 106°52'$. The water molecules are arranged about the cadmium ion in an almost regular octahedron, the average metal–oxygen distance being 2·28 Å.

Introduction

Cadmium ammonium sulfate hexahydrate is the only reported Tutton salt in which the metal ion belongs to the second long period in the periodic system. Its structure was therefore examined to see if it followed the pattern of the other Tutton's salts whose structures have already been established (Montgomery & Lingafelter, 1964*a*, 1964*b*, 1966).

Experimental

The procedure followed was essentially that for the isomorphous zinc salt (Montgomery & Lingafelter, 1964*a*) except that the crystal needle was ground to approximate a cylinder along c ($\mu = 78{\cdot}5$ cm^{-1}; $\mu R = 0{\cdot}40$). The cell dimensions were determined from rotation and zero-level ($hk0$) Weissenberg photographs (calibrated with $a_0 = 5{\cdot}6387$ Å for NaCl) and a precession photograph of the a^*c^* net (Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$). The results and their estimated standard deviations are $a_0 = 9{\cdot}433 \pm 0{\cdot}010$, $b = 12{\cdot}823 \pm 0{\cdot}015$, $c = 6{\cdot}286 \pm 0{\cdot}006$ Å, $\beta = 106°52' \pm 6'$. Systematic absences: $h0l$ when h is odd; $0k0$ when k is odd; space group $P2_1/a$, $Z = 2$.

The raw intensities were collected by photometer from singly-integrated equi-inclination Weissenberg photographs ($hk0$ through $hk4$) and were corrected for Lorentz and polarization factors and for absorption after Bond's (1959) method. The resulting structure factors were then scaled by levels to correspond to the calculated values, using the parameters of the isomorphous zinc salt. (It should be recognized that this procedure precludes physical interpretation of the anisotropic thermal parameters.) In all, 1136 reflections were used, of which 162 were below minimum observed value and 20 were given zero weight in the refinement because of secondary extinction effects. The intensities of the remainder varied from 1 to 1300.

The initial atomic parameters were taken from the isomorphous zinc salt for the heavy atoms and from the magnesium salt (Montgomery & Lingafelter, 1964*b*)

for the hydrogen atoms. The refinement was carried out by full-matrix least-squares, first in isotropic and then in anisotropic mode, where the anisotropic temperature factor was of the form

$$\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}.$$

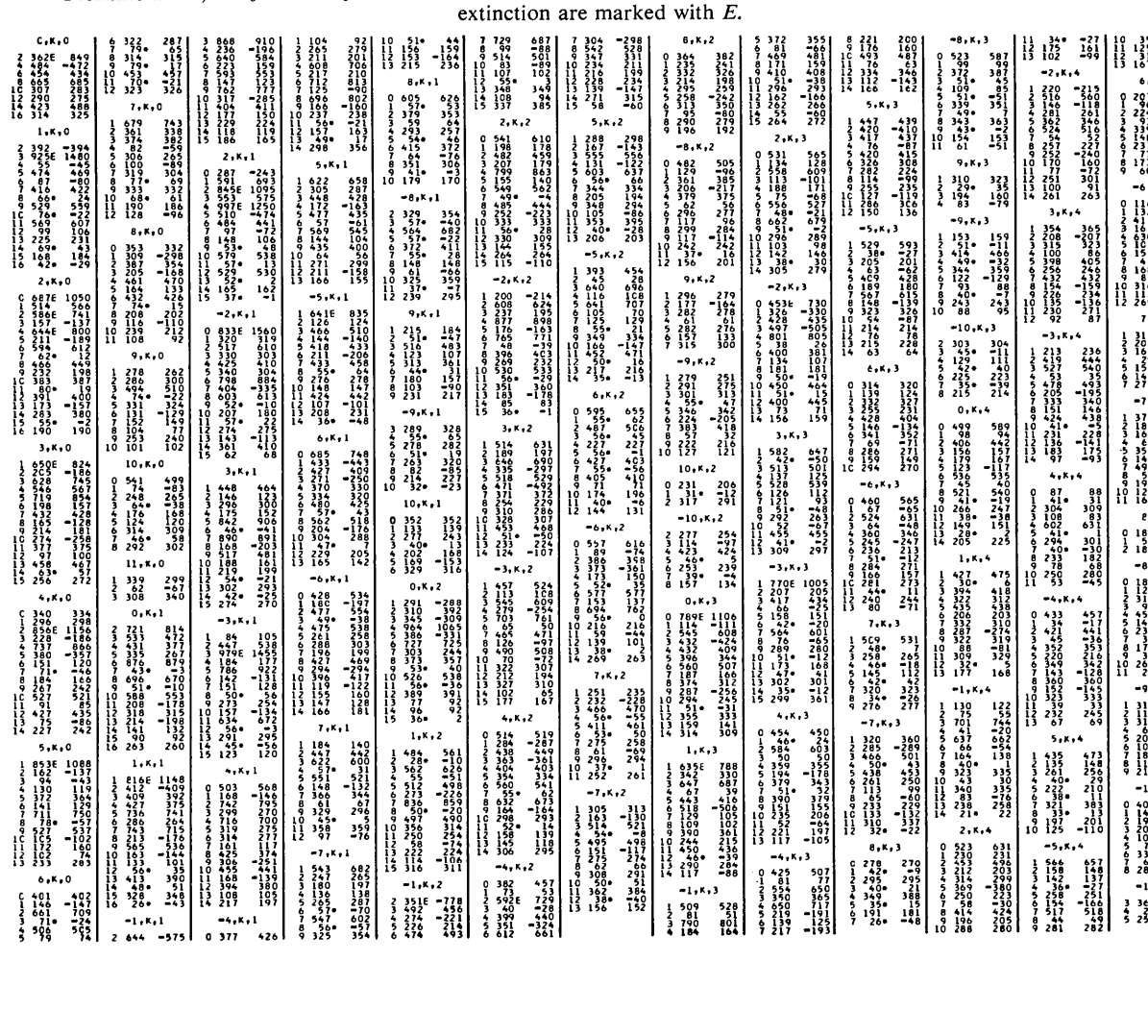
Scattering factors were taken from Thomas & Umeda (1957) for cadmium, from Viervoll & Øgrim (1949) for sulfur, from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for oxygen and nitrogen, and from McWeeny (1951) for hydrogen. A modified Hughes weighting scheme was used and the

Table 1. *Parameters (with least-squares standard errors in parentheses)*

Atom	Fractional positional parameters × 10⁴			Anisotropic thermal parameters × 10⁴					
	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cd	0	0	0	44 (1)	26 (0·5)	174 (6)	2·2 (0·3)	3 (2)	2·6 (0·6)
S(2)	4090 (2)	1362 (1)	7410 (4)	37 (2)	26 (0·8)	134 (10)	−6 (1)	0 (3)	−4 (2)
O(3)	4102 (7)	2234 (5)	5899 (11)	152 (10)	42 (4)	179 (25)	−34 (5)	42 (11)	1 (7)
O(4)	5471 (6)	784 (6)	7764 (12)	43 (7)	71 (5)	338 (31)	12 (4)	0 (9)	−24 (9)
O(5)	2847 (6)	661 (4)	6294 (10)	66 (7)	31 (3)	199 (23)	−12 (3)	25 (8)	−19 (6)
O(6)	3908 (6)	1741 (5)	9506 (10)	81 (7)	45 (3)	144 (25)	−8 (4)	23 (8)	−7 (7)
O(7)	1839 (6)	1149 (4)	1745 (12)	75 (7)	42 (3)	184 (25)	−16 (4)	−10 (9)	0 (6)
O(8)	−1730 (6)	1200 (4)	336 (12)	58 (6)	34 (3)	276 (27)	−6 (3)	34 (9)	−4 (6)
O(9)	1 (6)	−760 (4)	3210 (11)	88 (8)	36 (3)	250 (25)	13 (4)	43 (10)	11 (7)
N(10)	1366 (7)	3506 (6)	3654 (14)	64 (9)	49 (4)	197 (35)	4 (4)	−34 (11)	30 (8)

Table 2. *Observed and calculated structure factors*

Columns are k, $10F_o$ and $10F_c$. Unobserved reflections are marked with * and those omitted because of secondary extinction are marked with *E*.



function minimized was $\Sigma w(F_o-F_c)^2$. An attempt was made to refine the hydrogen atom positions ($B=2{\cdot}9$) but, as expected, the refinement was not satisfactory and in the final F_c calculation the original coordinates (from Table 1, Montgomery & Lingafelter, 1964*b*) and isotropic temperature factor ($B=2{\cdot}9$) were used. Although these hydrogen coordinates give somewhat short O–H distances and somewhat large H–O–H angles (the N–H distances and H–N–H angles are quite reasonable), it was felt that these are probably as satisfactory as calculated coordinates. The average shift during the final cycle of refinement of the position parameters of the heavy atoms was $0{\cdot}015\sigma$, with a maximum of $0{\cdot}04\sigma$. The corresponding shifts in temperature factors were $0{\cdot}018\sigma$ and $0{\cdot}06\sigma$. The final R index was 0·073. ($R=(\Sigma\,||F_o|-|F_c||)/\Sigma\,|F_o|$, not including unobserved reflections or those exhibiting secondary extinction effects). The final parameters are listed in Table 1, the observed and calculated structure factors in Table 2, bond lengths and angles in Table 3 and hydrogen bond distances in Table 4.

Table 3. *Bond lengths and angles with estimated standard deviations in parentheses for each bond type*

Bond lengths (Å)		Bond angles (°)	
Cd–O(7)(H_2O)	2·298 (0·007)	O(7)–Cd–O(8)	89·1 (0·2)
Cd–O(8)(H_2O)	2·297	O(7)–Cd–O(9)	92·6
Cd–O(9)(H_2O)	2·241	O(8)–Cd–O(9)	91·3
S —O(3)	1·469 (0·008)	O(3)–S —O(4)	108·2 (0·3)
S —O(4)	1·459	O(3)–S —O(5)	108·0
S —O(5)	1·483	O(3)–S —O(6)	110·8
S —O(6)	1·460	O(4)–S —O(5)	108·2
		O(4)–S —O(6)	111·4
		O(5)–S —O(6)	110·2

Table 4. *Hydrogen bond distances*

Bond	Relative position of second atom*			Bond length (Å)
O(7)—O(5)	x	y	z	2·810 (0·012)
O(7)—O(6)	x	y	$z-1$	2·821
O(8)—O(4)	$x-1$	y	$z-1$	2·719
O(8)—O(6)	$x-\frac{1}{2}$	$\frac{1}{2}-y$	$z-1$	2·790
O(9)—O(3)	$\frac{1}{2}-x$	$y-\frac{1}{2}$	$1-z$	2·715
O(9)—O(5)	$-x$	$-y$	$1-z$	2·796
N(10)–O(3)	x	y	z	3·033 (0·015)
N(10)–O(3)	$x-\frac{1}{2}$	$\frac{1}{2}-y$	z	3·033
N(10)–O(4)	$x-\frac{1}{2}$	$\frac{1}{2}-y$	z	3·079
N(10)–O(5)	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$1-z$	2·859
N(10)–O(6)	$x-\frac{1}{2}$	$\frac{1}{2}-y$	$z-1$	2·961

* This is the transformation relating each 'second atom' to the corresponding atom in the original asymmetric unit.

Discussion

The main point of interest is the arrangement of water molecules about the central ion. The bond length pattern of the other Tutton's salts is repeated, that is, the Cd–O(9) bond is shorter than the Cd–O(8) and Cd–O(7) bonds, but this has been accompanied by a distortion of the metal–oxygen bond angles; the O(7)–Cd–O(9) angle is 92·6°, whereas the corresponding angle in the zinc salt is 90·6°.

The average bond length Cd–O(H_2O) (2·28 Å) is the same as the Cd–O distance (2·28 Å) found in the cadmium formate–thiourea complex by Nardelli, Gasparri & Boldrini (1965).

The general packing of the ions and the hydrogen-bond network is essentially identical with that found in the other Tutton's salts; that is, each water molecule forms two hydrogen bonds (Table 4) which range in length from 2·72 to 2·82 Å. The ammonium ion is also hydrogen-bonded to the oxygen atoms of the sulfate groups; three bonds are normal but one (to O(3) and O(4) of the same sulfate ion), is 'bifurcated'.

In addition there is a fairly close approach of the water octahedra along the c axis, the distance separating O(9) from O(9′) being 2·978 Å.

This research was supported in part by the U.S. Public Health Service under Research Grant GM-10842 and in part by Defense Research Board of Canada Grant 9510-31.

References

Berghuis, J., Haanappel, IJ. M., Potters, J., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.

Bond, W. L. (1959). *Acta Cryst.* **12**, 375.

International Tables for X-ray Crystallography (1962). Vol. III. Table 3.3.1. Birmingham: Kynoch Press.

McWeeny, R. (1951). *Acta Cryst.* **4**, 513.

Montgomery, H. & Lingafelter, E. C. (1964*a*). *Acta Cryst.* **17**, 1295.

Montgomery, H. & Lingafelter, E. C. (1964*b*). *Acta Cryst.* **17**, 1478.

Montgomery, H. & Lingafelter, E. C. (1966). *Acta Cryst.* **20**, 659.

Nardelli, M., Gasparri, G. F. & Boldrini, P. (1965). *Acta Cryst.* **18**, 618.

Viervoll, H. & Øgrim, O. (1949). *Acta Cryst.* **2**, 277.