

The Determination of the Crystal Structure of Cadmium Nitrate Tetrahydrate by means of Neutron Anomalous Dispersion Measurements

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The method of solving the phase problem by use of neutron anomalous scattering measurements at a single wavelength has been tested in the structure determination of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{D}_2\text{O}$. It has been shown that the structure can be obtained independently from both the 'direct-phase' and sine Patterson procedures. The structural parameters have been refined by the method of least-squares to an R value of 0.074; the refined value of b_{Cd}'' is $0.105(9) \times 10^{-12}$ cm at a wavelength of 1.054 Å. The hydrogen bonding scheme has been elucidated.

Introduction

The method of determining phase angles in crystal-structure determinations with X-ray anomalous dispersion effects is well known. Peterson & Smith (1962) and Ramaseshan (1966) pointed out that the anomalous scattering effects are more pronounced in the case of neutrons and can be used to solve complex crystal structures; however, no structure determination has been reported by this method. It was the purpose of this investigation to carry out one such structural analysis and to observe whether the techniques used in X-rays can be applied to the neutron case.† For this study the compound cadmium nitrate tetrahydrate was chosen, the X-ray structure of which has been reported by Matković, Ribar, Zelenko & Peterson (1966).

Experimental

The anomalously scattering isotope ^{113}Cd is present in the proportion 12.26% in naturally occurring cadmium and this nuclide strongly absorbs thermal neutrons. In order to achieve a balance between absorption and resonance scattering, a wavelength in the region of 1 Å was chosen. The crystal was deuterated to minimize the background arising from the incoherent scattering arising from hydrogen atoms.

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{D}_2\text{O}$ was prepared by repeated crystallization and refluxing of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 99.8% D_2O . The resulting crystals had a 97.5% content of D_2O (determined spectroscopically). The crystals were hygroscopic and very soft. A large single crystal was grown from the melt (m. p. 58°C) by use of a modified crystal growing apparatus (Sherwood & Thomson, 1960) and from this a sphere of mass 18.6 mg was ground with a modified Bond sphere grinder. (As data

collection proceeded, the shape of this crystal changed to an oblate spheroid; the maximum change in radius was 19%.)

The crystal was orientated along the b axis by the use of X-rays and then covered with a silica cap to prevent interaction with the atmosphere. The Bragg neutron intensities were measured at the PLUTO reactor by use of the Harwell Mark I automatic neutron diffractometer (Arndt & Willis, 1963). A copper monochromator was used giving an incident thermal neutron flux of 2.3×10^5 n.cm²sec⁻¹ at a wavelength of 1.054 Å as determined from a standard KCl crystal. The cell dimensions $a=5.828$, $b=25.86$, $c=11.002$ Å determined by Matković *et al.* (1966) were consistent with the observed 2θ angles. The systematic absences corresponding to the space group $Fdd2$ were also confirmed. The intensities of the Bijvoet pairs of reflexions hkl and $\bar{h}\bar{k}\bar{l}$ were measured by the ω - 2θ scan method

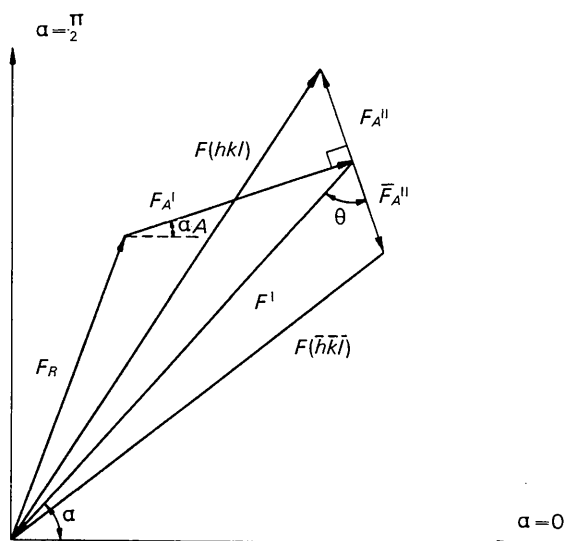


Fig. 1. Amplitude-phase diagram in the presence of anomalous dispersion scattering.

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† Professor S. W. Peterson and Dr D. Dale were associated with the earlier stages of this work but the results reported here are based entirely on data collected by the present authors.

out to a $\sin\theta/\lambda$ value of 0.56 \AA^{-1} . The reflexions were indexed according to a right-handed system.

The integrated intensities were corrected for variation in the incident flux, Lorentz factor and absorption (corrections for a sphere of radius $r=0.12 \text{ cm}$ were applied; the absorption coefficient was measured on a separate single crystal 0.99 mm thick and was

found to be 12.2 cm^{-1}). Standard deviations were derived from counting statistics and comparison of the pairs of hkl and $h\bar{k}\bar{l}$ when $h+k+l=4n+2$ (reflexions which do not show any anomalous dispersion effects) indicated that these were reliable estimates of the precision of the measurements. Reflexions of intensity less than one standard deviation were treated as un-

Table 1. Observed and calculated values of phase angles in $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{D}_2\text{O}$
The six columns in each set contain respectively the miller indices $h, k, l, \alpha_1, \alpha_2$ and α_0 .

0	2	2	135	45	109	1	5	7	190	80	78	3	21	1	179	45	46
1	1	1	100	350	76	3	1	5	135	135	125	3	1	9	210	60	30
1	3	1	315	315	304	3	3	5	45	45	58	2	0	10	90	90	15
1	5	1	160	291	271	1	13	5	91	359	335	1	13	9	166	284	109
0	6	2	241	299	203	1	7	7	225	225	195	5	3	5	197	93	161
1	1	3	257	13	286	4	2	2	234	308	237	3	5	9	315	315	161
1	7	1	135	135	117	2	8	6	203	337	0	1	25	1	101	349	32
1	3	3	61	29	22	0	16	4	141	38	86	2	22	4	165	15	165
0	0	4	109	71	77	0	18	2	159	21	134	0	10	10	202	338	316
0	0	3	308	324	337	3	11	3	279	351	54	5	5	5	85	5	293
1	1	7	2	155	24	0	0	8	124	56	86	4	16	4	173	6	0
0	4	4	128	52	120	2	16	2	199	341	358	0	24	4	191	349	4
1	9	1	186	264	190	1	17	3	237	33	78	5	13	1	144	305	211
2	4	2	139	41	0	2	14	4	239	301	212	3	21	3	81	8	342
1	7	3	45	45	36	3	7	5	225	225	189	3	15	7	237	33	244
0	10	2	270	270	290	1	9	7	205	65	127	3	7	9	225	225	132
1	11	1	206	64	63	1	15	5	211	59	239	3	19	5	124	326	76
1	9	3	217	53	102	1	19	1	135	135	102	2	24	2	290	270	269
0	8	4	198	342	1	0	14	6	183	357	311	2	20	6	183	357	97
1	1	5	184	266	194	3	13	3	161	290	330	1	23	5	135	135	296
2	8	2	134	47	34	3	9	5	315	315	7	1	15	9	315	315	0
2	1	3	233	37	25	4	0	4	160	20	53	1	25	3	279	351	290
2	2	4	228	312	288	3	15	1	187	263	256	2	8	10	127	53	61
1	5	5	114	336	63	0	8	8	176	4	358	0	26	2	110	70	81
3	1	1	315	315	18	2	12	2	173	7	137	4	14	6	214	326	201
1	11	3	94	356	148	1	19	3	88	1	264	5	13	3	297	333	68
3	3	1	165	285	300	3	11	5	108	342	311	5	9	5	60	30	29
1	13	1	45	45	18	4	10	2	90	90	71	3	23	1	140	310	307
2	6	4	206	334	350	1	17	5	169	281	336	1	5	11	215	55	39
0	2	6	249	291	304	3	15	3	315	315	233	6	0	2	147	33	32
1	7	5	182	88	110	3	3	7	174	95	191	1	21	7	201	69	59
3	5	1	248	22	250	1	13	7	190	80	238	3	17	7	45	45	131
0	14	2	191	349	190	3	17	1	221	49	218	1	7	11	103	347	317
3	1	3	116	334	354	3	13	5	202	68	70	6	4	2	186	354	146
3	7	1	45	45	103	0	20	4	137	43	112	0	14	10	139	41	10
0	12	4	230	310	326	2	18	4	174	6	317	5	11	5	315	315	202
0	6	6	157	23	145	1	5	9	97	352	305	0	20	8	159	21	180
3	3	3	174	96	106	0	12	8	178	2	61	1	27	1	258	12	335
1	13	3	236	34	26	2	20	2	218	322	255	3	23	3	234	36	89
1	9	5	176	274	328	5	3	1	215	55	83	3	21	5	233	37	87
2	12	2	173	7	137	0	22	2	135	45	46	1	17	9	128	322	66
1	15	1	315	315	321	3	17	3	173	277	111	5	3	7	157	293	0
3	5	3	225	225	202	1	15	7	45	45	3	2	12	10	181	359	149
3	9	1	315	315	286	0	18	6	230	310	232	1	25	5	225	225	141
2	10	4	194	346	158	3	9	7	96	353	21	5	17	1	45	45	352
3	7	3	216	54	209	2	16	6	153	27	39	5	5	7	246	23	9
2	0	6	139	41	137	3	15	5	181	269	197	3	13	9	162	87	87
1	11	5	236	34	26	4	12	4	90	90	100	0	0	12	194	346	282
1	15	3	113	337	41	5	5	3	156	144	77	1	27	3	70	20	40
0	10	6	216	323	295	3	11	7	254	16	29	4	20	4	159	21	330
1	1	3	102	348	255	5	7	3	225	225	246	0	4	12	174	5	212
3	3	3	225	225	188	1	21	5	25	225	263	4	22	2	154	26	178
1	17	1	181	269	162	3	13	7	176	274	312	1	19	9	241	28	52
						5	9	3	277	353	314	5	17	3	238	32	7

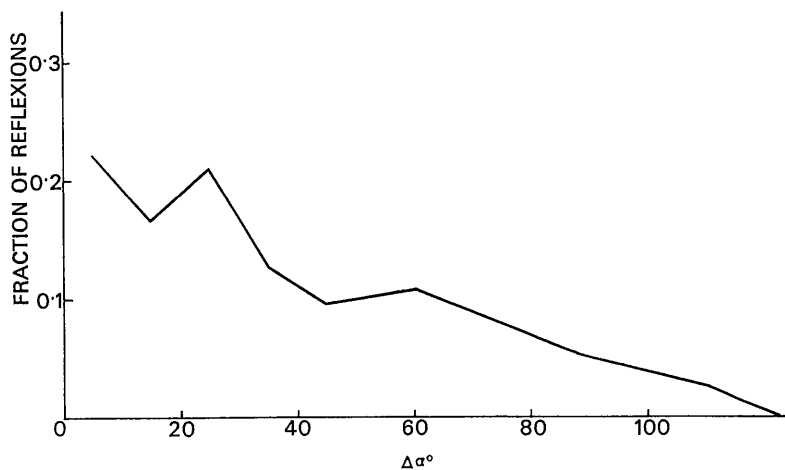


Fig. 2. The diagram showing the distribution of error on the measured value of the phase angle α .

observables. The derived structure factors were put on an absolute scale by comparing them with the intensity from a standard KCl crystal.

Solution of the structure from anomalous dispersion data

Two procedures have been used for the solution of crystal structures from X-ray anomalous dispersion measurements. One is the direct phase method proposed by Ramachandran & Raman (1956) and the other is the sine Patterson method suggested by Okaya, Saito & Pepinsky (1955). We have used both methods to determine the structure of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{D}_2\text{O}$.

(a) Direct phase method

The theory of this method has been described by Ramachandran & Raman (1956). The phase α of F' (see Fig. 1 for the relationship between these quantities) is given by

$$\alpha = \alpha_A + \frac{\pi}{2} + \theta$$

where

$$\theta = \pm \cos^{-1} \left[\frac{|F(hkl)|^2 - |F(\bar{h}\bar{k}\bar{l})|^2}{4 |F'| |F'_A|} \right].$$

The uncertainty in the sign of θ gives rise to an ambiguity in the value of the phase angle, α , which can have the following values

$$\alpha_1 = \alpha_A + \frac{\pi}{2} + \theta,$$

$$\alpha_2 = \alpha_A + \frac{\pi}{2} - \theta.$$

In the X-ray scattering case the ambiguity in phase angle is resolved by choosing that value of α which is closer to the heavy atom phase α_A since the anomalous scatterer is usually a 'heavy atom' [Raman (1959); Dale, Hodgkin & Venkatesan (1963); Hall & Maslen (1965)]. For $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{D}_2\text{O}$ the Cd atom contributes only 1.4% ($100 \Sigma (b_{\text{Cd}}^2 + b_{\text{Cd}}'^2) / \Sigma_j b_j^2$) of the total neu-

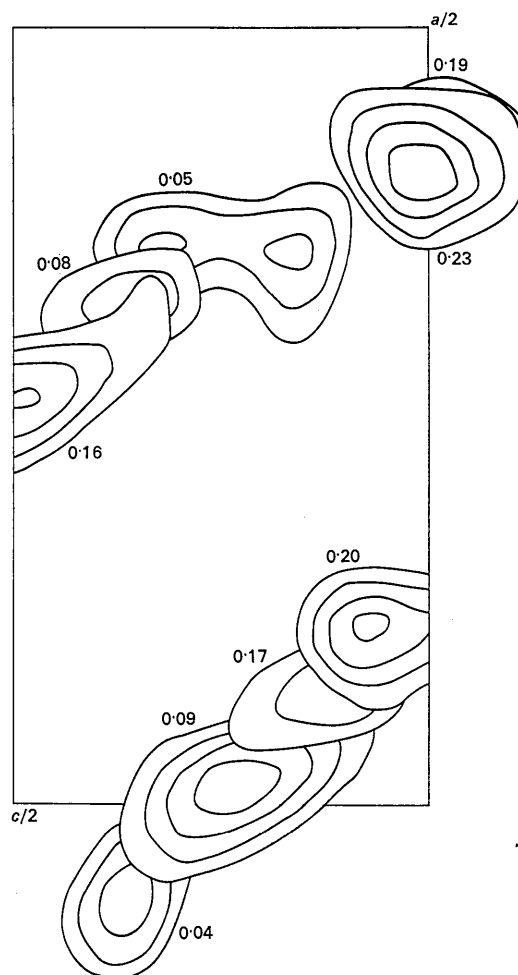


Fig. 3. Composite map of the double phased Fourier synthesis. The decimal fractions indicate the coordinates of the levels from which the contoured portions are taken. The contours are at equal arbitrary intervals. The zero and first contours are omitted.

Table 2. Final positional and temperature parameters*

The standard deviations are given in parentheses. All parameters are multiplied by 10^4 .

	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cd	0	0	0	123 (55)	5 (2)	14 (12)	-14 (12)	0	0
N	1791 (9)	879 (2)	5031 (14)	141 (18)	5 (1)	106 (8)	6 (3)	-2 (11)	-10 (2)
O(1)	1566 (15)	468 (2)	5627 (15)	295 (31)	0	18 (5)	5 (4)	-48 (13)	5 (2)
O(2)	3553 (18)	916 (4)	4434 (17)	259 (48)	15 (2)	60 (9)	-2 (9)	-4 (17)	8 (3)
O(3)	292 (20)	1229 (4)	5028 (15)	366 (44)	9 (1)	140 (13)	18 (8)	-60 (21)	13 (4)
O(4)	4888 (22)	3201 (4)	966 (22)	386 (56)	6 (1)	240 (24)	-16 (7)	201 (33)	-35 (5)
O(5)	1895 (22)	481 (4)	1437 (16)	280 (49)	11 (2)	52 (9)	-1 (7)	109 (20)	-7 (3)
D(1)	4947 (20)	1951 (5)	627 (15)	320 (34)	25 (3)	40 (8)	2 (9)	71 (17)	6 (4)
D(2)	5349 (26)	2509 (5)	314 (13)	779 (82)	26 (3)	62 (12)	-59 (15)	149 (25)	1 (5)
D(3)	1329 (21)	826 (4)	1587 (16)	456 (58)	17 (2)	62 (10)	26 (9)	54 (16)	-2 (3)
D(4)	3455 (21)	530 (4)	1174 (15)	352 (47)	12 (2)	67 (11)	-10 (7)	53 (19)	-3 (3)
$b'_{\text{Cd}} = 0.332 (20) \times 10^{-12}$ cm									
$b''_{\text{Cd}} = 0.105 (9) \times 10^{-12}$ cm									
$b_{\text{D/H}} = 0.609 (19) \times 10^{-12}$ cm									

* The expression for the temperature factor is:

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

tron scattering; hence the heavy atom method is inapplicable. The three wavelength method (Dale & Willis, 1966) which involves making measurements on the other side of the resonance peak (0.68 Å for ^{113}Cd) in order to overcome the phase ambiguity is not experimentally feasible for this compound.

The alternative approach of the use of a double-phased Fourier synthesis was adopted (Ramaseshan, 1964). In this method an electron density map is computed by the use of both $|F|, \alpha_1$ and $|F|, \alpha_2$. When the anomalous atom is centrosymmetrically disposed in the unit cell, this synthesis will yield to the true structure and its negative inverse. In the case of a non-centrosymmetrically placed anomalous atom, the relationship is not clear. In general the correct terms in the above synthesis will reinforce each other and the incorrect terms may cancel some of the correct terms or contribute to the general background.*

* See e.g. Ramachandran (1964).

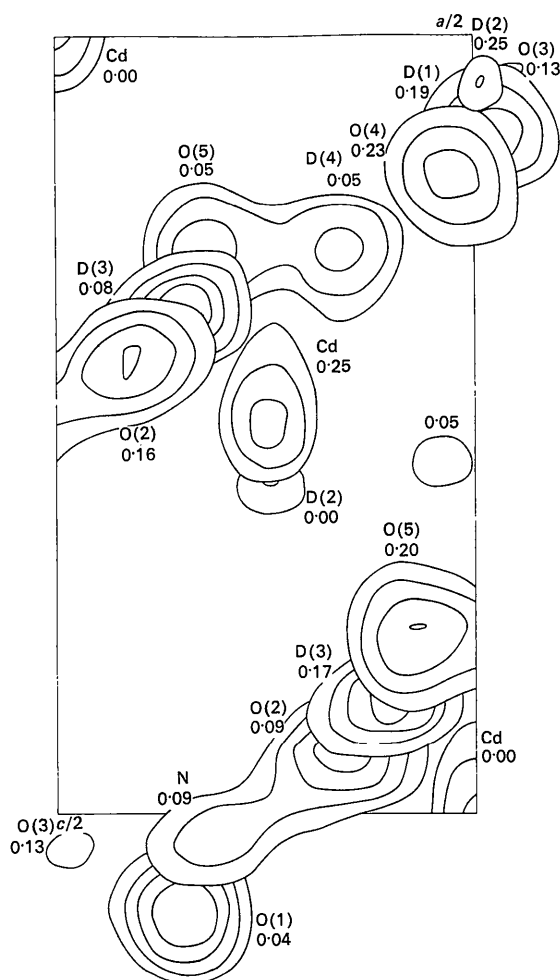


Fig. 4. Composite map of the Fourier synthesis calculated with measured phase angles which are closer to those calculated from the atoms located in the double phased Fourier synthesis.

For the calculation of α_1 and α_2 from the observed neutron Bijvoet differences, the values of α_a and F''_A for each reflexion were computed with the Cd atom placed at 0,0,0 (Cd lies at special position: $00z; \frac{1}{4}, \frac{1}{4}, \frac{1}{4} + z; +$ F.C.). Starting values adopted for the real and imaginary parts of the scattering amplitudes of the Cd atom were 0.38 and 0.12×10^{-12} cm respectively (Peterson & Smith, 1962). The magnitude of F' (see Fig. 1) was deduced from

$$F' = [\frac{1}{2}(|F(hkl)|^2 + |F(\bar{h}\bar{k}\bar{l})|^2) - F''_A{}^2]^{1/2}.$$

The criterion used to deal with those reflexions with $|\cos \theta| > 1$ † was as follows:

- (i) If $\cos \theta > 1$ θ was put equal to 0° ,
- (ii) If $\cos \theta < -1$ θ was put equal to 180° .

Reflexions of the type $hk0$ and $h+k+l=4n+2$, for which $F''_A=0$, were not included in this phase calculation. These computed values of α_1 and α_2 are listed for each reflexion in Table 1 together with α_0 , the phase angle calculated from the final least-squares refinement. It can be seen that either α_1 or α_2 is close to α_0 . This agreement is also indicated by Fig. 2 which is a plot of the distribution of the deviation $|\alpha_1 - \alpha_0|$ or $|\alpha_2 - \alpha_0|$.

The double-phased Fourier synthesis computed from $|F|, \alpha_1$ and $|F|, \alpha_2$ contained both positive and negative peaks whose coordinates were related by $\frac{1}{2} - x, y, \frac{1}{2} - z$. The composite map, showing only the positive peaks is given in Fig. 3. There were no other large positive peaks in the map. The seven atoms located were later identified as O(1), O(2), O(4), O(5), D(1), D(3) and D(4). At the position of the cadmium atom there was no peak; this occurred as a result of the exact superposition of two peaks of equal magnitude but opposite sign for this atom. [Once the structure was completely solved we could similarly account for the absence of atoms O(3), N and D(2) from this map]. The coordinates of the seven maxima were estimated and included in a structure factor calculation together with the Cd atom. All the atoms were assigned the same neutron scattering amplitude (0.58×10^{-12} cm). The value of α_1 or α_2 which was closer to the value calculated from the positions of the eight known atoms was chosen and another Fourier synthesis was computed. The $hk0$ and reflexions with $h+k+l=4n+2$ were also included with their phases determined by the eight atoms. This synthesis revealed the positions of all the 11 atoms in the asymmetric unit. Fig. 4 is a composite diagram based on this map. (The only spurious peak whose height was equal to that of O(3) is also included.)

† This may arise either as a result of experimental errors in the measurements of intensities or from systematic errors such as extinction.

(b) Sine Patterson method

The theory of this method has been presented in detail by Okaya & Pepinsky (1961). The method consists of evaluating the function

$$P_S = \sum_h \sum_k \sum_l [|F(hkl)|^2 - |F(h\bar{k}l)|^2] \sin 2\pi(hu + kv + lw)$$

This synthesis contains vectors between the anomalously scattering atom and the rest of the normally scattering atoms. The map is usually deconvoluted into the scattering density map by one of the image seeking functions.

For Cd(NO₃)₂·4D₂O, the form of the P_S function reduces to

$$P_S = \sum_h \sum_k \sum_l [|F(hkl)|^2 - |F(h\bar{k}l)|^2] \times \cos 2\pi hu \cos 2\pi kv \sin 2\pi lw$$

The map was interpreted with the help of the sum function. All the eight positions of the Cd atom (000, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ + F.C.) were made the basis for the computation of the eightfold sum function. This function could be expressed as

$$S(x, y, z) = P_S(x, y, z) + P_S(x - \frac{1}{4}, y - \frac{1}{4}, z - \frac{1}{4}) + P_S(x - \frac{1}{2}, y - \frac{1}{2}, z) + P_S(x - \frac{1}{2}, y, z - \frac{1}{2}) + P_S(x, y - \frac{1}{2}, z - \frac{1}{2}) + P_S(x - \frac{3}{4}, y - \frac{1}{4}, z - \frac{3}{4}) + P_S(x - \frac{3}{4}, y - \frac{3}{4}, z - \frac{1}{4}) + P_S(x - \frac{1}{4}, y - \frac{3}{4}, z - \frac{3}{4})$$

Table 3. Observed and calculated squared structure factors for Cd(NO₃)₂·4D₂O

The four columns in each set contain respectively h, l, 100|F_o|² and 100|F_c|².

k = 0				k = 5				k = 9				k = 15				k = 21				k = 27											
0	0	0	0	1	1	412	417	1	1	1255	1215	1	1	285	307	1	1	1598	1458	1	1	1598	1458	1	1	1598	1458	1	1	1598	1458
0	0	0	0	1	1	479	536	1	1	1465	1429	1	1	444	466	1	1	1759	1681	1	1	1759	1681	1	1	1759	1681	1	1	1759	1681
0	0	0	0	1	1	487	575	1	1	1615	1576	1	1	469	491	1	1	1870	1782	1	1	1870	1782	1	1	1870	1782	1	1	1870	1782
0	0	0	0	1	1	526	555	1	1	1785	1740	1	1	491	513	1	1	1998	1890	1	1	1998	1890	1	1	1998	1890	1	1	1998	1890
0	0	0	0	1	1	530	625	1	1	1920	1860	1	1	513	535	1	1	2154	2022	1	1	2154	2022	1	1	2154	2022	1	1	2154	2022
0	0	0	0	1	1	567	625	1	1	2070	1995	1	1	535	557	1	1	2322	2158	1	1	2322	2158	1	1	2322	2158	1	1	2322	2158
0	0	0	0	1	1	567	625	1	1	2170	2085	1	1	557	579	1	1	2496	2292	1	1	2496	2292	1	1	2496	2292	1	1	2496	2292
0	0	0	0	1	1	607	625	1	1	2320	2215	1	1	579	601	1	1	2718	2472	1	1	2718	2472	1	1	2718	2472	1	1	2718	2472
0	0	0	0	1	1	607	625	1	1	2470	2345	1	1	601	623	1	1	2976	2676	1	1	2976	2676	1	1	2976	2676	1	1	2976	2676
0	0	0	0	1	1	647	625	1	1	2620	2475	1	1	623	645	1	1	3174	2822	1	1	3174	2822	1	1	3174	2822	1	1	3174	2822
0	0	0	0	1	1	647	625	1	1	2770	2605	1	1	645	667	1	1	3330	2922	1	1	3330	2922	1	1	3330	2922	1	1	3330	2922
0	0	0	0	1	1	687	625	1	1	2920	2725	1	1	667	689	1	1	3486	3022	1	1	3486	3022	1	1	3486	3022	1	1	3486	3022

The peak heights in the resultant diagram at various atomic sites were (arbitrary scale):

O(1) 469; O(2) 215; O(3) 56; O(4) 577;
O(5) 482; D(1) 348; D(2) 365; D(3) 326;
D(4) 482; N 176.

The water molecule O(4) D(1)D(2) was distinctly visible in the map. In the asymmetric unit there were many other spurious peaks. One of these had a height of 390 and the others had heights of less than 350. It is interesting to note that 8 out of 16 atoms of each N, O(2), O(3) and D(3) in the unit cell lie very close to

Table 4. Bond distances (Å) and bond angles (°)

Uncorrected for thermal motion*.

Cd-oxygen distances

Cd—O(1) ^{I†}	2.438 (9)
Cd—O(2) ^I	2.590 (11)
Cd—O(4) ^{II}	2.247 (22)
Cd—O(5)	2.295 (12)

NO₃ group

N—O(1)	1.256 (15)	O(1)—N—O(2)	115.7 (0.8)
N—O(2)	1.223 (17)	O(1)—N—O(3)	122.5 (1.1)
N—O(3)	1.258 (12)	O(2)—N—O(3)	121.7 (1.2)
O(1)—O(2)	2.099 (21)	O(2)—O(1)—O(3)	60.4 (0.6)
O(1)—O(3)	2.204 (15)	O(3)—O(2)—O(1)	62.2 (0.5)
O(2)—O(3)	2.167 (17)	O(1)—O(3)—O(2)	57.4 (0.6)

Water molecules and hydrogen bonds

O(4)—D(1)	0.980 (20)	D(1)—O(4)—D(2)	103.2 (2.5)
D(1)···O(3) ^{III}	1.990 (18)	O(3) ^{III} ···O(4)···O(5) ^{IV}	106.9 (0.8)
O(4)···O(3) ^{III}	2.967 (17)	O(4)—D(1)···O(3) ^{III}	175.2 (1.9)
O(4)—D(2)	0.936 (26)	O(4)—D(2)···O(5) ^{IV}	167.5 (1.7)
D(2)···O(5) ^{IV}	1.951 (23)	Cd ^{VI} —O(4)—D(1)	121.3 (1.5)
O(4)···O(5) ^{IV}	2.872 (26)	Cd ^{VI} —O(4)—D(2)	128.5 (1.4)
O(5)—D(3)	0.965 (15)	D(3)—O(5)—D(4)	104.6 (1.5)
D(3)···O(2) ^V	2.004 (16)	O(2) ^V ···O(5)···O(1) ^{III}	103.2 (0.5)
O(5)···O(2) ^V	2.945 (16)	O(5)—D(3)···O(2) ^V	164.6 (1.4)
O(5)—D(4)	0.963 (19)	O(5)—D(4)···O(1) ^{III}	167.6 (1.2)
D(4)···O(1) ^{III}	1.917 (17)	Cd—O(5)—D(3)	117.0 (1.4)
O(5)···O(1) ^{III}	2.865 (17)	Cd—O(5)—D(4)	108.6 (1.4)
D(1)—D(2)	1.502 (22)	Cd—O(5)···D(2) ^{VII}	103.5 (0.6)
D(3)—D(4)	1.526 (17)	D(3)—O(5)···D(2) ^{VII}	118.1 (1.7)
		D(4)—O(5)···D(2) ^{VII}	104.1 (1.4)

* The errors have been computed from the standard deviations of the coordinates as listed in Table 2 and standard deviations of the cell constants determined in the X-ray study.

† Code for symmetry related atoms:

—	x,	y,	z	IV	$\frac{3}{4}-x, \frac{1}{4}+y, z-\frac{1}{2}$
I	$x-\frac{1}{2},$	y,	$z-\frac{1}{2}$	V	$x-\frac{1}{4}, \frac{1}{4}-y, z-\frac{1}{4}$
II	$\frac{1}{4}-x, y-\frac{1}{4},$	$z-\frac{1}{4}$		VI	$\frac{1}{4}+x, \frac{1}{4}-y, \frac{1}{4}+z$
III	$\frac{1}{2}+x,$	y,	$z-\frac{1}{2}$	VII	$\frac{3}{4}-x, y-\frac{1}{4}, \frac{1}{4}+z$

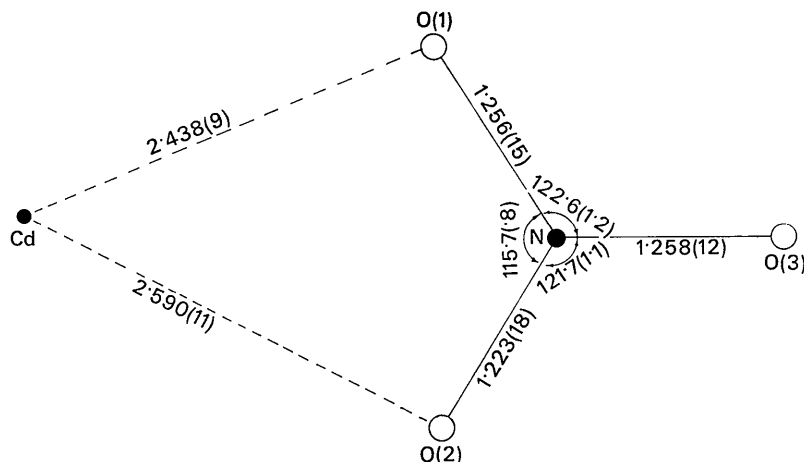


Fig. 5. Cd(NO₃)₂ bond lengths and angles.

either $z=0$ or 0.50 where the P_S function is zero. Therefore, when the sum function is taken these atoms contribute very little to their respective peaks and so have lower heights in the $S(x, y, z)$ map.

Structure refinement

A full-matrix least-squares refinement on the F_o^2 data was carried out by use of the program *ORFLS* (Busing, Martin & Levy, 1962); the parameters refined were the positional parameters of all the atoms in general positions derived from the phase method, the isotropic thermal parameters of all the atoms, the real and imaginary scattering lengths of the cadmium atom and the scattering length of the deuterium atoms. The scattering lengths used for the nitrogen and oxygen atoms were 0.94 and 0.577×10^{-12} cm (Bacon, 1962). The weighting scheme used was $w=1/\sigma^2(F_o^2)$ where $\sigma(F_o^2)$ was derived from counting statistics. After the first cycle of refinement it was apparent that the data suffered from extinction. Thereafter refinement by use of anisotropic thermal parameters) was carried out with the use of only those reflexions in which $F_c^2/\sin 2\theta \leq 600$. After six cycles of refinement this converged to an R value of 0.086 . The data were then corrected for extinction according to the method described by Sikka, Momin, Rajagopal & Chidambaram (1966).

The extinction factor is given by

$$E \approx \frac{F_o^2}{F_c^2} \approx 1 - c \frac{F_c^2}{\sin 2\theta} \frac{\frac{1}{V} \int T \exp(-\mu T) dV}{A(\mu)},$$

where c is a constant and T is the sum of the incident and diffracted-beam path lengths inside a volume element dV of the crystal. The value of c was derived from a graph of F_o^2/F_c^2 against $F_c^2/\sin 2\theta$ (the factor

$\frac{1}{V} \int T \exp(-\mu T) dV$ was treated as a constant). The

value found was $c=8.3 \times 10^{-5}$. This extinction correction was applied to the data and after three more cycles of least-squares refinement the parameter shifts were less than 0.20 standard deviations. The final agreement factors are

$$R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.074,$$

$$R(F^2) = \frac{\sum ||F_o|^2 - |F_c|^2|}{\sum |F_o|^2} = 0.105,$$

$$WR = \left(\frac{w||F_o| - |F_c||^2}{w|F_o|^2} \right)^{1/2} = 0.090.$$

Throughout the refinement the anisotropic thermal parameter β_{22} for atom O(1) tended to refine to slightly negative values, and so was restrained to a value 0. The final positional and thermal parameters are given in Table 2. The observed and calculated squared structure factors are given in Table 3. Interatomic distances

(uncorrected for thermal motion) and angles were calculated and the significant features of these calculations are given in Table 4.

Discussion

The neutron diffraction study confirms the gross molecular features as described by the X-ray study except that the absolute configuration is automatically established by the anomalous dispersion method. The coordinates of the non-hydrogen atoms given by the X-ray study are related to those determined in the present analysis by the transformation $(x, y, z) \rightarrow (\bar{x}, y, \bar{z})$. The differences in the positional parameters between the two studies are:

N 0.08 (4), O(1) 0.02 (4), O(2) 0.05 (5),
O(3) 0.14 (5), O(4) 0.16 (5), and O(5) 0.08 (4) Å,

where the quantities given in brackets are $(\sigma_{X\text{-ray}}^2 + \sigma_{\text{Neutrons}}^2)^{1/2}$.

The D_2O content of the water of hydration was determined spectroscopically to be 97.5% . When this is taken into consideration the corrected value taking $b_H = -0.378 \times 10^{-12}$ cm) of the deuterium scattering length is $b_D = 0.637(20) \times 10^{-12}$ cm. The refined value of $b_{Ca}^* = 0.105(9)$ agrees well with that calculated from the measured absorption coefficient ($b_{Ca}^* = \sigma_{Ca}/2\lambda = 0.114 \times 10^{-12}$ cm).

The Cd-O distances do not vary significantly from those reported previously and range from $2.295(13)$ and $2.247(22)$ Å for the Cd to water molecule contacts. The cadmium-nitrate ion configuration is shown in Fig. 5; the bond lengths and angles show good agreement with those measured for other similar systems (Taylor, Mueller & Hitterman, 1966).

The equation of the plane through the nitrate oxygen atoms is $0.452x + 0.432y + 0.780z - 5.766 = 0$, and the nitrogen atom deviates 0.01 Å from the plane.

Water molecules and hydrogen bonds

The deuterium atoms of the water molecules are involved in hydrogen bonding; the acceptor atoms being the three nitrate oxygen atoms and one water oxygen atom [O(5)]. The hydrogen bonding scheme suggested by Matkovic *et al.* (1966) is confirmed. All the hydrogen bond interactions in the structure are weak, the range of O-D...O distances being 2.86 to 2.97 Å. The O-D...O angles given in Table 4 indicate that the hydrogen bonds are bent. The values of the dihedral angles between the two sets of planes D(1)-O(4)-D(2)-O(3) III O(4)...O(5) IV and D(3)-O(5)-O(4), O(1) III O(5)...O(2) V are 12.3° and 3.4° respectively.

The lone pair coordination of the water molecule O(4) D(1) D(2) is of the type J (Chidambaram, Sequeira & Sikka, 1964) in which one of the lone pairs is directed towards the divalent Cd^{2+} atom and the other is not specifically directed; the angle between the O(4)-Cd and bisector of D(1) O(4) D(2) angle is 24° and the sum of the angles Cd-O(4)-D(1), Cd-O(4)-D(2),

D(1)–O(4)–D(2) is 352° . The coordination of the water molecule, O(5) D(3) D(4) is tetrahedral with one of the lone pairs pointing towards the Cd atom and the other acting as the negative end of the hydrogen bond from the water oxygen O(4). The relevant angles around O(5) are given in Table 4. It falls under the type H. The dimensions of the water molecules are normal. The angles D(1)–O(4)–D(2) and D(3)–O(5)–D(4) of 103.2° , 104.7° are not significantly different from the vapour value of 104.5° . This is consistent with the observation (Chidambaram, Sequeira & Sikka, 1964) that only in water molecules whose coordination is of type *D* (the group, metal–OH₂, is planar) is the HOH angle significantly greater than the value 104.5° .

Conclusion

The results of this study indicate that anomalous dispersion techniques can be successfully used in solving crystal structures directly from neutron diffraction data. In view of the difficulty in locating atoms which lie close to the antisymmetric axis in the sine function it would appear that the double phase Fourier method is superior in determining the atomic positions.

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The Crystal Structure of Ba[B(OH)₄]₂·H₂O

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Crystals of BaB₂O₄·5H₂O = Ba[B(OH)₄]₂·H₂O are monoclinic, space group *P*2₁/*c*, with four formula units in the unit cell of dimensions $a = 5.949 \pm 0.003$, $b = 8.535 \pm 0.004$, $c = 15.157 \pm 0.008$ Å and $\beta = 102.31 \pm 0.04^\circ$. The structure consists of discrete tetrahedral B(OH)₄⁻ groups. Each barium atom is bonded to ten oxygen atoms. Each barium polyhedron shares an edge each with two other barium polyhedra to form chains wound around the screw axis. The chains are linked in the [100] and [001] directions by boron tetrahedra. The water molecules and the hydroxyl groups form hydrogen bonds.

Introduction

The investigation of the structure was undertaken mainly to determine the configuration of the anion. From a study of two projections ($R_{hol} = 0.21$, $R_{okl} = 0.24$) Ozol, Vimba & Jevins (1960) suggested a structure with anions consisting of one tetrahedral and one triangular boron oxygen group each, with the two groups

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sharing an edge. The structure of the anion proposed by Ozol *et al.* is not in agreement with the results obtained by Kessler (1966), at the Institut für Anorganische und Anorganisch-Technische Chemie of the Technical University in Dresden, from an examination of infrared spectra. These indicate a structure containing isolated boron–oxygen tetrahedra and Kessler proposed the formula Ba[B(OH)₄]₂·H₂O. The structure determination