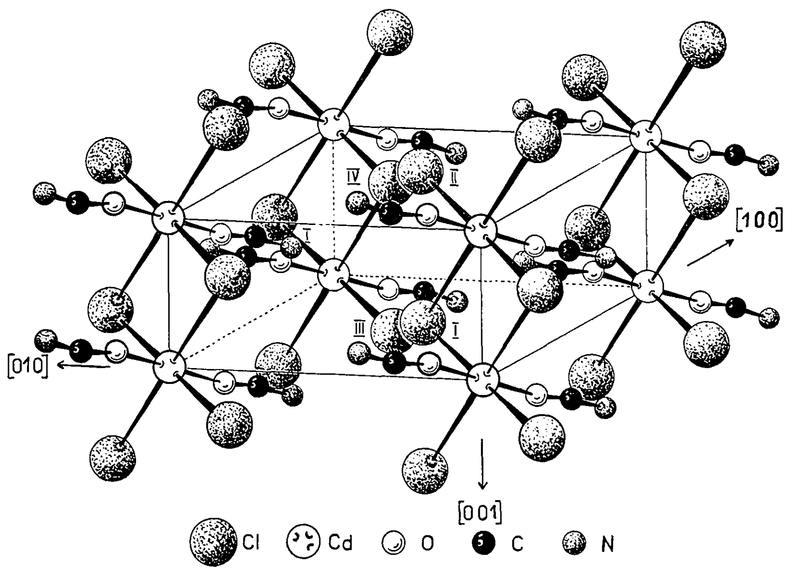

Fig. 4. Remplissage de la maille.

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Crystal Structures of Nitrates of Divalent Hexaquocations
I. Hexaquozinc Nitrate

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The crystal structure of hexaquozinc nitrate has been solved by three-dimensional methods and refined by differential syntheses. The crystals are orthorhombic, space group *Pnma*, with $a = 12{\cdot}34$, $b = 12{\cdot}85$, $c = 6{\cdot}29$ Å. The structure is composed of cations $[Zn(OH_2)_6]^{2+}$ and anions NO_3^-. The hexaquocation has practically octahedral symmetry, with $Zn\text{–}OH_2 = 2{\cdot}097 \pm 0{\cdot}010$ Å, which is very close to the values quoted in the literature. The nitrato anion has trigonal symmetry, with $N\text{–}O_{av} = 1{\cdot}242 \pm 0{\cdot}009$ Å, and is planar. The hexaquocations and the nitrato anions are held together by a network of hydrogen bonds, each H_2O forming two hydrogen bonds with oxygen atoms of nitrato groups. Hydrogen bond lengths are in the range $2{\cdot}778 - 2{\cdot}995$ Å.

Introduction

The hexaquocations of divalent metals are the most common complexes considered in coordination-compound chemistry. One could expect ions of similar size and properties such as Zn^{2+}, Mg^{2+}, Ni^{2+} to form isomorphous series of compounds. The crystal structure, however, of hexaquozinc nitrate, orthorhombic (Ferrari & Braibanti, 1958), of hexaquomagnesium nitrate, monoclinic (Ferrari & Braibanti, 1958; Mozzi

& Bekebrede, 1961) and of hexaquonickel nitrate, triclinic (Jayaraman, 1957; Weigel, Imelik & Laffitte, 1962) are different from one another. It seems therefore worth while to analyse the structures of these complexes in detail and the packing conditions in the crystal lattice.

The results of the structure determination of hexaquozinc nitrate are reported here.

Experimental

Crystals of hexaquozinc nitrate, $Zn(OH_2)_6(NO_3)_2$, were obtained by evaporation from an aqueous solution. As they are highly hygroscopic, crystals for X-ray analysis were sealed into Lindemann-glass capillary tubes.

Crystal data

Compound: hexaquozinc nitrate, $Zn(OH_2)_6(NO_3)_2$; F.W. 297·49.

Crystal habit: elongated prisms.

Crystal class: orthorhombic, dipyramidal.

Unit cell: (Cu $K\alpha$ radiation: $\lambda = 1{\cdot}5418$ Å; rotation axis: elongation axis, [001]).

$a = 12{\cdot}34 \pm 0{\cdot}01$, $b = 12{\cdot}85 \pm 0{\cdot}03$, $c = 6{\cdot}29 \pm 0{\cdot}01$ Å, $U = 997{\cdot}4$ Å^3, $D_m = 2{\cdot}067$ g.cm^{-3}, $D_x = 1{\cdot}979$ g.cm^{-3}.

$Z = 4$, $\mu = 42{\cdot}74$ cm^{-1} (Cu $K\alpha$).

Reflexions: hkl: no conditions; $0kl$: $k+l=2n$; $h0l$: no conditions; $hk0$: $h=2n$.

Possible space groups: *Pnma* [no. 62, $D_{2h}(16)$] or $Pbn2_1$ [no. 33, $C_{2v}(9)$] from systematic absences. *Pnma* was assumed and confirmed by the structure determination.

For the structure determination, integrated reflexions $hk0$, $hk1$, $hk2$, $hk3$, $hk4$, $hk5$ were recorded on a Weissenberg camera, with the use of the multiple film technique, and measured by a microdensitometer. Corrections for absorption as for cylindrical specimens ($\mu R = 0{\cdot}81$) and for Lorentz and polarization factors were applied.

The structure factors were calculated with atomic form factors obtained by the Forsyth & Wells (1959) formula with the improved constants given by Moore (1963).

Determination of the structure

The structure was solved by the Patterson function $P(UVW)$ and by a few Fourier functions $\varrho_0(xyz)$. Refinement was done by differential syntheses; the anisotropic thermal parameters were derived, following Nardelli & Fava (1960) and Nardelli, Fava & Giraldi (1963), by a program written by Nardelli, Musatti, Domiano & Andreetti (1965) (final disagreement index: $R = 8{\cdot}2\%$, observed reflexions only). Final atomic coordinates and observed and calculated electron densities at the atomic peaks are quoted in Table 1 and the anisotropic thermal parameters in Table 2. Observed and calculated structure factors are compared in Table 3.

Discussion of the structure

The whole structure is drawn in Fig. 1. The main interatomic distances and angles are quoted in Table 4.

The structure was clearly composed of $[Zn(OH_2)_6]^{2+}$ octahedra and NO_3^- triangular groups. The hexaquozinc cation (Fig. 2) has nearly octahedral symmetry as

Table 1. *Atomic coordinates (with e.s.d.'s* × 10^4) *and electron densities at the atomic peaks*

	x	y	z	$\varrho_o(xyz)$ (e.Å^{-3})	$\varrho_c(xyz)$ (e.Å^{-3})
Zn	0·6242 (1)	0·2500 (0)	0·4472 (2)	70·7	71·7
$H_2O(1)$	0·4923 (4)	0·2500 (0)	0·2353 (11)	12·3	12·2
$H_2O(2)$	0·7316 (3)	0·2500 (0)	0·1823 (10)	12·3	12·1
$H_2O(3)$	0·5205 (3)	0·2500 (0)	0·7179 (10)	11·9	11·8
$H_2O(4)$	0·7587 (3)	0·2500 (0)	0·6473 (9)	12·6	12·3
$H_2O(5)$	0·6257 (5)	0·0894 (3)	0·4457 (12)	11·5	11·6
O(6)	0·6440 (7)	0·0818 (4)	−0·0585 (18)	9·5	9·5
O(7)	0·6196 (5)	−0·0605 (3)	0·1155 (11)	11·0	10·9
O(8)	0·6144 (5)	−0·0596 (4)	−0·2313 (12)	11·3	11·5
N(9)	0·6270 (4)	−0·0124 (3)	−0·0578 (12)	11·3	11·5

Table 2. *Anisotropic thermal parameters* (Å^2)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zn	2·839	2·163	2·662	—	−0·164	—
$H_2O(1)$	2·603	2·273	3·338	—	−0·531	—
$H_2O(2)$	2·810	2·395	2·748	—	−0·331	—
$H_2O(3)$	3·121	2·413	2·527	—	0·100	—
$H_2O(4)$	2·717	2·583	2·511	—	−0·196	—
$H_2O(5)$	4·435	2·005	3·331	−0·092	0·241	−0·028
O(6)	5·503	2·654	4·575	−0·110	−0·532	−0·217
O(7)	4·785	3·052	3·060	0·217	0·055	0·157
O(8)	4·197	2·606	2·630	−0·473	0·137	−0·161
N(9)	2·876	2·091	2·452	0·073	−0·223	0·011

Average and maximum thermal parameter shift in the last cycle:
Zn: $|\Delta B_{av}| = 0{\cdot}034$, $|\Delta B_{max}| = 0{\cdot}040$.
Ligth atoms: $|\Delta B_{av}| = 0{\cdot}054$, $|\Delta B_{max}| = 0{\cdot}338$.

Table 3. *Observed and calculated structure factors*

Reflexions marked with an asterisk are probably affected by secondary extinction and were excluded from the refinement.

h	k	l	$10F_o$	$10F_c$
2	0	0	—	28-
4	0	0	1762	2157-
6	0	0	—	2
8	0	0	1554	1710
10	0	0	—	15
12	0	0	484	460-
14	0	0	—	26-
2	1	0	1179	1261-
4	1	0	143	127
6	1	0	680	679
8	1	0	136	104-
10	1	0	498	482-
12	1	0	—	36
14	1	0	205	179
0	2	0	445	334-
2	2	0	40	9-
4	2	0	1414	1213-
6	2	0	—	19
8	2	0	332	364-
10	2	0	—	2
12	2	0	—	24
14	2	0	—	5
2	3	0	1008	1073
4	3	0	374	343
6	3	0	652	666-
8	3	0	232	259-
10	3	0	519	508
12	3	0	120	126
14	3	0	232	201-
0	4	0	*976	1851
2	4	0	58	57
4	4	0	53	106-
6	4	0	100	95-
8	4	0	826	817
10	4	0	49	46
12	4	0	236	219-
14	4	0	—	21-
2	5	0	493	409-
4	5	0	166	167
6	5	0	243	241
8	5	0	155	151-
10	5	0	285	276-
12	5	0	—	66
14	5	0	127	109
0	6	0	*1344	2422-
2	6	0	—	26
4	6	0	877	805
6	6	0	—	23-
8	6	0	941	925-
10	6	0	—	3-
12	6	0	224	222
14	6	0	—	19
2	7	0	1405	1451
4	7	0	—	19
6	7	0	892	869-
8	7	0	—	17-
10	7	0	529	520
12	7	0	—	19
14	7	0	178	201-
0	8	0	573	657
2	8	0	—	6-
4	8	0	271	172
6	8	0	—	21
8	8	0	436	414
10	8	0	—	27-
12	8	0	142	112-
2	9	0	188	207-
4	9	0	136	103-
6	9	0	143	152
8	9	0	98	93
10	9	0	211	198-
12	9	0	68	53-
0	10	0	763	805-
2	10	0	—	50-
4	10	0	150	131
6	10	0	97	96
8	10	0	437	409-
10	10	0	75	74-
12	10	0	82	95
2	11	0	469	417
4	11	0	63	60-
6	11	0	281	271-
8	11	0	44	67
10	11	0	237	221
0	12	0	768	874
2	12	0	—	27-
4	12	0	361	347-
6	12	0	47	58
8	12	0	493	451
10	12	0	21	41-
2	13	0	568	550-
4	13	0	—	26-
6	13	0	387	364
8	13	0	—	34
0	14	0	327	287-
2	14	0	—	12-
4	14	0	—	19-
6	14	0	—	17
8	14	0	156	180-
2	15	0	105	111
4	15	0	—	14
6	15	0	73	88-
0	16	0	342	352
2	16	0	—	17
4	16	0	—	113-
1	0	1	82	84
2	0	1	—	23
3	0	1	85	54
4	0	1	307	264
5	0	1	358	361-
6	0	1	131	117
7	0	1	206	216
8	0	1	269	235
9	0	1	181	219
10	0	1	125	91-
11	0	1	73	91-
12	0	1	117	143
13	0	1	175	187-
14	0	1	—	58
15	0	1	90	88
0	1	1	407	464-
1	1	1	818	910-
2	1	1	—	26-
3	1	1	841	840-
4	1	1	332	324
5	1	1	516	522
6	1	1	—	5
7	1	1	555	612
8	1	1	244	249-
9	1	1	351	374-
10	1	1	119	101-
11	1	1	301	305-
12	1	1	90	96
13	1	1	142	138
14	1	1	—	39-
15	1	1	115	145
1	2	1	1097	1241-
2	2	1	591	598
3	2	1	979	1037
4	2	1	337	239-
5	2	1	862	879
6	2	1	377	384-
7	2	1	685	707-
8	2	1	239	248-
9	2	1	356	374-
10	2	1	174	165
11	2	1	253	261
12	2	1	150	118-
13	2	1	253	237
14	2	1	97	77-
15	2	1	138	144-
0	3	1	156	181
1	3	1	335	408
2	3	1	93	85-
3	3	1	99	167
4	3	1	118	102-
5	3	1	301	325-
6	3	1	156	158
7	3	1	111	137-
8	3	1	120	120
9	3	1	245	279
10	3	1	—	3
11	3	1	99	83
12	3	1	81	39-
13	3	1	117	91-
14	3	1	—	76
15	3	1	—	63-
1	4	1	326	320
2	4	1	155	132-
3	4	1	251	267-
4	4	1	290	247
5	4	1	334	308-
6	4	1	149	135
7	4	1	303	303
8	4	1	177	179
9	4	1	134	129
10	4	1	51	66-
11	4	1	96	94-
12	4	1	138	130
13	4	1	144	130-
14	4	1	—	39
15	4	1	54	68
0	5	1	474	450-
1	5	1	862	836-
2	5	1	53	39-
3	5	1	849	793-
4	5	1	360	324
5	5	1	526	502
6	5	1	—	42
7	5	1	586	579
8	5	1	253	233-
9	5	1	343	343-
10	5	1	112	109-
11	5	1	284	297-
12	5	1	—	89
13	5	1	135	133
14	5	1	—	22-
15	5	1	—	143
1	6	1	578	588-
2	6	1	275	257
3	6	1	429	438
4	6	1	134	145-
5	6	1	553	573
6	6	1	237	229-
7	6	1	395	400-
8	6	1	188	181-
9	6	1	289	317-
10	6	1	139	133
11	6	1	191	187
12	6	1	105	107-
13	6	1	213	215
14	6	1	—	73-
0	7	1	179	181
1	7	1	398	401
2	7	1	—	13-
3	7	1	357	371
4	7	1	141	132-
5	7	1	250	258-
6	7	1	—	43
7	7	1	305	310-
8	7	1	157	136
9	7	1	211	217
10	7	1	—	36
11	7	1	168	172
12	7	1	—	59-
13	7	1	95	83-
14	7	1	—	46
1	8	1	523	507
2	8	1	262	242-
3	8	1	441	424-
4	8	1	125	104
5	8	1	385	408-
6	8	1	176	176
7	8	1	306	323
8	8	1	130	159
9	8	1	180	188
10	8	1	—	77-
11	8	1	83	110-
12	8	1	—	70
13	8	1	129	135-
0	9	1	259	228-
1	9	1	464	441-
2	9	1	—	18
3	9	1	329	326-
4	9	1	180	158
5	9	1	352	334
6	9	1	—	46-
7	9	1	224	215
8	9	1	124	120-
9	9	1	234	241-
10	9	1	—	23-
11	9	1	122	113-
12	9	1	—	41
13	9	1	73	93
1	10	1	282	269-
2	10	1	103	116
3	10	1	248	249
4	10	1	124	124-
5	10	1	238	228
6	10	1	122	106-
7	10	1	243	239-
8	10	1	77	64-
9	10	1	120	111-
10	10	1	—	62
11	10	1	112	109
12	10	1	75	98-
0	11	1	147	140
1	11	1	235	257
2	11	1	—	9
3	11	1	255	261
4	11	1	—	102-
5	11	1	153	158-
6	11	1	—	11-
7	11	1	225	223-
8	11	1	120	94
9	11	1	124	125
10	11	1	—	52
11	11	1	108	131
1	12	1	237	233
2	12	1	119	107-
3	12	1	173	170-
4	12	1	—	34
5	12	1	220	242-
6	12	1	107	94
7	12	1	155	152
8	12	1	124	110
9	12	1	131	147
10	12	1	—	52-
0	13	1	148	119-
1	13	1	270	259-
2	13	1	—	7
3	13	1	242	236-
4	13	1	117	91
5	13	1	199	198
6	13	1	—	26-
7	13	1	200	188
8	13	1	—	88-
9	13	1	118	158-
1	14	1	273	258-
2	14	1	145	122
3	14	1	256	232
4	14	1	61	51-
5	14	1	219	213
6	14	1	109	99-
7	14	1	171	190-
8	14	1	—	52-
0	15	1	109	80
1	15	1	157	138
2	15	1	—	0
3	15	1	123	110
4	15	1	—	51-
5	15	1	102	101-
6	15	1	—	4
1	16	1	51	64
2	16	1	—	22-
3	16	1	—	56-
0	0	2	604	669
1	0	2	241	385-
2	0	2	290	328-
3	0	2	803	881-
4	0	2	1304	1508-
5	0	2	799	893
6	0	2	67	73
7	0	2	152	164
8	0	2	380	391
9	0	2	215	206-
10	0	2	107	140-
11	0	2	160	177-
12	0	2	326	328-
13	0	2	199	187
14	0	2	—	25
15	0	2	71	59
1	1	2	486	544-
2	1	2	965	1084-
3	1	2	699	720
4	1	2	—	10
5	1	2	512	554
6	1	2	740	826
7	1	2	336	344-
8	1	2	—	1
9	1	2	183	197-
10	1	2	289	313-
11	1	2	183	179
12	1	2	—	22-
13	1	2	131	119
14	1	2	190	178
15	1	2	64	69-
0	2	2	340	203
1	2	2	259	188-
2	2	2	163	105
3	2	2	570	554
4	2	2	805	843
5	2	2	413	407-
6	2	2	212	248
7	2	2	122	113-
8	2	2	100	113-
9	2	2	—	15-
10	2	2	—	57-
11	2	2	162	173
12	2	2	200	206
13	2	2	118	93-
14	2	2	—	60
15	2	2	55	55-
1	3	2	286	234-
2	3	2	280	165-
3	3	2	78	36
4	3	2	74	47
5	3	2	149	142-
6	3	2	151	175-
7	3	2	—	16-
8	3	2	—	32-
9	3	2	—	70
10	3	2	85	99
11	3	2	83	62-
12	3	2	—	24
13	3	2	96	83-
14	3	2	128	120-
15	3	2	—	41
0	4	2	108	25
1	4	2	74	23
2	4	2	167	141-
3	4	2	569	555-
4	4	2	868	873-
5	4	2	467	462
6	4	2	112	129-
7	4	2	154	138
8	4	2	179	199
9	4	2	—	58-
10	4	2	—	8-
11	4	2	172	178-
12	4	2	236	254-
13	4	2	135	131
14	4	2	—	24-
1	5	2	473	463-
2	5	2	911	913-
3	5	2	630	582
4	5	2	—	28-
5	5	2	469	466
6	5	2	664	696
7	5	2	294	289-
8	5	2	—	35
9	5	2	162	176-
10	5	2	248	267-
11	5	2	147	151
12	5	2	—	40-
13	5	2	103	105
14	5	2	113	149
0	6	2	288	274-
1	6	2	173	140
2	6	2	156	177
3	6	2	480	475
4	6	2	864	846
5	6	2	520	499-
6	6	2	—	5-
7	6	2	—	67-
8	6	2	178	186-
9	6	2	—	85
10	6	2	—	76
11	6	2	104	106
12	6	2	194	192
13	6	2	116	106-
14	6	2	—	2-
1	7	2	320	317
2	7	2	606	625
3	7	2	441	425-
4	7	2	—	45-
5	7	2	364	339-
6	7	2	544	532-
7	7	2	242	235
8	7	2	93	44
9	7	2	149	136
10	7	2	234	236
11	7	2	147	138-
12	7	2	—	11-
13	7	2	85	89-
0	8	2	277	319
1	8	2	163	158-
2	8	2	—	49-
3	8	2	486	483-
4	8	2	724	755-
5	8	2	403	389
6	8	2	138	144-
7	8	2	200	187
8	8	2	228	245
9	8	2	104	85-
10	8	2	—	38
11	8	2	171	171-
12	8	2	225	227-
13	8	2	86	113
1	9	2	—	36
2	9	2	98	40-
3	9	2	—	32
4	9	2	79	54-
5	9	2	128	109
6	9	2	128	135
7	9	2	—	3-
8	9	2	—	52
9	9	2	—	51-
10	9	2	—	55-
11	9	2	—	31
12	9	2	—	38-
0	10	2	196	157
1	10	2	136	112-
2	10	2	71	71
3	10	2	149	135
4	10	2	236	234
5	10	2	138	121-
6	10	2	—	40
7	10	2	—	4
8	10	2	—	7
9	10	2	—	33-
10	10	2	—	23
11	10	2	49	60
12	10	2	—	89
1	11	2	255	251
2	11	2	493	482
3	11	2	319	302-
4	11	2	—	2
5	11	2	260	252-
6	11	2	399	397-
7	11	2	190	178
8	11	2	—	5-
9	11	2	118	113
10	11	2	179	186
11	11	2	75	106-
0	12	2	327	332
1	12	2	215	186-
2	12	2	—	57-
3	12	2	313	302-
4	12	2	529	529-
5	12	2	329	308
6	12	2	—	21-
7	12	2	112	105
8	12	2	195	194
9	12	2	99	101-
10	12	2	—	22-
1	13	2	98	83-
2	13	2	188	176-
3	13	2	141	126
4	13	2	—	19
5	13	2	123	107
6	13	2	189	170
7	13	2	52	70-
8	13	2	—	24-
9	13	2	—	40-
0	14	2	—	67-
1	14	2	—	28
2	14	2	—	24
3	14	2	166	153
4	14	2	251	244
5	14	2	123	121-
6	14	2	—	50
7	14	2	53	58-
1	15	2	63	66
2	15	2	142	148
3	15	2	85	85-
4	15	2	—	31
5	15	2	81	103-
0	16	2	—	16-
1	16	2	—	12
2	16	2	—	27-
1	0	3	329	445
2	0	3	822	1018-
3	0	3	420	465-
4	0	3	268	294-
5	0	3	303	339-
6	0	3	543	605
7	0	3	84	99
8	0	3	92	98
9	0	3	322	329
10	0	3	427	429-
11	0	3	140	146-
12	0	3	141	148-
13	0	3	84	59-
14	0	3	126	125
0	1	3	244	347-
1	1	3	173	228-
2	1	3	71	93-
3	1	3	210	213-
4	1	3	499	549
5	1	3	226	247
6	1	3	—	4-
7	1	3	247	207
8	1	3	275	263-
9	1	3	83	69-
10	1	3	—	6
11	1	3	135	109-
12	1	3	241	231
13	1	3	106	103
14	1	3	—	21
1	2	3	187	195-
2	2	3	489	506
3	2	3	330	336
4	2	3	50	32-
5	2	3	101	100
6	2	3	296	290-
7	2	3	79	84-
8	2	3	182	189
9	2	3	206	192-
10	2	3	302	298
11	2	3	146	157
12	2	3	—	5-
13	2	3	—	8
14	2	3	103	95-
0	3	3	847	923
1	3	3	399	399
2	3	3	56	68
3	3	3	383	353
4	3	3	893	910-
5	3	3	350	336-
6	3	3	—	15
7	3	3	289	264-
8	3	3	377	375
9	3	3	103	92
10	3	3	—	7
11	3	3	136	123
12	3	3	241	231-
13	3	3	102	95-
14	3	3	50	40-
1	4	3	144	161
2	4	3	398	407-
3	4	3	259	255-
4	4	3	78	59-
5	4	3	84	95-
6	4	3	193	206
7	4	3	—	28
8	4	3	115	81-
9	4	3	167	175
10	4	3	204	211-
11	4	3	105	107-
12	4	3	58	51-
13	4	3	—	1-
14	4	3	—	41
0	5	3	50	74-
1	5	3	87	108-
2	5	3	48	45-
3	5	3	95	95-
4	5	3	291	281
5	5	3	156	157
6	5	3	65	49-
7	5	3	130	125
8	5	3	154	147-
9	5	3	—	46-
10	5	3	—	43
11	5	3	103	72-
12	5	3	195	177
13	5	3	81	89
1	6	3	402	378-
2	6	3	921	888
3	6	3	436	396
4	6	3	168	158
5	6	3	318	292
6	6	3	598	581-
7	6	3	136	133-
8	6	3	—	25-
9	6	3	282	279-
10	6	3	418	422
11	6	3	138	151
12	6	3	69	87
13	6	3	67	64
0	7	3	540	518
1	7	3	276	255
2	7	3	84	82
3	7	3	277	243
4	7	3	608	571-
5	7	3	234	221-
6	7	3	93	55-
7	7	3	199	206-
8	7	3	278	279
9	7	3	—	67
10	7	3	—	40
11	7	3	122	106
12	7	3	183	197-
13	7	3	51	78-
1	8	3	52	50
2	8	3	103	100-
3	8	3	138	133-
4	8	3	—	17
5	8	3	—	7-
6	8	3	—	34
7	8	3	—	13
8	8	3	115	117-
9	8	3	105	87
10	8	3	107	106-
11	8	3	77	79-
12	8	3	—	1-
0	9	3	451	439-
1	9	3	215	201-
2	9	3	—	13-
3	9	3	208	174-
4	9	3	495	465
5	9	3	204	187
6	9	3	—	46-
7	9	3	162	143
8	9	3	225	224-
9	9	3	82	66-
10	9	3	—	30
11	9	3	88	75-
12	9	3	—	162
1	10	3	194	200-
2	10	3	512	510
3	10	3	227	223
4	10	3	52	50
5	10	3	156	150
6	10	3	343	325-
7	10	3	94	76-
8	10	3	—	22
9	10	3	164	160-
10	10	3	225	241
11	10	3	69	94

Table 3 (*cont.*)

h	k	l	10F_o	10F_c
0	11	3	—	4
1	11	3	—	39
2	11	3	—	23
3	11	3	—	34
4	11	3	99	92-
5	11	3	—	57-
6	11	3	—	9
7	11	3	—	54-
8	11	3	—	34
9	11	3	—	8
10	11	3	—	12-
1	12	3	55	95
2	12	3	199	196-
3	12	3	122	115-
4	12	3	61	48-
5	12	3	70	73-
6	12	3	148	134
7	12	3	57	28
8	12	3	—	9-
9	12	3	79	102
0	13	3	425	395-
1	13	3	192	174-
2	13	3	65	34-
3	13	3	190	167-
4	13	3	428	400
5	13	3	163	148
6	13	3	—	30
7	13	3	122	142
8	13	3	—	233-
1	14	3	96	80-
2	14	3	205	190
3	14	3	106	105
4	14	3	—	1
5	14	3	—	51
6	14	3	—	120-
0	15	3	—	40
1	15	3	—	36
2	15	3	—	2-
3	15	3	—	23
0	0	4	225	295
1	0	4	* 549	932-
2	0	4	265	300
3	0	4	367	469-
4	0	4	129	142-
5	0	4	412	461
6	0	4	106	139
7	0	4	366	394
8	0	4	150	131
9	0	4	420	442-
10	0	4	115	108
11	0	4	166	175-
12	0	4	82	59-
13	0	4	130	147
1	1	4	569	720-
2	1	4	180	195-
3	1	4	426	470
4	1	4	—	2-
5	1	4	315	323
6	1	4	105	95
7	1	4	355	375-
8	1	4	—	12
9	1	4	312	318-
10	1	4	96	99-
11	1	4	180	188
12	1	4	—	6
13	1	4	95	101
0	2	4	143	162-
1	2	4	363	394
2	2	4	267	266-
3	2	4	144	145
4	2	4	86	43
5	2	4	80	6-
6	2	4	158	176-
7	2	4	285	276-
8	2	4	86	77-
9	2	4	180	175
10	2	4	82	74-
11	2	4	148	140
12	2	4	—	38
13	2	4	28	24-
1	3	4	162	205
2	3	4	57	93
3	3	4	57	12
4	3	4	35	29
5	3	4	39	40-
6	3	4	39	27-
7	3	4	136	104
8	3	4	49	44-
9	3	4	195	204
10	3	4	117	61
11	3	4	105	90-
12	3	4	—	17
13	3	4	55	67-
0	4	4	184	184
1	4	4	485	497-
2	4	4	252	250
3	4	4	228	237-
4	4	4	92	68-
5	4	4	139	146
6	4	4	121	129
7	4	4	311	312
8	4	4	90	85
9	4	4	259	260-
10	4	4	92	93
11	4	4	157	164-
12	4	4	—	42-
13	4	4	60	85
1	5	4	602	589-
2	5	4	161	154-
3	5	4	381	382
4	5	4	—	12
5	5	4	279	276
6	5	4	89	79
7	5	4	294	301-
8	5	4	45	6-
9	5	4	264	273-
10	5	4	92	86-
11	5	4	144	148
12	5	4	—	17
0	6	4	197	188-
1	6	4	541	526
2	6	4	205	203-
3	6	4	234	232
4	6	4	123	86
5	6	4	207	218-
6	6	4	102	119-
7	6	4	227	226-
8	6	4	105	91-
9	6	4	258	253
10	6	4	92	71-
11	6	4	99	95
12	6	4	30	42
1	7	4	532	496
2	7	4	165	145
3	7	4	382	350-
4	7	4	38	21
5	7	4	258	237-
6	7	4	95	75-
7	7	4	308	299
8	7	4	38	30-
9	7	4	248	239
10	7	4	82	73
11	7	4	148	167-
12	7	4	—	10
0	8	4	143	130
1	8	4	445	427-
2	8	4	141	155
3	8	4	290	267-
4	8	4	52	53-
5	8	4	161	160
6	8	4	103	107
7	8	4	304	294
8	8	4	71	68
9	8	4	229	213-
10	8	4	67	52
11	8	4	122	159-
1	9	4	147	123-
2	9	4	50	52-
3	9	4	—	8-
4	9	4	—	3-
5	9	4	—	30
6	9	4	—	19
7	9	4	—	41-
8	9	4	—	10
9	9	4	125	125-
10	9	4	—	40-
0	10	4	84	89-
1	10	4	145	141
2	10	4	126	130-
3	10	4	—	17
4	10	4	—	28
5	10	4	—	13
6	10	4	71	62-
7	10	4	97	92-
8	10	4	49	40-
9	10	4	75	89
10	10	4	—	64-
1	11	4	357	347
2	11	4	99	87
3	11	4	260	253-
4	11	4	—	0
5	11	4	190	188-
6	11	4	38	49-
7	11	4	198	210
8	11	4	—	4-
9	11	4	—	182
0	12	4	122	101
1	12	4	374	347-
2	12	4	104	87
3	12	4	221	210-
4	12	4	69	52-
5	12	4	188	189
6	12	4	—	70
7	12	4	145	186
1	13	4	181	169-
2	13	4	71	64-
3	13	4	115	109
4	13	4	—	11-
5	13	4	64	68
6	13	4	—	36
0	14	4	60	55-
1	14	4	130	147
2	14	4	59	70-
3	14	4	64	84
1	0	5	—	56
2	0	5	113	126-
3	0	5	—	10
4	0	5	—	10-
5	0	5	—	10-
6	0	5	234	237
7	0	5	—	54
8	0	5	49	13
9	0	5	—	37-
10	0	5	73	66-
11	0	5	—	6
12	0	5	—	7-
0	1	5	446	618-
1	1	5	84	98
2	1	5	—	5-
3	1	5	—	49-
4	1	5	418	429
5	1	5	—	17-
6	1	5	62	52
7	1	5	83	90-
8	1	5	374	373-
9	1	5	—	11
10	1	5	—	35-
11	1	5	—	18-
12	1	5	128	148
1	2	5	56	41
2	2	5	633	647
3	2	5	143	126-
4	2	5	—	9
5	2	5	—	27-
6	2	5	567	564-
7	2	5	—	30
8	2	5	—	18-
9	2	5	—	39
10	2	5	242	221
11	2	5	62	48-
12	2	5	—	17
0	3	5	255	267
1	3	5	75	67-
2	3	5	55	50-
3	3	5	97	93
4	3	5	128	137-
5	3	5	—	6
6	3	5	65	55
7	3	5	49	41
8	3	5	181	181
9	3	5	—	1
10	3	5	—	43-
11	3	5	52	44
12	3	5	38	52-
1	4	5	—	17
2	4	5	207	220-
3	4	5	51	54
4	4	5	—	10
5	4	5	—	11-
6	4	5	255	256
7	4	5	—	19
8	4	5	—	2-
9	4	5	—	20-
10	4	5	72	60-
11	4	5	—	15
0	5	5	613	621-
1	5	5	105	99
2	5	5	—	17-
3	5	5	—	28-
4	5	5	463	449
5	5	5	56	31-
6	5	5	67	67
7	5	5	80	83-
8	5	5	378	372-
9	5	5	—	21
10	5	5	39	50-
11	5	5	—	14-
1	6	5	—	2-
2	6	5	391	348
3	6	5	67	51-
4	6	5	—	14
5	6	5	—	16-
6	6	5	376	365-
7	6	5	—	7-
8	6	5	—	15-
9	6	5	38	41
10	6	5	144	159
11	6	5	14	29-
0	7	5	327	298
1	7	5	63	43-
2	7	5	—	10-
3	7	5	—	50
4	7	5	213	195-
5	7	5	—	10-
6	7	5	—	8-
7	7	5	57	58
8	7	5	218	207
9	7	5	—	9
10	7	5	—	3
1	8	5	—	6-
2	8	5	367	338-
3	8	5	80	58
4	8	5	—	13-
5	8	5	—	5
6	8	5	318	308
7	8	5	—	0
8	8	5	—	25
9	8	5	—	22-
0	9	5	326	319-
1	9	5	80	63
2	9	5	—	18
3	9	5	—	36-
4	9	5	216	219
5	9	5	42	26-
6	9	5	—	16-
7	9	5	35	35-
8	9	5	178	198-
9	9	5	—	16
1	10	5	—	1
2	10	5	157	162
3	10	5	—	40-
4	10	5	—	22-
5	10	5	—	0
6	10	5	168	187-
7	10	5	—	1-
8	10	5	—	22
0	11	5	242	243
1	11	5	—	37-
2	11	5	—	8
3	11	5	—	26
4	11	5	154	170-
5	11	5	—	2
6	11	5	32	33-
1	12	5	—	5
2	12	5	167	172-
3	12	5	—	21
4	12	5	—	21-
5	12	5	—	4
0	13	5	159	202-
1	13	5	—	31
2	13	5	—	7

Table 4. *Main interatomic distances and angles, with e.s.d.'s*

Hexaquozinc cation

$Zn-OH_2(1)$	2·104 ± 0·009 Å	$H_2O(5)-Zn-H_2O(1)$	90·2 ± 0·4°
$Zn-OH_2(2)$	2·129 ± 0·009	$H_2O(5)-Zn-H_2O(2)$	89·5 ± 0·4
$Zn-OH_2(3)$	2·130 ± 0·010	$H_2O(5)-Zn-H_2O(3)$	90·5 ± 0·4
$Zn-OH_2(4)$	2·083 ± 0·010	$H_2O(5)-Zn-H_2O(4)$	89·7 ± 0·4
$Zn-OH_2(5)$	2·064 ± 0·010	$H_2O(1)-Zn-H_2O(2)$	89·2 ± 0·3
		$H_2O(1)-Zn-H_2O(3)$	92·4 ± 0·4
		$H_2O(4)-Zn-H_2O(2)$	88·7 ± 0·4
		$H_2O(4)-Zn-H_2O(3)$	89·7 ± 0·4

Nitrato anion

N(9)-O(6)	1·228 ± 0·007 Å	O(6)-N(9)-O(8)	119·5 ± 0·9°
N(9)-O(7)	1·256 ± 0·010	O(6)-N(9)-O(7)	120·0 ± 0·8
N(9)-O(8)	1·258 ± 0·010	O(7)-N(9)-O(8)	120·4 ± 0·5

Hydrogen bonds

$H_2O(1)-O(8)_{II}$	2·778 ± 0·016 Å	$O(8)_{II'}-H_2O(1)-O(8)_{II}$	123·4 ± 0·3°
$H_2O(1)-O(8)_{II'}$	2·778 ± 0·016	Zn —— $H_2O(1)-O(8)_{II}$	111·9 ± 0·4
$H_2O(2)-O(6)$	2·852 ± 0·015	O(6′) — $H_2O(2)-O(6)$	98·6 ± 0·4
$H_2O(2)-O(6')$	2·852 ± 0·015	Zn —— $H_2O(2)-O(6)$	100·4 ± 0·4
$H_2O(3)-O(6)_{I}$	2·995 ± 0·016	$O(6)_{I}$ — $H_2O(3)-O(6)_{I'}$	92·4 ± 0·4
$H_2O(3)-O(6)_{I'}$	2·995 ± 0·016	Zn —— $H_2O(3)-O(6)_{I}$	94·0 ± 0·4
$H_2O(4)-O(7)_{III}$	2·868 ± 0·016	$O(7)_{III}-H_2O(4)-O(7)_{III'}$	116·2 ± 0·4
$H_2O(4)-O(7)_{III'}$	2·868 ± 0·016	Zn —— $H_2O(4)-O(7)_{III}$	112·0 ± 0·4
$H_2O(5)-O(7)$	2·834 ± 0·010	O(7) —— $H_2O(5)-O(8)_{I}$	93·8 ± 0·2
$H_2O(5)-O(8)_{I}$	2·795 ± 0·012	Zn —— $H_2O(5)-O(7)$	133·1 ± 0·4
		Zn —— $H_2O(5)-O(8)_{I}$	132·9 ± 0·4

Asymmetric units

No label	x	y	z	′	x	$\frac{1}{2}-y$	z
I	x	y	$1+z$	I′	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$
II	$1-x$	$\frac{1}{2}+y$	$\bar{z}$	II′	$1-x$	$\bar{y}$	$\bar{z}$
III	$\frac{3}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}+z$	III′	$\frac{3}{2}-x$	$\bar{y}$	$\frac{1}{2}+z$

shown by the distances Zn–OH_2(1) = 2·104, Zn–OH_2(2) = 2·129, Zn–OH_2(3) = 2·130, Zn–OH_2(4) = 2·083, Zn–OH_2(5) = 2·064 Å and by the observed angles.

The distances between zinc and water can be compared with distances found in other compounds of the hexaquozinc cation: 2·08 (Broomhead & Nicol, 1948), 2·12 (Yü & Beevers, 1935), 2·08, 2·05, 2·14 (Hargreaves, 1957), 2·129, 2·117, 2·075 Å (Montgomery & Lingafelter, 1964) with a weighted mean value Zn–OH_2 = 2·105 ± 0·025 Å against our weighted mean value Zn–OH_2 = 2·097 ± 0·010 Å; the total mean value is Zn–OH_2 = 2·099 ± 0·020 Å. For the distances between zinc and water, in octahedral complexes not formed exclusively by water molecules, the following values have been found: Zn–OH_2 = 2·14 (Niekerk, Schoening & Talbot, 1953), 2·09, 2·16, 2·21 (Doyne & Pepinsky, 1957), 2·21, 2·24 Å (Gladkova & Kondrašev, 1963) with a mean value Zn–OH_2 = 2·18 ± 0·05 Å. For bonds between zinc and oxygen atoms, not belonging to water molecules, the following bond distances in octahedral complexes have been found: Zn–O = 2·17, 2·18 (Niekerk, Schoening & Talbot, 1953), 2·16, 2·17 (Novacki & Silverman, 1961), 2·19, 2·08 (Doyne & Pepinsky, 1957), 2·147 (Ferrari, Braibanti, Bigliardi & Lanfredi, 1965*a*), 2·19, 2·20, 2·10 (Iitaka, Oswald & Locchi, 1962), 2·10, 2·12, 2·10, 2·16 (Ghose, 1964); however some lower values, 2·039 (Nardelli, Fava & Giraldi, 1963), 2·04, 1·96, 1·93 Å (Iitaka, Oswald & Locchi, 1962), 2·04 (Ghose, 1964), 2·05 (Ferrari, Braibanti, Bigliardi & Lanfredi, 1965*b*) have been found and these are of the same length as bonds in tetrahedral complexes: Zn–O = 2·02 (Novacki & Silverman, 1961), 2·00, 1·94, 2·06, 2·06 (Iitaka, Oswald & Locchi, 1962), 1·99, 1·98 (Ghose, 1964).

The identification of the atoms of the nitrato group, whose shape is well known, is out of the question, although the observed and calculated electron densities at the peaks corresponding to N(9), O(7) and O(8) are equal and that corresponding to O(6) is lower. This fact can be due to the thermal motion of the whole group, librating around the nitrogen atom. A survey of the thermal parameters confirms this point of view; but we cannot consider the refinement of the thermal parameters so reliable that we can use them with confidence to calculate librational motions.

The distances in the nitrato group (Fig. 3) are not significantly different: N–O(6) = 1·228, N–O(7) = 1·256 and N–O(8) = 1·258 Å with N–O_{av} = 1·242 ± 0·009 Å in good agreement with values quoted by *International Tables for X-ray Crystallography* (1962): N–O_{av} = 1·24 Å; the three angles O–N–O are practically equal to 120°; the plane passing through the four atoms is represented by $-0·98286X + 0·18172Y + 0·03102Z = -7·63647$ where X, Y, Z are coordinates in Å; the deviations from the plane are $\Delta = -0·00834$, $+0·00527$, $+0·00289$ and $+0·00041$ Å for N(9), O(6), O(7) and O(8) respectively. Therefore the nitrato group is planar and the nitrogen atom would be in the perfect sp^2 hybridization state.

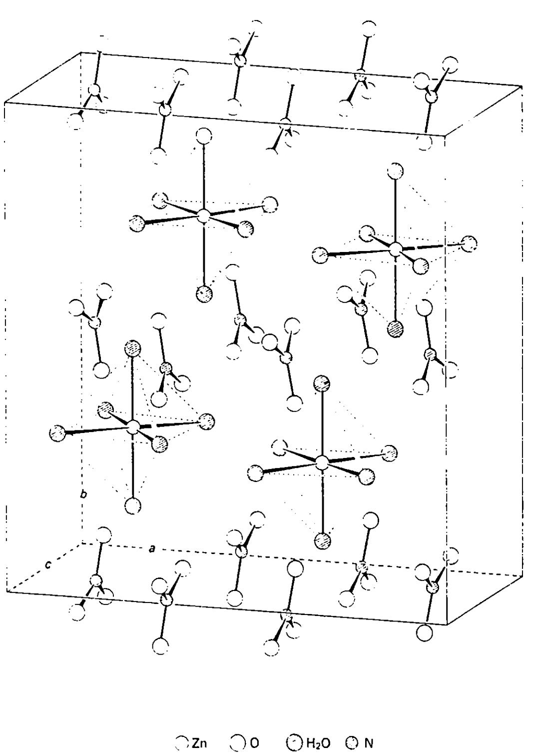

Fig. 1. Clinographic projection of the structure of $Zn(OH_2)_6(NO_3)_2$.

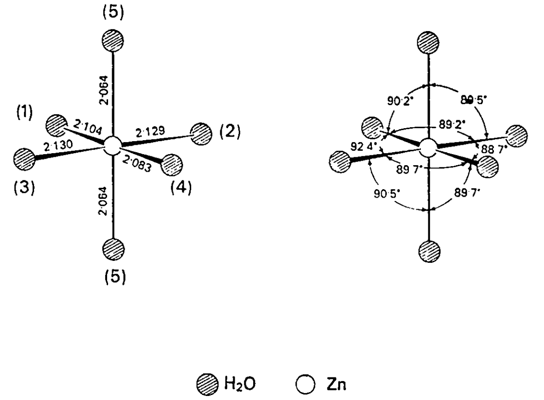

Fig. 2. Hexaquozinc cation, $[Zn(OH_2)_6]^{2+}$.

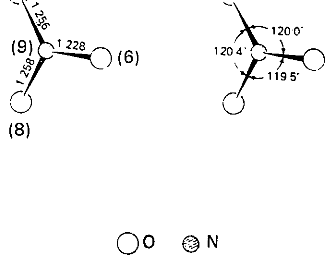

Fig. 3. Nitrato group, NO_3^-.

The question whether the three bonds N–O of the nitrato group must be equal, and which is their proper length, is still an open one. According to Barclay, Sabine & Taylor (1965), the difference between the values N–O = 1·21 and N–O = 1·26 Å, found in $RbUO_2(NO_3)_3$, is probably significant. Taylor & Mueller (1965) in the structure of $UO_2(NO_3)_2.6H_2O$, examined by neutron diffraction, find N–O = 1·207, 1·271 Å for the first NO_3^- and N–O = 1·231, 1·260 Å for the second NO_3^-, which are significantly different. Britton & Dunitz (1965) find significantly different values, N–O(1)–1·202, N–O(2) = 1·272 and N–O(3) = 1·309 Å in $AgCN.2AgNO_3$ and they attribute these differences to the different strength of the bonds O–Ag; they find angles O–N–O = 118·1, 119·6 and 122·2°, probably different. On the contrary, Sass, Vidale & Donohue (1957) find three equivalent bonds, N–O = 1·218 Å, in $NaNO_3$ and Hamilton (1957) finds, by neutron diffraction, three equivalent bonds in $Pb(NO_3)_2$, with length N–O = 1·268 Å. Swink & Atoji (1960) find three equal bonds N–O = 1·21 Å in triethylenediaminenickel(II) nitrate. The distances $N\text{–}O_{av} = 1·22 \pm 0·07$ Å, found by Šćavničar & Prodić (1965) in $Mg(OH_2)_6Th(NO_3)_6.2H_2O$, are not significantly different; the NO_3^- group, however, is significantly not planar. Also Komiyama & Lingafelter (1964) find, in the nitrato group, three equal bonds N–O = 1·258 Å but with nitrogen slightly out of the plane formed by the three oxygen atoms.

Distances between nitrogen and oxygen in nitrato ions are practically equal to those in nitric esters, nitric acid and nitro compounds, apart from bonds N–O(H) and N–O(R) (Luzzati, 1951; Millen & Morton, 1960; Trotter, 1963; Mak & Trotter, 1964; Jensen & Andersen, 1964; Coppens & Schmidt, 1964; Hanson, 1964; Mugnoli, Mariani & Simonetta, 1965).

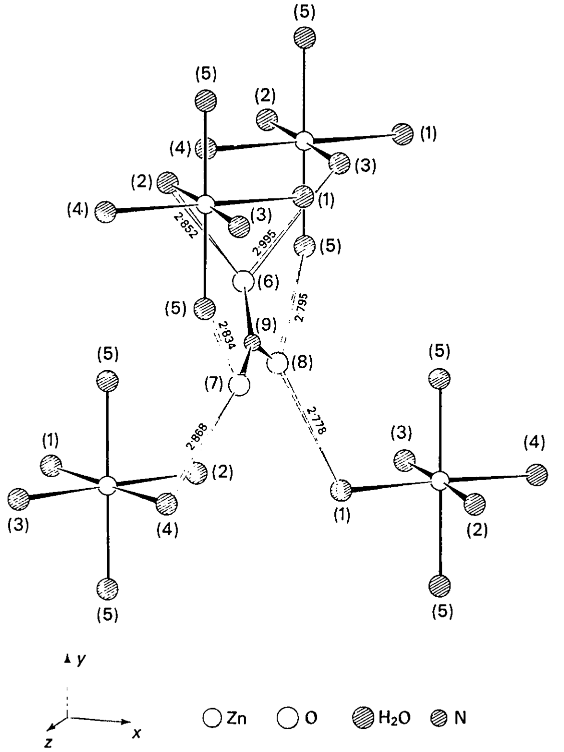

Fig. 4. Hydrogen bonds formed by oxygen atoms of one nitrato group with surrounding water molecules.

The whole structure is held together by a three-dimensional network of hydrogen bonds between water molecules and nitrato groups. Each oxygen atom of the nitrato group forms two hydrogen bonds (Fig. 4), with water molecules, in the range 2·778 – 2·995 Å. Each water molecule forms two hydrogen bonds with nitrato groups (Fig. 5). Two contact distances $OH_2(3)\cdots O(7) = 3·165$ Å and $OH_2(2)\cdots O(8) = 3·145$ Å have not been considered as hydrogen bonds. The two hydrogen bonds $H_2O(5)\cdots O(7)$ and $H_2O(5)\cdots O(8)$ and the bond $Zn\text{–}OH_2(5)$ are nearly in the same plane as shown by the sum of the interatomic angles, 359·8°. The planes of the remaining couples of hydrogen bonds of each water molecule are bent with respect to the corresponding $Zn\text{–}OH_2$ direction, as shown by the sum of the corresponding angles, $O\text{–}H_2O\text{–}O'$, $O\text{–}H_2O\text{–}Zn$ and $Zn\text{–}H_2O\text{–}O'$ which are less, and sometimes much less, than 360°.

We wish to thank Prof. L. Cavalca for computing facilities on the Olivetti Elea 6001/S of the Centro Calcolo Elettronico dell'Università di Parma, and the

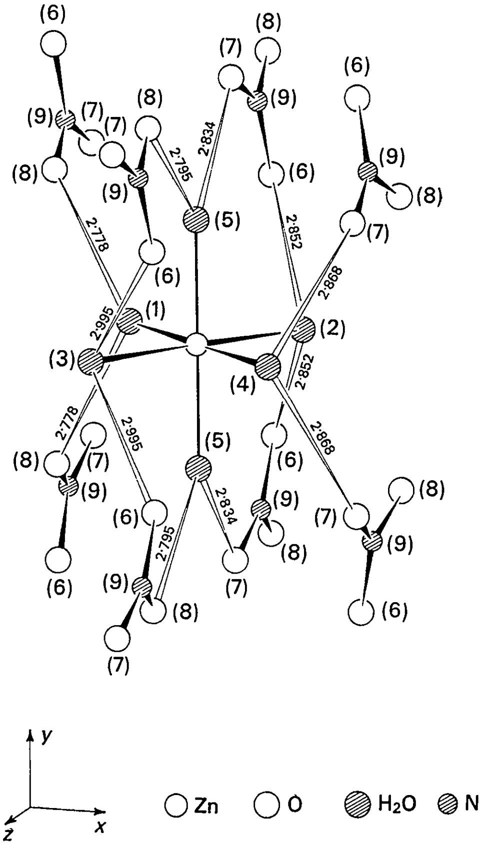

Fig. 5. Hydrogen bonds from water molecules, of one hexaquozinc cation, to oxygen atoms of neighbouring nitrato groups.

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Die Kristallstruktur des 1,4-Bis-(*N*-äthyl-1,2-dihydrobenzthiazol-2-yliden)tetrazens

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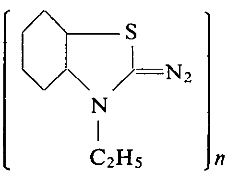
The structure of 1,4-bis-(*N*-ethyl-1,2-dihydrobenzthiazol-2-ylidene)tetrazen, $(C_9H_9N_3S)_2$, was solved by a three-dimensional Patterson synthesis with S as the heavy atom. Space group $P\bar{1}$, $a=7{\cdot}307\pm2$, $b=9{\cdot}145\pm2$, $c=7{\cdot}252\pm3$ Å, $\alpha=94{\cdot}95\pm4°$, $\beta=111{\cdot}06\pm4°$, $\gamma=84{\cdot}89\pm3°$; $Z=1$, $D_m=1{\cdot}40\pm1$, $D_x=1{\cdot}41$ g.cm^{-3}. By least-squares methods with 1888 reflexions, anisotropic temperature factors for S, N and C and isotropic temperature factors for H, the structure was refined to an R index of 8·4 %. The tetrazene chain is in the *trans*(*N*)-*trans*-*trans*(*N*) form with bond lengths: C=N 1·302, N–N 1·400 and N=N 1·257 Å. The plane of the tetrazene chain is inclined 4·8° to the benzthiazole planes.

Einleitung

Balli (1966) stellte durch 'Thermolyse' von 2-Tetrazo-3-äthylbenzthiazolin eine Verbindung



$=(C_9H_9N_3S)_n$ her, von der er annahm, dass sie dimer ($n=2$) sei und dass vier der darin enthaltenen Stickstoffatome ein Tetrazen bilden. Um diese Frage zu beantworten und um die Konfiguration der eventuellen Tetrazenkette aufzuklären, wurde die genannte Substanz einer Röntgenstrukturanalyse unterzogen. Diese bestätigte die Annahme eines Tetrazens, und zwar liegt dieses in der *trans*(*N*)-*trans*-*trans*(*N*)-Form vor.

Experimentelles

Die Kristalle der genannten Substanz wurden von Balli durch Kristallisation aus Dimethylformamid ge-