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The Crystal Structure of Ammonium di-μ-hydroxo-di[triscarbonato-zirconate(IV)]tetrahydrate

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The crystal structure of ammonium di-μ-hydroxo-di-[triscarbonatozirconate(IV)]tetrahydrate, $(NH_4)_6[Zr(OH)(CO_3)_3]_2 \cdot 4H_2O$, has been determined. The crystals are monoclinic, $P2_1/n$, with cell dimensions $a = 16.46 \pm 0.02$ Å, $b = 11.53 \pm 0.03$ Å, $c = 6.95 \pm 0.01$ Å and $\beta = 92.0 \pm 0.2$ Å. The observed density, 1.87 ± 0.05 g/cm^3, corresponds to four molecules per unit cell. The crystals consist of discrete dimeric species in which the metal atoms are bridged by hydroxo groups. Each carbonate ion behaves as a bidentate ligand forming with the hydroxo groups a distorted dodecahedron of oxygen atoms about each zirconium atom. The dimers are held in the crystal through the compensating electrostatic charge of the ammonium ions and a network of hydrogen bonds to the water molecules.

Introduction

Zirconium forms a variety of carbonate complexes. A number of these are crystalline and readily obtainable from aqueous solution.[1,2] Pospelova and Zaitsev proposed a number of interesting tetranuclear and dinuclear structures for these complexes in which the carbonato groups were depicted as monodentate ligands. The tris carbonato complex, $M_6[Zr_2O(CO_3)_6] \cdot 4H_2O$, was formulated as a dinuclear species with the two zirconium atoms linked through an oxo-bridge. This would result in a coordination number of 4 to 6 (depending upon the number ot water molecules in the metal coordination sphere) assuming the carbonates were monodentate.

In an earlier review of the structures of «oxygen-containing» zirconium compounds it was shown that in such compounds coordination numbers of less than six have never been observed.[3] It has further been shown that, in all basic salts whose structures were known, hydroxo bridges rather than oxo-bridges were present. Thus, a more likely structure would result if the metal atoms were linked through two hydroxo bridges and the carbonato groups were bidentate. The complex would then be eight coordinate. Such structures were previously proposed for hydroxo-tris-α-hydroxy carboxylates of zirconium.[3] It was, therefore, of interest to determine the structure of the triscarbonatozirconate species and the ammonium salt was chosen for study.

During the course of this work, a preliminary report on the structure of potassium di-μ-hydroxo-di[triscarbonatozirconate(IV)]hexahydrate, was published.[4] The structure was shown to have the double hydroxo bridging and to be eight coordinate as predicted. This paper provides additional evidence for the structure of the complex ion.

Experimental Section

Crystals were obtained from the Tizon Chemical Co., Flemington, New Jersey. They were clear, colorless prisms with 2/m symmetry.

The zirconium content was determined by igniting a weighed crystal to oxide. Carbon dioxide, ammonia and water were determined with a C, H, N analyser by standard methods. Found: ZrO_2, 32.58%; N, 10.97%; C, 9.18%; H, 4.48%. Required for $(NH_4)_3ZrOH(CO_3)_3.2H_2O$: ZrO_2, 32.74%; N, 11.07%; C, 9.50; H, 4.51%.

The crystals began to decompose with loss of ammonia as soon as they were removed from the mother liquor. Hence, it was necessary to seal them in Lindemann glass capillaries along with a drop of mother liquor. In this way the crystals could be kept for several days before they began to deteriorate.

The unit cell was found to be monoclinic with $a = 16.46 \pm 0.02$ Å, $b = 11.53 \pm 0.03$ Å, $c = 6.95 \pm 0.01$ Å and $\beta = 92.0 \pm 0.2°$. The unit cell constants were determined from Weissenberg photographs using CuKα radiation ($\lambda = 1.5418$ Å). Corrections for film shrinkage were made by recording a sodium chloride powder pattern on the photographs. The corrected d values were then plotted against $\cos^2\theta$ and extrapolated to $\theta = 90°$ by a least squares method.

The measured density obtained by flotation in a carbon tetrachloride, 1,1-dibromoethane mixed solvent was $1.87 \pm .05$ g/cm^3. The calculated density with $Z = 4$ is 1.911 g/cm^3.

Weissenberg photographs taken about the b axis ($h\ k\ \ell$, $k = 0\text{-}3$) and the c axis ($h\ k\ \ell$, $\ell = 0\text{-}3$) revealed the following systematic absences: $h\ 0\ \ell$

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[1] L. A. Pospelova and L. M. Zaitsev, *Zhur. Neorg. Khim.*, *11*, 1863 (1966).
[2] Yu. E. Gorbunova, V. G. Kuznetsov, and E. S. Kovaleva, *Zhur. Neorg. Khim.*, *13*, 102 (1968).
[3] A. Clearfield, *Rev. Pure and Appl. Chem.*, *14*, 91 (1964).
[4] Yu. E. Gorbunova, V. G. Kuznetsov, and E. S. Kovaleva, *Zh. Strukt. Khim.*, *9*, 918 (1968).

when h ± ℓ ≠ 2n and 0 k 0 when k ≠ 2n. This fixed the space group as $P2_1/n$.

Intensity data were gathered from multiple film Weissenberg photographs using CuKα (nickel filtered) radiation. Two separate crystals were used. One was mounted about the b axis and h 0 ℓ data recorded. The other was mounted about the c axis and h k 0 and h k 1 data obtained. The intensities were estimated visually by comparison with an intensity strip and corrected for Lorentz and polarization factors but not for absorption. They were then placed on the same scale by the least squares procedure of Monohan, Schiffer and Schiffer.[5] No corrections for spot extension were made but since the data did not extend beyond the first layer line the error is small. In all 685 intensities above background were obtained.

Structure Solution and Refinement. Patterson projections onto the (001) and (010) planes were prepared. The zirconium atom positional parameters and those of three of the light atoms were determined immediately from the Pattersons. A structure factor calculation based on only the zirconium atom parameters and another based on all 4 atoms showed a difference in sign for only 8 reflections. Thus, Fourier projections (on (001) and (010)) were made using the signs determined from positional parameters of all four atoms. As it turned out, 80% of the signs were correctly determined in this calculation. The parameters of six additional atoms were immediately obtained from the Fourier projections and their positions refined by two successive difference syntheses. A three-dimensional Fourier map was now obtained using signs calculated for the structure factors from all ten atoms. This Fourier resolved the positions of the remaining (except hydrogens) nine atoms.

The structural parameters were then refined by the block-diagonal least squares method.[6] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Neutral atom scattering factors used in the calculation were obtained from the tabulation in «International Tables».[7]

Initially, the zirconium atom was assigned an isotropic temperature factor $B = 1.0$ and the light atoms individual temperature factors of 1.5. A weighting scheme due to Cruickshank and Pilling was used.[8] The weights were $w = 1/(a + |F_o| + b|F_o|^2)$ where $a = 2|F_{min}|$ and $b = 2/|F_{max}|$.

In seven cycles of refinement the residual, $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, was reduced from 0.21 to 0.13. A difference synthesis was now made and clearly showed that the zirconium atom was vibrating anisotropically. Therefore, further refiniment was carried out with anisotropic temperature coefficient for zirconium. Also, 25 structure factors for which $\Delta F/\sigma = ||F_o| - |F_c||/\sigma$ was greater than 3 were eliminated from the refinement. Nine more cycles were computed to give a final R of 0.104 excluding these 25 structures factors and 0.114 if they are included.

Table I. X-ray Positional and Thermal Parameters with Estimated Standard Deviations[1]

Atom	X	Y	Z	$B(Å)^2$
Zr_1	0.05840(8)	0.1157(1)	−0.0810(4)	*
C_2	0.1018(12)	0.3295(21)	−0.0042(50)	1.5(4)
C_3	0.2114(12)	0.0579(21)	0.0135(52)	1.5(4)
C_4	−0.0205(11)	0.1653(18)	−0.4074(41)	0.9(3)
N_5	0.2976(11)	0.4635(18)	0.0256(43)	1.9(4)
N_6	−0.1069(13)	0.3938(21)	0.2619(52)	2.8(5)
N_7	0.1579(12)	0.3006(20)	0.4566(47)	2.3(4)
O_8	−0.0218(8)	0.0579(13)	0.1296(32)	0.9(2)
O_9	0.0510(10)	0.1186(17)	−0.4029(40)	2.5(4)
O_{10}	0.1572(9)	0.0853(15)	0.1379(36)	1.7(3)
O_{11}	−0.0494(8)	0.1873(13)	−0.2281(33)	1.1(3)
O_{12}	0.1300(9)	0.4272(16)	0.0584(37)	1.8(3)
O_{13}	0.1798(9)	0.0513(15)	−0.1587(35)	1.7(3)
O_{14}	0.0481(8)	0.2740(14)	0.1063(32)	1.2(3)
O_{15}	0.1253(9)	0.2769(14)	−0.1456(35)	1.7(3)
O_{16}	0.2843(9)	0.0425(15)	0.0521(36)	1.9(3)
O_{17}	−0.0642(10)	0.1812(17)	−0.5594(41)	2.5(4)
O_{18}	0.3119(11)	0.1970(18)	0.3789(44)	3.0(4)
O_{19}	0.4714(12)	0.0481(20)	0.2150(44)	3.3(4)

[1] Standard deviations in the least significant digits are in parentheses in all the tables. * Anisotropic thermal parameters for Zr: $B_{11} = 0.00056(4)$, $B_{22} = 0.00103(10)$, $B_{33} = 0.0050(5)$, $B_{23} = 0.0016(13)$, $B_{13} = 0.0008(3)$, $B_{12} = -0.0001(1)$. The form of the anisotropic thermal ellipsoid is $\exp[(-B_{11}h^2 + B_{22}k^2 + B_{33}\ell^2 + B_{23}k\ell + B_{13}h\ell + B_{12}hk)]$ so that $B_{11} = 2\pi^2 a^{*2} U_{11}$, etc. and $B_{12} = 4\pi^2 a^{*2} b^{*2} U_{12}$, etc.

The final parameters together with their standard deviations are listed in Table I and the observed and calculated structure factors in Table Ia. The final difference map revealed several positive regions the highest of which was 1.5 electrons/Å^3 between the metal and hydroxyl groups. Other positive regions ranged from 0.4 to 1.2 e/Å^3 compared to 110 e/Å^3 peak height for zirconium and an average of about 15 e/Å^3 for the oxygen and nitrogen atoms. None of the residual maxima could be assigned to hydrogen atoms. Therefore, they must arise from systematic errors such as series termination effects, absorption errors, etc.

Results and Discussion

The crystals contain discrete dinuclear anions in which the zirconium atoms are bridged by hydroxo groups (Figure 1). Three carbonate groups, acting as bidentate ligands, are bonded to each metal atom so that the coordination number of the zirconium atoms is eight. The dinuclear complexes form hydrogen bonds with the water and ammonium ions. The crystals are built up through this network of hydrogen bonds and the compensating electrostatic charge of the ammonium ions as shown in Figure 2.

The bond distances and angles for the three carbonate groups are given in Table II. Each carbonate ion is planar within the experimental error of the data. Table III lists the least squares planes formed

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(5) J. E. Monohan, M. Schiffer, and J. P. Schiffer, *Acta Cryst.*, 22, 322 (1967).

(6) The programs used in this work were as follows: (a) F. R. Ahmed, NRC-8 Fourier Program; (b) F. R. Ahmed, NRC-10 Structure Factor Least Squares; (c) M. E. and F. R. Ahmed, NRC-12 Scan of Interatomic Distances and Angles; (d) M. E. Pippy and F. R. Ahmed, NRC-21 mean plane, National Research Council, Ottawa, Canada.

(7) « International Tables for X-ray Crystallography » Vol. III, the Kynoch Press, Birmingham, England, 1962 p. 202.

(8) D. W. J. Cruickshank and D. E. Pilling, in « Computing Methods and the Phase Problem in X-ray Crystal Analysis », Pergamon Press, N. Y., 1960, p. 45.

Table Ia. Observed and Calculated Structure Amplitudes (× 10) in Electrons

H	FO	FC
K= 0, L= 0		
1	48*	0
2	1517	1675
3	51*	0
4	48*	71
5	48*	0
6	183	-235
7	45*	0
8	1671	-1582
9	149*	0
10	927	-1057
11	129*	0
12	792	-827
13	45*	0
14	188	214
15	45*	0
16	573	617
17	45*	0
18	736	703
19	45*	0
20	312	301
K= 1, L= 0		
1	1185	1376
2	1188	-1172
3	725	665
4	649	-660
5	570	464
6	138	60
7	949	-945
8	343	-306
9	1385	-1302
10	275	282
11	326	-325
12	736	787
13	45*	83
14	511	541
15	435	426
16	326	329
17	534	479
18	45*	-29
19	360	374
20	275	-310
K= 2, L= 0		
0	160	298
1	815	-820
2	624	-561
3	685	-633
4	635	511
5	1056	-1021
6	309	268
7	826	-785
8	45*	45
9	517	483
10	289	295
11	812	789
12	45*	-44
13	753	780
14	152	144
15	500	549
16	132	-106
17	132	179
18	45*	-39
19	348	-347
20	87	-85
K= 3, L= 0		
1	874	-926
2	817	-838
3	1564	-1422
4	593	-571
5	343	260
6	733	-673
7	941	761
8	309	-270
9	871	789
10	871	870
11	775	701
12	938	891
13	163	-143
14	677	682
15	329	-351
16	261	276
17	424	-406
18	180	-192
19	261	-261
20	289	-352
K= 4, L= 0		
0	1017	-1125
1	859	-917
2	1284	-1242
3	983	-871
4	171	99
5	699	-640
6	823	773
7	522	-469
8	961	886
9	45*	-35
10	941	847
11	374	347
12	121	89
13	272	261
14	258	-265
15	112	138
16	539	-561
17	309	308
18	556	-598
19	135	-147
20	244	-297
K= 5, L= 0		
1	1177	-1155
2	45*	-15
3	45*	-33
4	708	635
5	45*	-31
6	834	689
7	688	591
8	95	-75
9	1042	988
10	45*	-28
11	511	462
12	272	-213
13	45*	-77
14	140	-134
15	309	-336
16	45*	-38
17	477	-514
18	45*	-25
19	390	-436
K= 6, L= 0		
0	640	-669
1	469	426
2	154	-124
3	1680	1699
4	219	196
5	1191	1100
6	45*	-9
7	525	481
8	104	83
9	222	188
10	340	336
11	697	-680
12	216	184
13	865	-851
14	121	-125
15	609	-571
16	169	-192
17	95	-69
18	152	-180
19	239	295
K= 7, L= 0		
1	601	589
2	890	951
3	98	101
4	1236	1206
5	284	-245
6	1545	1368
7	219	-191
8	455	447
9	320	-286
10	264	-192
11	368	-389
12	921	-785
13	121	-111
14	756	-699
15	275	260
16	140	-140
17	278	281
18	166	170
K= 8, L= 0		
0	45*	9
1	101	105
2	581	656
3	371	383
4	45*	-10
5	376	375
6	663	-715
7	183	212
8	649	-595
9	250	-181
10	660	-627
11	284	-251
12	129	-144
13	132	-118
14	185	219
15	112	-93
16	489	533
K= 9, L= 0		
1	472	476
2	45*	-64
3	340	367
4	483	-526
5	371	-365
6	329	-360
7	570	-647
8	45*	-53
9	654	-657
10	213	208
11	427	-426
12	45*	124
13	45*	142
14	256	280
15	286	374
16	157	176
K= 10, L= 0		
0	329	342
1	256	-235
2	329	351
3	753	-791
4	219	-235
5	756	-811
6	286	-320
7	323	-327
8	424	-437
9	45*	27
10	458	-514
11	354	368
12	45*	-13
13	421	443
14	45*	122
15	239	306
K= 11, L= 0		
1	45*	58
2	351	-362
3	45*	98
4	719	-885
5	45*	-40
6	626	-628
7	45*	58
8	343	-342
9	45*	-37
10	267	268
11	163	-173
12	477	552
13	45*	37
14	275	368
K= 12, L= 0		
0	595	-667
1	166	-157
2	250	-281
3	430	-501
4	140	-175
5	360	-356
6	199	254
7	118	-162
8	517	602
9	45*	-80
10	272	354
11	166	189
12	185	235
K= 13, L= 0		
1	688	-708
2	45*	101
3	312	-335
4	45*	11
5	264	258
6	45*	64
7	441	572
8	45*	3
9	531	635
K= 14, L= 0		
0	455	-508
1	216	241
2	295	-335
3	348	347
4	45*	-111
5	435	432
6	270	314
K= 0, L= 1		
1	1295	1555
3	966	800
5	242	-222
7	506	-601
9	888	-1049
11	829	-714
13	430	-456
15	256*	86
17	767	746
19	584	611
-1	1152	1422
-3	621	-739
-5	910	-909
-7	115	-138
-9	475	-536
-11	191	-199
-13	149	112
-15	800	759
-17	480	547
-19	79*	31
K= 1, L= 1		
0	1435	1011
1	79*	-20
2	1031	754
3	1208	-1018
4	1034	975
5	820	-801
6	792	715
7	573	-545
8	416	-411
9	337	-328
10	593	-603
11	79*	42
12	275	-207
13	402	447
14	79*	-13
15	480	545
16	79*	141
17	362	280
18	663	616
19	270	-184
20	233	239
-1	1441	1391
-2	124	-209
-3	1348	1475
-4	101	-80
-5	1067	1103
-6	893	-1068
-7	228	-240
-8	758	-1038
-9	360	-377
-10	413	-423
-11	475	-529
-12	79*	126
-13	607	-790
-14	489	521
-15	79*	-85
-16	247	269
-17	225	262
-18	258	267
-19	365	356
-20	79*	-8
K= 2, L= 1		
0	826	893
1	343	279
2	216	-88
3	256	232
4	604	-600
5	177	226
6	1913	-1620
7	843	782
8	913	-886
9	461	-430
10	374	314
11	79*	-69
12	514	486
13	309	289
14	548	545
15	79*	-142
16	570	532
17	79*	8
18	79*	188
19	79*	-36
20	295	-277
-1	79*	93
-2	980	1537
-3	79*	4
-4	230	447
-5	348	-412
-6	289	441
-7	197	-160
-8	320	-368
-9	211	-145
-10	972	-1235
-11	79*	122
-12	772	-977
-13	211	156
-14	427	-465
-15	239	181
-16	270	245
-17	79*	88
-18	618	564
-19	79*	-32
-20	708	692
K= 3, L= 1		
0	278	304
1	851	-790
2	79*	-95
3	506	381
4	143	54
5	169	-23
6	79*	-20
7	1174	-1133
8	447	446
9	312	-328
10	882	872
11	270	221
12	396	371
13	624	627
14	79*	30
15	362	393
16	244	-237
17	348	314
18	312	-272
19	79*	-66
20	267	-306
-1	1121	1472
-2	79*	-85
-3	576	839
-4	270	327
-5	343	416
-6	331	362
-7	272	-292
-8	236	230
-9	764	-964
-10	79*	107
-11	570	-680
-12	320	-334
-13	581	-638
-14	480	-465
-15	79*	-30
-16	379	-372
-17	286	246
-18	298	-243
-19	517	455
-20	79*	-74
K= 4, L= 1		
0	152	-126
1	868	-940
2	590	-545
3	812	-743
4	719	-594
5	815	-710
6	340	-224
7	447	350
8	79*	49
9	809	768
10	511	414
11	680	642
12	79*	154
13	295	252
14	239	254
15	79*	-102
16	548	484
17	360	-324
18	79*	172
19	463	-524
-1	331	-445
-2	475	-505
-3	514	624
-4	452	-492
-5	865	1084
-6	146	-151
-7	879	1068
-8	354	-336
-9	463	482
-10	79*	-46
-11	79*	72
-12	79*	-76
-13	587	-582
-14	222	-197
-15	820	-734
-16	228	128
-17	615	-565
-18	79*	-66
-19	362	-289
K= 5, L= 1		
0	1138	-1275
1	756	-815
2	857	-917
3	264	240
4	947	-875
5	750	627
6	79*	52
7	315	242
8	761	689
9	385	324
10	553	467
11	216	-106
12	587	560
13	81*	-18
14	222	208
15	261	-215
16	354	-375
17	79*	-29
18	514	-534
19	79*	35
-1	143	117
-2	402	-489
-3	1039	-1093
-4	579	652
-5	416	-462
-6	868	915
-7	79*	37
-8	1031	1028
-9	345	269
-10	475	437
-11	570	581
-12	219	-187
-13	79*	-57
-14	697	-596
-15	79*	39
-16	685	-592
-17	264	-163
-18	348	-280
-19	396	-331
K= 6, L= 1		
0	739	-776
1	795	-836
2	79*	-42
3	385	-299
4	980	1001
5	385	-326
6	744	763
7	79*	-37
8	463	379
9	480	360
10	216	155
11	312	252
12	449	-405
13	79*	-1
14	649	-590
15	79*	-87
16	433	-430
17	219	-190
18	79*	2
19	79*	-161
-1	525	-602
-2	837	-1002
-3	169	178
-4	1042	-1227
-5	253	232
-6	228	-192
-7	256	218
-8	79*	21
-9	326	316
-10	286	217
-11	444	373
-12	831	804
-13	79*	-117
-14	404	345
-15	472	-365
-16	79*	-16
-17	79*	-116
-18	503	-376
-19	79*	19
K= 7, L= 1		
0	219	184
1	183	-81
2	365	350
3	427	427
4	79*	0
5	480	711
6	494	-418
7	770	670
8	303	-259
9	469	392
10	413	-363
11	390	-388
12	477	-474
14	79*	-83
15	643	-686
17	256	-253
18	79*	120
-1	239	-202
-2	222	196
-3	907	-1052
-4	351	-337
-5	199	-179
-6	744	-216
-7	79*	-94
-8	79*	-147
-9	309	224
-10	227	-180
-11	952	863
-12	79*	60
-13	466	355
-14	337	231
-15	79*	115
-16	570	459
-17	345	-251
-18	219	177
K= 8, L= 1		
0	225	-218
1	691	841
2	79*	-181
3	809	906
4	79*	42
5	211	191
6	472	451
7	404	-371
8	222	207
9	632	-642
10	79*	-61
11	565	-599
12	264	-152
13	233	-247
14	79*	-86
15	79*	103
16	208	-195
17	286	336
-1	261	258
-2	458	-506
-3	79*	-74
-4	360	-337
-5	635	-647
-6	79*	100
-7	809	-827
-8	261	201
-9	725	-687
-10	511	400
-11	239	-163
-12	463	394
-13	671	536
-14	79*	4
-15	716	595
-16	79*	31
-17	562	531
K= 9, L= 1		
0	565	536
1	213	-16
2	609	643
3	230	-47
4	382	387
5	270	-228
6	79*	-7
7	275	-184
8	449	-430
9	222	67
10	733	-703
11	79*	-11
12	427	-439
13	185	196
14	79*	-100
15	79*	96
16	261	283
-1	326	311
-2	430	452
-3	79*	-87
-4	579	-601
-5	219	180
-6	888	-861
-7	239	251
-8	727	-604
-9	222	-161
-10	233	-210
-11	211	-77
-12	567	403
-13	79*	-46
-14	640	528
-15	79*	-54
-16	635	577
K= 10, L= 1		
0	362	339
1	348	282
2	79*	-49
3	416	360
4	340	-392
5	295	241
6	390	-422
7	374	-389
8	354	-381
9	281	-272
10	79*	-39
11	191	-250
12	250	298
13	160	-196
14	388	435
15	138	149
-1	275	281
-2	570	563
-3	79*	-96
-4	551	541
-5	317	-313
-6	79*	83
-7	295	-279
-8	497	-365
-9	368	-247
-10	618	-484
-11	247	-133
-12	385	-344
-13	284	215
-14	348	-277
-15	337	291
K= 11, L= 1		
0	239	-187
1	376	314
2	222	-199
3	312	-301
4	270	-223
5	652	-692
6	213	-151
7	542	-559
8	79*	-88
9	267	-223
10	79*	-57
11	79*	143
12	79*	12
13	382	468
-1	413	469
-2	79*	90
-3	716	637
-4	79*	28
-5	677	590
-6	368	319
-7	191	-12
-8	348	253
-9	562	-463
-10	79*	-58
-11	761	-648
-12	79*	11
-13	559	-487
-14	79*	-27
K= 12, L= 1		
0	317	317
1	584	-525
2	208	-96
3	615	-621
4	461	-382
5	79*	-89
6	407	-429
7	183	172
8	278	-286
9	365	395
10	79*	-41
11	312	349
12	143	186
-1	275	-255
-2	671	649
-3	79*	-84
-4	528	458
-5	258	239
-6	79*	128
-7	517	479
-8	79*	52
-9	506	450
-10	385	-294
-11	79*	23
-12	416	-429
K= 13, L= 1		
0	677	-643
1	79*	27
2	666	-667
3	79*	54
4	258	-214
5	79*	27
6	79*	67
7	79*	-21
8	244	303
-1	79*	-3
-2	256	-188
-3	264	218
-4	275	171
-5	202	37
-6	584	514
-7	79*	22
-8	531	474
-9	79*	57
K= 14, L= 1		
0	211	-192
1	298	-302
2	256	238
3	368	-382
4	326	367
5	79*	3
6	270	334
-1	199	-137
-2	413	-366
-3	79*	12
-4	202	-184
-5	323	318
-6	79*	-132
K= 0, L= 2		
0	1368	1332
2	385	407
4	677	721
6	247	218
8	511	-501
10	312	-313
12	539	-515
14	146	140
16	199	225
18	573	627
20	486	588
-2	747	-565
-4	618	-633
-6	1073	-1166
-8	758	-751
-10	306	-268
-12	242*	63
-14	798	783
-16	326	324
-18	213*	-11
-20	256	-290
K= 0, L= 3		
1	654	-536
3	1910	1900
5	972	1154
7	579	632
9	177	216
11	744	-788
13	772	-716
15	601	-597
17	208*	-20
19	345	390
-1	357	-298
-3	961	-905
-5	2166	-2094
-7	913	-805
-9	315	338
-11	683	803
-13	758	812
-15	567	605
-17	219*	-42
-19	301	-339
K= 0, L= 4		
0	868	-741
2	124	-119
4	494	463
6	477	534
8	362	428
10	146	169
12	581	-550
14	416	-353
16	438	-487
18	143	-137
-2	1008	-878
-4	1022	-645
-6	986	-863
-8	368	414
-10	803	888
-12	719	666
-14	323	326
-16	247	-183
-18	199	-184
K= 0, L= 5		
1	913	-845
3	253	238
5	556	516
7	539	487
9	362	369
11	202	-189
13	298	-242
15	503	-564
17	295	-443
-1	601	-569
-3	753	-727
-5	390	-407
-7	404	310
-9	823	901
-11	767	945
-13	292	303
-15	124	-93
-17	362	-351
K= 0, L= 6		
0	938	-848
2	823	-788
4	388	-367
6	694	686
8	677	668
10	528	534
12	115	151
14	219	-198
-2	1118	-943
-4	256*	-32
-6	374	330
-8	688	704
-10	834	915
-12	404	398
-14	180	-231
K= 0, L= 7		
1	438	-422
3	536	-475
5	236*	90
7	379	441
9	472	563
11	354	409
-1	188	-105
-3	244	-205
-5	477	448
-7	522	514
-9	480	540
-11	278	283
-13	261	-299
K= 0, L= 8		
0	199	-157
2	337	-285
4	393	-401
6	163*	-39
8	247	178
-2	199*	-42
-4	382	402
-6	385	486
-8	331	375
-10	112	139

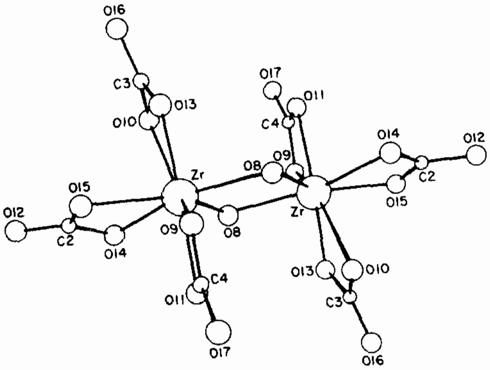

Figure 1. The di-μ-hydroxo-di[triscarbonatozirconate(IV)] ion. The two halves of the ion are related by a center of symmetry.

by the four atoms comprising each of the carbonate groups. The angle formed by the carbon atom and the two oxygen atoms which are bonded to the metal is, in each case, the smallest angle.

The interatomic distances within the dinuclear complex are given in Table IV. The coordination polyhedron about each zirconium atom. is a distorted dodecahedron. This is shown by the following criteria: a dodecahedron consists of two mutually perpendicular trapezoids, whose line of intersection contains the central metal atom and coincides with the $\bar{4}$ axis. Lippard and Russ have calculated this angle for many of the structures reported to have dodecahedral coordination and found that it ranges from 86.1 to close to 90°.[9] In the present structure the angle is 88.7°.

Table II. Bond Distances and Angles in the Carbonate Group

Bond	dist. (Å)	Angle	deg.
C_2—O_{12}	1.29(3)	O_{12}—C_2—O_{14}	117.2(2.3)
C_2—O_{14}	1.35(3)	O_{12}—C_2—O_{15}	125.6(2.5)
C_2—O_{15}	1.23(4)	O_{14}—C_2—O_{15}	116.8(2.3)
C_3—O_{10}	1.30(3)	O_{10}—C_3—O_{16}	125.1(2.5)
C_3—O_{16}	1.23(3)	O_{10}—C_3—O_{13}	111.5(2.3)
C_3—O_{13}	1.29(4)	O_{16}—C_3—O_{13}	123.4(2.5)
C_4—O_9	1.29(2)	O_9—C_4—O_{11}	113.5(2.0)
C_4—O_{11}	1.37(3)	O_9—C_4—O_{17}	124.6(2.2)
C_4—O_{17}	1.27(4)	O_{11}—C_4—O_{17}	121.5(2.1)

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(9) S. J. Lippard and B. J. Russ, *Inorg. Chem.*, 7, 1686 (1968).

Table III. Least Squares Planes of Carbonate Ions

Carbonate Ion	Equation of Plane	x^2
C_2—O_{12}—O_{14}—O_{15}	0.1901X+0.9704Y—0.1491Z—1.3067 = 0	0.270
C_3—O_{10}—O_{16}—O_{13}	−0.7159X+0.4485Y—0.5351Z—0.4782 = 0	2.86
C_4—O_8—O_{11}—O_{17}	0.3893X+0.9196Y—0.0532Z—1.3164 = 0	2.74

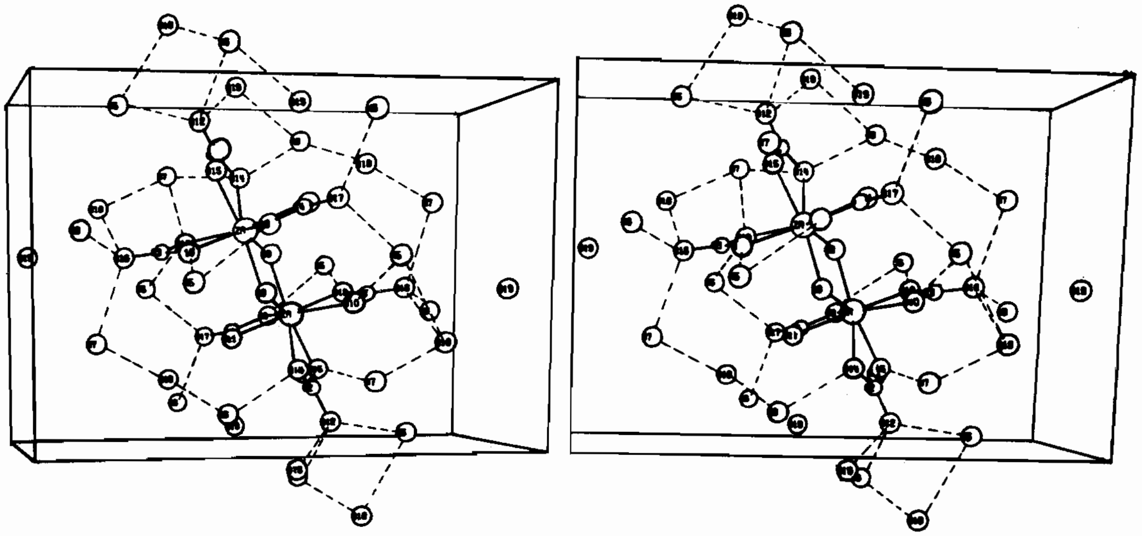

Figure 2. A stereoscopic view of the hydrogen bonding in ammonium di-μ-hydroxo-di[triscarbonatozirconate(IV)]tetrahydrate. The dashed lines represent possible hydrogen bonds out to a distance of 3.00 Å for O—H———O type bonds and 3.35 Å for N—H———O type bonds.

Table IV. Interatomic Distances in the Dinuclear Complex

Atoms	Dist. (Å)
Zr_I—Zr_I'	3.498(2)
Zr—O_8 (H)	2.11(1)
Zr—O_9	2.24(4)
Zr—O_{10}	2.21(2)
Zr—O_{11}	2.18(2)
Zr—O_{14}	2.25(2)
Zr—O_{15}	2.22(2)
Zr—O_{13}	2.22(2)
Avg. (non-OH)	2.22(2)

Oxygen-Oxygen Distances

Type	Atoms	Dist. (Å)
m	O_6—O_8'	2.37(3)
a	O_6—O_{14}	2.75(2)
g	O_6—O_{10}	2.96(2)
g	O_8—O_{11}	2.92(3)
m	O_9—O_{11}	2.23(3)
a	O_9—O_{13}	2.78(3)
g	O_9—O_9'	2.84(3)
g	O_9—O_{15}	2.81(3)
m	O_{10}—O_{13}	2.14(3)
g	O_{10}—O_{14}	2.82(2)
b	O_{10}—O_{15}	2.99(3)
b	O_{10}—O_8'	3.30(2)
g	O_{11}—O_{14}	2.95(3)
b	O_{11}—O_{15}	3.09(2)
b	O_{11}—O_8'	3.13(2)
m	O_{14}—O_{15}	2.20(3)
g	O_{15}—O_{13}	2.75(2)
g	O_{13}—O_8'	2.90(3)

Table V. Interatomic Distances Involving Possible Hydrogen Bonds*

Atoms	Distance
N_5'''—O_{13}	2.78(4)
N_5'''—O_{10}	2.81(2)
N_5—O_{12}	2.81(4)
N_5''—O_{17}	2.90(3)
N_5'''—O_9	3.21(3)
N_5'''—O_{18}	3.32(3)
N_6—O_{17}	2.82(3)
N_6''—O_{16}	2.84(4)
N_6—O_{19}	2.85(3)
N_6'—O_{12}	3.05(4)
N_6''—O_{18}	3.12(4)
N_6—O_{14}	3.13(3)
N_7—O_{15}	2.85(4)
N_7—O_{18}	2.87(3)
N_7—O_9	2.93(3)
N_7'''—O_{16}	2.95(3)
N_7—O_{14}	3.00(3)
N_7—O_{12}	3.15(4)
N_7''—O_{10}	3.32(3)
O_8—O_{17}	2.70(3)
O_{18}—O_{16}	2.91(3)
O_{19}—O_{12}	2.72(3)

* Unprimed atoms are in symmetry position x y z, singly primed in $\bar{x}\,\bar{y}\,\bar{z}$, doubly primed in 1/2+x, 1/2—y, 1/2+z, and triply primed in 1/2—x, 1/2+y, 1/2—z.

Hoard and Silverton have developed sets of shape parameters for the ideal dodecahedron and the square antiprism.[10] In the dodecahedron there are four different types of interatomic distances (exclusive of

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(10) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 2, 235 (1963).

the metal-ligand distances) labelled a, m, g and b. For the most favorable polyhedron, in which ligand-ligand repulsion is minimized, the ratios of these interatomic distances to the zirconium-oxygen bond length should ideally be type a, 1.17; type m, 1.17; type g, 1.24; type b, 1.49. In Table IV the oxygen-oxygen distances are labeled as to their different class of shape parameters. The average distances for the different types in the present complex are: a, 2.76 Å; m, 2.24 Å; g, 2.87 Å; b, 3.13 Å. These distances are compared with the average Zr—O bond length of 2.22 Å. This latter value is the average of the zirconium-carbonate oxygen bond lengths only. The ratios are then calculated to be: a, 1.24; m, 1.01; g, 1.29; b, 1.41. These ratios are in the correct order required for dodecahedral coordination but differ considerably from the ideal values. The distortion primarily arises from the very small intra-carbonato oxygen-oxygen distances and also the close approach of the bridging oxygens to each other.

The interatomic distances reported here are in good agreement with those given for the potassium salt.[4] The dinuclear species has the same structure in both salts. However, the water contents in the two salts are different. The potassium salt contains three moles of water whereas the ammonium salt contains two moles. Pospelova and Zaitsev reported the ammonium salt to contain one and one-half moles of water per formula weight or three moles per dimeric molecule. However, this would require one of the oxygen atoms to be in a special position. No such oxygen was found.

Other interatomic distances of interest are listed in Table V. The coordination about the nitrogens is quite irregular in all three cases. Thus, the ammonium groups must take up positions which reflect the minimum electrostatic repulsion potential. The two water molecule oxygens O_{18} and O_{19} form three and two hydrogen bonds, respectively. The former to two ammonium groups and one carbonate oxygen and the latter to one ammonium ion and one carbonate oxygen. Finally, the bridging hydroxyl oxygen lies 2.70 Å from O_{17} and presumably is hydrogen bonded to it.

Other compounds which contain somewhat similar dinuclear ions to the one reported here include $ZrF_4 . 3H_2O$[11] and a basic thorium nitrate.[12]

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(11) T. N. Waters, *Chem. Ind.*, 713 (1964).
(12) G. Johansson, *Acta Chem. Scand.*, 22, 389 (1968).