respectively 0·024 Å and −0·060 Å out of this plane; this is partly because the carboxylic group makes a small angle of 3·3° with the benzene ring plane and may partly be due to the fact that the oxygen atoms are drawn towards the centre of the dimer, presumably because of the force exerted by the hydrogen bonds. This is indicated by the unequal distances of the two oxygen atoms from the benzene ring plane and by the fact that the distance of the centre of the dimer from the plane of the carboxylic group (−0·047 Å) is less than its distance from the benzene ring plane (−0·118 Å).

The observed value of 1·501 Å for the exocyclic C–C bond length is the expected single bond distance between the carbon atoms in sp^2 states of hybridization. This indicates that there is no appreciable degree of conjugation across this bond; this fact again suggests that as expected, there is no contribution from quinonoid valence bond structure in *p*-nitrobenzoic acid.

The nitrogen atom N is −0·047 Å out of the plane of the benzene ring. The atom C(4) is 0·121 Å away from the plane of the nitro group; the angle between this and the benzene ring plane is 13·7°. The C–N bond length of 1·480 Å is significantly longer than the corresponding bond lengths in *p*-nitroaniline (1·460 Å), α-*p*-nitrophenol (1·442 Å) and β-*p*-nitrophenol (1·450 Å). The mean of the two N–O bond lengths in *p*-nitrobenzoic acid is 1·216 Å. In *p*-nitroaniline and β-*p*-nitrophenol, the corresponding lengths after correction for thermal motion are 1·247 Å and 1·242 Å respectively. There is pronounced torsional oscillation of the nitro group in these latter structures and the correction for torsional effects in N–O distances is about 0·018 Å. In the present study, anisotropic thermal parameters have not been obtained; however, the individual isotropic temperature factors for the oxygen atoms of the nitro group (Table 1) are not much larger than the values for other atoms; there is thus no suggestion of pronounced torsional oscillation of the nitro group. It thus appears that the N–O bonds in *p*-nitrobenzoic acid are significantly shorter than those in *p*-nitroaniline and *p*-nitrophenol. The shortening of the N–O bonds and the elongation of the C–N bond in *p*-nitrobenzoic acid from the corresponding values in *p*-nitroaniline and *p*-nitrophenol further supports the view that the bond length variations are due to minor contributions from quinonoid valence bond structures in the latter compounds.

The arrangement of molecules in the unit cell is shown in Fig. 2, in which the principal intermolecular distances are also shown.

We are grateful to Dr A. B. Biswas for his kind interest in this work.

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Refinement of the Structure of $Cd(NO_3)_2.4H_2O$

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(*Received* 29 *September* 1965 *and in revised form* 8 *February* 1966)

The crystal structure of $Cd(NO_3)_2.4H_2O$ has been refined by least-squares calculations to a final R index of 8·4 %. The estimated standard deviations of atomic coordinates ranged from 0·0005 to 0·0042. The essential features of the original structure are confirmed. Cadmium–oxygen distances (from water molecules) have values of 2·26 and 2·33 Å, and cadmium–oxygen distances (from nitrate groups) are 2·44 and 2·59 Å. The structure consists of tetra-aquocadmium nitrate groups joined by hydrogen bonds.

Introduction

This structure was first solved from Patterson and electron density projections (Matković & Ribar, 1963). The results obtained may be summarized as follows: The cadmium–oxygen (water) distances are smaller than cadmium–oxygen (nitrate group) distances and the compound was described as tetra-aquocadmium nitrate. Two of the three oxygen atoms from the nitrate group are much closer to the cadmium atom than the

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third one. The range of bond distances between cadmium and eight oxygen atoms (four from water molecules and four from nitrate groups) located around the cadmium atom was only about 0·3 Å; hence, the cadmium atom is assigned the coordination number eight.

In the previous work precise coordinates of all the atoms except cadmium, which lies in the special position, could not be derived from electron density projection because of overlapping of the maxima. From these data it was not possible to obtain accurate bond distances or to determine with certainty the shape of the molecule. The present paper describes the structure derived from a three-dimensional anisotropic refinement.

Experimental

Single crystals of cadmium nitrate tetrahydrate were obtained by slow evaporation of an aqueous solution. The crystals are orthorhombic, space group *Fdd*2 (C_{2v}^{19}), with unit-cell dimensions

$$\begin{aligned} a &= 5{\cdot}828 \pm 0{\cdot}005\ \text{Å} \\ b &= 25{\cdot}86\ \pm 0{\cdot}03 \\ c &= 11{\cdot}002 \pm 0{\cdot}005 \\ D_m &= 2{\cdot}46\ \text{g.cm}^{-3} \\ D_x &= 2{\cdot}47\ \text{g.cm}^{-3} \\ Z &= 8. \end{aligned}$$

The unit-cell dimensions were obtained from a powder diffractometer pattern calibrated with germanium lines. The uncertainties in the cell dimensions given above correspond to estimated maximum errors. The density was determined pycnometrically.

Specimens chosen for collecting the intensity data were sealed in Lindemann glass capillary tubes because the compound is not stable in air. The three-dimensional intensity data were recorded from crystals on multiple equi-inclination Weissenberg photographs, with Cu *Kα* radiation. A crystal was ground to a sphere of 0·19 mm radius ($\mu=227{\cdot}21$ cm^{-1}, $\mu r=4{\cdot}2$) in order to apply absorption corrections more easily and accurately. Such a ground specimen, mounted along the *a* axis, was used for collecting 0*kl* to 5*kl* intensity data. The maximum possible value of *h* index was 7 for Cu *Kα* radiation, but on account of the limitation of the camera design, reflections up to the fifth layer only could be recorded in the *a*-axis setting. Crystals mounted along *b* and *c* axes were used to collect almost all other reflections lying within the Cu *Kα* sphere. For this purpose one cylindrical specimen with a radius of 0·087 mm ($\mu r=2{\cdot}0$) oriented along [001] was used for collecting *hk*0 to *hk*4 reflections and another cylindrical specimen with a radius of 0·29 mm ($\mu r=6{\cdot}6$) oriented along [010] was used for collecting *h*0*l* to *h*4*l* reflections. The relative intensities were determined from the optical densities of each spot measured by means of a microdensitometer. The corrections for absorption, polarization and Lorentz factors were made in the usual way and the structure amplitude derived. The factors for translating the observed structure amplitude into the absolute scale were found for reflections of each layer and with the help of these factors, all structure amplitudes were scaled. The three-dimensional Fourier syntheses were computed on the ZUSE Z23 computer using the phase-angles as they were derived from the parameters of all the atoms resulting from the two-dimensional data. The calculation was carried out in the Institute Boris Kidrič, Vinča, Yugoslavia. The program was made by Zelenko & Zakrajšek (1964). The three-dimensional Fourier map confirmed the original structure.

Table 1. *Fractional coordinates for cadmium nitrate tetrahydrate*

The thermal parameters are of the form $T=\exp\,[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.
Each thermal parameter is multiplied by 10^4. Standard errors are given in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cd(1·00)	0·0	0·0	0·0	191	8	38	−3	are required to be zero by symmetry	
				(5)	(0·2)	(1)	(2)		
O(2·00)	0·3412	0·0469	−0·0645	215	5	100	5	8	2
	(0·0028)	(0·0005)	(0·0021)	(44)	(2)	(17)	(8)	(26)	(5)
O(3·00)	0·1427	0·0923	0·0524	292	18	157	−8	64	−3
	(0·0042)	(0·0009)	(0·0032)	(70)	(4)	(29)	(13)	(42)	(10)
O(4·00)	0·4650	0·1225	0·0096	316	12	109	−10	148	9
	(0·0031)	(0·0006)	(0·0035)	(76)	(2)	(23)	(9)	(45)	(10)
O(5·00)	0·2512	−0·0244	0·1456	378	15	104	20	−54	0
	(0·0038)	(0·0008)	(0·0023)	(70)	(3)	(20)	(14)	(44)	(7)
O(6·00)	0·1825	−0·0498	−0·1480	266	13	83	−2	−29	−4
	(0·0035)	(0·0007)	(0·0021)	(58)	(3)	(18)	(10)	(29)	(6)
N(7·00)	0·3198	0·0875	−0·0105	233	14	48	−5	−29	11
	(0·0038)	(0·0007)	(0·0021)	(53)	(3)	(15)	(10)	(28)	(6)

$R_1=\Sigma_{hkl}||F_o|-|F_c||/\Sigma_{hkl}|F_o|=0{\cdot}084$ (including unobserved reflections)
$R_2=\Sigma_{hkl}||F_o|-|F_c||/\Sigma_{hkl}|F_o|=0{\cdot}070$ (omitting unobserved reflections)
$R_3=\Sigma_{hkl}w||F_o|-|F_c||^2/\Sigma_{hkl}w|F_o|^2=0{\cdot}090$ (including unobserved reflections)

Table 2. *Observed and calculated structure factors*

Within each group, the numbers, reading from left to right are *l*, $10F_o$, $10F_c$, $10A$ and $10B$. A minus sign before $10F_o$ indicates an unobserved reflection. The numerical value is the estimated minimum observable value.

H= 0 K= 0				
4	3676	3201	3201	-35
8	2462	2227	2227	40
12	1641	1265	1264	24
H= 0 K= 2				
2	3691	4436	4425	-322
6	2874	2895	2881	-278
10	1163	1147	1146	49
14	779	945	944	-39
H= 0 K= 4				
0	2275	2826	2826	-0
4	1788	1335	882	-1002
8	1737	1617	1617	-2
12	1073	994	994	21
H= 0 K= 6				
2	1622	1509	1401	563
6	1507	2144	2114	-354
10	1392	1302	1293	157
H= 0 K= 8				
0	2284	2608	2608	-0
4	3219	3331	3319	279
8	2074	2052	2008	425
12	1111	1048	1046	-56
H= 0 K=10				
2	3269	3778	3419	1608
6	2273	2254	2250	141
10	1724	1602	1594	-153
H= 0 K=12				
0	1554	1507	1507	-0
4	2656	2718	2690	388
8	1596	1581	1580	-63
12	996	956	921	-256
H= 0 K=14				
2	1954	2023	2022	57
6	1699	1668	1666	70
10	1379	1241	1235	-122
H= 0 K=16				
0	1685	1693	1693	-0
4	2044	2002	2002	27
8	1482	1367	1366	-59
12	626	788	774	147
H= 0 K=18				
2	1941	1930	1760	-793
6	1290	1314	1306	148
10	919	900	896	87
H= 0 K=20				
0	1962	1947	1947	-0
4	1303	1299	1259	[illegible]
8	945	883	863	-184
H= 0 K=22				
2	1840	1948	1881	-507
6	1022	1081	1077	86
10	664	761	760	21
H= 0 K=24				
0	1842	1796	1796	-0
4	1405	1476	1475	-50
8	945	883	878	-87
H= 0 K=26				
2	1099	1167	1158	-140
6	881	881	877	-83
H= 0 K=28				
0	461	485	485	-0
4	805	823	823	-18
H= 0 K=30				
2	639	710	673	225
H= 0 K=32				
0	651	653	653	-0
H= 1 K= 1				
1	2008	2071	878	-1875
3	1963	1818	105	1815
5	1671	1473	1245	-787
7	1425	1414	979	1020
9	1077	1007	593	-814
11	831	825	550	615
13	549	597	405	-439
H= 1 K= 3				
1	2008	2803	1011	2615
3	2389	2662	552	-2604
5	2210	2424	1262	2070
7	1795	1757	1490	-931
9	1279	1237	819	927
11	908	838	504	-670
13	662	732	486	547
H= 1 K= 5				
1	2266	2540	1643	-1938
3	2681	2981	1350	2658
5	1761	1784	1202	-1318
7	1884	1866	1689	793
9	1447	1344	940	-961
11	976	964	626	732
13	639	676	509	-447
H= 1 K= 7				
1	2188	2354	2222	775
3	1402	1459	345	-1418
5	1952	2023	1847	824
7	1414	1274	1159	-528
9	1021	979	767	608
11	1032	938	615	-709
13	516	566	480	300
H= 1 K= 9				
1	1750	1612	1590	-266
3	2165	2280	1568	1655
5	1190	1240	837	-914
7	1043	1013	950	353
9	931	902	673	-600
11	639	629	445	445
13	583	650	494	-422
H= 1 K=11				
1	2536	2763	2004	1903
3	1907	2020	1325	-1525
5	1021	1051	721	765
7	987	1041	883	-553
9	1077	1018	559	850
11	819	800	589	-541
13	382	505	329	383
H= 1 K=13				
1	1694	1743	1155	-1306
3	1683	1787	1119	1393
5	2064	2087	1331	-1608
7	1100	1084	633	880
9	729	734	552	-484
11	718	756	461	599
H= 1 K=15				
1	1537	1558	1136	1065
3	1459	1463	872	-1175
5	606	593	408	430
7	998	1038	499	-911
9	1156	1084	748	785
11	639	643	428	-479
H= 1 K=17				
1	897	906	736	-529
3	1010	1014	876	511
5	1436	1365	844	-1072
7	1167	1045	676	797
9	718	657	357	-551
11	527	623	469	411
H= 1 K=19				
1	1369	1427	1243	700
3	1301	1213	1054	-600
5	1021	1044	623	838
7	1032	991	690	-711
9	763	804	593	544
11	516	578	426	-391
H= 1 K=21				
1	1211	1286	1072	-710
3	1077	1035	699	763
5	1057	1054	922	-510
7	953	896	647	620
9	763	751	555	-505
H= 1 K=23				
1	763	718	440	568
3	819	816	588	-566
5	875	876	573	662
7	752	764	608	-463
9	382	478	377	294
H= 1 K=25				
1	797	796	375	-702
3	774	716	328	636
5	527	461	318	-334
7	606	603	472	375
H= 1 K=27				
1	718	734	356	642
3	684	658	378	-538
5	897	897	663	603
7	494	535	410	-344
H= 1 K=29				
1	831	779	520	-580
3	763	829	642	524
5	415	462	333	-320
H= 1 K=31				
1	505	603	441	411
3	505	544	425	-339
H= 2 K= 0				
2	2870	3121	3121	49
6	2176	1927	1883	406
10	1719	1554	1551	97
H= 2 K= 2				
0	1198	1130	1130	0
2	1281	1210	427	-1133
4	2777	3101	3091	257
6	779	664	518	-417
8	1595	1562	1562	-21
10	-128	154	136	-72
12	980	943	943	22
H= 2 K= 4				
0	1294	1190	1190	-0
2	2299	2528	2500	-376
4	830	780	-156	-764
6	1583	1604	1604	21
8	-128	305	106	-286
10	1470	1401	1390	-179
12	-128	105	84	63
H= 2 K= 6				
0	2753	2993	2993	-0
2	879	786	114	-778
4	2526	2713	2704	221
6	-128	285	-259	119
8	1646	1618	1604	-215
10	-128	304	-296	67
12	1043	1005	1005	1
H= 2 K= 8				
0	1086	1009	1009	0
2	2840	3253	3207	-547
4	-128	441	-359	257
6	2111	2180	2167	239
8	-128	377	-359	116
10	1281	1236	1234	69
12	-128	144	-47	135
H= 2 K=10				
0	2631	2814	2814	-0
2	-128	235	230	65
4	1671	1769	1768	-64
6	-128	128	-13	128
8	1458	1394	1390	-95
10	-128	58	-11	57
12	866	875	868	104
H= 2 K=12				
0	643	595	-595	0
2	1458	1541	1491	-391
4	-128	272	228	-148
6	1483	1439	1433	-130
8	-128	126	126	6
10	904	854	853	36
12	-128	97	76	-61
H= 2 K=14				
0	2223	2349	2349	-0
2	-128	453	-346	293
4	1483	1496	1494	-81
6	-128	206	150	-142
8	1269	1224	1222	65
10	-128	222	196	-104
12	666	785	784	22
H= 2 K=16				
0	608	597	-597	0
2	2123	2250	2218	377
4	-128	354	322	147
6	1721	1698	1698	-34
8	-128	151	146	39
10	992	1018	1016	62
H= 2 K=18				
0	1962	1923	1923	-0
2	-128	393	84	384
4	1620	1607	1604	-109
6	-128	160	68	144
8	1306	1233	1230	88
10	-128	102	79	-64
H= 2 K=20				
0	-128	103	-103	0
2	1306	1215	1159	363
4	-128	209	-25	208
6	1181	1140	1123	-200
8	-128	53	-41	34
10	691	771	766	-81
H= 2 K=22				
0	1060	1065	1065	-0
2	-128	164	-102	-129
4	1043	1017	1017	-37
6	-128	100	-77	63
8	942	879	871	120
H= 2 K=24				
0	-128	227	227	0
2	1231	1152	1129	225
4	-128	140	-28	-137
6	1055	1038	1037	54
8	-128	68	42	-54
H= 2 K=26				
0	1346	1182	1182	-0
2	427	378	243	-290
4	917	929	929	17
6	-128	132	84	-102
H= 2 K=28				
0	304	310	310	-0
2	842	854	853	-50
4	-128	115	18	-114
6	666	759	757	-43
H= 2 K=30				
0	868	901	901	-0
2	-128	52	40	-33
4	540	657	656	-31
H= 3 K= 1				
1	1558	1604	923	1312
3	1818	2021	937	-1791
5	1373	1457	1388	444
7	1050	1009	430	-913
9	1050	973	664	711
11	875	785	505	-601
H= 3 K= 3				
1	2095	2072	1228	-1668
3	1737	1876	1340	1313
5	1374	1348	760	-1114
7	1023	969	562	789
9	1037	955	805	-514
11	741	695	471	511
H= 3 K= 5				
1	1548	1819	1098	1451
3	1656	1767	1653	-623
5	1319	1259	793	977
7	1104	964	797	-543
9	822	742	530	518
11	700	654	575	-312
H= 3 K= 7				
1	1279	1422	986	-1025
3	1050	997	853	516
5	1064	950	901	-303
7	1211	1069	681	823
9	875	817	601	-553
11	633	572	442	363
H= 3 K= 9				
1	969	952	590	747
3	969	874	729	-481
5	1629	1442	797	1202
7	1333	1256	647	-1076
9	888	813	652	486
11	606	601	371	-473
H= 3 K=11				
1	1495	1605	839	-1368
3	1131	1044	755	722
5	1360	1250	981	-774
7	1535	1427	909	1100
9	1172	994	594	-796
11	660	703	506	487
H= 3 K=13				
1	1104	1136	829	777
3	1481	1381	1170	-734
5	1548	1415	961	1039
7	1387	1279	938	-870
9	861	789	656	438
11	538	569	446	-353
H= 3 K=15				
1	1373	1273	1016	-767
3	875	847	656	536
5	942	889	744	-488
7	808	699	544	439
9	768	693	513	-465
11	499	544	467	279
H= 3 K=17				
1	902	819	504	646
3	1050	936	715	-604
5	902	772	570	520
7	552	544	362	-407
9	445	449	257	368
H= 3 K=19				
1	1050	1011	747	-682
3	1023	1065	763	742
5	754	713	364	-613
7	687	572	286	495
9	565	507	409	-300
H= 3 K=21				
1	1091	1037	765	701
3	1158	1032	660	-793
5	942	856	757	399
7	660	571	439	-366
9	499	605	381	470
H= 3 K=23				
1	888	815	577	-576
3	1023	902	786	441
5	822	756	419	-630
7	538	537	472	257
H= 3 K=25				
1	808	758	554	517
3	673	637	362	-525
5	485	477	388	277
7	364	440	305	-317
H= 3 K=27				
1	565	550	379	-398
3	606	580	363	452
5	485	504	411	-292
H= 3 K=29				
1	512	540	433	323
3	350	417	347	-231
H= 4 K= 0				
0	1841	1678	1678	-0
4	1665	1508	1507	43
8	1578	1410	1393	219
H= 4 K= 2				
0	304	249	-249	0
2	1497	1501	1449	391
4	-128	231	150	176
6	1748	1615	1612	-95
8	-128	110	13	109
10	791	931	931	18
12	-128	8	4	-7
H= 4 K= 4				
0	2023	1956	1956	-0
2	635	613	-195	581
4	1401	1374	1374	-33
6	-128	235	-232	38
8	1185	1129	1129	-37
10	-128	55	54	8
H= 4 K= 6				
0	929	815	-815	0
2	1760	1915	1901	226
4	-128	115	65	95
6	1497	1350	1350	2
8	-128	102	-13	101
10	695	793	792	-29
H= 4 K= 8				
0	2128	2169	2169	-0
2	-128	229	117	197
4	1509	1540	1539	-57
6	-128	213	193	-91
8	1102	1097	1089	137
10	-128	191	189	-29
H= 4 K=10				
0	313	278	278	0
2	1712	1557	1533	-270
4	-128	332	328	-51
6	1245	1208	1202	-119
8	-128	308	298	-75
10	755	841	840	43
H= 4 K=12				
0	1268	1301	1301	-0
2	-128	156	47	-149
4	1281	1206	1168	-301
6	-128	23	-17	-15
8	1102	908	900	-122
10	-128	65	-64	-13
H= 4 K=14				
0	-128	187	187	0
2	1389	1408	1401	-140
4	-128	460	-453	79
6	1066	961	960	45
8	-128	220	-217	-34
10	538	709	709	-3
H= 4 K=16				
0	1390	1406	1406	-0
2	-128	215	17	-214
4	1401	1375	1357	224
6	-128	79	-47	64
8	815	818	817	56
H= 4 K=18				
0	521	473	473	-0
2	1257	1206	1206	-10
4	-128	162	115	-114
6	1030	965	960	102
8	-128	147	146	-15
H= 4 K=20				
0	704	658	658	0
2	-128	196	179	-80
4	1138	981	980	45
6	-128	202	152	-132
8	611	743	732	-132
H= 4 K=22				
0	-128	61	-61	0
2	815	751	751	-27
4	-128	54	17	-51
6	767	738	737	37
H= 4 K=24				
0	747	721	721	-0
2	-128	205	-51	199
4	910	857	847	134
6	-128	46	-39	24
H= 4 K=26				
0	-128	128	-128	0
2	839	803	803	-3
4	-128	116	88	75
H= 4 K=28				
0	659	696	696	-0
H= 5 K= 1				
1	840	781	534	-570
3	675	659	507	421
5	719	773	544	-548
7	715	698	467	518
9	486	535	227	-485
H= 5 K= 3				
1	1224	1135	974	583
3	897	867	703	-506
5	903	797	403	688
7	934	785	501	-603
9	662	568	323	451
H= 5 K= 5				
1	1042	1081	956	-505
3	997	1006	807	601
H= 5 K= 7				
1	992	965	743	615
3	1097	1126	781	-811
H= 5 K= 9				
1	729	692	444	-531
3	768	788	457	642
H= 5 K=11				
1	780	777	493	600
3	818	752	421	-623
H= 5 K=13				
1	729	706	633	-314
3	911	935	658	664
H= 5 K=15				
1	890	847	706	467
3	608	632	449	-445
H= 5 K=17				
1	759	710	390	-594
3	658	697	442	539
H= 5 K=19				
1	678	665	389	540
3	578	531	283	-450
H= 5 K=21				
1	607	542	360	-405
3	409	471	326	339
H= 5 K=23				
1	476	459	397	231
3	389	440	397	-185
H= 6 K= 0				
2	1379	1280	1260	-225
6	802	778	770	115
H= 6 K= 2				
0	1138	1222	1222	-0
2	-128	211	209	27
4	981	930	930	-21
6	-128	228	205	101
8	587	650	643	-90
H= 6 K= 4				
0	-128	167	167	0
2	858	912	887	-210
4	256	116	43	108
6	736	726	723	-66
8	-128	53	50	-19
H= 6 K= 6				
0	669	655	655	-0
2	-128	202	-195	-52
4	864	829	829	6
H= 6 K= 8				
0	-128	115	-115	0
2	770	851	835	161
4	-128	94	-93	-11
H= 6 K=10				
0	834	772	772	-0
2	-128	53	51	-11
4	967	954	946	117
H= 6 K=12				
0	-128	93	93	0
2	770	859	844	160
4	-128	121	118	-26
H= 6 K=14				
0	704	712	712	-0
2	-128	93	88	30
4	644	704	704	5
H= 6 K=16				
0	-128	14	14	0
2	533	631	630	31
4	-128	93	81	-46
H= 6 K=18				
0	643	763	763	-0
2	-128	79	72	-31
H= 7 K= 1				
1	391	482	258	407
3	387	491	345	-349
H= 7 K= 3				
1	456	485	285	-392
3	457	489	213	440
H= 7 K= 5				
1	344	393	275	280
3	369	403	260	-305
H= 7 K= 7				
1	466	513	377	-348
3	329	458	390	241
H= 7 K= 9				
1	364	494	371	326
3	369	449	314	-321
H= 7 K=11				
1	385	535	360	-395

Refinement of the structure

The coordinates of the atoms obtained from two-dimensional data were subjected to a least-squares refinement by the ORFLS program of Busing, Martin & Levy (1962). Four cycles of weighted least-squares refinement with isotropic and two cycles with anisotropic temperature factors were performed. A modified version of the Hughes weighting scheme (Hughes, 1941) was used; the standard deviation for each reflection was computed by the equations

$$\sigma = |F_o|/4|F_{\min}| \text{ for } |F_o| > 4|F_{\min}|$$
$$\sigma = 4|F_{\min}|/|F_o| \text{ for } |F_o| \leq 4|F_{\min}|$$

Structure factors for unobserved reflections were assigned one-half the minimum observed $|F|$ and were omitted from the refinement if the calculated structure factor was less than the minimum observed structure factor. After the last cycle of refinement the shifts in the atomic coordinates were less than standard deviations. In the course of this refinement the R index decreased to 0·084. The refined atomic coordinates and temperature factors are listed in Table 1. The observed and calculated structure factors are listed in Table 2. The atomic scattering factors used in these calculations were from *International Tables for X-ray Crystallography* (1962). No dispersion correction for cadmium atomic scattering factors was applied. Bond distances and angles were computed with the Busing, Martin & Levy (1964) ORFFE, Fortran function and error program.

The refinement cycles and the calculation of bond lengths were carried out on the IBM 709 computer at Washington State University, where one of the authors (B.M.) has a postdoctoral fellowship.

Description and discussion of the structure

The numbering of the atoms, which is the same in all Figures and Tables, is listed in Table 3. The bond distances in the cadmium nitrate tetrahydrate group are listed in Table 4. Fig. 1 represents the projection of the structure on the xy plane, and Fig. 2 a view down one cadmium nitrate tetrahydrate group. There are two short cadmium–oxygen (water) distances, 2·26 and 2·33 Å, and two longer cadmium–oxygen (nitrate group) distances, 2·44 and 2·59 Å. The shorter cadmium–oxygen distances are indicated in Fig. 2 by broken lines, and

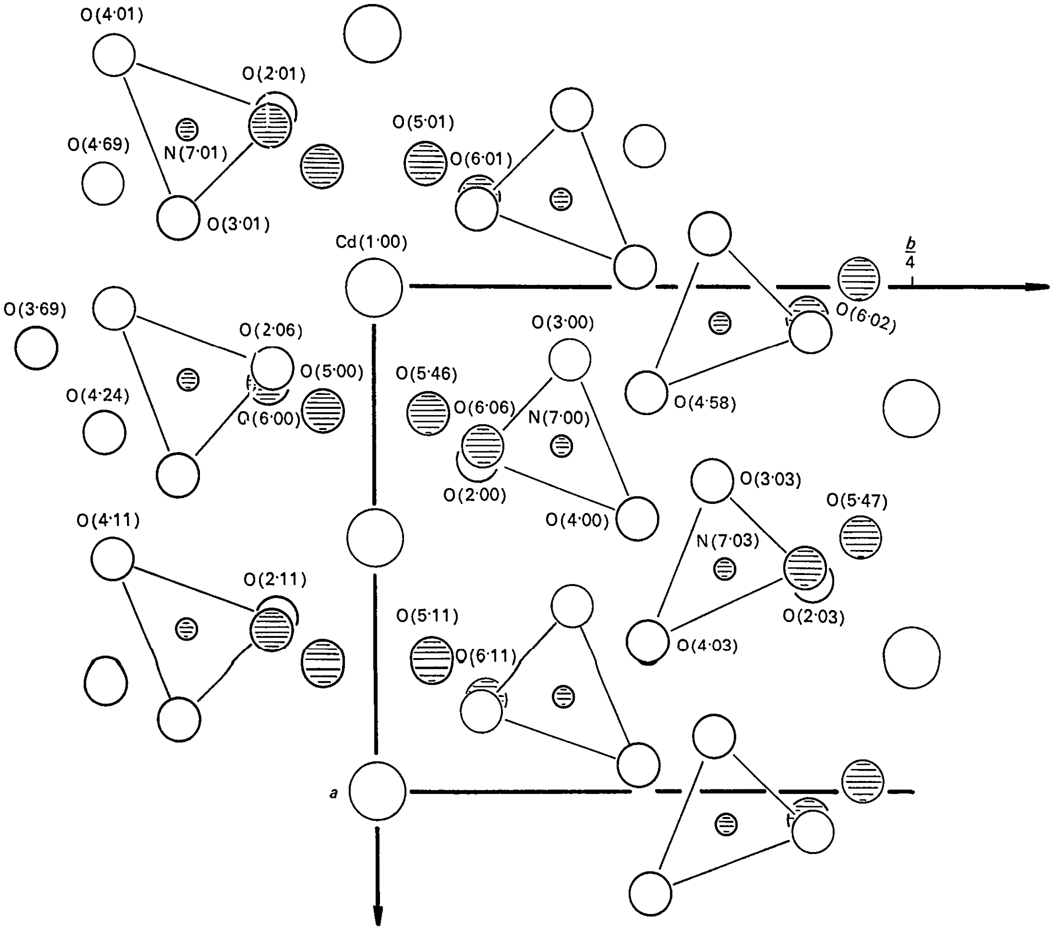

Fig. 1. Projection of the structure of cadmium nitrate tetrahydrate on a plane normal to [001]. Big open circles are cadmium atoms, medium open circles are nitrate-oxygen atoms, shaded medium circles are water molecules, and small shaded circles are nitrogen atoms. Only these atoms are numbered whose distances are mentioned in tables.

the nitrate-oxygen distances by full lines. The third oxygen atom of the nitrate group, O(4·00), is over 4 Å from the cadmium atom, and hence not listed in Table 4. The distances from the cadmium atom to the eight nearest oxygen atoms range from 2·26 to 2·59 Å, and it appears reasonable to assign cadmium a coordination number eight. Such a polyhedron is shown in Fig. 3, which represents the same view down the cadmium nitrate tetrahydrate group as in Fig. 2. The cadmium atom lies on the twofold axis inside the oxygen polyhedron and it is omitted from this figure. The oxygen polyhedron has eight vertices, four of which are nitrate oxygen atoms

Table 3. *Numbering of the atoms**

The atoms in the asymmetric unit and their closest neighbors

In asymmetric unit	The coordinates of atoms									
	Transformed by symmetry					Transformed by symmetry and translated by cell				
$x,$ $y,$ $z.$	$-x,$ $-y,$ $z.$	$\frac{1}{4}-x,$ $\frac{1}{4}+y,$ $\frac{1}{4}+z.$	$\frac{1}{4}+x,$ $\frac{1}{4}-y,$ $\frac{1}{4}+z.$	$\frac{1}{2}-x,$ $-y,$ $\frac{1}{2}+z.$	$1-x,$ $-y,$ $z.$	$\frac{3}{4}-x,$ $\frac{3}{4}+y-1,$ $\frac{1}{4}+z.$	$\frac{1}{2}-x,$ $-y,$ $\frac{1}{2}+z-1.$	$\frac{3}{4}-x,$ $\frac{1}{4}+y,$ $\frac{3}{4}+z-1.$	$\frac{3}{4}+x-1,$ $\frac{1}{4}-y,$ $\frac{3}{4}+z-1.$	$\frac{1}{4}-x,$ $\frac{3}{4}+y-1,$ $\frac{3}{4}+z-1.$
Cd(1·00)										
O(2·00)	O(2·01)		O(2·03)	O(2·06)	O(2·11)					
O(3·00)	O(3·01)		O(3·03)							O(3·69)
O(4·00)	O(4·01)		O(4·03)		O(4·11)	O(4·24)			O(4·58)	O(4·69)
O(5·00)	O(5·01)			O(5·06)	O(5·11)		O(5·46)	O(5·47)		
O(6·00)	O(6·01)	O(6·02)		O(6·06)	O(6·11)					
N(7·00)	N(7·01)		N(7·03)							

* Atoms are designated by a three place number which identifies the atom, the cell translation and the symmetry transformation. Only those atoms are numbered whose distances and angles are mentioned in tables.

Table 4. *Interatomic distances and bond angles in cadmium nitrate tetrahydrate group*

Standard errors are given in parenthesis.

$Cd-OH_2$ distances	
Cd(1·00)–O(5·00)	2·26 (0·02) Å
Cd(1·00)–O(6·00)	2·33 (0·02)

Cd–O (from NO_3) distances	
Cd(1·00)–O(2·00)	2·44 (0·02) Å
Cd(1·00)–O(3·00)	2·59 (0·02)

Cd–N distance	
Cd(1·00)–N(7·00)	2·93 (0·02) Å

O–N distances in NO_3 group	
O(2·00)–N(7·00)	1·21 (0·03) Å
O(3·00)–N(7·00)	1·25 (0·03)
O(4·00)–N(7·00)	1·26 (0·03)

H_2O-N distances	
O(5·00)–N(7·00)	3·39 (0·02) Å
O(6·00)–N(7·00)	3·94 (0·03)

O–O distances between NO_3 oxygens	
O(2·00)–O(3·00)	2·09 (0·03) Å
O(3·00)–O(4·00)	2·09 (0·03)
O(2·00)–O(4·00)	2·24 (0·03)

$O-OH_2$ distances	
O(2·00)–O(6·00)	2·82 (0·02) Å
O(2·00)–O(5·00)	3·00 (0·03)
O(3·00)–O(5·01)	3·07 (0·03)
O(3·00)–O(6·01)	3·10 (0·04)
O(2·00)–O(6·01)	3·18 (0·03)
O(3·00)–O(5·00)	3·25 (0·03)

H_2O-OH_2 distances	
O(5·00)–O(5·01)	3·19 (0·04) Å
O(5·00)–O(6·00)	3·32 (0·03)
O(6·00)–O(6·01)	3·34 (0·04)

O–N–O angles in NO_3 group	
O(2·00)–N(7·00)–O(3·00)	116·4°(2·1°)
O(2·00)–N(7·00)–O(4·00)	129·7 (2·3)
O(3·00)–N(7·00)–O(4·00)	112·7 (2·1)

O–Cd–O angles in Cd polyhedron	
O(2·00)–Cd(1·00)–O(3·00)	48·9°(0·7°)
O(6·00)–Cd(1·00)–O(2·00)	72·5 (0·6)
O(6·00)–Cd(1·00)–O(3·01)	77·9 (0·9)
O(5·00)–Cd(1·00)–O(3·01)	78·1 (0·9)
O(5·00)–Cd(1·00)–O(2·00)	79·5 (0·8)
O(6·00)–Cd(1·00)–O(2·01)	83·8 (0·7)
O(5·00)–Cd(1·00)–O(3·00)	83·9 (0·9)
O(5·00)–Cd(1·00)–O(5·01)	89·8 (1·2)*
O(6·00)–Cd(1·00)–O(6·01)	91·5 (1·1)*
O(5·00)–Cd(1·00)–O(6·00)	92·6 (0·8)
O(6·00)–Cd(1·00)–O(3·00)	121·1 (0·8)
O(5·00)–Cd(1·00)–O(2·01)	126·6 (0·7)
O(2·01)–Cd(1·00)–O(3·00)	141·8 (0·7)
O(2·00)–Cd(1·00)–O(2·01)	146·0 (1·1)*
O(3·00)–Cd(1·00)–O(3·01)	154·6 (1·6)*
O(5·00)–Cd(1·00)–O(6·01)	160·7 (0·7)

* All values of O–Cd–O angles, except those designated by asterisks, appear twice in the polyhedron.

[O(2·00), O(2·01), O(3·00) and O(3·01)] and four oxygen from water molecules [O(5·00), O(5·01), O(6·00) and O(6·01)]. The oxygen atoms which belong to this distorted polyhedron are connected in Fig. 3 with full lines and dotted lines, and the twofold axis is indicated by a full and broken line. The oxygen edges of the polyhedron vary in length over a fairly narrow range from 2·82 to 3·34 Å, apart from two much shorter edges (2·09 Å), which are sides of the NO_3 triangle adjoining the cadmium polyhedron [the distances between the atoms O(2·00)–O(3·00) and O(2·01)–O(3·01)]. The polyhedron around Cd may be described as a distorted dodecahedron. The distances between oxygen atoms which belong to this polyhedron and angles around Cd atom are listed in Table 4. For comparison, the regular dodecahedron has 4 longer and 14 shorter edges and 28 angles, which are as follows: 74°24′(14), 98°44′(4), 130°12′(4), 136°48′(2), 148°48′(4).

Intermolecular distances between atoms of the asymmetric unit and their nearest neighbors are listed in Table 5 and illustrated in Fig. 1. They require no special comment. Some O···O contacts between the atoms

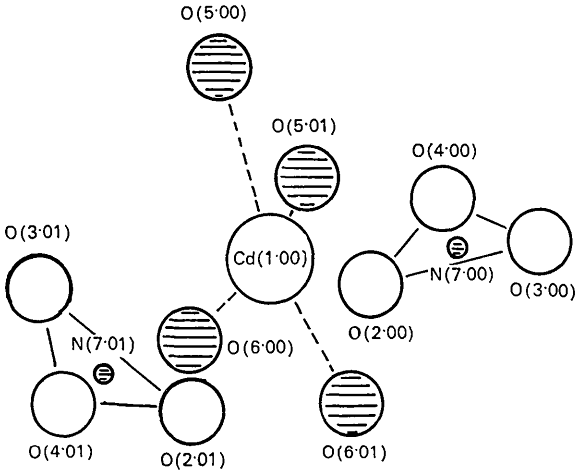

Fig. 2. A view down the cadmium nitrate tetrahydrate group. Big open circle is cadmium atom, medium open circles are nitrate-oxygen atoms, shaded medium circles are water molecules, and small shaded circles are nitrogen atoms.

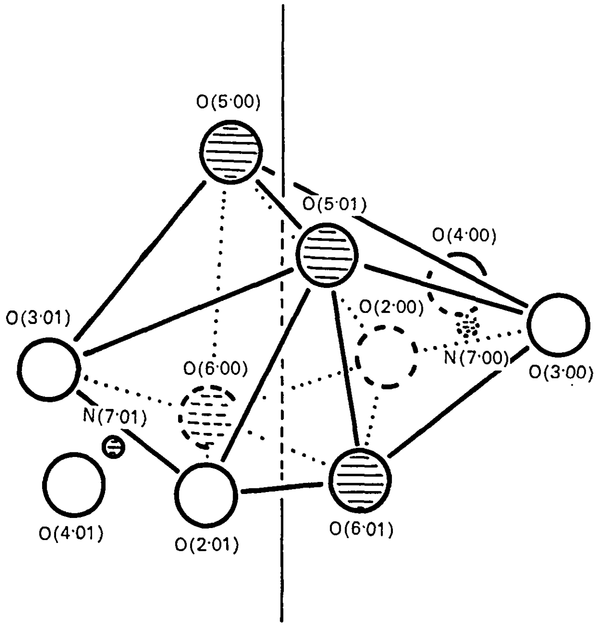

Fig. 3. A view down the polyhedron of oxygen atoms around the cadmium atom, which is omitted in the figure. It lies in the center of the molecule and a twofold axis is passing through it dividing the O(5·00)–O(5·01) and O(6·00)–O(6·01) distances. Open circles are nitrate-oxygen atoms, shaded circles are water molecules, and small shaded circles are nitrogen atoms.

Table 5. *Intermolecular distances less than* 3·40 Å *between the neighboring atoms of the asymmetric unit*

Standard errors are given in parenthesis.

O–O distances	
O(4·00)–O(2·03) O(2·00)–O(4·58)	2·93 (0·04) Å
O(2·00)–O(2·11)	3·06 (0·03)
O(4·00)–O(4·03) O(4·00)–O(4·58)	3·12 (0·02)
O(4·00)–O(3·03) O(3·00)–O(4·58)	3·36 (0·05)

O–N distances	
O(4·00)–N(7·03) N(7·00)–O(4·58)	2·79 (0·04) Å

H_2O–OH_2 distances	
O(5·00)–O(6·06) O(6·00)–O(5·46)	3·00 (0·03) Å
O(5·00)–O(5·11)	3·16 (0·05)

O–OH_2 distances	
O(3·00)–O(6·02) O(6·00)–O(3·69)	2·87 (0·03) Å
O(2·00)–O(6·11) O(6·00)–O(2·11)	2·93 (0·03)
O(4·00)–O(5·47) O(5·00)–O(4·24)	2·96 (0·03)
O(4·00)–O(6·02) O(6·00)–O(4·69)	3·23 (0·03)
O(2·00)–O(5·46) O(5·00)–O(2·06)	3·29 (0·03)
O(6·00)–O(4·11) O(4·00)–O(6·11)	3·28 (0·03)
O(2·00)–O(5·11) O(5·00)–O(2·11)	3·37 (0·03)
O(4·00)–O(5·11) O(5·00)–O(4·11)	3·37 (0·04)

of neighboring molecules have a range of values increasing from 2·87 Å. These distances between nitrate-oxygen and water-oxygen atoms or between water-oxygen atoms indicate possible hydrogen bonding between the atoms of neighboring cadmium nitrate tetrahydrate groups. Further evidence is provided by the list of angles around water molecules also given in Table 6. These angles, selected because their values were close to the HOH bond angle in H_2O, may be used in conjunction with the distances to select possible hydrogen bond locations. Based on the distances and angles hydrogen bonds are probably between O(4·24)–O(5·00)–O(6·06) and O(3·69)–O(6·00)–O(2·11) atoms.

Table 6. *Selected angles involving water oxygen atoms*

O(5·11)–O(5·00)–O(2·06)	102·8°(0·5°)
O(4·24)–O(5·00)–O(6·06)	104·1 (1·1)
O(4·24)–O(5·00)–O(6·00)	104·2 (1·0)
O(3·69)–O(6·00)–O(2·11)	103·2 (0·9)
O(5·46)–O(6·00)–O(4·69)	104·8 (1·0)
O(4·69)–O(6·00)–O(4·11)	105·0 (0·6)

The values of the intermolecular distances obtained during this refinement are not significantly different from the results obtained before. The cadmium–oxygen distances, obtained after refinement, are a little shorter than reported previously. The shortest one is 2·26 Å. This length is 0·09 Å shorter than the cadmium–oxygen distance in CdO which has a sodium chloride structure (Wyckoff, 1963). The values of two shorter cadmium–oxygen distances (2·26 and 2·33 Å) are also in good agreement with those already found in other cadmium compounds; *e.g.* the cadmium–oxygen distance in monomethylureacadmium chloride is 2·18 Å, in bisacetamide-cadmium chloride is 2·23 Å, in bisthiourea-cadmium formate is 2·28 Å, in bisurea-cadmium chloride is 2·28 Å and in bisbiuret-cadmium chloride is 2·34 Å (Nardelli, Fava-Gasparri & Boldrini, 1965). A still shorter cadmium–oxygen (water) distance of 2·12 Å was found in the structure of tricadmium sulphate octahydrate (Lipson, 1936). For comparison, in this structure the distances of six nearest atoms (four sulphate oxygen atoms and two from water molecules) located around the cadmium atom vary from 2·12 to 2·63 Å. In the structure of cadmium nitrate tetrahydrate the distances of eight nearest atoms (four from water molecules and four nitrate oxygens) around the cadmium atom range from 2·26 to 2·59 Å. The distances in the NO_3 group do not deviate significantly from the results obtained before and are in agreement with the known data (*International Tables for X-ray Crystallography*, 1962). The O–N–O angles in the NO_3 groups indicate that the nitrogen atom lies in the plane of the oxygen triangle within the error of experiment.

We would like to thank Dr R. Willett for his instructive help during the calculations, the Washington State University Computing Center for a grant of computing time, and the U.S. Atomic Energy Commission for partial support of this work.

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