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The Crystal Structure of Cadmium Nitrate Tetrahydrate

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The structure of cadmium nitrate tetrahydrate has been determined from two-dimensional X-ray data. The crystals are rhombic, space group Fdd2-C_{2v}^{19}, with a = 5.83, b = 25.75, c = 10.99 Å, Z = 8. They are piezoelectric. It follows from the interatomic distances that the compound is tetra-aquocadmium nitrate defined by the formula $[Cd(OH_2)_4](NO_3)_2$. The lengths of the cadmium-water distances (2.35 and 2.37Å) are almost the same as the cadmium-oxygen distances in the CdO (2.35 Å), and smaller than cadmium-oxygen from the nitrate group.

The crystal structure of cadmium nitrate tetrahydrate has been studied in order to determine the co-ordination of oxygen atoms (from water molecules and nitrate groups) around the cadmium atom. This is of interest not only for the structural chemistry of cadmium compounds but also for the crystal chemistry of hydrated metal nitrates, which are not sufficiently known.

EXPERIMENTAL

Crystallographic and X-Ray Data

Single crystals of cadmium nitrate tetrahydrate were obtained by slow evaporation of an aqueous solution. The crystals are colourless and transparent rhombic prisms. They are piezoelectric, as determined by the Bergmann method modified by Yoichi Iitaka[1]. The dimensions of the unit cell, which contains eight formula units (calculated density (D_c) 2.48 g.cm^{-3}, measured density (D_m) 2.46 g.cm^{-3}), are as follows: a = 5.83 Å, b = 25.75 Å, c = 10.99 Å and were determined from oscillation photographs. Nickel-filtered Cu-K radiation was used. The space group is Fdd2 (C_{2v}^{19}, No 43), since the following systematic absence of the reflexions were noted:

(hkl) with h+k, k+l, (l+h) ≠ 2n
(0kl) with k+l ≠ 4n; (k,l ≠ 2n)
(h0l) with l+h ≠ 4n; (l,h ≠ 2n)
(hk0) with h,k ≠ 2n
(h00) with h ≠ 4n
(0k0) with k ≠ 4n
(00l) with l ≠ 4n

In addition, all (hkl) reflexions with h+k+l ≠ 2n+1 or 4n were absent except some weak reflexions and only one medium reflection. These crystallographic data are in good agreement with the data obtained by P. Gallerot and D. Weigel[2].

Intensity Measurements

Specimens cylindrically ground along the a- and c- axes with diameters 0.46 and 0.17 mm, respectively, were sealed in Lindemann glass capillaries to protect them from atmospheric moisture. All possible (hk0) and (0kl) reflexions were recorded on multiple-film Weissenberg photographs by means of a Nonius integrating camera. The relative intensities of the reflexions were determined from the optical densities measured in the centre of each spot by means of a micro-densitometer and corrected by means of the characteristic curve of the film. The number of hk0 and 0kl reflexions was 40 and 50, respectively (out of 49 and 50 possible reflexions). The absorption correction ($\mu = 227$ cm^{-1}) was carried out with the help of Tables[3]. The correction for polarisation and Lorentz factors were made in the usual way.

Determination and Present Refinement of the Structure

Since there are eight molecules per unit cell, the cadmium atoms must occupy positions in the set (a): 0,0,z; $^1/_4$, $^1/_4$, $^1/_4$ + z with the value of z taken as z = 0. Successive Fourier projections along [001] with the (+) signs for the observed structure factors F_o(hk0) where h+k = 4n, and with the signs changed systematically for some structure factors F_o(hk0), with h+k = 4n+2, were used to locate oxygen and nitrogen atoms. (The number of observed hk0 reflexions with h+k = 4n+2 was 11, of which three reflexions were medium, three-weak, and the others-very weak). In this way quite a good resolution of two oxygen and one nitrogen atoms (from the nitrate-group) was obtained. The peaks of other three oxygen atoms (two from water molecules and one from the nitrate-group) were concealed in a broad maximum. In the next step the Fourier projections along [001] were computed with the signs of F_o(hk0) obtained by taking into account the contributions of all atoms. The z-coordinates of all light atoms from [100] Patterson projection were used to calculate the structure factors F_o(0kl), phase angles α (0kl), and Fourier projection along [100]. The refinement of these x,y and z co-ordinates was made with several successive structure-factor calculations and Fourier syntheses [100] (Fig. 1) and [001]. An improved resolution was achieved in the [001] difference Fourier projection which was computed with (F_o-F_{Cd}) as coefficients (Fig. 2). The values of the x,y and z co-ordinates at the present stage of the investigation, are listed in Table I. The work on a more exact determination of the co-ordinates of all light atoms on the basis of three-dimensional data is now in progress.

TABLE I

Atomic co-ordinates

	x/a	y/b	z/c
Cd	0.000	0.000	0.000
$O_{(1)}$	0.350	0.046	—0.067
$O_{(2)}$	0.133	0.095	0.046
$O_{(3)}$	0.467	0.118	0.000
$O_{(4)}$	0.227	—0.028	0.164
$O_{(5)}$	0.197	—0.056	—0.135
N	0.318	0.085	—0.006

Numbering: $O_{(1)}$, $O_{(2)}$ and $O_{(3)}$ belong to the nitrate-group, $O_{(4)}$ and $O_{(5)}$ to water.

Structure factors were calculated by using the values of the atomic scattering factors, given in Tables[4], multiplied by an average temperature factor exp (-B.sin$^2\,\Theta\,/\lambda^2$) with B = 3.1Å^2 for light atoms and B = 2.2Å^2 for the cadmium atom. These values of B as well as the scale factor were obtained and subsequently improved by plotting ln(F_o/F_c) against (sin$^2\,\Theta\,/\,\lambda^2$).

The observed F_o and calculated F_c structure amplitudes (with the real and imaginary parts) are given in Table II. The reliability indices have values R(hk0)= = 11.6 and R(0kl) = 11.4. The values of unobserved reflexions were taken as half of the minimum observable. Each unobserved structure factor which was estimated according to this method, but which was weaker than or equal to the calculated value F_c, was not used. When the calculated structure factors were based on the cadmium atom only, the values for the reliability indices were R(hk0)=24.2 and R(0kl)=17.6 (the unobserved reflexions were not included here).

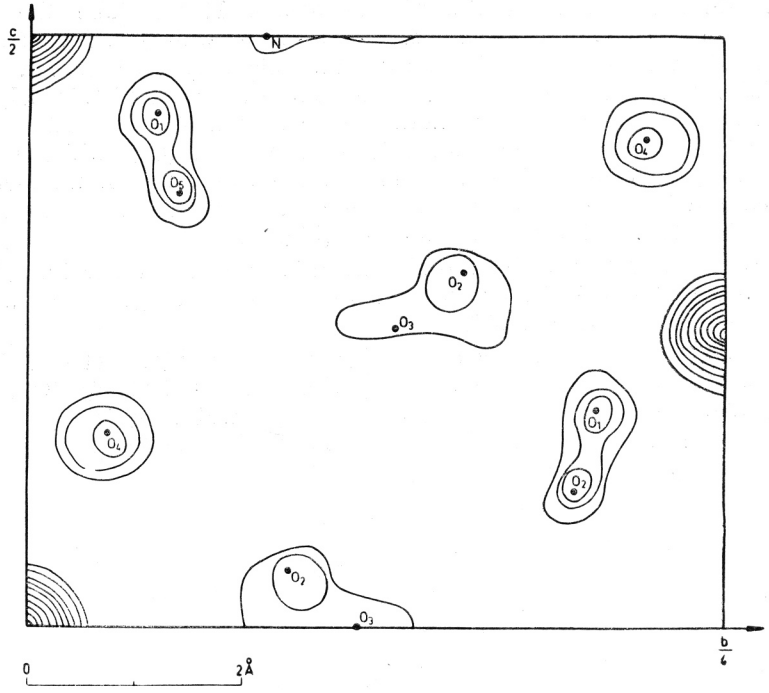

Fig. 1. Electron-density projection on (100).

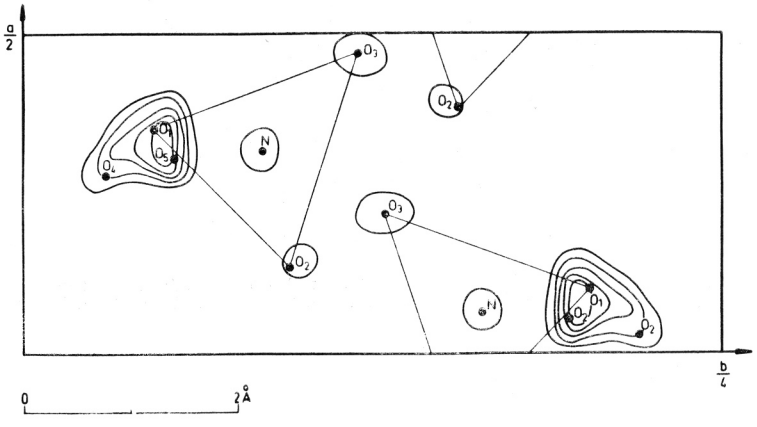

Fig. 2. Electron-density projection on (001), difference map. In Figs. 1 and 2. the contours are at arbitrary intervals. The numbering of the light atoms corresponds to the identification in the texst and tables.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The values of the intramolecular and intermolecular distances in the crystal structure of cadmium nitrate tetrahydrate are given in Table III. It follows from the crystal structure that the salt is tetra-aquocadmium nitrate defined by the formula $[Cd(OH_2)_4](NO_3)_2$. The lengths of the cadmium-water distances are almost the same as Cd-O in the CdO (2.35 Å)[5], and smaller than cadmium-oxygen from the nitrate group. If we take the nearest neighbours of the cadmium atom *i.e.* O_4, O_5 (from water) and O_1 (from the nitrate-group) for co-ordinated atoms, the distorted octahedron is the co-ordination polyhedron of oxygen atoms. The distortion of this polyhedron is influenced by the nearness of another oxygen atom from the nitrate-group (O_2). If we also take into account this oxygen atom (O_2), which seems to be reasonable, then the cadmium atom has the co-ordination number eight. In this case the co-ordination polyhedron of the oxygen atoms around the cadmium atom is a distorted dodecahedron (Fig. 3).

The NO_3^- ion does not deviate significantly from a regular triangle. The average N-O distance is 1.23 Å. This value is in good agreement with the known data for the nitrate ion[6,7].

The distances of the clossest approach between the atoms of neighbouring tetra-aquocadmium nitrate molecules are: $O_2 \ldots O_5 = 2.70$ and $O_1 \ldots O_5 = 2.76$ Å (between nitrate-oxygen (O_1), (O_2) and water-oxygen (O_5) atoms). These distances indicate the hydrogen bonding between the molecules of $[Cd(OH_2)_4](NO_3)_2$.

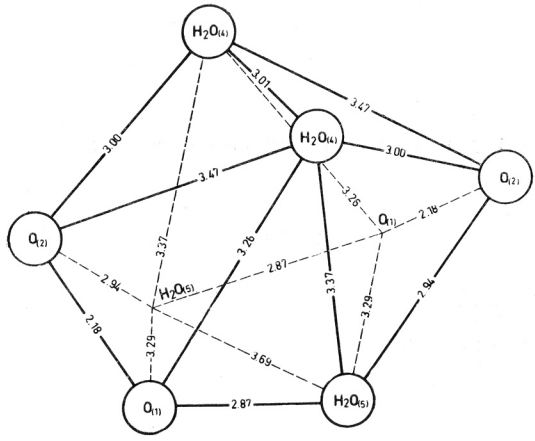

Fig. 3. The values of 0 . . . 0 distances in the distorted dodecahedron as the co-ordination polyhedron of the oxygen atoms around the cadmium atom.

TABLE II

Observed and calculated structure amplitudes with the components of the calculated structure factors

(The minimum observable values are given in parenthesis)

0kl	F_o	$\|F_c\|$	A	B	0kl	F_o	$\|F_c\|$	A	B
0.0.4	276	351	344	—67	0.12.12	91	74	72	—18
0.0.8	193	224	220	42	0.14.2	206	189	185	—38
0.0.12	132	117	117	10	0.14.6	173	160	160	3
0.2.2	428	468	466	—44	0.14.10	137	118	118	—5
0.2.6	252	284	283	23	0.16.0	181	166	166	0
0.2.10	103	106	106	4	0.16.4	211	171	170	9
0.2.14	89	78	78	10	0.16.8	149	167	163	—36
0.4.0	226	260	260	0	0.16.12	80	70	70	11
0.4.4	181	160	95	—128	0.18.2	214	166	144	—83
0.4.8	149	129	129	10	0.18.6	135	119	118	16
0.4.12	97	99	99	10	0.18.10	84	91	91	7
0.6.2	174	126	110	62	0.20.0	214	191	191	0
0.6.6	239	205	197	—58	0.20.4	138	129	127	22
0.6.10	126	128	128	0	0.20.8	97	86	86	—5
0.8.0	239	236	236	0	0.22.2	208	180	178	—27
0.8.4	332	359	358	27	0.22.6	115	82	82	5
0.8.8	183	178	177	18	0.22.10	77	66	64	12
0.8.12	104	106	105	—14	0.24.0	197	148	148	0
0.10.2	337	397	368	147	0.24.4	159	151	150	—14
0.10.6	215	242	241	23	0.24.8	97	88	88	—4
0.10.10	154	140	140	2	0.26.2	124	120	120	0
0.12.0	161	167	167	0	0.26.6	93	100	97	—24
0.12.4	274	284	271	86	0.28.0	52	68	68	0
0.12.8	156	152	152	—6	0.28.4	87	87	86	—7
0.32.0	71	82	82	0	0.30.2	71	86	68	19

hk0	F_o	F_c	hk0	F_o	F_c
0.4.0	226	260	4.2.0	37	—36
0.8.0	239	236	4.4.0	207	206
0.12.0	161	167	4.6.0	96	—95
0.16.0	181	166	4.8.0	218	209
0.20.0	214	191	4.10.0	41	28
0.24.0	197	148	4.12.0	140	124
0.28.0	52	68	4.14.0	0	—3
0.32.0	71	82	4.16.0	148	156
2.2.0	125	125	4.18.0	55	17
2.4.0	140	131	4.20.0	72	71
2.6.0	287	304	4.22.0	0	—5
2.8.0	117	103	4.24.0	77	79
2.10.0	263	316	4.26.0	24	—8
2.12.0	69	—57	4.28.0	49	73
2.14.0	231	232	6.2.0	120	123
2.16.0	64	—34	6.4.0	0(12)	32
2.18.0	207	205	6.6.0	72	81
2.20.0	0	5	6.8.0	0(12)	—21
2.22.0	117	115	6.10.0	88	95
2.24.0	47	—6	6.12.0	0(12)	16
2.26.0	145	128	6.14.0	74	87
2.28.0	32	23	6.16.0	0	—1
2.30.0	92	75	6.18.0	67	83
4.0.0	194	188	6.20.0	0	3

TABLE III

Interatomic distances

a) Intramolecular

Cd — $O_{(1)}$	= 2.47 Å	$O_{(1)}$ — $O_{(4)}$	= 3.26 Å
Cd — $O_{(2)}$	= 2.62	$O_{(1)}$ — $O_{(5)}$	= 2.87
Cd — $O_{(3)}$	= 4.08	$O_{(2)}$ — $O_{(4)}$	= 3.47
Cd — $O_{(4)}$	= 2.35	$O_{(4)}$ — $O_{(5)}$	= 3.37
Cd — $O_{(5)}$	= 2.37	$O_{(1)}$ — $O_{(1)}'$	= 4.24
Cd — N	= 2.87	$O_{(4)}$ — $O_{(2)}'$	= 3.00
		$O_{(4)}$ — $O_{(4)}'$	= 3.01
$O_{(1)}$ — N	= 1.22 Å	$O_{(5)}$ — $O_{(1)}'$	= 3.29
$O_{(2)}$ — N	= 1.25	$O_{(5)}$ — $O_{(2)}'$	= 2.94
$O_{(3)}$ — N	= 1.22	$O_{(5)}$ — $O_{(5)}'$	= 3.69
$O_{(1)}$ — $O_{(2)}$	= 2.18		
$O_{(1)}$ — $O_{(3)}$	= 2.12		
$O_{(2)}$ — $O_{(3)}$	= 2.10		

The co-ordinates of $O_{(1)}'$; $O_{(2)}'$; $O_{(4)}'$ and $O_{(5)}'$ are: $\bar{x}$; $\bar{y}$; z

b) Intermolecular distances between the nearest atoms

$O_{(1)}$ — $O_{(5)}'$	= 2.76 Å
$O_{(2)}$ — $O_{(4)}'$	= 3.01
$O_{(2)}$ — $O_{(5)}'$	= 2.94
$O_{(3)}$ — $O_{(5)}'$	= 2.93
$O_{(2)}$ — $O_{(5)}''$	= 2.70
$O_{(4)}$ — $O_{(1)}'''$	= 3.03
$O_{(4)}$ — $O_{(5)}'''$	= 3.12

The co-ordinates of $O_{(4)}'$; and $O_{(5)}'$ are: $\bar{x}$; $\bar{y}$; z.
The co-ordinates of $O_{(5)}''$ are: $\frac{1}{4} - x$; $\frac{1}{4} + y$; $\frac{1}{4} + z$.
The co-ordinates of $O_{(1)}'''$ and $O_{(5)}'''$ are: $\frac{1}{2} - x$; $\bar{y}$; $\frac{1}{2} + z$.

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IZVOD

Kristalna struktura kadmijeva nitrata tetrahidrata

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Struktura kadmijeva nitrata tetrahidrata određena je metodom rendgenske strukturne analize. Kristali su rompski, prostorna grupa Fdd2 (C_{2v}^{19}, No 43), sa dimenzijama elementarne ćelije : a = 5,83, b = 25,75, c = 10,99 Å, Z = 8; na kristalima je ustanovljen piezoelektrički efekt. Iz određenih međuatomskih razmaka proizlazi da je navedeni spoj tetra-akvokadmijev nitrat, $[Cd(OH_2)_4]$ $(NO_3)_2$.

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