Bekoe, D. A. & Trueblood, K. N. (1960). *Z. Kristallogr.* **113**, 1.

Bekoe, D. A. & Trueblood, K. N. (1964). A.C.A. Meeting, Bozeman, Montana, Abstract J–12, p. 87.

Bonham, R. A. & Bartell, L. S. (1959). *J. Amer. Chem. Soc.* **81**, 3491.

Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142.

Coulter, C. L. & Trueblood, K. N. (1963). *Acta Cryst.* **16**, 667.

Cram, D. J. & Bauer, R. H. (1959). *J. Amer. Chem. Soc.* **81**, 5971.

Cram, D. J. & Sheehan, M. (1969). *J. Amer. Chem. Soc.* **91**, 3553.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 754, 757.

Dewar, M. J. S. & Thompson, C. C. (1966). *Tetrahedron. Suppl.* **7**, 97.

Gantzel, P. K. & Trueblood, K. N. (1965). *Acta Cryst.* **18**, 958.

Herbstein, F. H. & Snyman, J. A. (1969). *Phil. Trans. Roy. Soc.* A**264**, 635.

Herndon, W. C. & Feuer, J. (1968). *J. Amer. Chem. Soc.* **90**, 5914.

Hoerni, J. A. & Ibers, J. A. (1954). *Acta Cryst.* **7**, 744.

Hope, H. (1968). *Acta Chem. Scand.* **22**, 1057.

Hope, H., Bernstein, J. & Trueblood, K. N. (1971). To be published.

Howells, E. R., Phillips, D. C. & Rogers, D. (1950). *Acta Cryst.* **3**, 210.

Ikemoto, I. & Kuroda, H. (1967). *Bull. Chem. Soc. Japan*, **40**, 2009.

Kuroda, H., Amano, T., Ikemoto, I. & Akamatu, H. (1967). *J. Amer. Chem. Soc.* **89**, 6056.

Kuroda, H., Ikemoto, I. & Akamatu, H. (1966). *Bull. Chem. Soc. Japan*, **39**, 547.

Leung, Y. C. & Marsh, R. E. (1958). *Acta Cryst.* **11**, 17.

Little, R. G., Pautler, D. & Coppens, P. (1971). To be published.

Long, R. E. (1965). Ph.D. Thesis, Univ. of California, L.A.

Maine, P. A. D. de (1957). *J. Chem. Phys.* **26**, 1189

Merrifield, R. E. & Phillips, W. D. (1958). *J. Amer. Chem. Soc.* **80**, 2778.

Mulliken, R. S. (1952). *J. Amer. Chem. Soc.* **74**, 811.

Orgel, L. E. & Mulliken, R. S. (1957). *J. Amer. Chem. Soc.* **79**, 4839.

Prout, C. K. & Wright, J. D. (1968). *Angew. Chem.* (*Int.*) **7**, 659.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

Williams, R. M. & Wallwork, S. C. (1967). *Acta Cryst.* **22**, 899.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139.

Acta Cryst. (1971). B**27**, 2089

The Crystal and Molecular Structures of Hexakis(imidazole)cadmium(II) Nitrate, $[Cd(C_3H_4N_2)_6](NO_3)_2$, and Hexakis(imidazole)cadmium(II) Hydroxide Nitrate Tetrahydrate, $[Cd(C_3H_4N_2)_6](OH)(NO_3).4H_20$

By A. D. Mighell and A. Santoro

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234, *U.S.A.*

(*Received* 21 *September* 1970)

The crystal and molecular structures of hexakis(imidazole)cadmium(II) nitrate, $Cd(C_3H_4N_2)_6]\,(NO_3)_2$, and hexakis(imidazole)cadmium(II) hydroxide nitrate tetrahydrate, $[Cd(C_3H_4N_2)_6]\,(OH)\,(NO_3).4H_2O$, have been determined by single-crystal X-ray diffraction techniques. $[Cd(C_3H_4N_2)_6]\,(NO_3)_2$ crystallizes in the trigonal system, space group $R\bar{3}$. The lattice parameters (hexagonal axes) are $a=12{\cdot}633$ (2), $c=15{\cdot}049$ (2) Å, $Z=3$, $\varrho_o=1{\cdot}54$ g.cm^{-3}, $\varrho_c=1{\cdot}54$ g.cm^{-3}. The final three-dimensional full-matrix least-squares refinement resulted in an R value of 3·6% based on 1343 observed reflections. $[Cd(C_3H_4N_2)_6]\,(OH)\,(NO_3).4H_2O$ crystallizes in the hexagonal system, space group $P6_3/m$. The lattice parameters are $a=9{\cdot}0376$ (8), $c=21{\cdot}729$ (3) Å, $Z=2$, $\varrho_c=1{\cdot}45$ g.cm^{-3}, $\varrho_o=1{\cdot}44$ g.cm^{-3}. The final three-dimensional full-matrix least-squares refinement resulted in an R value of 5·4% based on 996 observed reflections. Both structures consist of discrete $Cd(C_3H_4N_2)_6^{2+}$ cations and NO_3^- anions but as a result of the presence of water molecules and OH^- ions in the hydroxide complex, the packing of the cations in the two structures is considerably different. The ligand imidazole molecules are coordinated through the pyridine type nitrogen atoms (>N) to the Cd^{2+} ions with an average bond distance $Cd\cdots N$ of 2·363 Å and they are hydrogen bonded through the pyrrole type (– N–H) nitrogen atoms to the nitrate groups. However, to accommodate hydrogen bonding, there is considerable difference in the orientation of the imidazole rings in the two complexes. Specifically, each ring in one of the two complex cations is rotated, about the Cd–N(1) direction, approximately 130° with respect to its counterpart in the other cation. The bond distances and angles between the atoms of the imidazole molecules are practically identical in the two structures.

Introduction

The imidazole group occurs in a number of biologically important molecules such as histidine and hypoxanthine, and it plays an important rôle in the chemistry of several biological systems by providing possible binding sites in metal–protein interactions and in other interactions involving hydrogen bonds (Hofmann, 1953; Barnard & Stein, 1958). The adaptability of the imidazole group for a number of biological roles is due to the fact that bonding of this group to its environment is possible through a secondary 'pyrrole' (>NH) and a tertiary 'pyridine' (>N) nitrogen atom. Crystal structure analyses of complexes containing imidazole as ligand are important in clarifying the biological functions of the imidazole group as they provide direct evidence on the stereochemistry of the imidazole molecule which is simultaneously involved in a coordinate bond and in hydrogen bonding.

As a part of a program in the structural and spectroscopic investigation of imidazole coordination complexes, crystals of hexakis(imidazole)cadmium(II) nitrate $[Cd(C_3H_4N_2)_6](NO_3)_2$ [hereafter called $Im_6Cd(NO_3)_2$], were grown from an aqueous solution of $Cd(NO_3)_2$ and imidazole. Almost invariably, crystals of a second compound, hexakis(imidazole)cadmium (II) hydoxide nitrate tetrahydrate, $[Cd(C_3H_4N_2)_6]$ (OH) $(NO_3).4H_2O$ [hereafter called $Im_6Cd(OH)(NO_3).4H_2O$], were obtained from the same solution. Space group and lattice parameter measurements indicated that the structures of these two complexes are different. The presence of water molecules and hydroxide and nitrate ions indicates that hydrogen bonding and packing in the hydroxide complex must be substantially different from that in $Im_6Cd(NO_3)_2$. The complete structure determination of the two cadmium complexes was carried out to permit a comparison of the cation Im_6Cd^{2+} in two different environments. In addition, the present work is intended to provide the structural information needed for the analysis of the infrared spectra of the two complexes and to determine the relationships between their structures and those of related nickel and cobalt compounds now under investigation.

Experimental

Preparation

Crystals of $Im_6Cd(NO_3)_2$ and $Im_6Cd(OH)(NO_3).4H_2O$ were prepared by slow evaporation of an aqueous solution of $Cd(NO_3)_2$ and imidazole in molecular ratio of approximately 1:6. As the crystals of the nitrate complex have rhombohedral habit, they can be easily separated from those of the hydroxide nitrate complex which grow as hexagonal prisms from the same solution. The crystals of both species are colorless.

Crystal data

A summary of the crystal data for the complexes is given in Table 1. In this Table, as well as in all the others, numbers in parentheses are standard deviations in the last significant digits. Approximate unit-cell parameters, Laue symmetry, and systematic extinctions were obtained in both cases from zero and upper level precession and Weissenberg photographs. To determine precise unit-cell parameters, the 2θ angles of a number of reflections were determined with a single-crystal diffractometer. The unit-cell parameters were refined by least-squares to obtain the best fit between observed and calculated 2θ values. In the above measurements Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) was used. The density of the two complexes was measured by the flotation method in a mixture of chloroform and tetrabromoethane.

Intensity measurements

Intensity data for both complexes were obtained using Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) and a three-circle diffractometer with scintillation counter and pulse-height analyzer set to admit 90% of the Mo $K\alpha$ radiation. The intensities of reflections with $2\theta \le 60°$ were measured with a stationary-crystal stationary-counter method. This method was used because the crystals suffer appreciable radiation damage after exposure to X-rays for more than a few days. The background settings were those given by the expression $2\theta \pm (\frac{1}{2})\Delta 2\theta$ where $\Delta 2\theta = 1{\cdot}8 + \tan\theta$ (Alexander & Smith, 1962). The counting time was 10 seconds at each peak and background setting. Niobium foils were used as attenuators when the diffracted intensity exceeded 20000 counts/sec.

The crystal of $Im_6Cd(NO_3)_2$ was an almost perfect rhombohedron with an edge of 0·3 mm. This crystal was mounted on the diffractometer with the reciprocal vector $[0\bar{1}{\cdot}1]^*$ coincident with the axis of the φ-circle. The 2340 reflections measured were reduced by averaging equivalent reflections to a unique set of 1359 reflections of which 1343 were above background. The agreement of the equivalent reflections, expressed by the factor $(\sum | I - \bar{I} |)/(\sum \bar{I})$ ($\bar{I}$ is the average intensity of a group of equivalent reflections and I the intensity of each member of the group), was $\sim 3\%$.

The crystal of $Im_6Cd(OH)(NO_3).4H_2O$ was a hexagonal prism. The form $\{00{\cdot}1\}$ was a hexagon with a side of 0·16 mm and the height of the prism was 0·2 mm. The crystal was mounted with the reciprocal vector $[10{\cdot}0]^*$ coincident with the axis of the φ-circle. The 2045 reflections were reduced by averaging equivalent reflections to a unique set of 1539 of which 996 were above background. The agreement of the equivalent reflections was $\sim 5\%$. A reflection was considered 'unobserved' and assigned a value equal to twice the standard deviation if the net number of counts did not exceed zero by at least twice the standard deviation.

For both compounds, six standard reflections were measured at regular intervals to monitor source intensity, crystal stability and crystal orientation. Neither these reflections nor equivalent reflections showed significant variation of intensity ($< 2\%$) over the period of time in which the intensities were measured. Peak intensities (I_0) were converted to integrated intensities (I_i) by means of a curve I_i/I_0 *versus* 2θ. This curve was determined by measuring both integrated and peak intensities of a number of reflections uniformly distributed over the entire 2θ range. The maximum magnitude of this correction was $\sim 1{\cdot}2$ for both compounds. The intensities were corrected for Lorentz and polarization factors but no absorption corrections were applied as the linear absorption coefficients and the sizes of the crystals are small.

Determination and refinement of the structures*

(*A*) $Im_6Cd(NO_3)_2$

On the basis of the space groups and lattice parameters, it was assumed that $Im_6Cd(NO_3)_2$ and $Im_6Ni(NO_3)_2$ (Santoro, Mighell, Zocchi & Reimann, 1969) are isostructural. A model of the cadmium complex consisting of the coordinates of the atoms of $Im_6Ni(NO_3)_2$ was refined anisotropically with the following weighting scheme: $w^{1/2}=1$ for $F_o \le 70$ (absolute scale) and $w^{1/2}=70/F_o$ for $F_o > 70$. The hydrogen atoms were included in the structure factor calculations but they were assigned an isotropic temperature factor of 4·0 Å^2 and were kept fixed in calculated positions (Santoro *et al.*, 1969). After three cycles of refinement, the R and R_w values were 3·6 and 4·3%, respectively. In the last cycle of refinement the standard deviation of an observation of unit weight was 1·58, which indicates that the experimental errors have been slightly underestimated.

The final difference electron density was everywhere less than 10% of the value of an average carbon atom. The final atomic coordinates, the anisotropic thermal parameters and the structure factors for $Im_6Cd(NO_3)_2$ are reported in Tables 2 and 3 respectively.

(*B*) $Im_6Cd(OH)(NO_3).4H_2O$

The atoms of the complex cation and of the nitrate anion were readily located in a Patterson map. A difference electron density map, calculated assuming the space group $P6_3/m$, revealed peaks in positions $2(a)\bar{6}$, $2(c)\bar{6}$ and $6(h)m$ and well defined peaks at the ex-

---

* In the least-squares refinements in this paper (*a*) the quantity minimized is $\sum w(|F_o|-|F_c|)^2$, (*b*) the F_o's of 'unobserved reflections' are weighted zero or one depending on whether the corresponding F_c's are less or greater than the assigned values of the F_o's, (*c*) scattering factors for neutral cadmium, nitrogen, hydrogen, and carbon atoms and for the singly negative oxygen atom are taken from *International Tables for X-ray Crystallography* (1962), (*d*) the conventional R and weighted R_w values are defined by the expressions

$$R=\frac{\sum ||F_o|-|F_c||}{\sum |F_o|} \quad \text{and} \quad R_w=\left[\frac{\sum w(|F_o|-|F_c|)^2}{\sum w\, F_o^2}\right]^{1/2}$$

Table 1. *Crystal data for hexakis(imidazole)cadmium(II) nitrate and hexakis(imidazole)cadmium(II) hydroxide nitrate tetrahydrate*

The cell parameters of the nitrate and hydroxide nitrate complex were refined using 12 and 14 observed 2θ values, respectively.

	$[Cd(C_3H_4N_2)_6](NO_3)_2$	$[Cd(C_3H_4N_2)_6](OH)(NO_3).4H_2O$
a	12·633 (2) Å	9·0376 (8) Å
c	15·049 (2) Å	21·729 (3) Å
Volume	2080·0 Å^3	1537·0 Å^3
Z	3	2
ϱ_c	1·54 g.cm^{-3}	1·45 g.cm^{-3}
ϱ_o	1·54 g.cm^{-3}	1·44 g.cm^{-3}
Systematic extinctions	$-h+k+l\neq 3n$	$00\cdot l,\ l\neq 2n$
Space group	$R\bar{3}$	$P6_3/m$
Linear absorption coefficient for Mo $K\alpha$	8·5 cm^{-1}	7·6 cm^{-1}

Table 2. *Atomic coordinates* and thermal parameters† for* $Im_6Cd(NO_3)_2$

The anisotropic temperature factor has the form exp $[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cd	0	0	0	63·0 (4)	63·0 (4)	48·0 (2)	31·5 (2)	0	0
C(1)	1090 (3)	2858 (3)	567 (2)	94 (3)	73 (2)	71 (2)	37 (2)	−1 (2)	−4 (2)
C(2)	605 (5)	3011 (4)	1923 (4)	207 (6)	108 (4)	109 (3)	46 (4)	51 (4)	−39 (3)
C(3)	151 (4)	1827 (3)	1725 (3)	150 (4)	93 (3)	76 (2)	42 (3)	30 (2)	−9 (2)
N(1)	459 (2)	1732 (2)	870 (2)	87 (2)	66 (2)	54 (1)	37 (2)	−1 (1)	−8 (1)
N(2)	1170 (3)	3650 (2)	1178 (3)	119 (3)	65 (2)	107 (2)	29 (2)	20 (2)	−20 (2)
N(3)	0	0	3923 (3)	83 (3)	83 (3)	43 (2)	42 (2)	0	0
O(1)	700 (2)	1113 (2)	3922 (2)	112 (3)	89 (2)	113 (2)	37 (2)	−7 (2)	3 (2)
H(1)‡	147	309	0						
H(2)	45	336	245						
H(3)	−37	112	209						
H(4)	154	445	115						

* The atomic coordinates are multiplied by 10^4 for the non-hydrogen atoms and by 10^3 for the hydrogen atoms.

† The β_{ij}'s have been multiplied by 10^4.

‡ The hydrogen atoms H(1), H(2) and H(3) are labeled with the same numbers as the carbon atoms to which they are attached. The hydrogen atom H(4) is bonded to the nitrogen atom N(2).

pected positions of the hydrogen atoms of the imidazole ring. The positions 6(*h*)*m* can only be occupied by the oxygen atoms of water molecules because of charge balance. The oxygen atoms of the remaining two water molecules and of the two OH^- ions must be located in positions 2(*a*)$\bar{6}$ and 2(*c*)$\bar{6}$. In either case the two water

Table 3. *The columns are h, k,* $10F_o$, $10F_c$, *respectively*

Unobserved reflections are marked with an L.

h	k	10Fo	10Fc
L=0			
3	0	1204	1216
6	0	1040	1068
9	0	439	404
12	0	215	231
15	0	79	102
1	1	1923	1913
4	1	526	528
7	1	694	686
10	1	460	489
13	1	240	237
2	2	1509	1463
5	2	888	883
8	2	552	554
11	2	250	262
14	2	131	128
3	3	518	512
6	3	636	647
9	3	714	747
12	3	205	208
1	4	1120	1102
4	4	599	605
7	4	765	756
10	4	306	299
2	5	1470	1354
5	5	729	730
8	5	561	552
11	5	187	177
3	6	859	829
6	6	545	542
9	6	220	216
1	7	702	680
4	7	479	484
7	7	223	245
10	7	179	161
2	8	292	292
5	8	336	365
8	8	199	191
3	9	297	316
6	9	258	276
1	10	529	574
4	10	356	396
7	10	141	138
2	11	263	280
5	11	156	166
3	12	270	265
1	13	208	197
2	14	128	146
L=1			
1	0	1200	962
4	0	220	170
7	0	959	921
10	0	253	258
13	0	183	170
2	1	1686	-1621
5	1	994	943
8	1	244	248
11	1	350	347
14	1	138	142
0	2	1209	1100
3	2	425	405
6	2	456	499
9	2	369	390
12	2	272	257
-2	3	1489	1489
1	3	1732	1710
4	3	898	670
7	3	290	286
10	3	284	296
13	3	132	115
2	4	1382	1343
5	4	630	620
8	4	452	471
11	4	177	175
-1	4	104	78
-3	5	1671	1679
0	5	1667	1662
3	5	1247	1221
6	5	201	194
9	5	200	214
12	5	81	73
1	6	1242	1252
4	6	343	341
7	6	238	250
10	6	192	184
-2	6	907	872
-5	6	672	649
2	7	550	523
5	7	79	52
8	7	150	145
-1	7	971	968
-4	7	800	748
0	8	695	696
3	8	244	252
6	8	312	332
9	8	197	201
-3	8	79	134
-6	8	718	700
1	9	375	365
4	9	359	394
7	9	188	171
-2	9	281	284
-5	9	603	574
-8	9	331	333
2	10	387	403
5	10	249	263
-1	10	418	412
-4	10	281	287
-7	10	676	652
0	11	345	362
3	11	177	183
6	11	162	162
-3	11	414	432
-6	11	285	308
-9	11	311	319
1	12	170	183
4	12	188	200
-2	12	244	247
-5	12	383	384
-8	12	238	250
-11	12	454	470
2	13	214	224
-1	13	167	162
-4	13	250	254
-7	13	301	315
-10	13	363	401
0	14	125	114
-3	14	222	236
-6	14	167	176
-9	14	347	379
-12	14	266	274
-2	15	204	203
-5	15	256	254
-8	15	113	107
-11	15	234	233
-14	15	176	176
-4	16	164	152
-7	16	171	158
-10	16	150	169
-13	16	205	196
-6	17	178	159
-9	17	144	139
-12	17	140	147
L=2			
2	0	133	-117
5	0	754	752
8	0	756	748
11	0	289	305
14	0	233	233
0	1	2157	2332
3	1	1212	1232
6	1	1274	1241
9	1	96	118
12	1	250	260
1	2	672	632
4	2	685	682
7	2	753	736
10	2	437	446
13	2	240	244
-1	3	2776	2672
2	3	318	295
5	3	1033	975
8	3	511	518
11	3	230	217
-3	4	1467	1484
0	4	569	507
3	4	718	678
6	4	563	550
9	4	465	481
12	4	165	157
-2	5	1871	1832
1	5	654	595
4	5	607	614
7	5	342	341
10	5	177	167
-4	6	1585	1635
-1	6	435	424
2	6	536	498
5	6	245	246
8	6	286	292
11	6	159	132
0	7	289	254
3	7	444	467
6	7	324	319
9	7	239	233
-3	7	349	356
-6	7	1060	983
1	8	444	452
4	8	423	425
7	8	270	293
-2	8	528	536
-5	8	1106	1059
2	9	560	565
5	9	398	423
8	9	87	114
-1	9	561	572
-4	9	577	564
-7	9	688	696
0	10	721	727
3	10	298	329
6	10	125	126
-3	10	372	370
-6	10	808	836
-9	10	330	346
1	11	352	374
4	11	262	266
-2	11	535	542
-5	11	383	399
-8	11	290	310
2	12	248	237
5	12	101	110
-1	12	198	212
-4	12	573	564
-7	12	524	514
-10	12	134	146
0	13	222	234
3	13	165	170
-3	13	312	322
-6	13	367	362
-9	13	244	258
-12	13	151	159
1	14	137	125
-2	14	240	244
-5	14	231	234
-8	14	229	226
-11	14	290	306
-1	15	138	123
-4	15	217	210
-7	15	201	189
-10	15	212	214
-13	15	238	227
-3	16	150	143
-6	16	220	212
-9	16	213	195
-12	16	145	144
-5	17	147	141
-8	17	162	148
-11	17	159	165
L=3			
0	0	133	85
3	0	544	526
6	0	582	525
9	0	426	453
12	0	315	332
15	0	215	198
1	1	1454	1494
4	1	507	496
7	1	773	740
10	1	340	355
13	1	247	235
-1	2	2255	2312
2	2	1203	1167
5	2	655	580
8	2	567	597
11	2	378	389
14	2	125	112
0	3	1782	1820
3	3	887	886
6	3	941	921
9	3	400	427
12	3	188	156
-2	4	1895	1883
1	4	1750	1767
4	4	1023	957
7	4	419	438
10	4	186	203
2	5	905	874
5	5	516	512
8	5	409	418
11	5	137	127
-1	5	1115	1068
-4	5	93	48
0	6	691	701
3	6	786	774
6	6	167	188
9	6	262	262
-3	6	1218	1243
1	7	723	698
4	7	333	325
7	7	420	414
10	7	199	206
-2	7	687	683
-5	7	214	-152
2	8	536	541
5	8	319	313
8	8	202	211
-1	8	948	933
-4	8	749	756
-7	8	356	351
0	9	589	576
3	9	399	408
6	9	241	245
-3	9	330	346
-6	9	760	758
1	10	413	400
4	10	165	161
7	10	159	148
-2	10	484	491
-5	10	570	552
-8	10	550	595
2	11	85	59
5	11	206	210
-1	11	425	428
-4	11	593	605
-7	11	496	494
-10	11	283	299
0	12	197	216
3	12	201	204
-3	12	393	369
-6	12	545	549
-9	12	271	304
1	13	188	181
-2	13	213	222
-5	13	282	277
-8	13	562	553
-11	13	359	373
2	14	194	185
-1	14	171	162
-4	14	321	328
-7	14	224	228
-10	14	268	284
-13	14	229	226
0	15	140	124
-3	15	259	239
-6	15	246	232
-9	15	192	163
-12	15	180	186
-2	16	201	191
-5	16	199	186
-8	16	149	141
-11	16	135	129
-14	16	164	147
-7	17	155	147
-10	17	144	144
L=4			
1	0	499	-493
4	0	1115	1112
7	0	789	774
10	0	286	307
13	0	238	231
2	1	826	785
5	1	818	849
8	1	430	462
11	1	292	302
14	1	246	225
0	2	939	845
3	2	923	892
6	2	985	931
9	2	132	132
12	2	218	211
1	3	992	926
4	3	607	582
7	3	472	510
10	3	191	184
13	3	180	170
-2	3	149	-146
2	4	678	703
5	4	435	425
8	4	117	131
11	4	131	121
-1	4	1462	1451
0	5	430	411
3	5	283	313
6	5	196	184
9	5	255	210
-3	5	1414	1353
1	6	574	629
4	6	367	376
7	6	175	184
10	6	208	196
-2	6	870	858
-5	6	612	644
2	7	604	602
5	7	183	193
8	7	290	317
-1	7	675	694
-4	7	632	706
0	8	240	236
3	8	535	513
6	8	287	295
9	8	149	149
-3	8	741	718
-6	8	560	559
1	9	536	542
4	9	235	229
7	9	139	141
-2	9	249	256
-5	9	730	735
-8	9	558	582
2	10	339	337
5	10	178	183
-1	10	549	550
-4	10	55	49
-7	10	192	203
0	11	363	343
3	11	186	188
6	11	99	117
-3	11	272	287
-6	11	482	478
-9	11	268	292
1	12	277	279
4	12	173	173
-2	12	105	110
-5	12	312	314
-8	12	406	417
-11	12	165	176
2	13	166	148
-1	13	221	228
-4	13	195	198
-7	13	284	268
-10	13	265	292
0	14	151	144
-3	14	261	255
-6	14	88	86
-9	14	199	180
-12	14	209	222
-2	15	173	157
-5	15	177	177
-8	15	218	209
-11	15	115	134
-14	15	190	177
-4	16	178	169
-7	16	161	157
-10	16	193	183
-13	16	115	111
-6	17	171	167
-9	17	162	155
L=5			
2	0	1422	1489
5	0	1082	1077
8	0	489	521
11	0	276	293
14	0	220	203
0	1	1797	1937
3	1	1122	1125
6	1	906	873
9	1	500	525
12	1	259	276
1	2	1278	1276
4	2	662	649
7	2	775	796
10	2	278	294
13	2	186	180
2	3	983	955
5	3	727	696
8	3	434	450
11	3	217	227
-1	3	1558	1610
0	4	1247	1207
3	4	77	127
6	4	762	750
9	4	230	236
12	4	202	187
-3	4	1129	1148
1	5	605	591
4	5	646	636
7	5	450	462
10	5	167	174
-2	5	872	815
2	6	537	539
5	6	533	522
8	6	407	395
11	6	156	155
-1	6	432	430
-4	6	457	391
0	7	625	608
3	7	448	444
6	7	377	376
9	7	200	203
-3	7	1307	1269
-6	7	382	429
1	8	392	393
4	8	435	430
7	8	236	252
-2	8	353L	623
-5	8	494	500
2	9	590	604
5	9	154	153
8	9	152	131
-1	9	543	549
-4	9	457	467
-7	9	576	585
0	10	508	512
3	10	177	182
6	10	196	200
-3	10	587	598
-6	10	529	547
-9	10	414	439
1	11	258	274
4	11	169	177
-2	11	437	438
-5	11	877	875
-8	11	310	304
2	12	185	197
-1	12	307	303
-4	12	356	357
-7	12	546	552
-10	12	322	355
0	13	271	264
3	13	166	157
-3	13	261	256
-6	13	300	274
-9	13	283	282
-12	13	256	258
1	14	146	156
-2	14	164	168
-5	14	322	313
-8	14	284	265
-11	14	174	166
-1	15	138	131
-4	15	230	234
-7	15	202	205
-10	15	143	137
-13	15	116	116
-3	16	177	176
-6	16	166	168
-9	16	195	196
-12	16	134	132
-8	17	171	154
-11	17	152	142
L=6			
0	0	40	19
3	0	453	419
6	0	293	328
9	0	376	403
12	0	282	287
1	1	426	424
4	1	1080	1067
7	1	421	439
10	1	329	365
13	1	166	162
2	2	738	737
5	2	635	628
8	2	183	202
11	2	227	240
-1	2	498	486
0	3	1320	1325
3	3	748	695
6	3	485	506
9	3	114	123
12	3	143	142
1	4	741	769
4	4	434	448
7	4	368	367
10	4	133	135
-2	4	675	660
2	5	642	699
5	5	471	490
8	5	141	151
11	5	171	174
-1	5	755	756
-4	5	888	842
0	6	1244	1211
3	6	327	338
6	6	246	258
9	6	189	215
-3	6	536	546
1	7	475	461
4	7	344	357
7	7	257	249
-2	7	814	792
-5	7	136	167
2	8	436	443
5	8	249	241
8	8	151	151
-1	8	320	317
-4	8	443	438
-7	8	512	514
0	9	470	497
3	9	248	244
6	9	157	159
-3	9	375	375
-6	9	198	183
1	10	273	262
4	10	95	93
-2	10	584	588
-5	10	413	461
-8	10	355	349
2	11	222	202
5	11	163	164
-1	11	182	178
-4	11	212	225
-7	11	443	445
-10	11	387	412
0	12	299	286
3	12	116	109
-3	12	37L	35
-6	12	388	394
-9	12	399	394
1	13	177	169
-2	13	183	168
-5	13	211	204
-8	13	136	135
-11	13	253	269
-1	14	182	181
-4	14	197	235
-7	14	219	211
-10	14	172	157
-13	14	167	165
-3	15	193	175
-6	15	156	149
-9	15	187	191
-12	15	138	142
-5	16	215	197
-8	16	196	178
-11	16	126	125
L=7			
1	0	509	487
4	0	1206	1158
7	0	473	477
10	0	301	336
13	0	154	158
2	1	724	705
5	1	975	955
8	1	317	343
11	1	210	235
14	1	147	121
0	2	770	772
3	2	1027	976
6	2	500	530
9	2	247	258
12	2	180	163
1	3	331	316
4	3	369	398
7	3	361	349
10	3	222	211
-2	3	1169	1193
2	4	277	318
5	4	597	588
8	4	200	194
11	4	192	192
-1	4	984	954
0	5	466	487
3	5	383	379
6	5	376	370
9	5	161	162
-3	5	476	513
1	6	395	383
4	6	381	360
7	6	303	308
10	6	122	129
-2	6	665	659
-5	6	730	746
2	7	84	91
5	7	469	460
8	7	176	184
-1	7	329	316
-4	7	782	740
0	8	452	461
3	8	484	482
6	8	159	165
-3	8	543	543
-6	8	452	467
1	9	432	433
4	9	234	224
7	9	115	137
-2	9	619	635
-5	9	259	258
-8	9	562	589
2	10	251	246
5	10	179	181
-1	10	379	379
-4	10	544	542
-7	10	524	527
0	11	245	253
3	11	176	176
-3	11	217	192
-6	11	463	475
-9	11	301	314
1	12	275	266
4	12	98	106
-2	12	255	256
-5	12	191	182
-8	12	158	158
-11	12	220	233
2	13	142	125
-1	13	236	243
-4	13	190	182
-7	13	240	232
-10	13	171	158
0	14	210	209
-3	14	117	123
-6	14	252	244
-9	14	160	143
-12	14	117	126
-2	15	151	151
-5	15	209	206
-8	15	231	218
-11	15	148	143
-14	15	130	123
-4	16	141	140
-7	16	208	203
-10	16	149	134
L=8			
2	0	1131	1136
5	0	607	574
8	0	511	514
11	0	266	287
14	0	124	117
0	1	630	651
3	1	921	886
6	1	189	184
9	1	379	388
12	1	179	175
1	2	1148	1163
4	2	744	745
7	2	315	320
10	2	356	355
13	2	105	95
2	3	637	616
5	3	453	438
8	3	302	261
11	3	178	192
-1	3	1021	1029
0	4	496	527
3	4	784	761
6	4	524	531
9	4	193	202
-3	4	614	589
1	5	598	593
4	5	431	435
7	5	306	310
10	5	187	198
-2	5	520	547
2	6	332	315
5	6	397	405
8	6	219	239
-1	6	791	741
-4	6	308	326
0	7	499	494
3	7	481	480
6	7	291	295
9	7	131	95
-3	7	535	542
-6	7	228	223
1	8	439	444
4	8	351	367
7	8	132	132
-2	8	551	581
-5	8	317	311
2	9	157	158
5	9	168	163
-1	9	629	629
-4	9	659	656
-7	9	483	478
0	10	139	139
3	10	159	171
6	10	148	143
-3	10	512	506
-6	10	356	346
-9	10	448	451
1	11	194	201
4	11	135	135
-2	11	303	302
-5	11	224	234
-8	11	480	406
2	12	143	136
-1	12	241	246
-4	12	212	231
-7	12	262	251
-10	12	278	263
0	13	208	211
-3	13	209	205
-6	13	324	341
-9	13	195	195
-12	13	162	174
-2	14	206	202
-5	14	213	208
-8	14	202	211
-11	14	202	187
-4	15	218	202
-7	15	229	226
-10	15	170	143
-13	15	149	138
-6	16	164	161
-9	16	191	187
L=9			
0	0	103	112
3	0	812	778
6	0	422	407
9	0	415	425
12	0	139	134
1	1	519	512
4	1	756	758
7	1	154	140
10	1	210	210
13	1	117	100
2	2	740	727
5	2	314	319
8	2	256	258
11	2	143	140
-1	2	216	248
0	3	270	311
3	3	528	527
6	3	263	274
9	3	191	189
12	3	105	102
1	4	339	355
4	4	333	323
7	4	98	107
10	4	185	181
-2	4	314	335
2	5	584	599
5	5	198	210
8	5	137	138
-1	5	465	466
-4	5	345	359
0	6	230	245
3	6	291	301
6	6	284	268
9	6	125	108
-3	6	393	411
1	7	367	372
4	7	373	385
7	7	134	135
-2	7	479	501
-5	7	578	583
2	8	285	272
5	8	113	123
8	8	107	102
-1	8	453	469
-4	8	496	506
-7	8	436	430
0	9	234	196
3	9	219	207
6	9	121	106
-3	9	469	480
-6	9	240	244
1	10	101	93
4	10	191	197
-2	10	174	183
-5	10	150	134
-8	10	366	373
2	11	196	180
-1	11	211	199
-4	11	110	112
-7	11	157	149
-10	11	179	183
0	12	176	164
3	12	125	122
-3	12	225	219
-6	12	126	132
-9	12	196	200
1	13	174	174
-2	13	187	190
-5	13	119	123
-8	13	178	165
-11	13	174	172
-1	14	197	187
-4	14	187	182
-7	14	189	170
-10	14	192	189
-13	14	110	109
-3	15	114	105
-6	15	203	181
-9	15	168	152
-12	15	117	117
-5	16	182	183
L=10			
1	0	927	919
4	0	639	658
7	0	398	407
10	0	216	212
13	0	134	118
2	1	924	927
5	1	438	446
8	1	442	435
11	1	166	172
0	2	718	738
3	2	445	451
6	2	163	153
9	2	355	351
12	2	116	111
1	3	562	566
4	3	468	468
7	3	329	327
10	3	188	210
-2	3	634	631
2	4	501	515
5	4	330	324
8	4	246	229
11	4	151	150
-1	4	134	143
0	5	384	385
3	5	362	360
6	5	421	385
9	5	219	220
-3	5	367	375
1	6	439	439
4	6	346	326
7	6	255	255
-2	6	500	495
-5	6	586	591
2	7	487	487
5	7	274	266
8	7	111	108
-1	7	398	391
-4	7	587	624
0	8	336	334
3	8	275	270
6	8	129	136
-3	8	571	546
-6	8	514	511
1	9	133	113
4	9	208	213
-2	9	326	317
-5	9	365	361
-8	9	355	359
2	10	196	215
5	10	145	137
-1	10	239	239
-4	10	381	369
-7	10	207	213
0	11	164	170
3	11	189	189
-3	11	363	349
-6	11	176	166
-9	11	246	253
1	12	184	182
-2	12	264	267
-5	12	286	273
-8	12	241	235
-11	12	165	168
-1	13	190	195
-4	13	225	224
-7	13	209	199
-10	13	214	213
-3	14	222	213
-6	14	227	219
-9	14	170	164
-12	14	139	126
-5	15	162	151
-8	15	186	172
-11	15	160	143
L=11			
2	0	443	451
5	0	298	315
8	0	238	233
11	0	178	172
0	1	645	656
3	1	456	471
6	1	172	161
9	1	249	242
12	1	123	130
1	2	397	392
4	2	343	345
7	2	211	213
10	2	136	156
2	3	336	327
5	3	252	270
8	3	248	249
11	3	119	115
-1	3	213	228
0	4	435	453
3	4	425	426
6	4	170	176
9	4	189	200
-3	4	246	229
1	5	618	630
4	5	231	227
7	5	180	192
-2	5	243	250
2	6	502	513
5	6	270	269
8	6	85	103
-1	6	416	424
-4	6	475	486
0	7	377	368
3	7	176	191
6	7	125	126
-3	7	340	341
-6	7	553	554
1	8	264	262
4	8	99	104
7	8	107	112
-2	8	263	254
-5	8	346	342
2	9	163	151
5	9	124	114
-1	9	127	130
-4	9	231	235
-7	9	174	161
0	10	151	153
3	10	179	183
-3	10	238	234
-6	10	139	146
-9	10	202	184
1	11	119	120
-2	11	211	209
-5	11	222	211
-8	11	242	229
2	12	158	149
-1	12	149	152
-4	12	197	199
-7	12	160	155
-10	12	208	194
0	13	118	121
-3	13	227	214
-6	13	162	151
-9	13	181	177
-12	13	148	138
-2	14	96	94
-5	14	184	172
-8	14	95	108
-11	14	179	169
-7	15	101	118
L=12			
0	0	526	526
3	0	350	359
6	0	485	492
9	0	109	104
12	0	126	125
1	1	409	410
4	1	247	236
7	1	261	261
10	1	129	140
2	2	158	152
5	2	264	266
8	2	241	249
11	2	138	130
-1	2	522	539
0	3	259	274
3	3	330	339
6	3	157	151
9	3	157	159
1	4	368	386
4	4	371	357
7	4	219	196
10	4	146	138
-2	4	250	246
2	5	303	303
5	5	233	216
8	5	155	157
-1	5	393	408
-4	5	421	426
0	6	360	366
3	6	196	199
6	6	172	175
-3	6	408	412
1	7	323	314
4	7	136	107
7	7	103	87
-2	7	154	153
-5	7	520	517
2	8	182	175
5	8	144	140
-1	8	140	130
-4	8	210	214
-7	8	253	264
0	9	223	205
3	9	158	167
-3	9	188	188
-6	9	254	267
1	10	179	168
4	10	141	149
-2	10	189	178
-5	10	242	233
-8	10	191	194
2	11	177	173
-1	11	169	177
-4	11	245	219
-7	11	198	180
-10	11	130	123
0	12	165	146
-3	12	192	176
-6	12	138	140
-9	12	154	145
-2	13	163	155
-5	13	171	166
-8	13	113	121
-11	13	119	121
-4	14	97	112
-7	14	133	127
-10	14	135	130
L=13			
1	0	531	555
4	0	176	181
7	0	271	266
10	0	164	168
2	1	357	347
5	1	207	211
8	1	183	181
11	1	142	147
0	2	413	430
3	2	234	250
6	2	309	304
9	2	172	180
1	3	252	260
4	3	412	405
7	3	256	234
10	3	170	157
-2	3	380	387
2	4	341	337
5	4	246	233
8	4	192	203
-1	4	519	531
0	5	449	465
3	5	331	319
6	5	174	179
-3	5	387	403
1	6	273	280
4	6	198	185
7	6	129	115
-2	6	260	280
-5	6	397	408
2	7	228	213
5	7	145	148
-1	7	236	231
-4	7	219	212
0	8	277	255
3	8	108	118
-3	8	167	176
-6	8	275	270
1	9	204	217
4	9	135	141
-2	9	211	208
-5	9	286	278
-8	9	167	153
2	10	150	138
-1	10	198	199
-4	10	248	226
-7	10	265	245
0	11	155	150
-3	11	197	188
-6	11	204	196
-9	11	153	145
-2	12	182	182
-5	12	188	181
-8	12	205	184
-11	12	110	101
-4	13	164	161
-7	13	158	147
-10	13	131	124
L=14			
2	0	291	295
5	0	183	180
8	0	111	116
11	0	47L	65
0	1	179	178
3	1	104	97
6	1	253	257
9	1	143	139
1	2	180	168
4	2	180	181
7	2	167	178
10	2	110	96
2	3	269	262
5	3	234	230
8	3	108	114
-1	3	249	263
0	4	333	328
3	4	265	272
6	4	85	98
9	4	119	92
-3	4	261	253
1	5	130	142
4	5	168	175
7	5	46L	88
-2	5	360	361
2	6	156	153
5	6	87	72
-1	6	202	199
-4	6	209	208
0	7	173	173
3	7	117	120
6	7	47L	77
-3	7	120	122
-6	7	178	171
1	8	188	186
4	8	90	93
-2	8	143	148
-5	8	201	201
2	9	140	125
-1	9	138	137
-4	9	148	142
-7	9	180	186
0	10	152	142
-3	10	112	112
-6	10	158	151
-9	10	104	91
1	11	87	96
-2	11	134	115
-5	11	111	114
-8	11	134	125
-1	12	132	110
-4	12	110	103
-7	12	117	128
-10	12	70	75
-6	13	90	86
L=15			
0	0	310	310
3	0	266	265
6	0	181	181
9	0	155	155
1	1	292	310
4	1	152	150
7	1	216	223
10	1	102	101
2	2	291	284
5	2	280	268
8	2	168	166
-1	2	236	237
0	3	293	301
3	3	199L	235
6	3	191	200
9	3	117	114
1	4	230	225
4	4	197	192
7	4	133	135
-2	4	364	380
2	5	144	136
5	5	139	128
-1	5	274	275
-4	5	260	255
0	6	156	152
3	6	190	185
6	6	130	104
-3	6	216	249
1	7	166	167
4	7	135	118
-2	7	232	210
-5	7	190	195
2	8	185	174
-1	8	159	161
-4	8	214	202
-7	8	169	176
0	9	165	157
3	9	109	113
-3	9	170	159
-6	9	181	183
1	10	163	143
-2	10	142	137
-5	10	170	163
-8	10	81	94
-1	11	145	131
-4	11	139	145
-7	11	161	165
-10	11	81	82
-3	12	129	114
-6	12	122	124
-9	12	146	129
L=16			
1	0	193	188
4	0	161	163
7	0	152	146
10	0	96	83
2	1	190	190
5	1	172	161
8	1	156	153
0	2	168	157
3	2	197	182
6	2	169	184
1	3	276	277
4	3	132	144
7	3	118	112
-2	3	208	216
2	4	154	145
5	4	117	124
-1	4	211	226
0	5	180	176
3	5	118	126
6	5	100	91
-3	5	194	195
1	6	124	128
4	6	109	112
-2	6	191	185
-4	6	118	108
2	7	125	138
-1	7	157	161
-4	7	136	148
0	8	120	126
3	8	113	90
-3	8	129	126
-6	8	119	113
1	9	156	139
-2	9	107	113
-5	9	110	110
-8	9	81	72
-1	10	47L	86
-4	10	130	132
-7	10	102	103
-3	11	99	91
-6	11	131	128
L=17			
2	0	135	121
5	0	133	126
8	0	106	103
0	1	140	137
3	1	168	158
6	1	155	158
1	2	170	173
4	2	130	142
7	2	120	115
2	3	152	158
5	3	115	113
-1	3	157	151
0	4	153	156
3	4	76	73
6	4	105	92
-3	4	192	182
1	5	108	100
4	5	96	99
-2	5	151	151
2	6	83	74
-1	6	151	149
-4	6	146	137
0	7	120	108
3	7	93	89
-3	7	103	103
-6	7	122	107
1	8	111	106
-2	8	104	102
-5	8	89	81
-1	9	89	89
-4	9	118	111
-7	9	56L	56
-3	10	114	91
-6	10	116	124
L=18			
0	0	154	174
3	0	155	163
6	0	118	128
1	1	135	144
4	1	145	161
7	1	121	118
2	2	167	183
5	2	125	133
-1	2	149	161
0	3	153	159
3	3	119	122
6	3	185	104
1	4	137	141
4	4	104	102
-2	4	171	173
2	5	92	83
-1	5	144	150
-4	5	132	139
0	6	128	124
3	6	91	96
-3	6	132	123
1	7	91	85
-2	7	111	119
-5	7	90	77
-1	8	145	139
-4	8	82	91
-7	8	84	70
-3	9	123	122
-6	9	111	106
L=19			
1	0	86	75
4	0	118	109
2	1	93	98
5	1	95	93
0	2	83	84
3	2	114	113
1	3	105	96
4	3	79L	68
-2	3	95	98
2	4	61	73
-1	4	84	80
0	5	40L	63
-3	5	94	97
1	6	47L	48
-2	6	91	69
-5	6	40L	54
-1	7	102	101
-4	7	55L	41
L=20			
2	0	89	98
5	0	91	91
0	1	102	101
3	1	128	124
1	2	115	104
2	3	112	103
-1	3	85L	93
0	4	47L	64
-3	4	114	138
-2	5	73	75
L=21			
0	0	76	84
1	1	74L	78
-1	2	73L	74

Table 4. *Atomic coordinates* and thermal parameters† for* $Im_6Cd(OH)(NO_3).4H_2O$

	x	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cd	0	0	0	147 (1)	147 (1)	13·3 (1)	73·7 (6)	0	0
C(1)	2653 (6)	1855 (6)	1172 (2)	154 (8)	179 (8)	23 (1)	81 (7)	−6 (3)	−4 (3)
C(2)	4146 (7)	4575 (7)	1000 (3)	192 (11)	166 (9)	40 (2)	38 (8)	−31 (4)	−10 (4)
C(3)	3104 (7)	3822 (7)	526 (3)	203 (10)	166 (8)	27 (1)	64 (8)	−12 (3)	7 (3)
N(1)	2155 (5)	2099 (5)	633 (2)	145 (6)	151 (6)	16·8 (7)	63 (5)	−4 (2)	−3 (2)
N(2)	3857 (5)	3325 (6)	1413 (2)	143 (7)	203 (8)	21·7 (8)	87 (6)	−17 (2)	−14 (2)
N(3)	$\frac{2}{3}$§	$\frac{1}{3}$§	$\frac{1}{4}$§	180 (17)	180 (17)	12 (2)	90 (8)	0	0
O(1)	5653 (6)	3947 (6)	$\frac{1}{4}$§	144 (8)	171 (8)	26 (1)	112 (7)	0	0
O(2)	0	0	$\frac{1}{4}$§	237 (17)	237 (17)	34 (3)	118 (8)	0	0
O(3)	$\frac{1}{3}$§	$\frac{2}{3}$§	2693 (11)	180 (20)	180 (20)	70 (14)	90 (10)	0	0
O(4)	617 (8)	3309 (9)	2639 (6)	188 (12)	232 (13)	41 (6)	132 (10)	5 (5)	5 (5)
H(1)‡	222	77	137						
H(2)	438	349	176						
H(3)	495	577	106						
H(4)	299	436	16						

* † and ‡ as in Table 2.

§ These values are not multiplied by 10^4.

molecules, as well as the two OH⁻ ions, will have symmetry $\bar{6}$ imposed by the space group. This feature suggests either a space group of lower symmetry or disorder of the hydrogen atoms of the hydroxide ions and of the two water molecules.

The model of the structure was refined by full-matrix anisotropic least-squares analysis with the weighting scheme $w^{1/2}=1$ for $|F_o| \le 50$ (absolute scale) and $w^{1/2}=50/|F_o|$ for $|F_o|>50$. The hydrogen atoms of the water molecules and of the OH⁻ ions were not included in this refinement. However, the hydrogen atoms of the imidazole rings were included in the calculations but they were kept fixed in the positions determined as indicated in Santoro *et al.* (1969) and they were given a fixed isotropic temperature factor of 4·0 Å². At the end of the refinement the R and R_w values were 5·4 and 6·3%, respectively. The standard deviation of an observation of unit weight was 1·62.

An analysis of the thermal parameters showed that, with the exception of the oxygen atoms O(3) and O(4), the root-mean-square displacements (r.m.s.d.) of all atoms in the structure were reasonable, ranging from 0·16 to 0·33 Å. The r.m.s.d. for the oxygen atoms O(3) and O(4) ranged from 0·21 to 0·25 Å in the plane normal to the c axis, but in the direction of the c axis they were found to be 0·72 and 0·53 Å, respectively. These unusually large apparent thermal vibrations were interpreted as disordering of the water molecules. Accordingly, an anisotropic refinement was carried out with the oxygen atoms O(3) and O(4) slightly removed from the symmetry plane so that each atom is split into two half-atoms related by the mirror operation. After three cycles of refinement the R and R_w values were 5·4 and 6·2%, respectively. The standard deviation of an observation of unit weight was 1·61. The atomic coordinates and the thermal parameters of the atoms of the complex cation and of the nitrate anion are not sensitive to the way in which the atoms O(3) and O(4) are treated and they agree to within one standard deviation for the two types of anisotropic refinement. The results of the refinement with split atoms are reported here because it seems more reason-

Table 5. *The columns are h, k, $10F_o$, $10F_c$, respectively*

		L=0	
1	0	1206	1082
2	0	946	909
3	0	1446	1409
4	0	580	552
5	0	737	681
6	0	309	319
7	0	172	176
8	0	98	99
9	0	141	126
10	0	111	114
1	1	185	196
2	1	235	210
3	1	460	446
4	1	636	603
5	1	364	360
6	1	276	275
7	1	245	254
8	1	226	232
9	1	130	151
10	1	123	107
1	2	595	545
2	2	463	457
3	2	414	400
4	2	574	565
5	2	389	394
6	2	322	335
7	2	196	210
8	2	136	127
9	2	70	60
1	3	1030	1014
2	3	784	772
3	3	448	457
4	3	239	243
5	3	174	169
6	3	249	252
7	3	101	110
8	3	61L	49
9	3	68L	70
1	4	913	871
2	4	430	422
3	4	47L	43
4	4	408	420
5	4	264	286
6	4	136	136
7	4	112	114
8	4	77	76
1	5	560	544
2	5	423	432
3	5	158	159
4	5	346	365
5	5	185	200
6	5	125	122
7	5	107	114
1	6	196	191
2	6	131	132
3	6	265	260
4	6	135	133
5	6	111	110
6	6	95	52
1	7	315	313
2	7	219	237
3	7	101	108
4	7	164	166
5	7	64L	57
1	8	221	230
2	8	126	130
3	8	125	124
4	8	79	53
1	9	135	124
2	9	73	79
3	9	66L	18
1	10	151	137
		L=1	
1	0	248	263
2	0	83	51
3	0	310	286
4	0	182	-158
5	0	165	-151
6	0	45L	17
7	0	145	147
8	0	53L	-43
9	0	55L	-25
10	0	61L	2
1	1	720	724
2	1	84	-61
3	1	371	342
4	1	70	67
5	1	221	-205
6	1	98	109
7	1	48L	-15
8	1	52L	-61
9	1	57L	7
10	1	63L	3
1	2	93	-110
2	2	168	144
3	2	165	-150
4	2	147	-134
5	2	46L	20
6	2	48L	24
7	2	88	98
8	2	55L	-6
9	2	61L	0
1	3	111	118
2	3	112	96
3	3	92	-67
4	3	98	90
5	3	48L	27
6	3	87	-87
7	3	54L	9
8	3	60L	8
9	3	65L	-11
1	4	108	-108
2	4	126	-109
3	4	114	-103
4	4	64	68
5	4	51L	-24
6	4	55L	-52
7	4	59L	29
8	4	64L	-17
1	5	48	-32
2	5	59	41
3	5	159	165
4	5	52L	-17
5	5	54L	-1
6	5	60L	-21
7	5	64L	1
1	6	48L	-34
2	6	51	46
3	6	55	-50
4	6	55L	-2
5	6	59L	29
6	6	63L	-7
1	7	50L	40
2	7	53L	-11
3	7	61	-61
4	7	60L	13
5	7	65L	-14
1	8	54L	44
2	8	57L	16
3	8	61L	2
4	8	64L	20
1	9	60L	-23
2	9	63L	15
3	9	67L	-55
1	10	64L	-25
		L=2	
0	0	723	727
1	0	1280	1205
2	0	844	795
3	0	404	381
4	0	801	752
5	0	567	512
6	0	296	281
7	0	216	207
8	0	221	219
9	0	178	173
10	0	148	138
1	1	237	219
2	1	1078	1050
3	1	493	471
4	1	551	519
5	1	554	536
6	1	325	331
7	1	163	157
8	1	128	131
9	1	123	126
10	1	64	58
1	2	148	174
2	2	443	405
3	2	438	440
4	2	202	197
5	2	194	197
6	2	147	145
7	2	209	205
8	2	160	138
9	2	69	76
1	3	228	244
2	3	651	651
3	3	192	208
4	3	267	269
5	3	284	307
6	3	203	212
7	3	120	119
8	3	93	76
9	3	65L	57
1	4	610	566
2	4	550	555
3	4	328	333
4	4	183	191
5	4	279	285
6	4	153	158
7	4	113	112
8	4	78	83
1	5	393	393
2	5	106	93
3	5	285	235
4	5	295	298
5	5	103	114
6	5	131	130
7	5	73	71
1	6	211	218
2	6	227	234
3	6	124	128
4	6	148	155
5	6	102	93
6	6	87	83
1	7	173	174
2	7	200	211
3	7	157	140
4	7	124	117
5	7	88	66
1	8	151	163
2	8	90	87
3	8	104	79
4	8	92	77
1	9	132	127
2	9	77	97
3	9	67L	62
1	10	100	92
		L=3	
1	0	282	-322
2	0	429	412
3	0	38L	-73
4	0	101	95
5	0	47	31
6	0	47L	29
7	0	49L	45
8	0	69	-71
9	0	55L	26
10	0	61L	-24
1	1	1524	1452
2	1	775	721
3	1	205	199
4	1	285	-274
5	1	72	51
6	1	46L	-23
7	1	48L	67
8	1	52L	-1
9	1	56L	-38
10	1	63L	-13
1	2	99	-69
2	2	125	-88
3	2	64	-63
4	2	228	-210
5	2	61	50
6	2	67	70
7	2	51L	22
8	2	56L	2
9	2	60L	23
1	3	216	233
2	3	89	67
3	3	142	-117
4	3	171	-118
5	3	128	120
6	3	51L	51
7	3	54L	-34
8	3	60L	-11
9	3	65L	-13
1	4	47	12
2	4	44L	8
3	4	46L	-26
4	4	48L	0
5	4	51L	-28
6	4	78	-93
7	4	60L	-20
8	4	64L	-7
1	5	86	-73
2	5	87	92
3	5	48L	13
4	5	55	28
5	5	55L	-20
6	5	60L	32
7	5	64L	6
1	6	87	-83
2	6	189	205
3	6	52L	-2
4	6	55L	-33
5	6	59L	25
6	6	64L	-8
1	7	50L	-27
2	7	52L	8
3	7	56L	-43
4	7	60L	-18
5	7	64L	5
1	8	54L	5
2	8	77	51
3	8	61L	-15
4	8	65L	-33
1	9	60L	0
2	9	64L	-48
3	9	67L	-23
1	10	65L	9
		L=4	
0	0	488	438
1	0	690	662
2	0	566	539
3	0	862	796
4	0	551	513
5	0	460	429
6	0	479	468
7	0	325	324
8	0	200	192
9	0	169	167
10	0	91	90
1	1	1537	1530
2	1	995	942
3	1	1062	1023
4	1	520	503
5	1	553	525
6	1	167	167
7	1	172	159
8	1	245	254
9	1	91	77
10	1	83	74
1	2	765	724
2	2	637	647
3	2	215	235
4	2	551	564
5	2	407	415
6	2	117	114
7	2	145	147
8	2	173	157
9	2	96	82
1	3	691	672
2	3	344	313
3	3	537	532
4	3	331	343
5	3	242	242
6	3	171	173
7	3	176	179
8	3	126	127
9	3	49	44
1	4	480	480
2	4	406	403
3	4	363	365
4	4	368	361
5	4	238	244
6	4	144	153
7	4	130	91
8	4	65L	61
1	5	189	197
2	5	451	478
3	5	187	192
4	5	111	113
5	5	247	254
6	5	96	92
7	5	56	90
1	6	372	356
2	6	301	315
3	6	207	212
4	6	150	151
5	6	150	148
6	6	86	80
1	7	276	284
2	7	85	74
3	7	96	106
4	7	91	79
5	7	84	87
1	8	99	101
2	8	150	154
3	8	108	116
4	8	80	78
1	9	143	172
2	9	93	107
3	9	88	89
1	10	89	63
		L=5	
1	0	74	-83
2	0	678	-654
3	0	115	102
4	0	573	-520
5	0	173	-158
6	0	64	58
7	0	103	-107
8	0	80L	64
9	0	57L	33
10	0	67L	-19
1	1	147	-122
2	1	189	195
3	1	358	341
4	1	146	112
5	1	132	123
6	1	136	134
7	1	49L	17
8	1	58	65
9	1	57L	-11
10	1	63L	15
1	2	266	241
2	2	421	407
3	2	120	125
4	2	44L	-51
5	2	46L	-10
6	2	114	115
7	2	66	34
8	2	87	-85
9	2	62L	-34
1	3	186	-180
2	3	265	-222
3	3	143	-127
4	3	219	-230
5	3	48L	-18
6	3	50L	0
7	3	65	-66
8	3	61L	-3
9	3	65L	1
1	4	125	-111
2	4	73	-60
3	4	61	-59
4	4	49L	-26
5	4	69	60
6	4	54L	6
7	4	60L	15
8	4	65L	-11
1	5	46L	-26
2	5	56	67
3	5	137	139
4	5	52L	-44
5	5	56L	4
6	5	60L	0
7	5	65L	4
1	6	87	45
2	6	56L	-22
3	6	52L	-8
4	6	55L	0
5	6	60L	17
6	6	65L	36
1	7	106	123
2	7	52L	36
3	7	55L	-8
4	7	60L	-19
5	7	65L	-26
1	8	55L	-8
2	8	58L	-27
3	8	63L	-50
4	8	66L	-2
1	9	61L	6
2	9	63L	5
3	9	67L	-13
1	10	66L	2
		L=6	
0	0	982	-919
1	0	655	695
2	0	632	647
3	0	570	551
4	0	308	341
5	0	204	228
6	0	311	309
7	0	214	208
8	0	233	231
9	0	86	97
10	0	90	76
1	1	570	568
2	1	788	836
3	1	418	411
4	1	332	339
5	1	313	309
6	1	300	296
7	1	245	243
8	1	83	69
9	1	108	106
10	1	68	76
1	2	913	971
2	2	455	451
3	2	782	756
4	2	377	379
5	2	266	211
6	2	247	288
7	2	179	181
8	2	117	117
9	2	123	117
1	3	276	279
2	3	289	310
3	3	425	414
4	3	278	267
5	3	274	292
6	3	107	122
7	3	125	123
8	3	164	113
1	4	263	285
2	4	356	373
3	4	406	415
4	4	188	189
5	4	138	127
6	4	136	143
7	4	148	145
8	4	95	81
1	5	418	425
2	5	137	137
3	5	335	360
4	5	131	147
5	5	72	75
6	5	112	110
7	5	65L	60
1	6	283	301
2	6	248	262
3	6	109	113
4	6	121	133
5	6	93	93
6	6	87	84
1	7	168	169
2	7	168	180
3	7	151	160
4	7	108	114
5	7	97	106
1	8	154	163
2	8	118	122
3	8	65	75
4	8	109	96
1	9	70	71
2	9	72	74
1	10	66L	53
		L=7	
1	0	208	-232
2	0	64L	-71
3	0	122	-140
4	0	137	132
5	0	101	104
6	0	48L	42
7	0	121	-126
8	0	66	68
9	0	58L	37
10	0	62L	6
1	1	192	179
2	1	37L	11
3	1	193	-231
4	1	54	33
5	1	85	69
6	1	49	-52
7	1	50L	36
8	1	53L	24
9	1	58L	-24
10	1	64L	-11
1	2	216	221
2	2	173	-168
3	2	268	260
4	2	90	84
5	2	47L	13
6	2	79	86
7	2	61	-69
8	2	58L	8
9	2	62L	-28
1	3	113	-109
2	3	42L	4
3	3	139	-143
4	3	177	-181
5	3	61	45
6	3	57	51
7	3	56L	-30
8	3	74	-17
1	4	224	215
2	4	64	-46
3	4	47L	-9
4	4	50L	-66
5	4	51L	-21
6	4	55L	19
7	4	65	-41
8	4	65L	6
1	5	46L	-5
2	5	59	60
3	5	69	-66
4	5	51L	11
5	5	66	58
6	5	60L	40
7	5	65L	15
1	6	53	75
2	6	75	81
3	6	53L	-2
4	6	56L	-15
5	6	60L	-1
6	6	65L	-5
1	7	52L	5
2	7	54L	8
3	7	58L	20
4	7	61L	-37
5	7	66L	0
1	8	58L	-43
2	8	59L	4
3	8	63L	-13
4	8	68	-26
1	9	61L	9
2	9	63L	-7
1	10	66L	18
		L=8	
0	0	1546	1509
1	0	493	500
2	0	765	757
3	0	705	711
4	0	268	297
5	0	305	302
6	0	255	265
7	0	264	272
8	0	123	122
9	0	71	67
10	0	65L	42
1	1	771	816
2	1	354	348
3	1	451	458
4	1	368	321
5	1	159	185
6	1	309	311
7	1	306	306
8	1	149	144
9	1	131	138
10	1	94	45
1	2	964	924
2	2	681	694
3	2	564	565
4	2	477	483
5	2	370	379
6	2	403	419
7	2	154	158
8	2	125	125
9	2	93	93
1	3	844	868
2	3	551	569
3	3	527	543
4	3	335	347
5	3	206	198
6	3	186	181
7	3	132	138
8	3	106	103
1	4	368	396
2	4	246	250
3	4	250	264
4	4	244	248
5	4	75	63
6	4	120	116
7	4	102	108
8	4	74	79
1	5	335	355
2	5	426	449
3	5	266	213
4	5	111	114
5	5	110	111
6	5	73	86
7	5	105	97
1	6	254	266
2	6	189	201
3	6	258	268
4	6	132	135
5	6	106	112
6	6	85	79
1	7	220	227
2	7	201	208
3	7	166	166
4	7	131	121
5	7	85	84
1	8	149	162
2	8	138	144
3	8	123	116
4	8	68L	65
1	9	63	49
2	9	89	64
1	10	106	72
		L=9	
1	0	255	274
2	0	42L	-18
3	0	210	205
4	0	43L	-4
5	0	44	-43
6	0	48L	29
7	0	94	93
8	0	54L	0
9	0	58L	-32
10	0	63L	20
1	1	124	141
2	1	216	-212
3	1	113	-88
4	1	165	153
5	1	210	-219
6	1	49L	5
7	1	64	-75
8	1	64	-46
9	1	60L	11
1	2	100	-89
2	2	109	-77
3	2	52	36
4	2	46L	-19
5	2	48L	4
6	2	51L	21
7	2	53L	21
8	2	58L	41
9	2	63L	1
1	3	42L	-39
2	3	109	96
3	3	46L	-6
4	3	145	152
5	3	50L	-8
6	3	79	-82
7	3	62	34
8	3	63L	13
1	4	80	77
2	4	46L	-39
3	4	54	-45
4	4	50L	45
5	4	52L	-32
6	4	56L	-7
7	4	62L	5
1	5	62	-61
2	5	48L	0
3	5	83	94
4	5	53L	-29
5	5	56L	36
6	5	61L	-15
7	5	66L	1
1	6	50L	12
2	6	59	-50
3	6	54L	-51
4	6	57L	6
5	6	63	-2
6	6	66L	-18
1	7	52L	-10
2	7	55L	-13
3	7	59L	-18
4	7	63L	15
5	7	66L	0
1	8	57L	11
2	8	60L	15
3	8	64L	28
1	9	63L	-11
2	9	65L	25
		L=10	
0	0	401	-391
1	0	508	547
2	0	713	718
3	0	126	155
4	0	512	513
5	0	215	220
6	0	199	196
7	0	274	280
8	0	166	162
9	0	113	116
10	0	76L	66
1	1	575	589
2	1	597	586
3	1	267	279
4	1	389	380
5	1	213	212
6	1	350	352
7	1	248	232
8	1	95	88
9	1	109	99
1	2	401	428
2	2	719	691
3	2	395	410
4	2	155	159
5	2	254	260
6	2	193	179
7	2	157	150
8	2	96	78
9	2	69	75
1	3	395	408
2	3	503	512
3	3	233	245
4	3	419	423
5	3	237	248
6	3	203	213
7	3	132	124
8	3	121	102
1	4	276	288
2	4	278	301
3	4	350	372
4	4	50L	41
5	4	95	89
6	4	116	114
7	4	75	65
1	5	205	209
2	5	255	266
3	5	212	214
4	5	139	133
5	5	83	75
6	5	107	97
1	6	241	251
2	6	214	222
3	6	174	181
4	6	155	149
5	6	109	92
6	6	106	103
1	7	91	104
2	7	190	196
3	7	156	157
4	7	69	75
1	8	88	97
2	8	107	100
3	8	82	43
1	9	63L	55
2	9	109	86
		L=11	
1	0	129	-158
2	0	223	235
3	0	43L	-44
4	0	47L	30
5	0	47L	20
6	0	49L	-14
7	0	52L	-4
8	0	69	-64
9	0	61L	-11
10	0	65L	-15
1	1	89	-87
2	1	42L	63
3	1	43L	-7
4	1	201	-185
5	1	47L	14
6	1	50L	-54
7	1	52L	-20
8	1	57L	-16
9	1	62L	5
1	2	204	-180
2	2	92	-84
3	2	77	-69
4	2	47L	26
5	2	49L	-11
6	2	98	-106
7	2	54L	-18
8	2	64	34
9	2	65L	41
1	3	44L	-17
2	3	46	19
3	3	131	139
4	3	72	82
5	3	51L	-15
6	3	54L	22
7	3	59L	14
8	3	64L	34
1	4	40L	-15
2	4	76	75
3	4	200	194
4	4	61	50
5	4	53L	-6
6	4	56L	-3
7	4	63L	7
1	5	48L	-15
2	5	69	-58
3	5	93	-93
4	5	54L	28
5	5	59L	-55
6	5	62L	-15
1	6	135	-143
2	6	52L	-53
3	6	55L	9
4	6	59L	-11
5	6	63L	-6
1	7	76	-80
2	7	56L	-25
3	7	61L	35
4	7	64L	36
1	8	58L	16
2	8	61L	14
3	8	65L	19
1	9	63L	5
2	9	67L	-20
		L=12	
0	0	529	576
1	0	429	442
2	0	618	627
3	0	411	434
4	0	414	423
5	0	384	387
6	0	312	318
7	0	257	261
8	0	139	136
9	0	136	138
10	0	86	68
1	1	751	756
2	1	459	453
3	1	548	545
4	1	416	420
5	1	253	254
6	1	193	188
7	1	141	132
8	1	158	158
9	1	90	87
1	2	509	534
2	2	466	479
3	2	300	307
4	2	386	392
5	2	256	263
6	2	155	147
7	2	103	106
8	2	106	98
1	3	444	473
2	3	262	264
3	3	316	333
4	3	364	321
5	3	150	156
6	3	168	170
7	3	121	131
8	3	124	105
1	4	263	286
2	4	223	229
3	4	256	264
4	4	239	237
5	4	149	155
6	4	129	125
7	4	81	77
1	5	250	265
2	5	359	360
3	5	166	173
4	5	151	151
5	5	173	166
6	5	86	101
1	6	250	260
2	6	153	162
3	6	186	174
4	6	118	107
5	6	115	109
1	7	160	170
2	7	106	150
3	7	83	79
4	7	65L	64
1	8	124	122
2	8	109	111
3	8	89	93
1	9	122	113
		L=13	
1	0	48L	91
2	0	90	-112
3	0	46L	-14
4	0	93	-105
5	0	55L	-35
6	0	60	-64
7	0	52L	-8
8	0	57L	-14
9	0	63L	-10
1	1	333	-299
2	1	130	-136
3	1	45L	7
4	1	47L	37
5	1	98	98
6	1	57	-23
7	1	54L	-29
8	1	59L	17
9	1	63L	19
1	2	183	-164
2	2	56	64
3	2	98	-83
4	2	49L	44
5	2	51	-37
6	2	76	-83
7	2	57	10
8	2	62L	-27
1	3	46L	10
2	3	50	-59
3	3	174	176
4	3	79	79
5	3	76	-61
6	3	57L	-8
7	3	62L	9
8	3	66L	23
1	4	153	-152
2	4	128	121
3	4	50L	14
4	4	52L	3
5	4	56L	57
6	4	60L	21
7	4	65L	37
1	5	56L	23
2	5	85	-78
3	5	53L	-13
4	5	56L	-31
5	5	62	-41
6	5	64L	-13
1	6	52L	-25
2	6	117	-121
3	6	57L	29
4	6	61L	24
5	6	64L	0
1	7	55L	-4
2	7	58L	4
3	7	62L	16
4	7	65L	23
1	8	60L	-10
2	8	63L	-23
3	8	66L	16
1	9	65L	3
		L=14	
0	0	393	363
1	0	562	578
2	0	344	372
3	0	464	455
4	0	371	390
5	0	320	340
6	0	257	258
7	0	110	112
8	0	171	165
9	0	117	120
1	1	297	334
2	1	345	366
3	1	282	282
4	1	353	352
5	1	269	265
6	1	142	143
7	1	121	133
8	1	93	72
9	1	123	103
1	2	438	460
2	2	221	231
3	2	419	429
4	2	297	312
5	2	139	144
6	2	154	156
7	2	135	123
8	2	95	86
1	3	241	258
2	3	143	157
3	3	227	225
4	3	145	144
5	3	175	172
6	3	90	101
7	3	90	78
1	4	304	318
2	4	236	246
3	4	204	208
4	4	189	201
5	4	176	176
6	4	140	136
7	4	111	105
1	5	375	399
2	5	97	110
3	5	240	242
4	5	192	201
5	5	136	121
6	5	109	102
1	6	195	193
2	6	125	121
3	6	60	58
4	6	107	94
5	6	91	68
1	7	131	133
2	7	91	108
3	7	45	85
4	7	102	86
1	8	154	146
2	8	133	91
1	9	93	92
		L=15	
1	0	54L	-75
2	0	47L	51
3	0	94	-126
4	0	159	172
5	0	95	94
6	0	69	-63
7	0	54L	8
8	0	59L	1
9	0	64L	11
1	1	49L	-85
2	1	151	-170
3	1	48L	-59
4	1	49L	46
5	1	51L	8
6	1	52L	-37
7	1	57L	37
8	1	61L	-16
9	1	65L	8
1	2	46L	-8
2	2	89	-98
3	2	48L	-3
4	2	79	86
5	2	52L	-7
6	2	56L	-47
7	2	60L	-20
8	2	63L	13
1	3	48L	61
2	3	81	85
3	3	50L	26
4	3	51L	22
5	3	54L	15
6	3	59L	7
7	3	63L	24
1	4	50L	33
2	4	52	-42
3	4	52L	-54
4	4	56L	-29
5	4	59L	-36
6	4	63L	28
1	5	68	93
2	5	52L	-25
3	5	96	-79
4	5	59L	28
5	5	63L	30
6	5	66L	17
1	6	53L	28
2	6	56L	55
3	6	59L	6
4	6	63L	5
5	6	67L	0
1	7	57L	-15
2	7	60L	-24
3	7	63L	0
1	8	62L	-9
2	8	65L	6
1	9	67L	-15
		L=16	
0	0	899	882
1	0	531	541
2	0	262	276
3	0	341	350
4	0	339	356
5	0	364	368
6	0	200	209
7	0	134	134
8	0	119	113
9	0	105	99
1	1	416	437
2	1	256	276
3	1	419	407
4	1	278	291
5	1	268	264
6	1	148	148
7	1	133	127
8	1	139	123
1	2	275	293
2	2	250	271
3	2	226	231
4	2	209	221
5	2	206	204
6	2	179	177
7	2	93	105
8	2	94	83
1	3	389	408
2	3	325	333
3	3	218	226
4	3	102	113
5	3	168	164
6	3	129	127
7	3	103	100
1	4	439	468
2	4	269	279
3	4	141	145
4	4	227	233
5	4	160	167
6	4	114	116
1	5	218	233
2	5	164	164
3	5	123	133
4	5	131	129
5	5	149	136
1	6	123	127
2	6	133	130
3	6	161	153
4	6	114	118
1	7	161	159
2	7	112	97
3	7	111	101
1	8	109	107
2	8	117	88
		L=17	
1	0	59L	123
2	0	49L	-10
3	0	61L	69
4	0	57L	67
5	0	55L	-3
6	0	54L	16
7	0	58L	50
8	0	61L	11
9	0	60L	-14
1	1	52L	22
2	1	50L	11
3	1	51L	-52
4	1	51L	43
5	1	55	-61
6	1	55L	22
7	1	59L	-2
8	1	63L	-4
1	2	73	80
2	2	49L	60
3	2	49L	-22
4	2	51L	-30
5	2	54L	4
6	2	68	30
7	2	62L	16
1	3	50L	55
2	3	55L	16
3	3	56	-51
4	3	54L	46
5	3	57L	-11
6	3	61L	-18
7	3	65L	15
1	4	51L	4
2	4	52L	-32
3	4	62	-80
4	4	57L	-9
5	4	61L	-4
6	4	65L	8
1	5	52L	13
2	5	54L	21
3	5	57L	45
4	5	61L	-6
5	5	71	20
1	6	57L	59
2	6	58L	-7
3	6	62L	0
4	6	65L	11
1	7	59L	21
2	7	62L	13
3	7	65L	-7
1	8	64L	4
		L=18	
0	0	415	414
1	0	447	463
2	0	254	260
3	0	244	239
4	0	347	352
5	0	210	219
6	0	138	140
7	0	130	120
8	0	109	111
1	1	237	258
2	1	339	352
3	1	239	253
4	1	248	246
5	1	276	267
6	1	183	163
7	1	110	109
8	1	94	91
1	2	161	180
2	2	271	275
3	2	159	153
4	2	122	121
5	2	161	165
6	2	106	82
7	2	158	124
1	3	278	292
2	3	328	339
3	3	136	139
4	3	166	174
5	3	173	170
6	3	120	124
7	3	84	74
1	4	312	326
2	4	259	261
3	4	163	160
4	4	83	96
5	4	153	147
6	4	72	79
1	5	171	151
2	5	92	105
3	5	119	115
4	5	146	136
5	5	118	92
1	6	143	149
2	6	151	150
3	6	96	109
4	6	113	109
1	7	97	96
2	7	126	103
3	7	95	90
1	8	83	74
		L=19	
1	0	57L	-68
2	0	52L	63
3	0	51L	34
4	0	54L	-41
5	0	54L	-10
6	0	58	41
7	0	65L	-16
8	0	65L	1
1	1	53L	2
2	1	152	195
3	1	53L	58
4	1	100	-122
5	1	55L	8
6	1	61	44
7	1	62L	39
8	1	66L	11
1	2	115	123
2	2	88	116
3	2	52L	-22
4	2	54L	-45
5	2	57L	5
6	2	60L	19
7	2	63L	0
1	3	51L	-30
2	3	53L	-57
3	3	80	-75
4	3	58L	-57
5	3	60L	5
6	3	63L	30
1	4	52L	1
2	4	54L	-28
3	4	90	70
4	4	60L	16
5	4	64L	0
1	5	59L	-5
2	5	58L	21
3	5	60L	-10
4	5	64L	24
1	6	65	-14
2	6	60L	18
3	6	64L	24
1	7	62L	13
2	7	65L	13
1	8	67L	26
		L=20	
0	0	504	490
1	0	219	239
2	0	346	346
3	0	346	350
4	0	168	176
5	0	209	206
6	0	179	168
7	0	125	123
8	0	76	80
1	1	284	296
2	1	292	313
3	1	281	273
4	1	213	221
5	1	189	184
6	1	131	128
7	1	103	103
1	2	262	269
2	2	230	233
3	2	179	192
4	2	221	216
5	2	164	152
6	2	117	109
7	2	98	87
1	3	216	223
2	3	215	219
3	3	221	215
4	3	162	155
5	3	121	97
6	3	109	95
1	4	153	167
2	4	176	178
3	4	119	127
4	4	188	164
5	4	116	110
1	5	156	172
2	5	203	189
3	5	114	111
4	5	126	123
1	6	142	135
2	6	109	104
3	6	112	99
1	7	157	134
2	7	78	89
		L=21	
1	0	54L	29
2	0	55L	-33
3	0	54L	28
4	0	55L	-56
5	0	56L	-7
6	0	59L	7
7	0	63L	12
8	0	66L	9
1	1	56L	84
2	1	58L	101
3	1	55L	17
4	1	56L	3
5	1	58L	17
6	1	61L	17
7	1	65L	6
1	2	53L	32
2	2	54L	52
3	2	55L	-18
4	2	58L	-54
5	2	60L	9
6	2	63L	36
1	3	52L	8
2	3	54L	-25
3	3	57L	-35
4	3	60L	-27
5	3	62L	12
6	3	66L	1
1	4	55L	-24
2	4	57L	18
3	4	60L	-38
4	4	63L	-5
5	4	66L	18
1	5	65	-23
2	5	60L	14
3	5	63L	33
4	5	67L	-15
1	6	61L	26
2	6	64L	20
3	6	66L	16
1	7	66L	20
		L=22	
0	0	141	162
1	0	199	199
2	0	301	304
3	0	282	280
4	0	147	135
5	0	113	114
6	0	138	122
7	0	118	101
1	1	160	192
2	1	289	284
3	1	174	176
4	1	155	156
5	1	171	143
6	1	136	129
7	1	104	90
1	2	293	290
2	2	189	194
3	2	239	237
4	2	166	182
5	2	125	117
6	2	97	92
1	3	128	135
2	3	143	147
3	3	173	169
4	3	146	141
5	3	112	97
1	4	75	89
2	4	165	155
3	4	163	150
4	4	124	106
1	5	178	165
2	5	115	116
3	5	138	128
1	6	138	130
2	6	130	112
1	7	107	111
		L=23	
1	0	55L	-46
2	0	56L	-8
3	0	57L	-44
4	0	57L	24
5	0	60L	16
6	0	62L	-10
7	0	66L	1
1	1	58L	79
2	1	58L	-57
3	1	57L	23
4	1	58L	24
5	1	61L	-4
6	1	64L	0
1	2	57L	-14
2	2	57L	-45
3	2	59L	28
4	2	61L	16
5	2	64L	17
6	2	66L	-4
1	3	56L	11
2	3	58L	34
3	3	60L	-29
4	3	63L	-25
5	3	65L	20
1	4	58L	18
2	4	61L	-38
3	4	63L	-33
4	4	65L	-14
1	5	61L	15
2	5	64L	24
3	5	65L	-7
1	6	64L	11
2	6	68L	57
		L=24	
0	0	139	130
1	0	184	180
2	0	203	209
3	0	177	167
4	0	135	125
5	0	106	98
6	0	125	115
1	1	278	273
2	1	212	215
3	1	218	204
4	1	100	115
5	1	125	115
6	1	123	114
1	2	205	201
2	2	235	224
3	2	152	145
4	2	128	119
5	2	145	133
1	3	197	177
2	3	191	181
3	3	198	170
4	3	117	117
1	4	148	139
2	4	147	149
3	4	151	131
1	5	66	68
2	5	138	129
1	6	89	97
		L=25	
1	0	58L	18
2	0	59L	-42
3	0	60L	5
4	0	61L	-16
5	0	63L	-20
6	0	65L	7
1	1	60L	-7
2	1	60L	-39
3	1	61L	-9
4	1	62L	20
5	1	64L	10
1	2	60L	-39
2	2	61L	-18
3	2	62L	26
4	2	63L	11
5	2	66L	-1
1	3	61L	-12
2	3	62L	-9
3	3	64L	18
4	3	66L	3
1	4	62L	-4
2	4	64L	15
3	4	66L	-5
1	5	64L	-8
2	5	66L	9
		L=26	
0	0	93	95
1	0	214	195
2	0	155	151
3	0	136	128
4	0	156	139
5	0	88	76
1	1	167	164
2	1	178	160
3	1	130	123
4	1	102	91
5	1	120	98
1	2	190	172
2	2	174	165
3	2	161	131
4	2	100	100
1	3	192	173
2	3	184	153
3	3	142	118
1	4	115	111
2	4	142	115
1	5	99	87
		L=27	
1	0	62L	-25
2	0	62L	16
3	0	63L	7
4	0	65L	-28
5	0	66L	-5
1	1	61L	-43
2	1	62L	-3
3	1	64L	-1
4	1	66L	-25
1	2	63L	-20
2	2	64L	-17
3	2	65L	11
1	3	65L	-42
2	3	65L	-8
1	4	65L	10
		L=28	
0	0	208	194
1	0	134	137
2	0	168	144
3	0	153	146
4	0	105	99
1	1	170	153
2	1	117	105
3	1	135	113
1	2	173	149
2	2	129	116
3	2	130	123
1	3	147	124
2	3	102	90
		L=29	
1	0	65L	23
2	0	66L	5
3	0	67L	9
1	1	65L	1
2	1	66L	-15
1	2	67L	-27
2	2	67L	-26
		L=30	
0	0	87	107
1	0	165	132
2	0	147	121
1	1	122	107

able to interpret the large thermal parameters in terms of disorder rather than in terms of thermal vibrations. The final atomic coordinates, the thermal parameters and the structure factor for $Im_6Cd(OH)(NO_3).4H_2O$ are reported in Tables 4 and 5.

A Fourier difference map showed peaks near the oxygen atoms of the water molecules and of the OH^- ion. The peaks were interpreted as being due to the remaining hydrogen atoms. The highest residual density was found at about 0·8 Å above and below the cadmium atom. Everywhere else the electron density was less than 10% of the average value of the carbon atom.

Description of the structure

(*A*) $Im_6Cd(NO_3)_2$

As mentioned earlier, $Im_6Cd(NO_3)_2$ is isostructural with $Im_6Ni(NO_3)_2$. The structure consists of discrete Im_6Cd^{2+} cations and NO_3^- anions whose packing in the hexagonal unit cell is practically identical with that of the nickel compound.

The cadmium ions are located in the special positions $3(a)\bar{3}$ of space group $R\bar{3}$ and therefore the symmetry of the complex cation imposed by the space group is $\bar{3}$. The structure of the cation Im_6Cd^{2+} is shown in Fig. 1 and the unique bond distances and angles are given in Table 6. The coordination polyhedron is a distorted octahedron. The type of distortion may be described as a compression along one of the threefold axes of a regular octahedron. As a result of this compression, the angle between the threefold axis and the Cd–N(1) bond is 56·3° (in a regular octahedron the angle between these two directions is 54·75°).

The unique bond distances and angles of the imidazole ring are compared in Table 6 with the corresponding bond distances and angles found in other compounds. The imidazole ring is planar within experimental error (Table 7).

Table 6. *Unique bond distances and angles in* $Im_6Cd(NO_3)_2$ *and* $Im_6Cd(OH)(NO_3).4H_2O$ *and comparison with related compounds*

	Imidazole* −150°C	$Im_6Ni(NO_3)_2$†	$Im_6Cd(NO_3)_2$	$Im_6Cd(OH)(NO_3).4H_2O$
Cd—N(1)			2·361 (3) Å‡	2·364 (3) Å
Ni—N(1)		2·129 Å		
N(1)–C(1)	1·326 Å	1·316	1·316 (4)	1·313 (7)
C(1)–N(2)	1·349	1·329	1·325 (5)	1·333 (6)
N(2)–C(2)	1·369	1·352	1·357 (6)	1·361 (8)
C(2)–C(3)	1·358	1·366	1·340 (6)	1·331 (8)
C(3)–N(1)	1·378	1·372	1·366 (5)	1·370 (6)
C(3)–N(1)–C(1)	105·4°	105·4°	106·1 (3)°	105·7 (4)°
N(1)–C(1)–N(2)	111·3	111·6	110·6 (3)	111·1 (4)
C(1)–N(2)–C(2)	107·2	107·9	107·7 (3)	106·9 (4)
N(2)–C(2)–C(3)	106·3	106·1	106·6 (4)	107·0 (5)
C(2)–C(3)–N(1)	109·8	109·1	108·9 (4)	109·3 (5)
Cd—N(1)–C(3)			130·9 (2)	127·6 (3)
Cd—N(1)–C(1)			123·0 (2)	126·8 (3)
N(1)–Cd—N(1′)			87·71 (7)	90·4 (1)
N(1)–Ni—N(1′)		88·1		
[00.1] ∧ Cd–N(1)		56·1	56·3	54·5
N(3)–O(1)		1·239	1·231 (2)	1·286 (6)

* Martinez-Carrera, 1966.
† Santoro *et al.*, 1969.
‡ The standard deviations on bond distances and angles were estimated from the errors in coordinates and in lattice parameters.

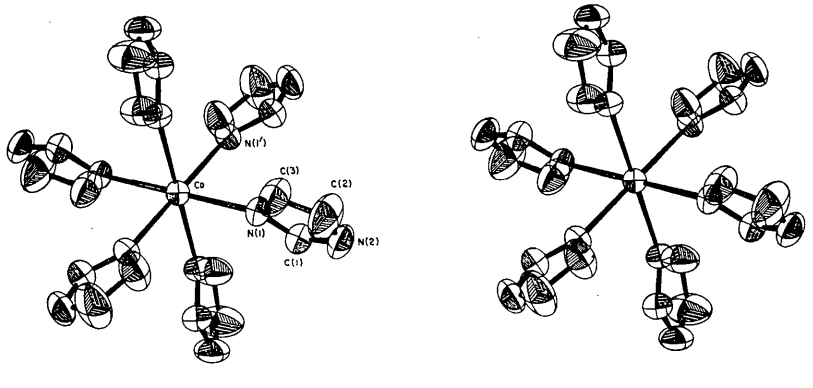

Fig. 1. Stereo view of the cation in $[Cd(C_3H_4N_2)_6](NO_3)_2$.

Table 7. *Distances from the ring atoms to the least-squares plane of the coordinated imidazole ring*

The equation of the plane in direct space is

$$PX+QY+RZ=S$$

For $Im_6Cd(NO_3)$: $P=11{\cdot}929$, $Q=-5{\cdot}2552$, $R=4{\cdot}8590$, $S=0{\cdot}6310$. For $Im_6Cd(OH)(NO_3).4H_2O$: $P=-8{\cdot}0191$, $Q=5{\cdot}0101$, $R=9{\cdot}6283$, $S=-0{\cdot}06840$.

	$Im_6Cd(NO_3)_2$	$Im_6Cd(OH)(NO_3).4H_2O$
N(1)	−0·003 Å	0·001 Å
N(2)	−0·013	0·001
C(1)	0·011	−0·001
C(2)	0·011	−0·001
C(3)	−0·005	0·000

The nitrogen atoms of the NO_3^- groups are located in special positions 6(*c*)3. The unique N–O distance in these groups is 1·231(2) Å. The NO_3^- ion is planar as the nitrogen atom is well within one standard deviation from the plane defined by the oxygen atoms. The shortest cation–anion distances (3·00 Å) are between the pyrrole type nitrogen atom of the imidazole rings and the oxygen atoms of the nitrate groups. These distances and the orientation of the imidazole rings are consistent with a hydrogen bonding scheme very similar to that already described for $Im_6Ni(NO_3)_2$ (Santoro *et al.*, 1969).

(*B*) $Im_6Cd(OH)(NO_3).4H_2O$

The structure of this complex consists of discrete Im_6Cd^{2+} cations, hydroxide and nitrate anions and water molecules. The packing of the structure in the hexagonal unit cell is shown in Fig. 2. For clarity, the atoms repeated by the 6_3 symmetry operation have been omitted from the Figure.

As in $Im_6Cd(NO_3)_2$, $\bar{3}$ symmetry is imposed on the complex cation by the space group. The structure of the cation is shown in Fig. 3, and the unique bond distances and angles are given in Table 6. The coordination polyhedron is an almost perfect octahedron very slightly elongated along the threefold axis. The angle N(1)–Cd–N(1′) is 90·4° (1) and the angle between the threefold axis and the Cd–N(1) bond is 54·5°.

The imidazole ring was found by least-squares analysis to be planar. The distances of the ring atoms from the least-squares plane are given in Table 7. The bond distances and angles in the ring are given in Table 6.

The planarity of the NO_3^- ion is required by the symmetry of the space group, as this ion lies on the symmetry plane. The unique N–O distance is 1·286 (6). Although it is not possible from crystallographic considerations to determine if the oxygen atom of the OH^- ion is O(2) or O(3), it seems chemically more

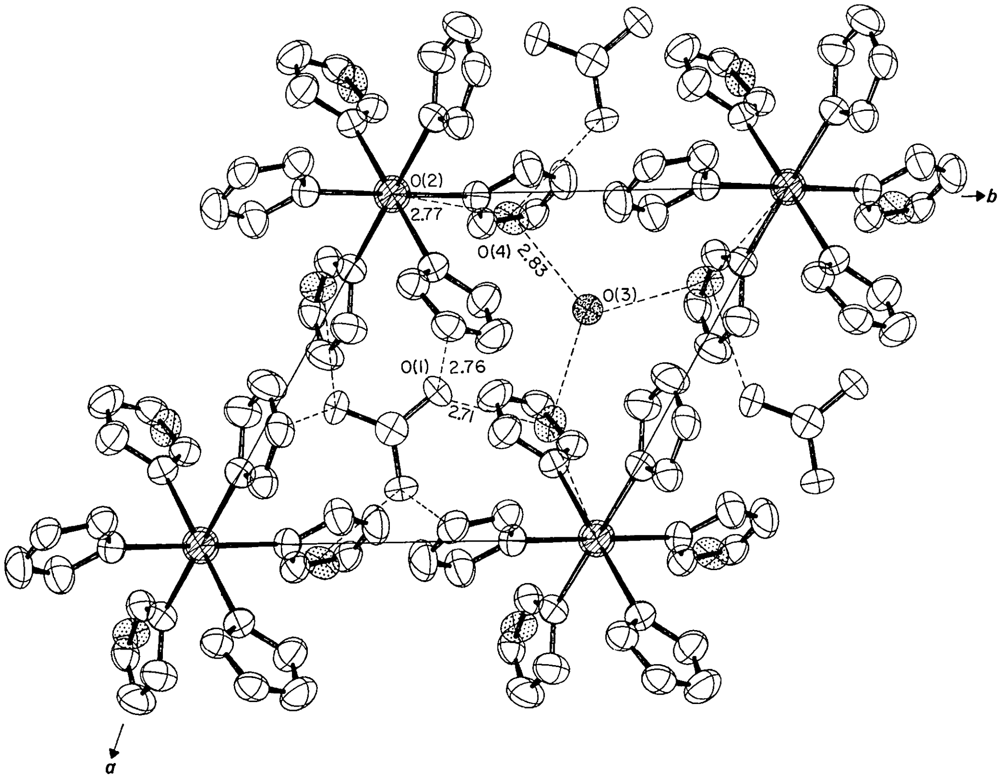

Fig. 2. The packing in the structure $[Cd(C_3H_4N_2)_6](OH)(NO_3).4H_2O$ viewed along the *c* axis. For clarity, atoms repeated by the 6_3 symmetry operation have been omitted. Oxygen atoms which are probably hydrogen bonded are indicated by the dashed lines and the unique distances between these oxygen atoms are given.

reasonable to assume that the hydroxide is O(2), as it is located between two complex cations.

The imidazole rings are oriented so that each nitrate oxygen atom O(1) forms hydrogen bonds with two pyrrole type (>NH) nitrogen atoms belonging to a pair of imidazole rings related by the mirror operation of the space group (Fig. 2). The interatomic distances involving the oxygen atoms O(1), O(2), O(3) and O(4) are consistent with hydrogen bonding (see Fig. 2). However, in view of the uncertainties in the location of the hydrogen atoms of the water molecules and of the OH^- ions, the existence and the details of such bonding can only be assumed. A possible scheme of hydrogen bonding is as follows. As mentioned above the OH^- ion is probably located in position $2(a)\bar{6}$ rather than in position $2(c)\bar{6}$. In either case it may act as donor in forming hydrogen bonds with any of three equivalent oxygen atoms O(4) (see Fig. 2). Once the hydrogen atom of this ion is assigned to any particular bond, the assignment of the hydrogen atoms involved in the bonds between O(3) and O(4) is uniquely defined. For each of the three initial possibilities there is a distinct network of hydrogen bonds in the structure. The three networks are equivalent as they are related to each other by the symmetry operations of the threefold axis and it seems reasonable to assume that all three are present in the structure so that the symmetry of the space group is preserved on the average.

Discussion

A comparison of the structures of $Im_6Cd(NO_3)_2$ and $Im_6Cd(OH)(NO_3).4H_2O$ shows that the coordination of cadmium is in both cases octahedral. However, as a result of the presence of the H_2O molecules and OH^- ions in the hydroxide complex, the packing of the two structures is considerably different.

In both complexes the orientation of the imidazole rings is such that the $\geq$N–H groups can form hydrogen bonds with the oxygen atoms of the nitrate groups. However, because of a different utilization of the threefold axes of the space groups $R\bar{3}$ and $P6_3/m$, the NO_3^- groups and the imidazole rings are located differently with respect to each other in the two structures. As a consequence, there is considerable difference in the orientation of the imidazole rings. Specifically, each ring in one of the two complex cations is rotated, about the Cd–N(1) direction, approximately 130° with respect to its counterpart in the other cation. The difference in the relative positions of the rings in the two structures can be clearly seen in Figs. 1 and 3. The two pictures have been drawn in the same orientation with respect to the threefold axis.

The corresponding bond distances and angles of the imidazole rings in the two cadmium complexes agree with each other to within two standard deviations. In Table 6 these distances and angles are compared with those found in $Im_6Ni(NO_3)_2$ and in molecular imidazole at -150°C (Martinez–Carrera, 1966). From the Table it is evident that the bond distances in coordinated imidazole as found in the two cadmium complexes are very similar but are systematically smaller than those found in molecular imidazole at -150°C. Almost certainly this discrepancy is due to thermal motion. No accurate correction for thermal motion was attempted, however, in view of the fact that the intensities were not corrected for absorption and were measured with the peak-height method. The above results show that, although the interaction of the imidazole rings with their environments is different in the cadmium and nickel complexes and in imidazole, bond distances and angles within the ring are remarkably constant. The values of the bond distances given in Table 6 are also in rather close agreement with those found in di-imidazolezinc(II) dichloride (Lundberg, 1966).

The unique N–O distances of the nitrate groups are also given in Table 6. The value for this distance found in $ImCd(NO_3)_2$ (1·231 Å) agrees closely with the value found in $Im_6Ni(NO_3)_2$ (1·239 Å) but it is significantly smaller than the value (1·286 Å) found in $Im_6Cd(OH)(NO_3).4H_2O$. The change in the N–O distance reflects the fact that in $Im_6Cd(NO_3)_2$ each oxygen atom of the NO_3^- group is involved in a weak hydrogen bond (N–H···O, 3·00 Å), while in the hydroxide nitrate complex each oxygen atom is involved in three moder-

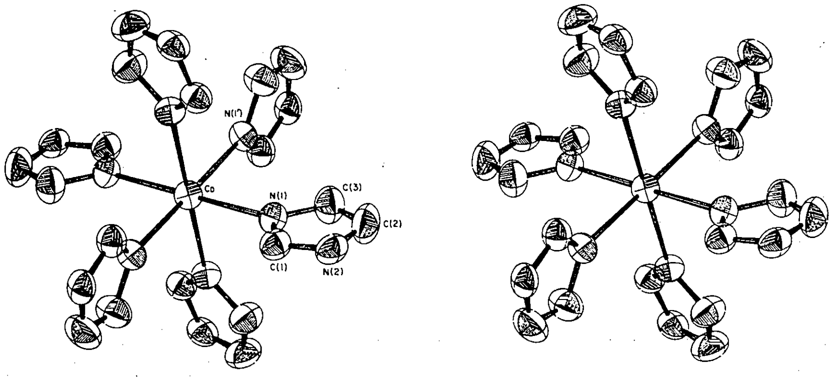

Fig. 3. Stereo view of the cation in $[Cd(C_3H_4N_2)_6](OH)(NO_3).4H_2O$.

ately strong hydrogen bonds, two with the pyrrole nitrogen atoms of the imidazole rings and one with an oxygen atom O(4) (see Fig. 2 for distances). Variations in the N–O distances as a function of the strength of the hydrogen bonding in which the oxygen atom is involved have been observed in the study of other complexes. For example, in the structure of $Cu(NO_3)_2Pz$ (Pz = pyrazine, $C_4N_2H_4$) (Santoro, Mighell & Reimann, 1970), the three independent N–O distances range from 1·21 to 1·29 Å and in the structure of nitratobis(dipyridine)-cobalt(III) hydroxide nitrate tetrahydrate (Reimann, Zocchi, Mighell & Santoro, 1971), the four independent distances range from 1·19 to 1·31 Å.

The computer calculations were made with local programs, with the *Program System for X-ray Crystallography* (1967) developed at the University of Maryland in collaboration with the National Bureau of Standards and the Geological Survey, and with C.K. Johnson's *ORTEP* plotting program.

Thanks are due to Dr C. W. Reimann for suggesting the problem and for the preparation of the crystals.

References

ALEXANDER, L. E. & SMITH, G. S. (1962). *Acta Cryst.* **15**, 983.
BARNARD, E. A. & STEIN, W. D. (1958). *Advances in Enzymology*, Vol. XX, New York: Interscience.
HOFMANN, K. (1953). *Imidazole and Its Derivatives.* New York: Interscience.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
LUNDBERG, B. K. S. (1966). *Acta Cryst.* **21**, 901.
MARTINEZ-CARRERA, S. (1966). *Acta Cryst.* **20**, 783.
Program System for X-ray Crystallography (1967). Univ. of Maryland.
REIMANN, C. W., ZOCCHI, M., MIGHELL, A. D. & SANTORO, A. (1971). *Acta Cryst.* In the press.
SANTORO, A., MIGHELL, A. D. & REIMANN, C. W. (1970). *Acta Cryst.* B**26**, 979.
SANTORO, A., MIGHELL, A. D., ZOCCHI, M. & REIMANN, C. W. (1969). *Acta Cryst.* B**25**, 842.

Acta Cryst. (1971). B**27**, 2097

The Crystal and Molecular Structure of Portulal *p*-Bromophenylsulphonylhydrazone

BY SUNAO YAMAZAKI AND SABURO TAMURA
Department of Agricultural Chemistry, Faculty of Agriculture, The University of Tokyo, Bunkyo-ku, Tokyo 113, *Japan*

AND FUMIYUKI MARUMO AND YOSHIHIKO SAITO
The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, *Japan*

(*Received* 28 *October* 1970)

The crystal structure of portulal *p*-bromophenylsulphonylhydrazone has been determined by a three-dimensional X-ray analysis. The stereochemistry and absolute configuration of portulal, a naturally occurring diterpene isolated from *Portulaca grandiflora* as a plant growth regulator, has thus been established. The crystals are orthorhombic, space group $P2_12_12_1$, with four molecules of $C_{26}H_{37}O_5N_2SBr$ in a unit cell of dimensions, $a = 10{\cdot}68$, $b = 36{\cdot}98$ and $c = 6{\cdot}67$ Å. The structure has been refined by least-squares methods to a final R value of 0·123 for 2089 observed reflexions collected by the photographic method. Portulal belongs to a new type of bicyclic diterpene containing a perhydroazulene nucleus.

Introduction

Portulal, $C_{20}H_{32}O_4$, was first isolated by Mitsuhashi & Shibaoka (1965) from leaves of *Portulaca grandiflora Hook.* as a plant growth regulator. At the initial stage, it was thought to be an inhibitor of plant growth induced by indoleacetic acid. Subsequent studies, however, revealed that it specifically accelerates adventitious root formation of plant cuttings such as *Raphanus*, *Phaseolus* and *Azukia*.

In an attempt to establish the molecular structure and to extend the physiological studies of portulal, X-ray analysis of its *p*-bromophenylsulphonylhydrazone was carried out.

Experimental

Treatment of portulal (168 mg) with an equivalent amount of *p*-bromophenylsulphonylhydrazine (128 mg) in dry methanol at room temperature overnight gave the corresponding hydrazone. Recrystallization from methanol yielded well-formed transparent plates. Elementary analysis gave: C, 54·57; H, 6·51; N, 4·92%. $C_{26}H_{37}O_5N_2SBr$ requires C, 54·83; H, 6·55; N, 4·92%.

Oscillation and Weissenberg photographs were taken with crystals mounted along the c and a axes respectively with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}542$ Å). The unit-cell dimensions were determined from the two zero-layer Weissenberg photographs, on which the powder pat-