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A Refinement of the Crystal Structure of the Cadmium Sulfate $3CdSO_4 \cdot 8H_2O$

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The crystal structure of $3CdSO_4 \cdot 8H_2O$ has been refined from three-dimensional diffractometer data. The final R value for 1340 observed independent reflections is 0.022. The positions of the hydrogen atoms were located from a difference map. Each Cd atom is coordinated to two water molecules and four SO_4 tetrahedra. The coordination is octahedral with an average Cd–O bond length of 2.29 Å.

In an X-ray scattering investigation of aqueous cadmium sulfate solutions [1] evidence was found for a bonding of sulfate groups within the inner coordination sphere of the cadmium ion. For the interpretation of the solution scattering data a comparison with the bonding in crystalline cadmium sulfates then became of interest. In one of these sulfates, $(NH_4)_2Cd(SO_4)_2(H_2O)_6$ only water molecules are coordinated directly to the cadmium ion.[2] In $3CdSO_4 \cdot 8H_2O$, however, the sulfate groups are bonded to cadmium, and the bonding, which is monodentate, is apparently analogous to that found in the aqueous solutions. The crystal structure was solved in 1936 by Lipson [3] and a refinement has now been carried out in order to get more accurate bond lengths for comparison with the solution scattering data.

EXPERIMENTAL

For the data collection a crystal with the largest dimension less than 0.2 mm was selected from a commercial sample (Merck, reagent grade). The unit cell dimensions and the space group symmetry were checked by Weissenberg and precession photographs and intensity data were collected with a Syntex *P*21 automatic four circle diffractometer with the use of Mo*K*α-radiation. Accurate parameters for the monoclinic unit cell were determined from 10 centered, high-angle reflections with the use of a least-squares procedure. The values found were: $a=14.818(11)$ Å, $b=11.903(9)$ Å, $c=9.468(6)$ Å, $\beta=97.39(6)°$. The values given by Lipson [3] are: $a'=9.44\pm0.01$, $b'=11.87\pm0.01$, $c'=16.49\pm0.01$, $\beta'=117°16'\pm5'$, which, after transformation to the unit cell used here, correspond to $a=14.78$ Å, $b=11.87$ Å, $c=9.44$ Å, $\beta=97.33°$. With four formula weights in the unit cell the calculated density is 3.09 g cm^{-3}. Experimental values for the density have been reported to be 3.09 g cm^{-3}.[4]

Omega scanning was used for the intensity measurements with the scan speed varying from 0.49 to 29.36° min^{-1}. Four check reflections were repeatedly measured, but no systematic changes in their intensities could be observed during the data collection. All *hkl* and *hk̄l* and part of the *hkl̄* and *hk̄l̄* reflections were measured up to $2\theta=50°$. A semi-empirical absorption correction ($\mu=42.6$ cm^{-1}), obtained by measuring intensities for selected reflections when rotating around the diffraction vector, was applied.[5]

After averaging over equivalent reflections a total of 1469 independent reflections were obtained, 129 of which had intensities below 1.96 σ.

The Syntex XTL program system [6] (version 2 for a NOVA 32*K* computer with a disc memory unit) was used for the calculations. The thermal ellipsoid plot program [7] for crystal structure illustrations, ORTEP2, was also used.

STRUCTURE SOLVING AND REFINEMENT

Systematically absent reflections are *hkl* with $h+k=2n+1$ and *h*0*l* with $l=2n+1$. This is con-

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sistent with the space groups No. 15: $C2/c$ and No. 9: Cc. The intensity distribution indicated a centrosymmetric structure and the results of the structure determination confirmed that the correct space group is the centrosymmetric $C2/c$.

The positions of the 12 Cd atoms in the unit cell were derived from the three-dimensional Patterson function. A three-dimensional electron density map, based on the Cd positions, revealed the positions of all S and O atoms.

The parameters determined were in agreement with those of Lipson,[3] after transferring his parameters from the space group $I2/a$ to $C2/c$, which is used here. His original numbering of the oxygen atoms has been kept unchanged in the following.

An isotropic least squares refinement, in which $\sum w \| F_o | - | F_c \|^2$ was minimized, led to an R value of 0.037. Anisotropic temperature parameters further lowered the R factor to 0.026. In a difference map calculated at this stage, the highest peaks were between 0.90 and 0.60 el $Å^{-3}$ and could all be identified as possible positions for the hydrogen atoms. The highest of the remaining spurious peaks was 0.47 el/$Å^3$.

With the H atoms included with isotropic temperature factors the least squares refinement was continued until all parameter shifts were less than 1 % of the corresponding standard deviations. The weighting scheme used in the final refinement was $\frac{1}{w} = \sigma^2(F_o) + (0.02F_o)^2$ for $F_o > 3.92\sigma$. The final R factor was 0.022. With unobserved reflections included it was 0.026. The corresponding values for R_w were 0.024 and 0.037, respectively. The function

$$\left[\frac{\sum w(F_o - F_c)^2}{N_o - N_v}\right]^{1/2} = 1.15.$$

Final parameter values are given in Table 1 and selected bond lengths and angles in Table 2. A stereoscopic drawing of the atomic arrangement in the unit cell is given in Fig. 1.

DISCUSSION OF THE STRUCTURE

The two non-equivalent cadmium atoms in the unit cell, Cd1 and Cd2, have very similar surroundings. Each of them is octahedrally coordinated by oxygen atoms, two of which belong to water molecules and four to sulfate groups. A CdO_6 octahedron and a SO_4 tetrahedron are joined by a common corner (Fig. 2). Within the CdO_6 octahedra there are no significant differences between the $Cd-O_{H_2O}$ distances (av. value 2.292 Å) and the $Cd-O_{SO_4}$ distances (av. value 2.287 Å) (Table 2). Similar Cd–O bond lengths for an octahedrally coordinated Cd^{2+} ion have been found in other structures, for example 2.292(3) Å in $Cd(ClO_4)_2(H_2O)_6$[8] and 2.28 Å in $(NH_4)_2Cd(SO_4)_2(H_2O)_6$.[2] For $3CdSO_4 \cdot 8H_2O$ Lipson reported values between 2.12 and 2.63 Å,[3] but the average value, 2.293 Å, is nearly the same as that found here for the refined structure.

All oxygens of the sulfate groups are bonded to different cadmium ions, thus joining them into a three-dimensional framework (Fig. 1). The bonding angles at the bridging oxygens, that is the Cd–O–S angles, range between 125 and 136°, with an average value of 130.9°. The corresponding Cd–S distances have values between 3.352(1) and 3.480(1) Å with an average of 3.436 Å. A corresponding distance in crystals of β-$Cd_2(OH)_2SO_4$ has been found to be 3.50 Å.[9]

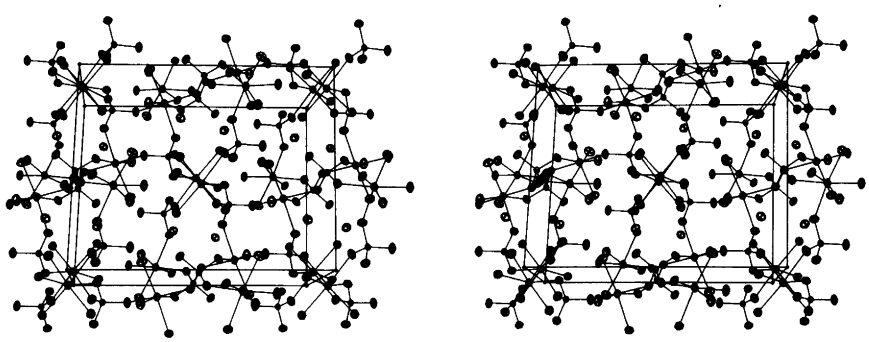

Fig. 1. A stereoscopic drawing of the contents of the unit cell of $3CdSO_4 8H_2O$ viewed along the c axis with the a axis horizontal and the b axis vertical. Hydrogen atoms are not included. The ellipsoids are drawn to include 50% probability.

Table 1a. Final positional parameters. Standard deviations are given within parentheses.

	x	*y*	*z*
Cd1	0.15443(2)	0.40511(2)	0.03500(3)
Cd2	0	−0.05363(3)	1/4
S1	0	0.50828(10)	1/4
S2	0.12978(6)	0.11705(7)	0.05632(8)
O1	0.0258(2)	0.4358(2)	0.1357(3)
O2	0.4224(2)	0.0799(2)	0.1936(3)
O3	0.3962(2)	0.4709(2)	0.0521(3)
O4	0.1008(2)	0.2269(2)	0.0033(3)
O5	0.0848(2)	0.0936(2)	0.1832(3)
O6	0.2296(2)	0.1152(2)	0.0982(3)
O7[a]	0.0936(2)	0.1928(3)	0.6827(4)
O8[a]	0.2796(4)	0.0746(4)	0.4019(4)
O9[a]	0.2214(3)	0.3584(3)	0.2573(4)
O10[a]	0.0955(2)	0.2506(3)	0.4077(3)
H1	0.083(3)	0.252(4)	0.716(5)
H2	0.095(4)	0.209(5)	0.601(7)
H3	0.251(5)	0.079(7)	0.406(10)
H4	0.271(5)	0.075(5)	0.309(8)
H5	0.195(4)	0.326(5)	0.288(6)
H6	0.273(4)	0.347(4)	0.273(6)
H7	0.094(3)	0.203(4)	0.346(5)
H8	0.060(4)	0.300(5)	0.402(6)

[a] H_2O.

The sulfate groups form regular tetrahedra with an average S−O distance of 1.475 Å (Table 2). This is similar to values found in other structures, for example 1.47 Å in $NiSO_4 \cdot 6D_2O$[10] and 1.471 Å in $MgSO_4 \cdot 7D_2O$.[11]

There are four independent water molecules in the structure only one of which, O10, is not bonded to cadmium. The arrangement around O10 is approximately tetrahedral. It forms two hydrogen bonds to sulfate oxygens, O1 and O5, and accepts two bonds from water molecules coordinated to cadmium, O9 and O7 (Table 2). The arrangement around the other water molecules is varied. For O7 it is approximately tetrahedral. It forms bonds to Cd2, H1 and H2 and accepts a hydrogen bond from O9. For O8 and O9 the arrangement seems closer to being planar trigonal. Each of them forms only three bonds, to Cd1, H3, H4 and Cd1, H5, H6, respectively (Table 2). The arrangements around the different water molecules are illustrated in Fig. 2.

With the suggested assignment of hydrogen bonds all of the sulfate oxygens, except O4, are engaged in

Table 1b. Final thermal parameters in Å^2. The anisotropic temperature factors, B_{ij}, are defined by the expression $\exp\{-\frac{1}{4}(B_{11}h^2a^{*2}+\cdots+2B_{23}klb^*c^*)\}$. The isotropic temperature factors B, used for the hydrogen atoms, are defined by $\exp\{-B\sin^2\theta/\lambda^2\}$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cd1	1.00(1)	1.51(1)	1.23(1)	−0.04(1)	0.23(1)	−0.06(1)
Cd2	1.03(2)	1.35(2)	1.24(2)	0	0.09(1)	0
S1	0.80(5)	1.09(5)	0.81(4)	0	0.14(4)	0
S2	0.80(3)	1.07(3)	0.86(3)	−0.07(3)	0.19(3)	0.06(2)
O1	1.38(11)	1.69(10)	1.59(11)	−0.12(9)	0.56(9)	−0.50(8)
O2	1.45(12)	1.87(11)	1.63(11)	0.49(9)	−0.01(9)	−0.02(8)
O3	1.71(12)	1.44(10)	1.34(10)	0.14(9)	−0.06(9)	−0.48(8)
O4	1.95(12)	1.22(11)	1.97(11)	0.07(9)	−0.28(10)	0.22(9)
O5	1.77(12)	2.12(11)	1.32(11)	−0.37(10)	0.87(9)	−0.30(8)
O6	0.94(11)	2.65(12)	1.48(11)	0.06(10)	0.01(9)	−0.03(9)
O7[a]	1.57(12)	1.81(12)	1.76(12)	−0.11(10)	0.27(10)	0.17(10)
O8[a]	2.45(19)	2.12(14)	1.96(17)	0.40(13)	0.53(13)	0.22(10)
O9[a]	1.79(16)	2.97(16)	2.22(14)	0.06(14)	0.11(12)	0.66(11)
O10[a]	2.05(13)	1.92(12)	1.91(12)	0.02(12)	0.32(10)	−0.08(10)
H1	1.5(10)	H5	3.0(17)			
H2	3.5(13)	H6	2.7(13)			
H3	3.9(28)	H7	1.5(9)			
H4	4.5(15)	H8	4.1(16)			

[a] H_2O.

Table 2. Selected interatomic distances (Å) and angles (°).

Within the CdO_6 octahedra			
Cd1–O1	2.268(3)	Cd2–O3	2.284(3)
–O2	2.319(3)	–O3	2.285(3)
–O4	2.280(3)	–O5	2.291(3)
–O6	2.272(3)	–O5	2.293(3)
–O8 (H_2O)	2.289(4)	–O7 (H_2O)	2.301(3)
–O9 (H_2O)	2.289(4)	–O7 (H_2O)	2.303(3)
Cd–S distances for bound SO_4 groups			
Cd1–S1	3.478(1), 3.461(1)	Cd2–S2	3.476(1), 3.461(1)
–S2	3.456(1), 3.428(1)		3.456(1), 3.428(1)
Within the sulfate tetrahedra			
S1–O1	1.474(3)	S2–O3	1.484(3)
–O1	1.471(3)	–O4	1.464(3)
–O2	1.474(3)	–O5	1.473(3)
–O2	1.475(3)	–O6	1.481(3)
O1–S1–O1	108.3(2)	O3–S2–O4	109.1(2)
O1–S1–O2	109.7(2)	O3–S2–O5	109.1(2)
O1–S1–O2	110.0(2)	O3–S2–O6	109.6(2)
O1–S1–O2	109.9(2)	O4–S2–O5	109.9(2)
O1–S1–O2	109.6(2)	O4–S2–O6	110.5(2)
O2–S1–O2	109.4(2)	O5–S2–O6	108.7(2)
Hydrogen bonding distances			
O7–H1···O2	2.973(4)		
O7–H2···O10	2.695(5)		
O7···H6–O9	2.794(5)		
O8–H3···O3	2.965(6)		
O8–H4···O6	2.915(5)		
O9–H5···O10	2.799(5)		
O9–H6···O7	2.794(5)		
O10–H7···O5	2.823(4)		
O10–H8···O1	2.840(4)		
O10···H5–O9	2.799(5)		
O10···H2–O7	2.695(5)		

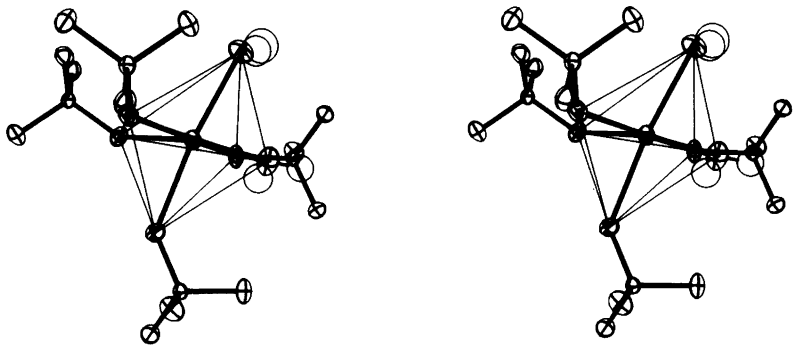

Fig. 2a. Stereoscopic drawing of the coordination around the Cd1 atom, including the sulfate groups (S1 and S2) and the water molecules (O8 and O9). The ellipsoids are scaled to include 50% probability.

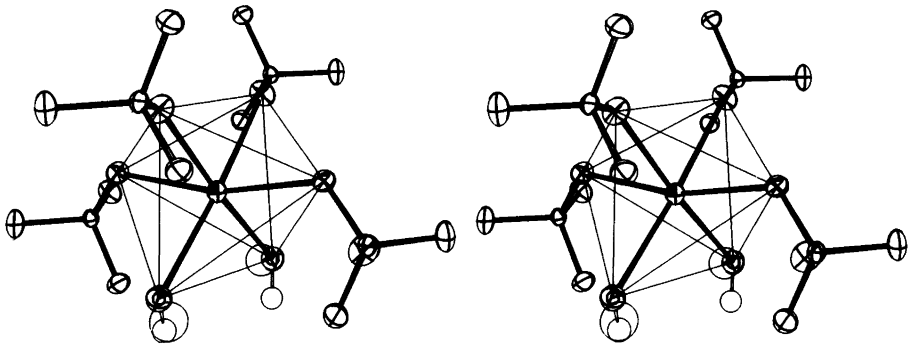

Fig. 2b. Stereoscopic drawing of the coordination around the Cd2 atom, including the sulfate groups (S2) and the water molecules (O7). Ellipsoids include 50% probability.

one hydrogen bond each. Perhaps because of this, the shortest of the S–O distances within the sulfate tetrahedra is that between S2 and O4, which is only 1.464(3) Å, compared to the average value of 1.475 Å (Table 2).

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