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A neutron-diffraction study of hemimorphite

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Abstract

The hydrogen atoms in hemimorphite, $Zn_4Si_2O_7(OH)_2 \cdot H_2O$, have been located and its crystal structure refined using 415 three-dimensional single-crystal neutron-diffraction data. The mineral is orthorhombic, space group *Imm*2, with $a = 8.367(5)$, $b = 10.730(6)$, $c = 5.115(3)$ Å, and $Z = 2$. The structure consists of three-membered rings of corner-sharing $Zn(OH)O_3$ ($\times 2$) and SiO_4 tetrahedra arranged in compact sheets parallel to (010). Three oxygen atoms in each tetrahedron are bonded to two zinc atoms and one silicon atom, while a fourth oxygen atom forms a bridging bond to an equivalent cation in an adjacent sheet. The water molecules are oriented parallel to (010) inside large cavities between the tetrahedral sheets and are held in place by hydrogen bonds to and from the hydroxyl groups of the Zn—OH—Zn bridging linkages. Mulliken population analyses calculated using constant bond lengths and the observed angles within and between the tetrahedra allow a rationalization of the bond-length variations in the SiO_4 group, but are less successful in the case of $Zn(OH)O_3$. Detailed analysis of observed bond length and calculated overlap-population variations in a variety of tetrahedral oxyanions suggests that the poorer agreement in the case of the Zn tetrahedron is more a function of the larger overall size of the group than of the relative ionic character of the bonds.

Introduction

The crystal structure of hemimorphite has been of interest following the discovery by Zambonini (1908), and later confirmed by Faust (1951), Roy and Mumpton (1956) and Taylor (1962), that the mineral dehydrates in two stages. Crystal-structure analyses by ITO and WEST (1932), BARCLAY and COX (1960) and MCDONALD and CRUICKSHANK (1967) have served to rationalize these dehydration properties by establishing the presence of hydroxyl groups strongly bonded to two zinc atoms, and water molecules located in a series of interconnected cavities parallel to the *c* axis.

The release of water over the temperature range 400–650 °C (FAUST, 1951), without disruption of the structure, represents the loss of the H_2O molecules, whereas the breakdown of the structure to β Zn_2SiO_4 at about 740 °C is a result of the expulsion of the hydroxyl groups (FAUST, 1951; TAYLOR, 1962).

Although the positions of the non-hydrogen atoms in hemimorphite are known with moderate precision (MCDONALD and CRUICKSHANK, 1967), the exact location of the hydroxyl and water oxygen atoms, and of course the protons, remains in some doubt. Indeed, MCDONALD and CRUICKSHANK have suggested that the water molecule may be rather free to move inside the cavity and to form hydrogen bonds to a variety of neighbouring oxygen atoms. Since the channels containing the water (and hydroxyl) are parallel to the polar *c* axis of the cell, a study of the mechanism of dehydration of this mineral is of particular interest. Moreover, TAYLOR (1962) has indicated that the product of complete dehydration of hemimorphite shows a marked preferred orientation with preservation of the repeat distance in the *c*-axis direction. The present neutron-diffraction study was initiated in order to locate the protons associated with the water molecule and hydroxyl group as a preliminary to a detailed x-ray study of the structure as a function of temperature. We also plan to undertake an analysis and comparison of the experimental charge-deformation distribution with theoretical electron-density maps obtained from accurate molecular-orbital theory.

Experimental

The sample selected for data collection was a 31 mg transparent fragment of hemimorphite from Chihuahua, Mexico, displaying well-developed {010} faces, and having approximate dimensions 1.6 × 2.6 × 2.1 mm. The crystal was oriented with the *c* axis parallel to the φ axis of a fully automated Electronics and Alloys four-circle diffractometer at the CP-5 reactor at Argonne National Laboratory. The unit-cell parameters were refined by least-squares methods to give the best fit between calculated and observed angles 2θ, χ and φ (measured[1] at $22 \pm 2\,^{\circ}$C with $\lambda = 1.142(1)$ Å) for 29 automatically centered reflections in the range $2\theta = 33-63\,^{\circ}$. The resulting cell dimensions ($a = 8.367(5)$, $b = 10.730(6)$, $c = 5.115(3)$ Å) and unit cell volume [459.2(4)Å^3] agree well with values reported previously by McDonald and Cruickskank (1967)

Density measurements were made by the volume displacement method (in toluene) using six crystals in the range 21–58 mg and yielded a value of 3.475(10) g cm^{-3}; the calculated density based on the ideal formula $Zn_4Si_2O_7(OH)_2 \cdot H_2O$ and $Z = 2$ is 3.484 g cm^{-3}. Several samples of hemimorphite with weights in the range 158–277mg were held at a temperature of 800 °C for several hours and yielded weight losses between 7.3 and 7.8%, again consistent with the presence of a single H_2O group in the ideal formula (theoretical leight loss = 7.48%).

Intensity data for the structure analysis were collected at $22 \pm 2\,^{\circ}$C using a neutron wavelength 1.142(1) Å produced by diffraction from the (110) plane of a Be monochromator crystal[2]. Each reflection was step-scanned using the $\theta-2\theta$ technique at 2θ intervals of 0.1° over a scan range of width 4.2–6.4° in 2θ. Backgrounds were determined from stationary counts taken at both ends of the scan. A total of 818 reflections of the types hkl and $\bar{h}kl$, consistent with a body-centered lattice, were collected to a maximum $(\sin\theta)/\lambda = 0.72$. Two reflections were measured every 50 regular reflections in order to monitor crystal and instrument stability: their integrated intensities were observed to have a maximum random variation of 2.1%. The intensity of each reflection was corrected for background, Lorentz, polarization and absorption effects using a μ value of 0.913 cm^{-1} (the corresponding transmission factors ranged from 0.83 to 0.88). All data were placed on an absolute scale by calibration with a well-characterized NaCl crystal using a method described by Petersen *et al.* (1974). Multiply measured and symmetry-equivalent reflections (consistent with point group *mm*2) were averaged (using weights based on counting statistics) to yield a set of 433 unique structure factors, each with a standard deviation estimated from the equation $\sigma = [\sigma_I^2 + 0.03I^2]^{0.5}/2I^{0.5}$, where I is the corrected raw intensity and σ_I is derived from counting and averaging statistics. The "agreement factor" between

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[1] Parenthesized figures here, and elsewhere in the text, represent the e.s.d. in terms of the least significant figure quoted.

[2] Further details are given by Roziere and Williams (1976).

Table 1. *Observed (F_o) and calculated (F_c)*

K	FO	FC	AC	BC
H= 0 L= 0				
2	573	578	-578	0
4	99	141	-141	0
6	1011	979	979	0
8	177	161	-161	0
10	6	41	41	0
12	349	369	369	0
14	439	449	449	0
H= 1 L= 0				
1	530	505	505	0
3	565	532	-532	0
5	472	495	495	0
7	247	242	242	0
9	89	115	-115	0
11	97	60	60	0
13	277	261	261	0
15	60	40	40	0
H= 2 L= 0				
0	226	213	-213	0
2	137	136	136	0
4	102	127	-127	0
6	123	101	-101	0
8	103	136	136	0
10	190	168	-168	0
12	32	20	-20	0
14	46	27	-27	0
H= 3 L= 0				
1	67	41	41	0
3	420	426	426	0
5	281	276	-276	0
7	596	584	584	0
9	43	27	27	0
11	141	138	138	0
13	313	314	314	0
H= 4 L= 0				
0	660	670	670	0
2	372	376	376	0
4	134	151	-151	0
6	773	758	758	0
8	302	315	315	0
10	336	320	-320	0
12	645	641	641	0
14	77	77	77	0
H= 5 L= 0				
1	177	167	167	0
3	1207	1147	-1147	0
5	114	125	125	0
7	224	220	220	0
9	691	689	-689	0
11	57	42	-42	0
13	235	227	227	0
H= 6 L= 0				
0	1139	1120	1120	0
2	195	206	-206	0
4	174	172	172	0
6	642	625	625	0
8	89	72	-72	0
10	246	244	244	0
12	83	75	75	0
H= 7 L= 0				
1	233	236	236	0
3	38	8	8	0
5	411	412	412	0
7	27	50	-50	0
9	454	459	459	0
11	79	72	72	0
H= 8 L= 0				
0	63	44	-44	0
2	56	41	-41	0
4	141	147	-147	0
6	105	100	-100	0
8	66	57	57	0
10	204	210	-210	0
H= 9 L= 0				
1	259	250	250	0
3	202	197	-197	0
5	109	105	-105	0
7	691	675	675	0
9	397	407	-407	0
H= 10 L= 0				
0	597	608	608	0
2	170	177	177	0
4	297	299	-299	0
6	768	761	761	0
8	203	197	197	0
H= 11 L= 0				
1	118	123	123	0
3	358	355	-355	0
5	48	72	72	0
H= 12 L= 0				
0	238	238	238	0
H= 0 L= 1				
1	141	142	137	-38
3	133	103	-103	-8
5	291	289	-24	-288
7	543	547	465	287
9	598	607	-448	-410
11	272	262	260	33
13	365	348	334	95
15	509	536	-430	-319
H= 1 L= 1				
0	219	215	-209	-47
2	31	16	-10	-12
4	242	268	-143	-227
6	148	148	-49	139
8	180	174	-171	-31
10	308	301	-199	-226
12	251	263	121	230
14	388	388	-340	-187
H= 2 L= 1				
1	562	560	-553	88
3	378	374	27	-373
5	301	294	-244	163
7	745	736	-727	-113
9	215	217	109	-188
11	119	123	-123	1
13	569	578	-572	-85
15	101	102	16	-101
H= 3 L= 1				
0	432	432	32	431
2	492	490	59	-486
4	566	542	540	-49
6	243	246	-211	127
8	357	355	-98	-341
10	589	601	591	109
12	369	366	-334	-150
14	44	58	45	37
H= 4 L= 1				
1	179	188	-31	186
3	454	450	-331	-305
5	368	374	191	322
7	206	213	-200	-72
9	58	84	-83	-13
11	96	89	73	50
13	52	41	-38	16
H= 5 L= 1				
0	41	47	43	-19
2	350	349	-319	-141
4	460	464	-400	-236
6	61	64	63	11
8	405	398	-373	-138
10	550	545	-475	-267
12	170	169	151	74
H= 6 L= 1				
1	174	184	-166	-79
3	152	161	153	-51
5	320	312	-189	-249
7	285	281	109	259
9	370	366	-161	-329
11	166	162	157	40
13	114	119	36	114
H= 7 L= 1				
0	498	500	-498	49
2	451	455	424	163
4	343	337	311	-129
6	370	364	-294	215
8	119	112	106	36
10	311	307	245	-185
12	281	287	-50	282
H= 8 L= 1				
1	440	450	-448	-48
3	364	368	-20	-368
5	248	250	-250	3
7	505	511	-505	-77
9	260	262	-18	-261
11	73	85	-81	26
H= 9 L= 1				
0	498	506	323	389
2	388	397	-262	-298
4	43	17	17	-3
6	211	217	145	162
8	369	367	-274	-244
H= 10 L= 1				
1	252	239	201	129
3	436	435	-329	-284
5	436	433	348	258
7	115	109	3	-109
H= 11 L= 1				
0	209	215	-202	73
2	174	174	-105	-138
4	102	109	-6	-109
H= 0 L= 2				
0	975	1047	804	670
2	468	503	323	-385
4	210	192	31	189
6	771	761	703	290
8	395	398	359	-172
10	404	415	-147	388
12	479	479	473	-75
14	414	421	309	287
H= 1 L= 2				
1	342	347	-119	326
3	293	294	-245	-162
5	474	483	-216	432
7	105	93	93	5
9	157	161	-118	109
11	216	215	-182	115
13	138	127	105	72
H= 2 L= 2				
0	369	351	-348	-46
2	187	194	183	64
4	227	223	154	-162
6	432	436	-423	107
8	173	164	147	71
10	221	223	102	-198
12	498	496	-440	229
14	147	144	127	-67
H= 3 L= 2				
1	92	93	18	91
3	542	552	469	291
5	212	204	33	-201
7	556	559	23	559
9	606	599	572	-181
11	179	185	-39	181
13	314	318	36	316
H= 4 L= 2				
0	312	317	296	113
2	369	372	8	372
4	55	79	-79	-2
6	348	356	165	315
8	257	264	131	230
10	180	173	-142	-100
12	405	407	21	407
H= 5 L= 2				
1	45	66	66	5
3	652	631	-522	-355
5	149	143	-95	106
7	249	243	229	-81
9	372	389	-366	-131
11	201	199	-191	58
13	232	240	233	-57
H= 6 L= 2				
0	731	744	190	719
2	325	315	243	-201
4	260	257	72	247
6	369	372	172	330
8	285	288	260	-125
10	344	345	-11	345
12	127	119	101	-64
H= 7 L= 2				
1	296	297	-149	257
3	463	475	430	-202
5	472	465	-185	427
7	37	62	-51	-35
9	435	430	386	190
11	138	132	-92	95
H= 8 L= 2				
0	272	279	-272	59
2	128	119	117	-22
4	103	91	45	-79
6	287	295	-291	48
8	137	141	138	32
10	142	143	21	-142
H= 9 L= 2				
1	145	142	133	51
3	262	266	-196	180
5	165	165	22	-163
7	426	423	187	379
9	159	164	-51	-156
H= 10 L= 2				
0	489	485	485	-9
2	264	263	-20	262
4	121	119	-89	-79
6	425	437	376	222
H= 11 L= 2				
1	98	103	-24	100
3	124	131	-22	-129
H= 0 L= 3				
1	223	236	219	-88
3	423	429	-250	348
5	556	578	534	-223
7	193	198	-115	162
9	173	190	189	24
11	205	210	210	3
13	144	140	126	61
H= 1 L= 3				
0	413	400	12	-400
2	63	52	-48	19
4	292	282	252	-127
6	296	321	-176	-269
8	150	153	-149	-37
10	282	283	226	-171
12	241	243	-216	-110
H= 2 L= 3				
1	680	663	-603	-277
3	633	658	630	-190
5	514	494	-461	-177
7	575	556	-434	-348
9	351	358	352	-68
11	221	209	-73	-196
13	453	447	-369	-252
H= 3 L= 3				
0	778	778	-757	178
2	828	813	811	-55
4	543	519	472	217
6	394	405	-404	-27
8	433	430	426	-56
10	373	369	275	245
12	211	206	12	-206
H= 4 L= 3				

averaged reflections was 0.021. Of these data only those 415 observations with $I > 2\sigma_I$ were included in the subsequent least-squares refinement.

structure factors (× 100) for hemimorphite

K	FO	FC	AC	BC
1	288	294	-246	-160
3	239	240	219	-98
5	285	287	-286	-33
7	278	278	44	-275
9	106	121	-96	74
11	156	138	76	-115
13	148	147	-11	-147
H= 5 L= 3				
0	400	405	164	-370
2	142	142	-129	-58
4	125	132	-15	-131
6	327	331	107	-314
8	234	219	-200	-90
10	176	186	-12	-185
12	183	191	49	-185
H= 6 L= 3				
1	154	157	-34	-154
3	237	241	59	234
5	403	391	291	-261
7	389	401	-393	80
9	352	336	335	-24
11	133	119	105	-56
H= 7 L= 3				
0	455	448	-356	-272
2	196	200	140	143
4	580	581	580	-34
6	540	525	-508	-130
8	46	75	38	65
10	601	605	600	-82
H= 8 L= 3				
1	405	407	-362	-187
3	503	510	504	-83
5	274	285	-251	-135
7	417	413	-353	-215
9	347	348	343	-57
H= 9 L= 3				
0	343	344	-344	-4
2	304	287	242	-153
4	77	62	-24	52
6	170	160	-98	-126
8	190	192	127	-144
H= 10 L= 3				
1	31	51	38	-34
3	178	173	173	-1
5	105	88	-57	67
H= 0 L= 4				
0	300	300	300	2
2	505	523	192	486
4	551	558	-475	293
6	513	523	515	90
8	431	416	199	366
10	711	696	-671	182
12	588	602	585	141
H= 1 L= 4				
1	169	170	-71	-154
3	342	346	-297	176
5	361	348	-295	-184
7	285	279	278	-18
9	378	395	-380	108
11	161	151	-137	-62
H= 2 L= 4				
0	137	121	-10	-120
2	101	104	-77	71
4	138	124	81	94
6	260	270	-210	-170
8	108	91	-58	70
10	151	139	125	61
12	444	440	-404	-176
H= 3 L= 4				
1	122	113	-18	111
3	341	346	-216	270
5	262	269	207	172
7	376	377	-376	21
9	506	502	323	384
11	146	152	-148	38
H= 4 L= 4				
0	589	575	574	-19
2	344	349	-334	100
4	227	235	-146	185
6	272	273	253	-103
8	181	179	-124	129
10	205	198	-123	155
H= 5 L= 4				
1	195	182	128	-129
3	588	580	-562	143
5	187	177	-104	-144
7	362	360	353	-71
9	527	519	-507	109
11	189	196	-165	-105
H= 6 L= 4				
0	181	189	-132	-135
2	350	341	187	285
4	330	335	-307	134
6	119	111	102	-43
8	294	292	182	229
10	434	435	-430	69
H= 7 L= 4				
1	159	155	-155	-7
3	426	430	313	295
5	337	337	-329	-72
7	178	171	125	117
9	176	175	39	170
H= 8 L= 4				
0	166	159	-79	-138
2	138	129	-81	100
4	106	108	-85	67
6	159	178	-129	-123
H= 9 L= 4				
1	199	206	200	-52
3	603	592	-585	93
5	247	255	254	-8
H= 10 L= 4				
0	709	708	705	67
H= 0 L= 5				
1	310	316	298	106
3	519	535	-520	-126
5	560	591	448	385
7	335	307	134	-277
9	396	401	-276	291
11	314	319	312	65
H= 1 L= 5				
0	401	397	386	91
2	169	164	-44	-163
4	166	154	117	99
6	300	309	294	-94
8	200	199	-135	-146
10	178	185	133	129
H= 2 L= 5				
1	274	277	-169	-220
3	346	339	335	48
5	283	272	-35	-270
7	154	160	-156	-37
9	243	225	194	-113
H= 3 L= 5				
0	417	405	-258	-313
2	519	523	325	410
4	248	257	257	-11
6	120	113	-112	-11
8	265	270	123	241
10	225	241	193	-144
H= 4 L= 5				
1	175	182	127	-131
3	198	204	-80	187
5	273	266	136	-229
7	251	232	200	117
9	186	206	-183	-96
H= 5 L= 5				
0	535	533	531	-49
2	245	236	-199	-127
4	119	113	-113	-7
6	481	478	467	-104
8	293	282	-224	-171
H= 6 L= 5				
1	137	135	133	26
3	231	228	-148	-173
5	411	417	228	257
7	293	304	-66	-297
H= 7 L= 5				
0	231	234	-58	227
2	170	155	123	-95
4	423	418	358	217
H= 8 L= 5				
1	201	202	-136	-149
3	172	183	182	18
H= 0 L= 6				
0	699	704	703	-35
2	472	492	-411	270
4	394	384	-350	-158
6	483	492	449	201
8	259	254	-178	181
H= 1 L= 6				
1	101	105	102	-24
3	487	491	-470	-142
5	164	160	51	-151
7	213	206	82	189
H= 2 L= 6				
0	324	334	-160	293
2	273	264	55	-258
4	149	130	-55	-118
6	206	199	-148	133
8	234	209	54	-202
H= 3 L= 6				
1	229	245	-140	201
3	433	412	50	-409
5	460	469	-270	383
7	129	137	58	-125
H= 4 L= 6				
0	488	479	234	418
2	240	239	-93	-220
4	351	344	-344	12
6	318	322	262	187
H= 5 L= 6				
1	207	211	204	-56
3	685	685	-651	-214
5	155	152	76	-132
H= 6 L= 6				
0	381	377	371	-70
2	274	275	-215	172
4	222	229	-127	-190
H= 0 L= 7				
1	155	152	-38	147
3	178	165	136	-94
H= 1 L= 7				
0	300	319	-246	203
2	258	259	257	-37
4	77	91	84	35
H= 2 L= 7				
1	217	209	-209	3
3	422	429	422	-76
H= 3 L= 7				
0	163	163	-112	118
2	133	138	-5	138

Loction of hydrogen atoms and refinement

Refinement of the heavy-atom positions and isotropic temperature factors was initiated in space group *Imm*2 using the atomic coordinates

Table 2. *Fractional atomic coordinates and temperature factor coefficients for hemimorphite**

Atom	x	y	z	β_{11}
Zn	0.2047(1)	0.1613(1)	0	0.0029(1)
Si	0	1465(2)	0.5076(5)	23(2)
O(1)	1602(2)	2055(1)	6362(4)	38(1)
O(2)	0	1669(2)	1938(4)	27(2)
O(3)	3050(2)	0	410(6)	50(2)
O(4)	0	0	5912(6)	54(3)
O(5)	5000	0	5195(13)	164(10)
H(35)	3740(8)	0	190(2)	154(9)
H(53)	4256(14)	0	643(4)	247(21)

Atom	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
			−0.0005	−0.0001 (2)	0.0003 (2)
Zn	0.0020(1)	0.0066(4)	5(1)	0.1(2)	3(2)
Si	13(1)	45(6)	0	0	0(3)
O(1)	26(1)	70(4)	−17(1)	9(2)	9(2)
O(2)	33(1)	55(5)	0	0	4(2)
O(3)	18(1)	271(10)	0	—30(4)	0
O(4)	10(2)	124(9)	0	0	0
O(5)	227(12)	221(9)	0	0	0
H(35)	56(4)	692(41)	0	−224(18)	0
H(53)	247(18)	1163(101)	0	102(45)	0

* Parenthesized figures here and in all subsequent tables represent the e.s.d. in terms of the least significant figure to the left.

of McDonald and Cruickshank (1967). As in the previous study, the unit-cell origin was defined by fixing the z coordinate of Zn at 0.0. Minimization of the function $\Sigma w(F_o - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors and $w = 1/\sigma^2$, resulted in convergence at a conventional R value of 0.123. The hydrogen atoms were then located from a Fourier difference map and the refinement was continued to convergence at $R = 0.081$. When the isotropic temperature-factor model was converted to an anisotropic model of the form $\exp\left[-\sum_{i=1}^{3}\sum_{j=1}^{3}\beta_{ij}h_ih_j\right]$ with the symmetry restrictions of

Table 3. *Magnitudes and orientations of the principal axes of thermal ellipsoids in hemimorphite*

Atom	Axis	Root-mean-square displacement	Angle to		
			$+a$	$+b$	$+c$
	1	0.090(3) Å	46(20)°	52(7)°	112(37)°
Zn	2	0.094(3)	113(28)	97(23)	156(34)
	3	0.116(2)	127(4)	39(4)	81(5)
	1	0.077(5)	90	89(29)	1(29)
Si	2	0.086(5)	90	179(29)	89(29)
	3	0.091(5)	0	90	90
	1	0.082(3)	43(5)	48(2)	95(14)
O(1)	2	0.092(3)	103(11)	84(9)	166(6)
	3	0.151(2)	130(1)	43(1)	77(2)
	1	0.085(4)	90	95(3)	5(3)
O(2)	2	0.098(3)	180	90	90
	3	0.139(3)	90	5(3)	85(3)
	1	0.104(4)	90	0	90
O(3)	2	0.125(4)	162(2)	90	108(2)
	3	0.195(3)	108(2)	90	18(2)
	1	0.076(6)	90	0	90
O(4)	2	0.128(5)	90	90	180
	3	0.138(4)	0	90	90
	1	0.171(7)	90	90	0
O(5)	2	0.241(7)	180	90	90
	3	0.364(9)	90	0	90
	1	0.146(9)	35(2)	90	55(2)
H(35)	2	0.181(6)	90	180	90
	3	0.354(10)	55(2)	90	145(2)
	1	0.285(13)	17(6)	90	107(6)
H(53)	2	0.379(14)	90	180	90
	3	0.401(18)	73(6)	90	17(6)

Levy (1956), the R value dropped to 0.051. Further refinement with the inclusion of an isotropic extinction parameter (g), as defined and scaled by Coppens and Hamilton (1970), proceeded smoothly to convergence (parameter shifts in the final cycle were less than one tenth of the corresponding e.s.d). The final values of R and R_w[3] were 0.028 and 0.035, respectively (0.031 and 0.035 for the entire data set of 433 structure factors), with the error in an observation of unit weight = 1.58. Although nearly one third of the data were affected more than 10% by extinction [$g = 0.61(4)$], only 5% of the reflections needed correction factors between 1.3 and the highest value of 2.2. The final scale factor was 0.989(7), close to the ideal value of unity expected for a data set placed on an absolute scale. The major positive and negative peaks in a Fourier difference synthesis were all located in the immediate environment of the water molecule but had maximum magnitudes somewhat less than 13% of the density of peaks corresponding to O and H atoms. The residual nuclear density may be a function of a small quantity of excess water present in a slightly different orientation within the channels, but could also be indicative of a minor amount of positional disorder in a single H_2O species.

Values for F_o and F_c ($\times 100$) are listed in Table 1. Atomic coordinates and thermal parameters along with their standard deviations estimated from the variance-covariance matrix are given in Table 2. The root-mean-square components of thermal displacement, and thermal-ellipsoid orientations appear in Table 3. The coherent neutron-scattering amplitudes used during least-squares refinement for Zn, Si, O and H were respectively 0.57, 0.42, 0.580 and −0.374, all in units of 10^{-12} cm (BACON, 1972). Programs utilized for solution, refinement and geometry calculations were local modifications of DATALIB, DATASORT, FOURIER, ORFLS3, ORFFE3 and ORTEP2[4].

Discussion of the structure

Hemimorphite crystallizes with the topology displayed in Fig. 1 and the bonding dimensions summarized in Table 4. The framework consists of an assembly of three-membered rings of corner-sharing $Zn(OH)O_3$ ($\times 2$) and SiO_4 tetrahedra arranged in compact sheets parallel to (010). Three of the oxygen atoms in each tetrahedron are bonded to one silicon and two zinc atoms, while the fourth oxygen (or, in the case of the zinc polyhedron, the hydroxyl group) forms a bridging bond to an equivalent cation in an adjacent sheet. The cross-linking of the sheets produces additional rings of four, six and eight tetrahedra and forms a series of large cavities connected along the

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[3] $R_w = [\Sigma w(F_o|F_c|)^2/\Sigma wF_o^2]^{0.5}$.

[4] All programs are listed in the *World list of crystallographic computer programs* (3rd ed. and supplements).

Table 4. *Interatomic distances and angles in hemimorphite**

SiO_4 tetrahedron:

Si—O(2)	1.620(3) Å	O(2) ··· O(1) (×2)	2.662(2) Å	∠O(2)—Si—O(1)(×2)	110.4(1)°
O(1) (×2)	1.622(2)	O(4)	2.709(3)	O(4)	113.0(2)
O(4)	1.629(2)	O(1) ··· O(1)^{i}	2.681(3)	O(1)—Si—O(1)^{i}	111.5(2)
<Si—O>	1.623(2)	O(4) (×2)	2.591(2)	O(4) (×2)	105.7(1)
		<O ··· O>	2.649(2)	<∠O—Si—O>	109.5(1)

ZnO_4 tetrahedron:

Zn—O(3)	1.935(2) Å	O(3) ··· O(1)^{ii}	3.211(2) Å	∠O(3)—Zn—O(1)^{ii}	111.4(1)°
O(1)^{ii}	1.951(2)	O(1)^{iii}	3.259(3)	O(1)^{iii}	113.7(1)
O(1)^{iii}	1.956(2)	O(2)	3.214(3)	O(2)	110.4(1)
O(2)	1.980(2)	O(1)^{ii} ··· O(1)^{iii}	3.116(2)	O(1)^{ii}-Zn—O(1)^{iii}	105.82(7)
<Zn—O>	1.956(1)	O(2)	3.169(2)	O(2)	107.47(9)
		O(1)^{iii} ··· O(2)	3.179(3)	O(1)^{iii}-Zn—O(2)	107.71(8)
		<O ··· O>	3.191(2)	<∠O—Zn—O>	109.4(1)

Framework anions:

∠Zn^{iv}—O(1)—Zn^{v}	114.01(7) Å	∠Zn—O(2)—Zn^{i}	119.8(1)°	∠Zn—O(3)—Zn^{vi}	126.9(1)°	∠Si—O(4)—Si^{vii}	149.5(2)
Zn^{iv}—O(1)—Si	116.7(1)	Zn—O(2)—Si (×2)	119.47(6)	Zn—O(3)—H(35) (×2)	110.4(2)		
Zn^{v}—O(1)—Si	128.3(1)						

Water molecule and hydroxyl group:

O_d	H	O_a	O_d—H	H ··· O_a	O_d ··· O_a	∠O_d—H···O_a	H ··· H	∠H—O_d—H
O(3)	H(35)	O(5)	0.957(7)	1.986(8)	2.941(6)	175.0(8)	—	—
O(5)	H(35)×2	O(3)^{iv}	0.888(17)	2.271(19)	3.127(6)	161.8(15)	1.25(2)	89(2)

* Symmetry transformations for atoms outside the asymmetric unit:
i. $-x, y, z$ *ii.* $0.5-x, 0.5-y, -0.5+z$ *iii.* $x, y, z-1.0$ *iv.* $x, y, 1.0+z$ *v.* $0.5-x, 0.5-y, 0.5+z$ *vi.* $x, -y, z$ *vii.* $-x, -y, z$

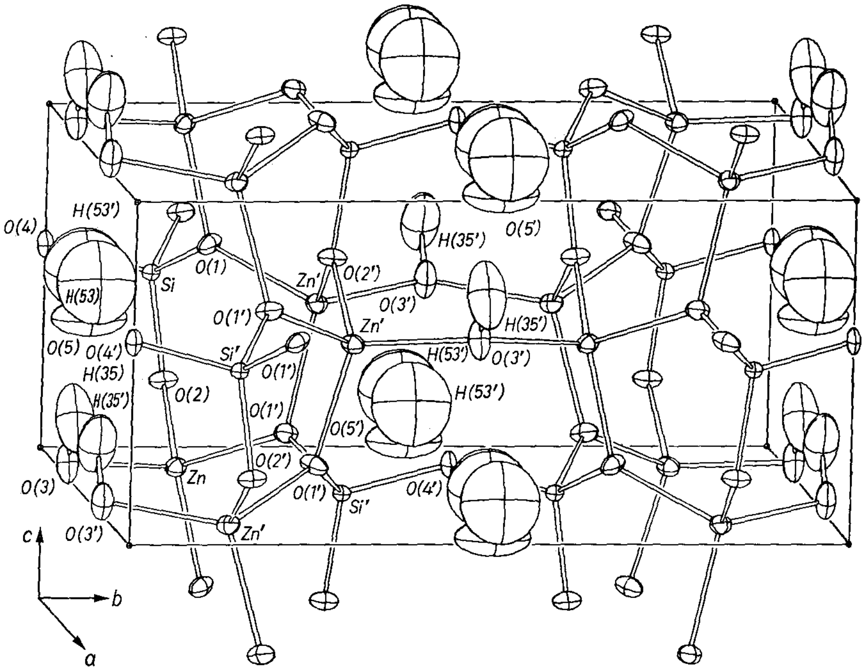

Fig. 1. Unit-cell diagram of the hemimorphite crystal structure. Thermal ellipsoids for all atoms represent 50% probability surfaces. Atoms outside the asymmetric unit are labelled with superscript primes

c axis. The water molecules near the centers of these cavities (in the plane of the eight fold rings), are orientented parallel to (010), and are held in place by hydrogen bonds to the hydroxyl groups (Fig. 2). On heating, it is apparent that the H_2O molecule is able to pass through the 6-membered ring (possibly by a process of proton exchange with the hydroxyl group) into an anjacent (vacated) cavity above or belong it in the *c*-axis direction without disruption of the structure.

Although the nuclear coordinates determined in the present study (Table 2) for the atoms not involved in bonds to hydrogen are similar to the values derived by x-ray diffraction as reported by McDonald and Cruickshank (1967), the positions of the oxygen atoms of the hydroxyl group, O(3), and water molecule, O(5), differ by 0.03 and 0.07 Å, respectively. The significance of these differences is, of course, markedly reduced by the large e.s.d.'s associated with the atomic coordinates in the earlier study, but it is interesting to note that in the

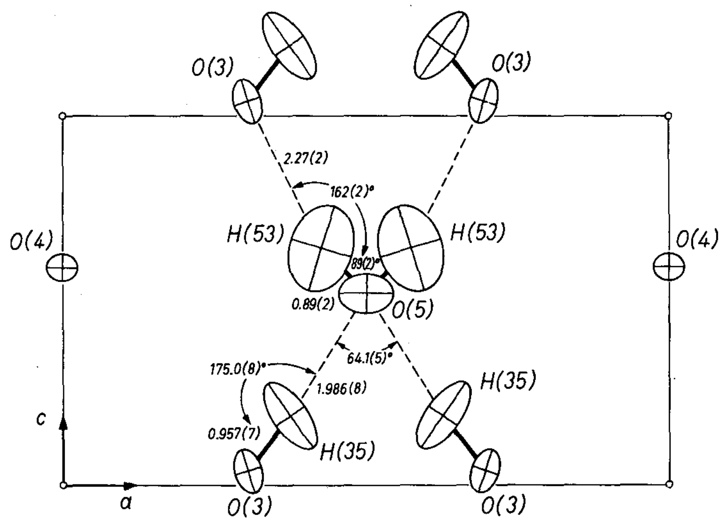

Fig. 2. Section through the cavity at $y = 0$ in the hemimorphite unit cell. Thermal ellipses for all atoms represent 50% probability surfaces. Hydrogen bonds are indicated by dashed lines

case of O(3) and O(5) the oxygen position in the x-ray study is displaced, relative to the neutron diffraction position, toward the region of space expected to be occupied by the oxygen lone pair electrons. Similar shifts due to asphericity of the electron distribution, as determined in the x-ray study, have been reported in a number of other structures containing terminal O, N and H atoms (see, for example, Coppens, 1977), but the magnitudes of the nonhydrogen-atom displacements in these instances are only about 0.01 Å. We are at present collecting a set of room-temperature x-ray data in an attempt to verify the apparently larger shift observed for the more isolated water-molecule oxygen atom in hemimorphite.

The O(5) atom lies slightly below the center of a rectangle of nearest-neighbor O(3) atoms in the plane at $y = 0$ (Fig. 2). Based on the relative sizes of the angles subtended by the O(3) atom pairs above and below O(5), McDonald and Cruickshank (1967) inferred that the water-molecule protons are directed towards the O(3) atoms below O(5) in the unit cell but in positions considerably displaced from the O(5)—O(3) lines. In fact, the present study indicates that the H_2O group is oriented in the reverse direction, and although the O(5)—H(53) $\cdots$ O(3) angle does deviate significantly from 180° (Table 4), the value is only slightly smaller than the mean angle (164°) documented for hydrogen bonds in other structures (BAUR, 1970a). The O(3)—H(35) · · · O(5) angle, on the other hand, is much wider (175°). Indeed, the orientation of the water molecule appears to be controlled by the arrangement of the Zn—O(3)—Zn linkage which dictates that the H(35) atom is directed in the positive z-axis direction in an attempt to fulfill the requirements of sp^2 hybridization on O(3). The H(53) atoms respond to this situation by positioning themselves on the opposite side of O(5), in which arrangement they are able to form hydrogen bonds to O(3) from below. Since H(35) is bonded to the bridging O(3) atom in a Zn—O—Zn linkage, it is not surprising that its thermal vibration parameters are lower and its hydrogen bonds to O(5) therefore stronger than those involving the H(53) atom. Under these circumstances the observed location of the O(5) atom in a site closer to the O(3) atoms below it in the unit cell is to be anticipated. However, both sets of hydrogen bonds are relatively long (Table 4) and would not be expected to anchor the H_2O group firmly in one place. Nevertheless, the absence of any significant peaks of residual nuclear density suggests that the H_2O group is not disordered over a number of markedly different sites within the cavity as suggested by MCDONALD and CRUICKSHANK (1967). Instead, the rather narrow H(53)—O(5)—H(53) valence angle, together with the large thermal parameters for H(53), indicates that the protons are disordered over a few closely spaced sites, each of which violates the overall $mm2$ symmetry of the cavity but lies within the observed "thermal" ellipsoid of vibration. With this in mind it is interesting to note that the O(3)—H(35) bond distance of 0.957(7) Å is close to the mean value (0.96 Å) in other structures (BAUR, 1970a), whereas the O(5)—H(53) distance of 0.888(17) Å is at the lower limit of the observed range. When these bond lengths are corrected for thermal motion under the "riding" approximation of BUSING and LEVY (1964), the values increase to 1.103(7) and 0.95(2) Å, respectively.

Molecular-orbital study

MCDONALD and CRUICKSHANK (1967) were able to justify the classification of hemimorphite as a framework structure rather than as a pyrosilicate (first proposed by ZOLTAI, 1960) by drawing attention to the approximate equality of the Si—O bond lengths in the pyrosilicate ion, and to the likelihood of sp^2 hybridization of the orbitals on O(1) and O(2) due to the close proximity of their valence angles to

120° (Table 4). Of course, the small range in Si—O bond lengths may also be rationalized in terms of an electrostatic model since all the oxygen atoms are completely charge balanced (BAUR, 1970b). However neither of these models is able to account for the relatively large range in Zn—O bond lengths from 1.935 to 1.980 Å. Therefore, in view of the apparent success of extended Hückel theory (EHT) in accounting for structural trends in a number of moderately complex systems (GIBBS *et al.*, 1972; TOSSELL and GIBBS, 1977) we were tempted to apply these concepts to the Si and Zn tetrahedral oxyanions in hemimorphite.

All calculations were performed with the program originally written by HOFFMANN (1963) assuming a minimum-valence *sp* basis for Si, Zn and O, and an *s* basis for H, with the corresponding valence-orbital ionization energies and Slater orbital exponents listed in Table 5. In an attempt to account for the influence of the surrounding framework on the individual T—O bond lengths within each tetrahedron, the "first coordination sphere" of tetrahedral groups was included in the calculations in both instances: the theoretical basis for the neglect of more distant atoms has been discussed by KIER (1968) In addition, since shorter bonds necessarily tend to produce larger overlap populations, we have removed this induced correlation from consideration by fixing all Si—O and Zn—O bond lengths within each oxyanion cluster to values of 1.623 and 1.956 Å, respectively (the O—H bond was left at 0.957 Å), while maintaining the O—T—O and T—O—T angles at their observed values. During the calculations, the

Table 5. *Valence orbital ionization potentials (VOIP) and Slater exponents* (ξ)

Atom	Orbital	VOIP*	ξ**
Si	3*s*	14.83 eV	1.634
	3*p*	7.75	1.428
Zn	4*s*	8.41	1.491
	4*p*	3.58	1.445
O	2*s*	32.33	2.246
	2*p*	15.79	2.227
H	1*s*	13.60	1.200

* VOIP's for Si, O and H are from BASCH *et al.* (1965); for Zn, from CUSACHS and CORRINGTON (1970).

** Slater exponents for Si, Zn and O are from CLEMENTI and RAIMONDI (1963); for H, from BARTELL, SU and YOW (1970).

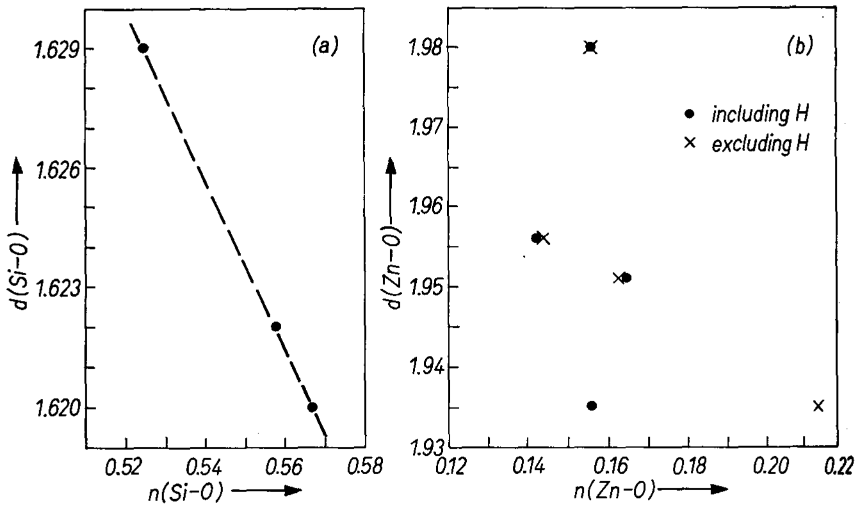

Fig. 3. (*a*) Observed bond length, *d* (Si—O), for the central SiO_4 tetrahedron of the $Si_2Zn_6O_{22}^{24-}$ cluster in hemimorphite, plotted against the corresponding Mulliken bond-overlap population, *n* (Si—O). (*b*) Observed bond length, *d*(Zn—O for the central ZnO_4 tetrahedron of the $Si_3Zn_5O_{22}H^{21-}$ cluster in hemimorphite, plotted against the corresponding Mulliken bond-overlap population, *n*(Zn—O). In both (*a*) and (*b*) the overlap population was calculated assuming observed valence angles, and constant bond lengths of 1.623 and 1.956 Å for Si—O and Zn—O respectively

energy and shape of the molecular-orbital wave functions respond to the angular distortions by establishing different overlap populations for the inidividual bonds.

Figure 3(*a*) is a plot of the observed bond length, *d*(Si—O) *vs* *n* (Si—O), the calculated bond overlap population, for the four bonds in the central SiO_4 tetrahedron of the $Si_2Zn_6O_{22}^{24-}$ cluster. Despite the very small range in Si—O bond lengths, it is clear that *n*(Si—O) correlates very well with *d*(Si—O), shorter bonds tending to involve larger overlap populations. Although the calculated value of *n*(*T*—O) cannot be regarded as the actual number of electrons localized in the internuclear region, the general belief that they are closely related (Coulson, 1970) is consistent with the above results. Encouraged by the discovery that the correlation between *d*(Si—O) and *n*(Si—O) was not as well developed when the calculation was repeated without the influence of the zinc tetrahedra (*i.e.*, on the $Si_2O_7^{6-}$ group alone), we were surprised to find that EHT was not able to rationalize the bond-length variations within the ZnO_4 group at the center of the $Si_3Zn_5H^{21-}$

cluster (Fig. 3b). With the removal of the proton from consideration, EHT successfully predicts that the Zn—O(3) bond should be the shortest, and also that O(3) is the point of attachment of the proton (by assigning a significantly larger value of calculated electrical charge to that atom), but the lengths of the other bonds remain essentially independent of overlap population (Fig. 3*b*). In both cases the results were unaffected by the inclusion of the completely filled 3*d* orbitals on the zinc atoms.

Earlier studies of the isolated tetrahedral oxyanions of a large number of second-, third- and fourth-row elements have indicated that a moderate to very strong correlation exists between $n(T-\mathrm{O})$ and $\langle \mathrm{O}-T-\mathrm{O}\rangle_3$, the mean of the three O—T—O angles common to the bond (Louisnathan and Gibbs, 1972; Tossell and Gibbs, 1977). The results of these calculations have been used to rationalize similar correlations observed between $d(T-\mathrm{O})$ and $\langle \mathrm{O}-T-\mathrm{O}\rangle_3$ in more than 100 precisely determined crystal structures containing the corresponding $T\mathrm{O}_4^{n-}$ groups. In both cases the correlation is observed to increase from left to right along each row of the periodic table. In other words, for a given range of $\langle \mathrm{O}-T-\mathrm{O}\rangle_3$ the range of observed bond lengths, $\Delta d(T-\mathrm{O})$, and of calculated bond-overlap populations, $\Delta n(T-\mathrm{O})$, is greater for B, S and Se than for T atoms of lower electronegativity in the same period (Tossell and Gibbs, 1977).

In the past it has been suggested that these trends are a reflection of a general increase in the directional properties of the bond as the electronegativity difference between the bonded atoms decreases along each period (Tossell and Gibbs, 1977). The poor correlations obtained above for the zinc cluster in hemimorphite, and also from an analysis of the relationship between $n(\mathrm{Zn}-\mathrm{O})$, $d(\mathrm{Zn}-\mathrm{O})$ and $\langle \mathrm{O}-\mathrm{Zn}-\mathrm{O}\rangle_3$ in a number of other precisely determined crystal structures (Hill and Gibbs, in preparation) are, therefore, consistent with the overall trend observed for the fourth-row elements. However, in spite of the fact that the electronegativity of Si is only slightly larger than that of Zn, EHT was clearly far more successful in rationalizing
in spite of the fact that the electronegativity of Si is only slightly larger than that of Zn, EHT was clearly far more successful in rationalizing
the bond-length variations for the silicate cluster. Indeed, the intraperiod relationship for $\Delta n(T-\mathrm{O})$ and $\Delta d(T-\mathrm{O})$ with electronegativity consistently breaks down for elements in different periods, even though the bonds may be predicted (Pauling, 1960) to have the same degree of covalent character. For example, small changes in $\langle \mathrm{O}-T-\mathrm{O}\rangle_3$

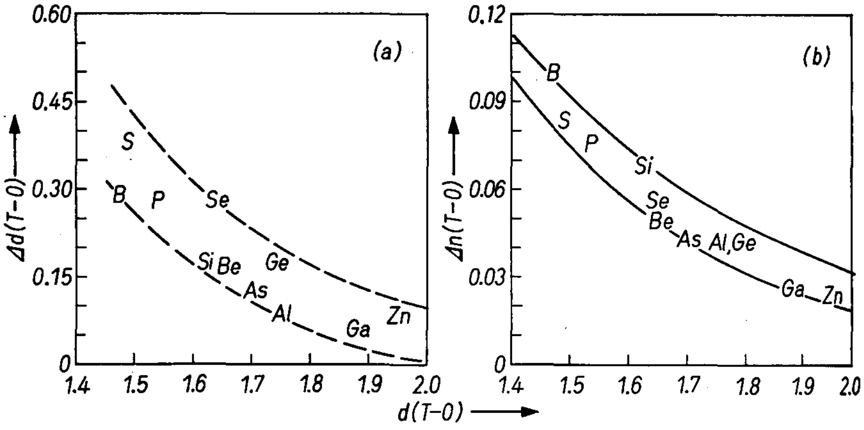

Fig. 4. (*a*) Variation of $\Delta d(T-O)$ as a function of $d(T-O)$ for second-, third, and fourth-row $TO_4{}^{n-}$ tetrahedral oxyanions. $\Delta d(T-O)$ is defined as $d(T-O) - <d(T-O)>$, where $<d(T-O>)>$ is the mean $d(T-O)$ value calculated at valence angles of 100° and 120° from published value calculated at valence angles of 100° and 120° from published linear regression equations relating $d(T-O)$ and $<O-T-O>_3$ (Tossell and Gibbs, 1977). (*b*) Variation of $\Delta n(T-O)$ as a function of $d(T-O)$ for the same oxyanions as in (*a*). $\Delta n(T-O)$ is defined as $n(T-O) - <n(T-O)>$, where $<n(T-O)>$ is the mean $n(T-O)$ value calculated at valence angles of 100° and 120° assuming a constant $d(T-O)$ value and C_{3v} point symmetry for each ion. The lower curve represents the relationship between $\Delta n(\mathrm{Zn-O})$ and $d(\mathrm{Zn-O})$ for the bond lengths in the range 1.4—2.0 Å; the upper curve gives the equivalent relationship for the SiO_4 group

within the borate group are observed to produce a greater change in the length of the common bond than the same angular changes occurring in the somewhat larger arsenate group, even though B and As have the same electronegativity. On the other hand, tetrahedral oxyanions about As and Be have approximately the same mean bond length and display very similar bond-length changes as a function of $<O-T-O>_3$, despite the fact that the cations have significantly different electronegativities. From a detailed analysis of bond-length and valence-angle variations in a wide variety of tetrahedral oxyanions it is now clear that the dependence of bond length on the average of the three valence angles common to the bond is more a function of the mean $T-O$ bond length itself than of the electronegativity difference between the bonded atoms (Fig. 4*a*).

Despite the fact that EHT is based on a totally covalent-bonding model and would therefore be expected to be strongly influenced by the electronegativities of the atoms incorporated into the calculations, values of $\Delta n(T-O)$ far all tetrahedral oxyanions studied show a monotonic dependence on $d(T-O)$ which is very similar to the relationship between $\Delta d(T-O)$ and $d(T-O)$ (Fig. 4*b*). Indeed, this same relationship may be replicated by artificially changing the bond length over the range 1.4 to 2.0 Å for any of the $TO_4{}^{n-}$ group considered. In Fig. 4*b* the relationship between $\Delta n(T-O)$ and $d(T-O)$ for $T = \mathrm{Zn}$ and Si have been plotted over the entire range of $d(T-O)$ values. The displacement of the two curves is a reflection of the different VOIP's and Slater exponents used to characterize the orbitals in the EHT calculations, but their overall shapes are remarkably similar. Therefore, although the observed changes in bond length may indeed be rationalized in terms of changes in bond-overlap population [$\Delta d(T-O)$ and $\Delta n(T-O)$ are linearly related with a correlation coefficient of 0.86], the fact that $\Delta n(T-O)$ is essentially independent of the exact EHT parameterization suggests that these changes are really a *geometric* function of orbital overlap.

Under these circumstances, the success with which EHT is able to simulate changes in bond length within tetrahedral oxyanions is not so much a function of the classical (Pauling) covalent character of the bond, but of the overall size of the tetrahedral oxyanion itself. For large $TO_4{}^{n-}$ groups, like the zinc tetrahedron in hemimorphite, orbital overlap is little affected by changes in $O-T-O$ angle, and in these cases the observed bond-length distortions probably reflect the influence of other factors, perhaps electrostatic in nature, not modelled in the EHT calculation.

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