ACTA CHEMICA SCANDINAVICA 23 (1969) 2016–2020

The Crystal Structure of γ-$Zn(OH)_2$

A. NØRLUND CHRISTENSEN

Department of Inorganic Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

The crystal structure of γ-$Zn(OH)_2$ was determined from three dimensional Patterson and Fourier functions and was refined to a conventional R-value of 8.8 %. The space group is $Imm2$, with $a = 23.07$ Å, $b = 8.04$ Å, $c = 3.30$ Å, and the cell contains 12 formula units. Zinc atoms are tetrahedrally coordinated with oxygen atoms and the structure is hydrogen bonded.

Zinc hydroxide is polymorphic.[1] The crystal structure of the stable modification of zinc hydroxide, ε-$Zn(OH)_2$, was reported by Schnering.[2] Giovanoli, Oswald and Feitknecht[3] investigated the unstable modifications β-, δ-, and γ-$Zn(OH)_2$ using Debye-Scherrer technique and electron diffraction, and reported the unit cell dimensions of the compounds. The crystal structure of the unstable modifications have not been reported in the literature. A three-dimensional single crystal X-ray analysis of γ-$Zn(OH)_2$ was undertaken in order to compare the structure with that of ε-$Zn(OH)_2$.

EXPERIMENTAL

Chemistry. Zinc hydroxide was precipitated from a 0.1 M solution of zinc sulphate with a 4 M solution of ammonia. The hydroxide was washed with water and was dissolved in concentrated ammonia. This solution was slowly evaporated in a desiccator with concentrated sulfuric acid. Within a few days crystals of γ-$Zn(OH)_2$ were formed. Zinc was determined by EDTA titration. (Found: Zn 64.3. Calc. for $Zn(OH)_2$: Zn 65.8).

Physical measurements. Differential thermal analysis of γ-$Zn(OH)_2$ was obtained on a Du Pont 900 Differential Thermal Analyzer, with a heating rate of 10°C/min. Fig. 1 shows the diagram obtained. The infra-red spectrum was obtained over the frequency range 400–4000 cm^{-1} with a Perkin-Elmer Model 521 spectrophotometer using the pellet technique with a mixture of 4 mg of sample and 200 mg of CsI. The infra-red spectrum had a broad band from 3000 to 3600 cm^{-1}.

X-Ray technique. A crystal of dimensions $0.03 \times 0.1 \times 0.3$ mm^3 was investigated by Weissenberg and precession methods using Mo$K\alpha$-radiation, $\lambda = 0.7107$ Å. Weissenberg photographs were taken of $hk0$, $hk1$, and $hk2$, and precession photographs were taken of $h0l$, $h1l$, and $0kl$. The photographs showed reflections with streaks and satellite spots indicating that the sample was not a single crystal. Integrated Weissenberg photographs were taken of $hk0$, $hk1$, $hk2$, using multiple film technique and integrated precession photographs were taken of $h0l$; Zr-filtered Mo$K\alpha$-radiation was used. 226 independent

intensities were measured photometrically. The usual Lorentz-polarisation corrections were applied, but no absorption correction was made. 330 independent reflections were measured on the same sample using a single crystal diffractometer with a scintillation counter and monochromatic Mo$K\alpha$-radiation. The two sets of data were treated separately.

STRUCTURE DETERMINATION

Conditions limiting possible reflections hkl were $h+k+l=2n$. Possible space groups are $I222$, $Imm2$, or $Immm$. A three-dimensional Patterson function $P(u,v,w)$ gave a solution with a zinc atom in a general position (0.088, 0.225, 0) and an other zinc atom in a special position (0.225, 0, 0). Based on this a three-dimensional Fourier map gave oxygen atoms in the general positions (0.175, 0.223, 0), (0.0625, 0.330, 0.5) and oxygen atoms in the special positions (0.230, 0, 0.5) and (0.055, 0, 0) in space group $I222$. In the refinement of the structure a program written by Danielsen [4] was used. The refinement gave R-values of 7.94 %, 7.67 %, and 8.24 % at the end of isotropic refinement in the space groups $I222$, $Imm2$, and $Immm$, and isotropic refinement of the diffractometer data gave the R-values 9.04 %, 8.76 %, and 9.37 %, respectively. The number of parameters refined in the three space groups were 19, 22, and 16, respectively. Only the refinement of the two sets of data in the space group $Imm2$ gave meaningful isotropic temperature factors to all the atoms. A final difference Fourier map did not give the positions of the hydrogen atoms.

Table 1. Atomic coordinates and temperature factors with standard deviations. Film data, 226 reflections, $R=7.7$ %.

Atom	x	y	z	B (Å^2)
O_1	0.1724(9)	0.199(3)	−0.047(8)	0.4(4)
O_2	0.0629(10)	0.332(3)	0.527(12)	1.1(4)
O_3	0.2653(13)	0	0.526(13)	0.4(5)
O_4	0.0599(17)	0	−0.067(15)	0.8(7)
Zn_1	0.0886(2)	0.2224(5)	0.018(2)	0.65(5)
Zn_2	0.2189(3)	0	0.035(2)	0.67(7)

Diffractometer data, 330 reflections, $R=8.8$ %.

Atom	x	y	z	B (Å^2)
O_1	0.1732(7)	0.200(2)	−0.048(5)	1.3(3)
O_2	0.0615(7)	0.329(2)	0.512(5)	1.0(3)
O_3	0.2653(9)	0	0.544(7)	0.7(3)
O_4	0.0584(12)	0	−0.049(9)	2.0(5)
Zn_1	0.0887(1)	0.2226(4)	0.0381(8)	0.90(4)
Zn_2	0.2188(2)	0	0.010(1)	0.85(6)

CRYSTAL DATA

The compound γ-$Zn(OH)_2$ has 12 formula units in the unit cell. Crystal system: orthorhombic, $a=23.07$ Å, $b=8.04$ Å, $c=3.30$ Å. Systematic absences: $hkl:h+k+l=2n+1$. Space group: $Imm2$. Density calculated for 12 formula units in the cell is 3.24 g/cm^3. Density reported in Ref. 3 is 3.234 g/cm^3. The absorption coefficient for Mo-radiation is 119 cm^{-1}, ($\lambda=0.7107$ Å). The structure factors were calculated using the atomic scattering factors from Vol. III of *International Tables of X-ray Crystallography*, approximated by Bassi polynomials.[5] Atomic coordinates and temperature factors are given in Table 1 and interatomic distances and bond angles in Table 2. A list of observed and calculated structure factors is given in Table 3.

Table 2. Interatomic distances (Å) and bond angles (degrees) with standard deviations, calculated from the diffractometer data.

Zn_1-O_1	1.98(2)	Zn_2-O_1	1.93(2)
Zn_1-O_2	1.89(3)	Zn_2-O_3	2.07(4)
Zn_1-O_2'	2.03(3)	Zn_2-O_3'	1.88(4)
Zn_1-O_4	1.94(1)		
$O_1-Zn_1-O_2$	119.2 (0.9)	$O_1-Zn_2-O_3$	111.7 (0.8)
$O_1-Zn_1-O_2'$	102.7 (0.9)	$O_1-Zn_2-O_1'$	112.8 (0.9)
$O_1-Zn_1-O_4$	104.5 (0.9)	$O_1-Zn_2-O_3'$	103.4 (0.8)
$O_2-Zn_1-O_2'$	114.4 (1.3)	$O_3-Zn_2-O_3'$	113.4 (0.9)
$O_2-Zn_1-O_4$	114.8 (1.3)		
$O_2'-Zn_1-O_4$	98.6 (1.5)		

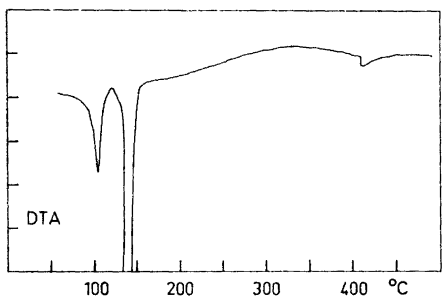

Fig. 1. DTA diagram of γ-$Zn(OH)_2$.

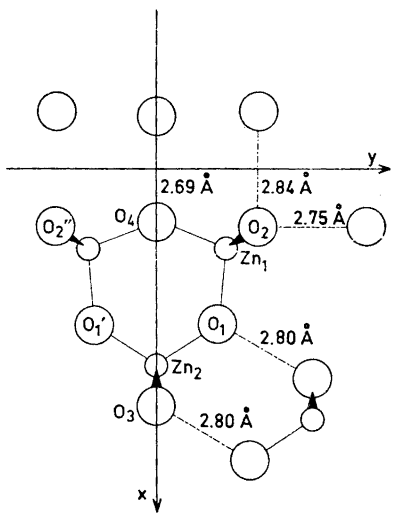

Fig. 2. Projection of ZnO_4 tetrahedra along[001]. O—O distances interpreted as hydrogen bonds are given in Å.

Table 3. Observed and calculated structure factors ($\times 10$). Diffractometer data.

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
0	2	0	1042	1146	23	7	0	411	260	17	6	1	428	369	17	5	2	773	725
0	4	0	2320	2525	24	0	0	593	454	18	1	1	605	545	17	7	2	618	435
0	6	0	462	493	24	2	0	634	640	18	3	1	838	749	18	2	2	1110	1069
0	8	0	529	593	24	4	0	472	386	18	7	1	837	867	18	6	2	742	721
0	10	0	480	604	24	6	0	486	376	19	0	1	495	310	19	3	2	569	555
1	1	0	579	637	25	1	0	575	436	19	2	1	741	727	19	7	2	472	436
1	5	0	1042	1195	25	3	0	665	616	20	1	1	458	322	21	3	2	603	600
1	7	0	822	836	25	7	0	538	388	20	3	1	457	280	21	7	2	618	568
1	9	0	943	914	26	0	0	713	613	20	5	1	362	259	22	0	2	964	884
1	11	0	458	428	27	3	0	520	535	21	2	1	766	855	22	2	2	545	484
2	2	0	1816	1905	28	0	0	600	489	21	6	1	532	457	22	4	2	699	688
2	4	0	416	432	28	2	0	710	761	22	1	1	385	257	23	1	2	605	584
2	6	0	782	825	29	5	0	558	492	22	5	1	758	628	23	5	2	904	863
2	8	0	782	825	30	0	0	668	490	22	7	1	650	488	24	2	2	568	475
3	1	0	749	740	30	4	0	441	450	23	0	1	1480	1446	25	3	2	669	496
3	5	0	663	769	0	1	1	1373	1710	23	2	1	539	583	26	0	2	456	450
4	0	0	470	472	0	3	1	649	663	23	4	1	905	865	28	2	2	652	650
4	2	0	2410	2318	0	5	1	2046	2106	25	2	1	612	548	29	1	2	458	254
4	6	0	931	958	0	7	1	608	550	25	4	1	379	288	0	3	3	267	292
5	1	0	517	553	0	9	1	1058	1029	26	1	1	416	342	0	5	3	977	1054
5	3	0	1120	1110	1	0	1	1700	1918	26	3	1	532	461	1	2	3	513	655
5	7	0	1275	1272	1	2	1	975	1076	27	2	1	792	737	1	4	3	496	724
5	9	0	506	457	1	4	1	1378	1471	28	3	1	566	534	1	6	3	411	345
5	11	0	660	738	1	6	1	581	493	29	0	1	844	685	2	1	3	249	296
6	0	0	2856	2734	2	1	1	280	305	29	4	1	637	514	2	3	3	560	644
6	2	0	873	920	2	3	1	956	997	31	2	1	387	144	2	7	3	429	473
6	4	0	1532	1579	2	7	1	659	683	0	2	2	673	736	3	0	3	520	533
6	8	0	403	481	2	11	1	509	387	0	4	2	1600	1694	4	3	3	472	548
7	1	0	1064	1044	3	0	1	1435	1372	0	8	2	480	478	4	7	3	422	541
7	3	0	736	668	3	4	1	487	576	1	1	2	283	339	5	2	3	1088	1252
7	5	0	1202	1275	4	1	1	245	274	1	5	2	708	802	5	6	3	654	691
7	9	0	1000	1009	4	3	1	1051	1048	1	7	2	525	650	6	3	3	366	483
8	0	0	1560	1377	4	7	1	916	917	1	9	2	690	709	6	5	3	605	709
8	2	0	946	874	5	0	1	516	624	2	2	2	1307	1374	7	0	3	1066	1100
8	4	0	332	272	5	2	1	2217	2140	2	6	2	606	637	7	4	3	811	956
9	1	0	674	723	5	4	1	405	438	2	8	2	415	350	7	8	3	386	444
9	5	0	620	690	5	6	1	1188	1182	3	1	2	437	477	9	0	3	912	898
10	0	0	1110	1106	6	1	1	631	627	3	5	2	470	515	9	4	3	504	563
10	2	0	1017	971	6	3	1	658	584	4	0	2	284	329	10	1	3	248	275
10	4	0	1022	1015	6	5	1	1023	1097	4	2	2	1435	1473	10	5	3	341	533
10	6	0	533	484	6	7	1	581	639	4	6	2	668	717	11	0	3	459	555
11	1	0	321	207	6	9	1	801	721	5	1	2	365	409	11	2	3	1290	1256
11	3	0	1750	1674	7	0	1	2181	2064	5	3	2	874	928	11	4	3	313	284
11	5	0	572	678	7	4	1	1818	1786	5	7	2	960	1015	11	6	3	569	590
11	7	0	1328	1320	7	8	1	635	714	5	9	2	449	400	12	3	3	568	670
12	0	0	1384	1251	7	10	1	512	430	6	0	2	1969	1888	12	7	3	630	709
12	2	0	2271	2128	8	1	1	645	628	6	2	2	850	925	13	0	3	733	743
12	4	0	592	569	8	3	1	453	430	6	4	2	1140	1149	13	4	3	496	588
12	6	0	786	838	8	5	1	639	676	6	8	2	465	340	14	1	3	440	434
13	1	0	438	413	9	0	1	1470	1409	7	1	2	738	730	14	5	3	348	360
13	5	0	786	710	9	2	1	418	409	7	3	2	391	488	15	0	3	558	631
13	7	0	367	306	9	4	1	832	848	7	5	2	922	950	16	1	3	344	426
13	9	0	440	546	9	6	1	453	499	7	9	2	720	801	16	5	3	562	644
14	0	0	871	753	9	8	1	478	461	8	0	2	694	710	17	0	3	846	844
14	2	0	695	718	10	1	1	398	377	8	2	2	594	541	17	2	3	632	729
14	4	0	480	539	10	5	1	702	804	9	1	2	712	628	17	4	3	372	468
14	6	0	445	503	10	7	1	452	497	9	3	2	297	257	18	1	3	307	323
14	8	0	442	389	10	9	1	640	717	9	5	2	603	625	18	3	3	419	472
15	3	0	634	702	11	0	1	1071	1065	10	0	2	928	954	20	3	3	335	237
15	5	0	651	590	11	2	1	2620	2493	10	2	2	708	677	21	2	3	497	572
15	7	0	572	436	11	4	1	465	323	10	4	2	830	797	23	0	3	875	877
16	0	0	1645	1540	11	6	1	955	961	11	3	2	1160	1132	0	2	4	226	366
16	2	0	426	364	11	8	1	382	369	11	5	2	492	485	0	4	4	600	739
16	4	0	1401	1347	12	3	1	1388	1315	11	7	2	921	985	1	5	4	301	338
17	1	0	447	406	12	5	1	474	459	11	9	2	485	361	2	2	4	554	671
17	3	0	470	498	12	7	1	1130	1178	12	0	2	885	818	4	2	4	549	626
17	5	0	848	819	12	9	1	411	365	12	2	2	1542	1460	5	1	4	233	227
17	7	0	501	508	13	0	1	1401	1324	12	4	2	426	445	5	3	4	422	490
17	9	0	541	562	13	4	1	1144	1006	12	6	2	572	650	5	5	4	289	322
18	2	0	1452	1393	13	8	1	475	373	13	1	2	353	327	6	0	4	821	906
18	6	0	884	939	14	1	1	823	745	13	5	2	680	543	6	2	4	380	551
19	3	0	855	765	14	3	1	619	619	13	9	2	535	447	6	4	4	524	568
19	7	0	550	557	14	5	1	549	512	14	0	2	652	604	7	1	4	260	329
20	2	0	477	422	14	7	1	505	477	14	2	2	472	505	7	5	4	478	471
20	6	0	409	360	15	0	1	1261	1225	14	4	2	445	421	9	1	4	378	358
21	1	0	363	403	15	2	1	659	632	14	8	2	413	303	10	0	4	565	506
21	3	0	699	738	15	4	1	569	555	15	3	2	425	433	10	2	4	273	346
21	7	0	698	663	16	1	1	704	646	15	5	2	475	427	10	4	4	357	423
22	0	0	1248	1153	16	5	1	1017	974	16	0	2	1249	1224	11	3	4	590	486
22	2	0	555	631	16	9	1	897	860	16	2	2	333	330	12	0	4	397	381
22	4	0	887	869	17	0	1	1181	1200	16	4	2	1027	1051	12	2	4	668	641
23	1	0	784	750	17	2	1	1209	1146	17	1	2	415	361	16	0	4	631	657
23	5	0	1078	1098	17	4	1	732	647	17	3	2	474	397					

DISCUSSION

The crystal structure is built of fairly regular ZnO_4 tetrahedra (see Table 2 and Fig. 2). Three tetrahedra are sharing corners (O_1, O_1', and O_4) and are forming a ring. The rings are stacked in the [001] direction by corner sharing

of the tetrahedra (O_3, O_2, and O_2'') and are forming a string where the unit repeated is $(Zn(OH)_2)_3$. Each oxygen atom is coordinated with two zinc atoms and one hydrogen atom, and the strings are held together by hydrogen bonds. The average value of the zinc-oxygen bonds is 1.96 Å with a standard deviation of 0.02 Å. These distances are comparable with the bond distances (1.94 to 1.98 Å) found in ε-$Zn(OH)_2$. The isotropic temperature factors of all the atoms had only meaningful values in the space group *Imm*2. Refinement with anisotropic temperature factor parameters yielded for both sets of data in the space groups *I*222, *Imm*2, and *Immm* sets of anisotropic temperature factor parameters, that were not physically meaningful. This is probably caused by the fact that the sample investigated was not a single crystal.

Acknowledgements. I am indebted to Mr. J. Danielsen and Mr. J. Nyborg for the use of some of their ALGOL programs, to Professor S. Brodersen of the Department of Chemical Physics, Aarhus University, for the use of the spectrophotometer, to Professor L. T. Muus of the Department of Physical Chemistry, Aarhus University, for the use of the differential thermal analyzer, and to Professor S. E. Rasmussen for interest in this work. *Statens Almindelige Videnskabsfond* is acknowledged for the diffractometer.

REFERENCES

1. Gmelins Handbuch der anorganischen Chemie, *Zink Ergänzungsband*, System-Nummer 32. Verlag Chemie, Weinheim 1956, p. 826.
2. Schnering, H. G. *Z. anorg. Chem.* **330** (1964) 170.
3. Giovanoli, R., Oswald, H. R. and Feitknecht, W. *J. Microscopie* **4** (1965) 711.
4. Danielsen, J. *Program D45*, Department of Chemistry, University of Aarhus.
5. Bassi, M. G. *Acta Cryst.* **15** (1962) 617.

Received November 25, 1968.