Acta Cryst. (1973). B**29**, 1929

The Crystal Structures of Barium Hexahydroxocuprate(II) and Strontium Hexahydroxocuprate(II), $Ba_2[Cu(OH)_6]$ and $Sr_2[Cu(OH)_6]$

BY ERICH DUBLER, PETER KORBER AND HANS R. OSWALD

Institut für anorganische Chemie, Universität Zürich, Rämistrasse 76, 8001 Zürich, Switzerland

(*Received 22 March 1973; accepted 23 March 1973*)

The crystal structure of $Ba_2[Cu(OH)_6]$ has been determined by Patterson and Fourier synthesis with data collected on an automated four-circle diffractometer. The crystals are monoclinic, space group $P2_1/c$ with $a=6{\cdot}030$ (2), $b=6{\cdot}440$ (2), $c=10{\cdot}115$ (2) Å, $\beta=124{\cdot}03$ (1)°. The structure was refined by full-matrix least-squares techniques to a conventional R index of 0·028 for 955 independent reflexions. Corrections were made for absorption, anomalous dispersion and isotropic secondary extinction. The structure contains isolated highly distorted $[Cu(OH)_6]^{4-}$ octahedra which appear to be held together primarily by barium ions. The structure may also be described as built up from close packed layers (011) consisting of Ba^{2+} and OH^- ions, the Cu^{2+} ions occupying distorted octahedral sites between every two of these layers. Thus, it represents a strongly distorted version of the well known cubic K_2PtCl_6-structure, which is built up from layers containing K^+ and Cl^- with Pt^{4+} at octahedral sites in a quite similar way. Average values for the Cu–O distances are 1·965 Å for four equatorial ligands and 2·805 Å for two axial ligands. The configuration of the barium–oxygen polyhedron can best be described as a distorted di-capped trigonal prism with Ba–O distances ranging from 2·642 to 2·954 Å. Single crystals of the isomorphous compound $Sr_2[Cu(OH)_6]$ have also been prepared; $a=5{\cdot}786$ (1), $b=6{\cdot}154$ (1), $c=9{\cdot}744$ (2), $\beta=124{\cdot}15$ (1)°.

Introduction

As part of a study on correlations between crystal structures and thermal-decomposition behaviour of hydroxy complexes we have determined the structure of barium hexahydroxocuprate(II). Several hydroxometallates are well known (Scholder 1962), but until now there has existed little information about the structural details of these compounds. We have grown single crystals of $Ba_2[Cu(OH)_6]$ and $Sr_2[Cu(OH)_6]$ by interdiffusion of aqueous Ba^{2+}– or Sr^{2+}– and Cu^{2+} solutions in a 50% NaOH solution.

Crystal data and experimental

Preliminary Weissenberg and precession photographs showed the crystals to be monoclinic, space group $P2_1/c$. Accurate unit-cell dimensions were calculated from X-ray powder photographs registered on a Guinier-de Wolff focusing camera using Cu $K\alpha$ radiation and high purity KCl as an internal standard. These lattice parameters were refined by the method of least squares. The calculated densities for 2 formula units per cell are in agreement with the pycnometrically measured values.

Crystal data for both compounds are listed in Table 1. An investigation of the powder X-ray patterns of $Ba_2[Cu(OH)_6]$ and $Sr_2[Cu(OH)_6]$ confirms that these salts are isostructural.

A $Ba_2[Cu(OH)_6]$ single crystal with approximate dimensions $0{\cdot}19 \times 0{\cdot}10 \times 0{\cdot}08$ mm was chosen for data collection on an automated four-circle Picker diffractometer using Mo $K\alpha$ radiation (pyrolytic graphite monochromator, 002). Intensity data were collected by a conventional moving-crystal moving-counter θ–2θ scan over a 2θ range of 2° (plus the α_1–α_2 dispersion) with a scan speed of 0·5°/min. Background counts of 40 s were taken at each side of the peak.

Table 1. *Crystal data*

	$Ba_2[Cu(OH)_6]$	$Sr_2[Cu(OH)_6]$
Crystal system	Monoclinic	Monoclinic
Systematic absences	$h0l$, $l=2n+1$ $0k0$, $k=2n+1$	$h0l$, $l=2n+1$ $0k0$, $k=2n+1$
Space group	$P2_1/c$	$P2_1/c$
a	6·030 (2) Å	5·786 (1) Å
b	6·440 (2)	6·154 (1)
c	10·115 (2)	9·744 (2)
β	124·03 (1)°	124·15 (1)°
d_{calc}	4·51 g cm^{-3}	3·94 g cm^{-3}
d_{obs}	4·40	3·84
Z	2	2
μ (for Mo $K\alpha$)	153 cm^{-1}	225 cm^{-1}
Colour	Blue	Blue

Two selected standard reflexions were measured after every 10 reflexions and used for an internal scaling of the data by least-squares methods. Intensities were collected up to $2\theta \le 60°$. Of the 1263 reflexions measured (including standards), 955 remained after averaging equivalent reflexions and 907 were judged to be observed according to the criterion $I \ge 3\sigma(I)$, $\sigma(I)$ being the estimated standard deviation in the net intensity based on counting statistics. The intensities were reduced to F_o in the usual way by applying Lorentz and polarization factors. Absorption corrections were made by an enlarged version (Schwarzenbach, 1972) of the program *ORABS* 2 (Busing, 1966) and resulted in a significantly better agreement between intensities of measured equivalent reflexions. The calculated transmission varied from 0·25 to 0·44.

All the computations, including subsequent refinement of the structure, were performed using the program system XRAY 67 (Stewart, Kundell & Baldwin, 1970), which was enlarged and modified for use on a CDC 6400–6500 computer system by Schwarzenbach (1972).

Structure determination and refinement

Approximate positions of the heavy atoms could be deduced from a three-dimensional Patterson map. The four barium atoms are situated in a fourfold general position 4(*e*) of $P2_1/c$, with $z \simeq \frac{1}{4}$; the two copper atoms are in the special position 2(*c*). Structure factor calculations based on refined positions of these heavy atoms yielded a conventional R ($\sum||F_o|-|F_c||/\sum|F_o|$) of about 0·20. A difference electron density map showed the positions of all the oxygen atoms, which were included in the subsequent cycles of full-matrix least-squares refinement. The function minimized was $\sum w(|F_o|-|F_c|)^2$, where w is the weight derived from counting statistics and defined as $w=1/\sigma^2(F_o)$. Structure factors were calculated with the atom scattering factors tabulated in *International Tables for X-ray Crystallography* (1962) including real and imaginary parts of anomalous dispersion corrections for barium and copper.

After several cycles of least-squares refinement in which individual isotropic temperature factors were used, R decreased to 0·059 and the weighted $R_w\{=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}\}$ to 0·079. Anisotropic temperature factors were then introduced and the isotropic secondary extinction was included as a parameter in the least-squares refinement (Larson, 1967). A final cycle of full-matrix anisotropic refinement gave $R=$ 0·028 and $R_w=0{\cdot}029$ for 955 reflexions (including those not observed). The resulting fractional positional coordinates are listed in Table 2 and vibrational parameters in Table 3. The corresponding observed and calculated structure factors are presented in Table 4.

Table 2. *Atomic positional coordinates in* $Ba_2[Cu(OH)_6]$

Standard deviations in the last digit calculated in the final least-squares refinement are given in parentheses.

	Position	x	y	z
Ba	4(*e*)	0·2821 (1)	0·0674 (1)	0·2489 (1)
Cu	2(*c*)	0·00	0·00	0·50
O(1)	4(*e*)	0·4327 (8)	0·2575 (6)	0·0586 (4)
O(2)	4(*e*)	0·1956 (8)	0·7629 (5)	0·0393 (4)
O(3)	4(*e*)	0·1387 (8)	0·4750 (6)	0·2267 (4)

Discussion of the structure

The crystal structure of $Ba_2[Cu(OH)_6]$ contains highly distorted octahedra of $[Cu(OH)_6]^{4-}$. These octahedra

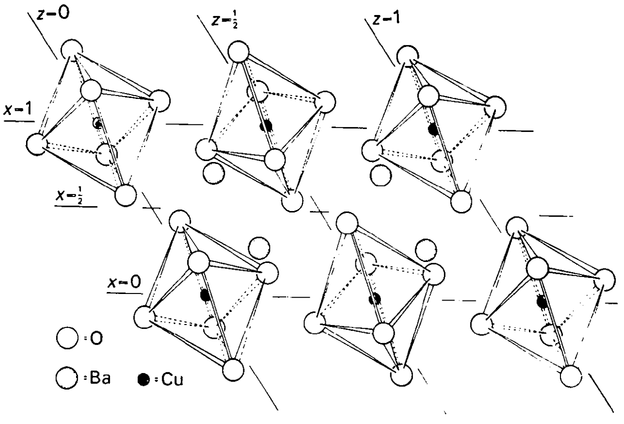

Fig. 1. Arrangement of discrete, distorted $[Cu(OH)_6]^{4-}$ octahedra in $Ba_2[Cu(OH)_6]$, projected along [010].

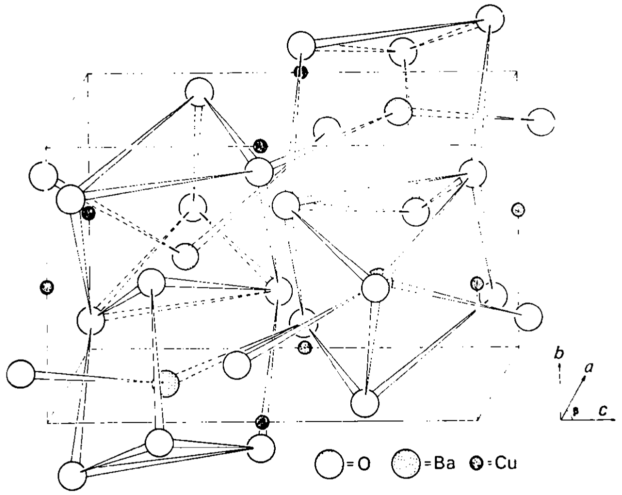

Fig. 2. Three-dimensional view of the $Ba_2[Cu(OH)_6]$ structure, showing the di-capped trigonal prismatic coordination of barium by oxygen.

Table 3. *Mean-square amplitudes of vibration* ($Å^2 \times 10^{-4}$)

The temperature factors were calculated from the expression:

$$\exp\left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\right].$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba	138 (1)	123 (1)	126 (1)	3 (1)	69 (1)	7 (1)
Cu	133 (4)	128 (4)	104 (3)	24 (4)	61 (3)	1 (3)
O(1)	197 (19)	181 (19)	148 (16)	−30 (17)	94 (15)	−14 (13)
O(2)	178 (19)	145 (17)	166 (16)	−49 (16)	104 (15)	−36 (13)
O(3)	142 (18)	128 (16)	119 (14)	5 (15)	66 (13)	18 (12)

Extinction factor $g=4{\cdot}93\ (5)\times 10^{-3}$ (Larson, 1967).

do not share any edges or corners and appear to be held together primarily by barium ions. The arrangement of the isolated copper polyhedra within the structure is shown in Fig. 1.

The coordination of the barium ion may be described as a polyhedron of eight oxygens forming a distorted di-capped trigonal prism (Fig. 2). These prisms are linked together into chains parallel to [010] by edge-sharing of the trigonal base.

The crystal structure can also be described in terms of close-packed hexagonal layers (011) consisting of Ba^{2+} and OH^- ions. The cupric ions then occupy octahedral sites between every two of these layers.

Table 4. *Calculated and observed structure factors for* $Ba_2[Cu(OH)_6]$

The columns are l, F_o, F_c. Unobserved reflexions are those less than $3\sigma(I)$ and are marked by *.

0,0,L		
2	1036	1035
4	1020	[illegible]
6	998	1015
8	1116	1100
10	672	654
0,1,L		
1	520	499
2	67	76
3	381	381
4	25	1
5	390	408
6	16*	12
7	240	243
8	79	80
9	217	210
10	21*	30
11	153	150
0,2,L		
0	1201	1176
1	1173	1174
2	1115	1078
3	1076	1057
4	1240	1217
5	895	887
6	486	492
7	772	778
8	947	933
9	597	537
10	253	237
11	494	471
0,3,L		
1	457	446
2	24*	9
3	340	345
4	120	87
5	306	305
6	95	98
7	217	213
8	30	26
9	217	203
10	123	112
11	131	117
0,4,L		
0	560	557
1	1190	1130
2	595	589
3	1032	1076
4	283	261
5	1034	1032
6	285	263
7	821	825
8	46	35
9	722	708
10	161	153
0,5,L		
1	281	266
2	61	55
3	217	219
4	51	50
5	250	253
6	60	64
7	134	132
8	106	105
9	160	152
0,6,L		
0	675	675
1	452	467
2	800	807
3	502	512
4	522	527
5	335	345
6	811	802
7	417	408
8	334	320
0,7,L		
1	219	214
2	15*	14
3	172	170
4	51	49
5	214	210
6	72	58
7	137	133
0,8,L		
0	447	445
1	211	239
2	877	858
3	242	235
4	407	433
5	149	144
0,9,L		
1	131	117
1,0,L		
-12	124	82
-10	506	518
-8	111	107
-6	907	921
-4	302	306
-2	800	803
0	129	130
2	323	347
4	151	107
6	305	333
8	123	131
10	210	208
1,1,L		
-12	263	251
-11	769	765
-10	335	331
-9	530	540
-8	460	475
-7	1163	1189
-6	442	462
-5	710	704
-4	765	805
-3	1375	1424
-2	672	692
-1	859	883
0	822	813
1	1432	1408
2	861	867
3	827	862
4	326	340
5	1269	1286
6	546	554
7	830	830
8	312	310
9	864	855
10	239	231
1,2,L		
-12	26*	4
-11	116	115
-10	322	320
-9	160	168
-8	87	93
-7	194	195
-6	320	344
-5	214	227
-4	50	37
-3	303	327
-2	525	530
-1	265	264
0	513	488
1	334	333
2	649	632
3	232	224
4	433	431
5	147	154
6	346	330
7	139	133
8	163	161
9	99	94
10	170	151
1,3,L		
-12	573	541
-11	322	315
-10	721	708
-9	26	13
-8	849	868
-7	476	499
-6	1104	1146
-5	93	90
-4	1143	1169
-3	657	691
-2	1332	1349
-1	143	130
0	1372	1308
1	736	725
2	1066	1074
3	27*	11
4	1219	1201
5	564	556
6	809	798
7	76	74
8	768	732
9	370	356
10	603	566
1,4,L		
-11	187	166
-10	221	215
-9	167	163
-8	303	300
-7	224	230
-6	356	347
-5	268	276
-4	469	461
-3	254	265
-2	308	310
-1	302	369
0	308	374
1	270	269
2	91	85
3	289	281
4	286	275
5	221	205
6	96	86
7	165	151
8	225	221
9	131	115
1,5,L		
-10	553	531
-9	553	543
-8	697	691
-7	251	264
-6	748	764
-5	700	778
-4	955	963
-3	377	392
-2	959	962
-1	675	674
0	926	944
1	364	371
2	1005	995
3	769	765
4	701	700
5	246	240
6	736	724
7	557	543
8	536	515
1,6,L		
-9	107	94
-8	211	211
-7	112	97
-6	51	58
-5	100	102
-4	305	311
-3	185	178
-2	29*	20
-1	37	103
0	463	464
1	130	188
2	104	103
3	123	108
4	406	403
5	120	116
6	60	54
7	96	79
1,7,L		
-8	128	119
-7	491	492
-6	180	190
-5	906	906
-4	149	152
-3	586	594
-2	201	202
-1	1032	1070
0	223	217
1	601	597
2	104	102
3	911	895
4	211	207
5	522	511
6	72	60
1,8,L		
-6	45*	45
-5	24*	19
-4	343	339
-3	41*	45
-2	48	10
-1	35*	22
0	247	272
1	45*	28
2	42*	31
3	15*	17
4	214	203
1,9,L		
-1	570	550
2,0,L		
-12	456	436
-10	1115	1104
-8	732	807
-6	1521	1474
-4	1133	1173
-2	1501	1545
0	1021	1048
2	1398	1466
4	742	755
6	976	991
8	511	502
2,1,L		
-13	400	376
-12	76	71
-11	152	136
-10	234	231
-9	690	653
-8	185	169
-7	234	232
-6	90	104
-5	990	1010
-4	572	565
-3	367	373
-2	202	161
-1	1129	1068
0	510	504
1	294	305
2	152	163
3	684	671
4	93	78
5	152	148
6	244	242
7	496	491
8	10*	19
9	76	66
2,2,L		
-13	237	374
-12	346	338
-11	505	496
-10	720	710
-9	549	649
-8	466	400
-7	750	773
-6	1152	1143
-5	637	674
-4	597	533
-3	949	998
-2	1344	1323
-1	900	977
0	523	545
1	951	943
2	1685	1608
3	614	620
4	552	547
5	732	703
6	740	733
7	504	551
8	212	200
9	433	436
2,3,L		
-12	250	333
-11	60	61
-10	249	233
-9	300	371
-8	414	423
-7	124	123
-6	544	565
-5	506	568
-4	263	256
-3	93	91
-2	737	702
-1	623	631
0	274	270
1	60	34
2,3,L		
2	433	433
3	457	447
4	393	336
5	55	56
6	184	170
7	265	261
8	291	278
2,4,L		
-12	231	221
-11	565	552
-10	166	168
-9	697	733
-8	273	275
-7	797	813
-6	163	[illegible]
-5	960	972
-4	313	324
-3	1016	1029
-2	177	177
-1	1063	1062
0	418	416
1	1036	1017
2	142	142
3	923	926
4	346	341
5	813	738
6	46	42
7	606	621
8	211	205
2,5,L		
-11	273	239
-10	325	319
-9	34*	13
-8	284	233
-7	351	351
-6	278	279
-5	64	37
-4	455	403
-3	436	430
-2	163	175
-1	141	121
0	395	334
1	454	436
2	263	290
3	121	110
4	154	153
5	337	322
6	263	256
7	47*	31
2,6,L		
-10	325	313
-9	276	233
-8	666	660
-7	373	376
-6	391	378
-5	375	375
-4	667	885
-3	471	469
-2	452	448
-1	458	450
0	900	886
1	479	476
2	457	452
3	429	419
4	757	733
5	394	390
6	353	335
2,7,L		
-8	67	55
-7	401	421
-6	37	65
-5	123	106
-4	67	60
-3	492	473
-2	119	111
-1	133	130
0	74	69
1	411	390
2	51	11
3	135	122
4	41*	26
5	313	293
2,8,L		
-6	412	404
-5	175	165
-4	704	684
-3	166	184
-2	480	463
-1	171	162
0	745	717
1	148	142
2	430	420
3,0,L		
-12	636	610
-10	287	304
-8	924	916
-6	203	243
-4	1020	1042
-2	360	423
0	800	839
2	415	439
4	646	657
6	237	233
8	491	485
3,1,L		
-13	576	544
-12	311	299
-11	350	335
-10	183	182
-9	904	906
-8	528	551
-7	496	515
-6	293	305
-5	1181	1264
-4	461	497
-3	663	701
-2	641	636
-1	1254	1323
0	229	253
1	673	691
2	510	521
3	1054	1094
4	253	263
5	506	516
6	268	250
7	716	714
8	220	213
3,2,L		
-13	317	249
-12	460	449
-11	370	309
-10	147	125
-9	465	470
-8	579	613
-7	521	545
-6	112	118
-5	623	647
-4	716	753
-3	629	634
-2	65	47
-1	632	633
0	821	820
1	535	531
2	53	54
3	443	430
4	584	582
5	359	351
6	77	73
7	270	254
3,3,L		
-13	257	278
-12	471	457
-11	73	60
-10	745	751
-9	365	386
-8	612	633
-7	55	40
-6	955	988
-5	536	542
-4	913	932
-3	40	33
-2	630	649
-1	622	615
0	990	997
1	63	67
2	685	685
3	526	518
4	703	695
5	60	61
6	555	537
7	350	343
3,4,L		
-12	90	84
-11	454	443
-10	269	261
-9	536	537
-8	137	134
-7	623	634
-6	415	420
-5	676	687
-4	126	123
-3	717	723
-2	386	368
-1	689	673
0	61	30
1	595	583
2	247	250
3	524	516
4	76	51
5	396	373
6	206	193
3,5,L		
-11	425	414
-10	418	412
-9	171	169
-8	653	662
-7	602	608
-6	575	565
-5	150	151
-4	663	673
-3	695	694
-2	755	752
-1	127	131
0	530	532
1	578	574
2	652	643
3	130	124
4	449	441
5	397	386
6	425	402
3,6,L		
-10	468	450
-9	283	264
-8	236	236
-7	289	287
-6	596	593
-5	371	364
-4	263	260
-3	315	314
-2	689	675
-1	350	343
0	182	177
1	278	272
2	600	585
3	233	225
4	143	133
5	206	191
3,7,L		
-9	349	335
-8	54	31
-7	659	651
-6	105	103
-5	458	449
-4	102	97
-3	725	710
-2	73	63
-1	450	448
0	143	135
1	685	604
2	37*	30
3	355	347
3,8,L		
-6	512	496
-5	56	51
-4	247	240
-3	43*	42
-2	509	456
-1	76	52
0	271	251
4,0,L		
-14	265	221
-12	722	654
-10	433	354
-8	955	962
-6	641	644
-4	654	688
-2	567	558
0	998	950
2	279	286
4	759	773
6	238	260
4,1,L		
-14	253	236
-13	375	347
-12	200	190
-11	838	816
-10	269	263
-9	513	517
-8	376	392
-7	1096	1128
-6	250	250
-5	609	625
-4	456	464
-3	1169	1152
-2	322	324
-1	532	535
0	330	333
1	898	919
2	275	281
3	354	350
4	245	240
5	583	578
6	175	166
4,2,L		
-13	322	299
-12	462	452
-11	364	350
-10	172	154
-9	470	477
-8	741	704
-7	513	551
-6	33	26
-5	495	513
-4	322	324
-3	642	633
-2	71	54
-1	103	135
0	690	657
1	552	552
2	225	222
3	443	446
4	394	397
5	362	373
6	193	105
4,3,L		
-13	35*	45
-12	520	516
-11	361	378
-10	571	571
-9	76	72
-8	607	613
-7	519	536
-6	772	786
-5	73	57
-4	730	690
-3	503	571
-2	753	741
-1	39*	3
0	684	675
1	455	429
2	573	571
3	35*	28
4	495	494
5	264	255
4,4,L		
-12	126	126
-11	443	428
-10	224	224
-9	512	508
-8	76	62
-7	599	610
-6	220	221
-5	681	687
-4	14*	15
-3	677	670
-2	304	297
-1	730	719
0	98	95
1	582	550
2	354	351
3	500	502
4	141	134
5	430	427
4,5,L		
-11	65	50
-10	411	402
-9	445	437

Table 4 (*cont.*)

4,5,L		
-7	83	53
-6	450	446
-5	530	516
-4	580	553
-3	122	103
-2	510	459
-1	504	492
0	537	492
1	136	113
2	430	422
3	406	369
4	358	374
4,6,L		
-10	470	454
-9	252	255
-8	354	353
-7	253	249
-6	675	655
-5	320	320
-4	236	[illegible]
-3	353	339
-2	570	605
-1	315	309
0	259	202
1	335	331
2	489	475
3	264	257
4,7,L		
-8	49	33
-7	345	331
-6	84	76
-5	630	605
-4	37*	43
-3	344	331
-2	70	59
-1	626	590
0	73	74
1	290	283
4,8,L		
-4	325	313
5,0,L		
-14	633	551
-12	543	514
-10	802	787
-8	630	627
-6	1081	1121
-4	523	529
-2	1125	1139
0	474	452
2	655	677
4	425	422
5,1,L		
-14	111	93
-13	135	115
-12	152	154
-11	540	515
-10	163	[illegible]
-9	222	[illegible]
-8	194	191
-7	730	753
-6	185	193
-5	339	310
-4	254	258
-3	737	812
-2	137	134
-1	293	305
0	242	250
1	626	647
2	130	130
3	222	225
4	127	136
5,2,L		
-13	441	418
-12	112	113
-11	524	510
-10	714	714
-9	585	547
-8	207	211
-7	620	630
-6	745	751
-5	678	677
-4	428	420
-3	643	631
-2	657	650
-1	583	577
0	400	390
1	569	563
2	505	505
3	399	395
4	232	223
5,3,L		
-13	43*	54
-12	236	283
-11	271	257
-10	340	338
-9	56	45
-8	397	402
-7	387	392
-6	417	421
-5	46	21
-4	405	408
-3	431	427
-2	466	463
-1	23*	12
0	342	346
1	346	346
2	359	359
3	9*	15
4	307	301
5,4,L		
-12	169	157
-11	629	615
[illegible]	40*	30
-9	[illegible]	650
-8	[illegible]	[illegible]
-7	[illegible]	775
-6	[illegible]	306
-5	[illegible]	[illegible]
-4	[illegible]	[illegible]
-3	773	752
-2	[illegible]	[illegible]
-1	[illegible]	[illegible]
0	306	304
1	567	570
2	[illegible]	121
3	495	467
[illegible]		
-11	6*	4
-10	[illegible]	[illegible]
-9	[illegible]	[illegible]
-8	266	[illegible]
-7	45	[illegible]
-6	222	[illegible]
-5	[illegible]	[illegible]
-4	343	330
-3	24*	[illegible]
-2	255	[illegible]
-1	327	[illegible]
0	337	[illegible]
1	[illegible]	17
2	[illegible]	[illegible]
5,6,L		
[illegible]	267	252
-9	354	342
-8	602	645
-7	344	336
-6	364	365
-5	360	372
-4	608	585
-3	333	320
-2	409	358
-1	385	391
0	517	489
5,7,L		
-7	166	148
-6	57	8
-5	402	401
-4	24*	16
-3	163	155
-2	41*	34
6,0,L		
-14	251	231
-12	36*	26
-10	415	418
-8	90	90
-6	465	492
-4	41	10
-2	404	416
0	65	80
2	333	335
6,1,L		
-13	740	701
-12	249	238
-11	496	487
-10	367	359
-9	689	699
-8	737	740
-7	552	551
-6	451	436
-5	942	919
-4	355	393
-3	[illegible]	[illegible]
-2	[illegible]	[illegible]
-1	756	764
0	347	342
1	[illegible]	[illegible]
2	[illegible]	[illegible]
[illegible]		
-13	[illegible]	[illegible]
-12	[illegible]	46
-11	[illegible]	155
-10	[illegible]	207
-9	[illegible]	[illegible]
-8	[illegible]	11
-7	[illegible]	[illegible]
-6	[illegible]	[illegible]
-5	222	[illegible]
-4	26*	42
-3	226	229
-2	327	[illegible]
-1	[illegible]	100
0	24*	26
1	180	181
2	271	[illegible]
6,3,L		
-13	316	360
-12	581	551
-11	73	68
-10	597	588
-9	384	388
-8	752	755
-7	63	30
-6	686	663
-5	414	404
-4	756	734
-3	0*	8
-2	712	698
-1	339	329
0	549	532
1	22*	14
6,4,L		
-12	197	195
-11	220	217
-10	132	131
-9	203	204
-8	287	292
-7	278	270
-6	158	141
-5	260	255
-4	248	246
-3	267	262
-2	112	92
-1	240	235
0	158	157
6,5,L		
-10	545	518
-9	170	159
-8	479	450
-7	486	466
-6	634	609
-5	220	210
-4	537	509
-3	472	440
-2	536	505
-1	221	205
6,6,L		
-8	257	248
-7	146	139
-6	42	84
-5	122	123
-4	299	291
-3	162	157
7,0,L		
-12	785	747
-10	538	526
-8	669	404
-6	584	588
-4	883	910
-2	515	517
0	705	712
7,1,L		
-13	281	197
-12	49	47
-11	55	48
-10	53	44
-9	260	255
-8	54	55
-7	59	48
-6	56	45
-5	264	265
-4	112	117
-3	66	52
-2	38*	21
-1	286	213
0	41*	52
7,2,L		
-12	513	496
-11	469	456
-10	318	302
-9	513	504
-8	634	630
-7	519	504
-6	380	353
-5	531	508
-4	610	609
-3	476	458
-2	330	379
-1	430	424
7,3,L		
-12	74	69
-11	91	95
-10	53	26
-9	207	210
-8	40*	11
-7	115	113
-6	139	139
-5	210	202
-4	40*	16
-3	139	130
-2	143	137
7,4,L		
-10	207	196
-9	209	263
-8	35	42
-7	615	579
-6	213	193
-5	624	562
-4	99	104
-3	565	530
7,5,L		
-8	57	37
-7	114	113
-6	45*	10
-5	91	83
8,0,L		
-10	261	255
-8	106	96
-6	188	187
-4	75	67
8,1,L		
-11	609	582
-10	300	242
-9	593	565
-8	234	210
-7	657	673
-6	277	255
-5	376	353
-4	253	245
8,2,L		
-10	146	143
-9	46*	29
-8	53*	45
-7	71	49
-6	156	147
-5	46*	21
8,3,L		
-8	615	577
-7	261	240

A model of the structure shows that it bears a close relationship to the well known $K_2[PtCl_6]$-type. The copper atoms define a highly distorted cubic face-centered pseudocell which corresponds to the arrangement of platinum in $K_2[PtCl_6]$. The edge lengths of this deformed cube (8·80 × 8·80 × 8·40 Å) are equal to the diagonals of the planes *ab* and to the short diagonal of the plane *ac* of the $Ba_2[Cu(OH)_6]$ structure. In comparison, $K_2[PtCl_6]$ has a cubic cell constant of 9·755 Å. It is possible to describe $K_2[PtCl_6]$ in terms of a cubic close-packed assembly of layers containing the K as well as the Cl atoms, with the Pt atoms occupying one half of the octahedral holes between six Cl. In fact, corresponding layers (011) of Ba and OH are observed in the $Ba_2[Cu(OH)_6]$ structure too, as was mentioned above. The formation of close packed layers is favoured by the similarity of the ionic radii of Ba^{2+} and OH^-. The marked distortion of the structure compared with $K_2[PtCl_6]$, connected with a decrease of the ideal coordination number of 12 Cl atoms around K to 8 OH groups around Ba can be explained by the known crystal chemical behaviour of bivalent copper.

The stereochemistry of copper and barium

The coordination polyhedron of the cupric ion in $Ba_2[Cu(OH)_6]$ is formed by four equatorial and two much more distant axial oxygen atoms completing a highly distorted octahedron. Interatomic distances and bond angles of the $[Cu(OH)_6]^{4-}$ octahedron are given in Fig. 3.

Table 5. *Copper*(II)*-oxygen bond lengths* (Å) *of selected* (4+2) *or* (4+1+1) *distorted octahedra in recently published crystal structures*

Compound	Reference	Central atom	Coordination number	Average of 4 equatorial bonds (Å)	Average of 2 axial bonds (Å)
$Ba_2[Cu(OH)_6]$	This work	Cu	4(+2)	1·965	2·805
CuO	Åsbrink & Norrby (1970)	Cu	4(+2)	1·956	2·784
$Cu_3AsO_4(OH)_3$	Ghose, Fehlmann & Sundaralingam (1965)	Cu(1)	4+1+1	1·942	2·917
		Cu(2)	4+1+1	1·974	2·642
		Cu(3)	4+1+1	1·964	2·576
$CuHPO_3.2H_2O$	Handlovič (1969)	Cu	4+1+1	1·980	2·695
$CuMoO_4$	Abrahams, Bernstein & Jamieson (1968)	Cu(1)	4+1+1	1·950	2·416
		Cu(2)	4+2	1·956	2·313
$CuUO_4$	Siegel & Hoekstra (1968)	Cu	4+2	1·955	2·590
$Cu_2P_4O_{12}$	Laügt, Guitel, Tordjman & Bassi (1972)	Cu(1)	4+2	1·948	2·471
		Cu(2)	4+2	1·954	2·369
$Cu_2SO_3.CuSO_3.2H_2O$	Kierkegaard & Nyberg (1965)	Cu	4+2	1·979	2·467
$CuWO_4$	Kihlborg & Gebert (1970)	Cu	4+2	1·976	2·395
$CuSO_4$ $3H_2O$	Zahrobsky & Baur (1968)	Cu	4+2	1·961	2·424

This coordination is commonly referred as to (4+2) and is explained as a consequence of the Jahn–Teller theorem. In $Ba_2[Cu(OH)_6]$, however, the elongation of the axial bonds is considerable and it could be argued that the coordination is actually square planar. Table 5 contains bond lengths in recently published (4+2) and (4+1+1) distorted copper(II)–oxygen octahedra. It shows that the mean of the four equatorial bond lengths of 1·965 Å is in very good agreement with other structure determinations. The axial bonds of 2·805 Å are at the upper limit of what usually is called a (4+2) coordination; but since these axial atoms lay very close to the expected octahedral positions, as evidenced by the O_{axial}–Cu–O_{eq} angles of 91·7, 88·3, 93·1 and 86·9° (Fig. 3), it is reasonable to describe the coordination of the cupric ion as tetragonal distorted octahedral.

The configuration of the barium–oxygen polyhedron can be best described as follows: six of the coordinating oxygen atoms form a distorted trigonal prism with the barium at its centre; the remaining two oxygen atoms lie just outside the centres of two of the prism faces. For interatomic distances see Table 6.

Table 6. *Barium–oxygen interatomic distances in* $Ba_2[Cu(OH)_6]$ *less than* 3·20 Å

Ba^i–$O(1^i)$	2·826 (5) Å
Ba^i–$O(1^{iii})$	2·642 (3)
Ba^i–$O(1^{iv})$	2·954 (4)
Ba^i–$O(2^i)$	2·716 (4)
Ba^i–$O(2^{ii})$	2·931 (3)
Ba^i–$O(2^{iii})$	2·922 (3)
Ba^i–$O(3^i)$	2·733 (4)
Ba^i–$O(3^{iii})$	2·749 (5)
Mean value	2·809

Symmetry code

i	$x, \; y, \; z;$	iii	$-x, \frac{1}{2}+y, \frac{1}{2}-z$
ii	$-x, -y, -z;$	iv	$x, \frac{1}{2}-y, \frac{1}{2}+z$

As shown in Table 7, this coordination number of eight for barium is rather common, and the mean barium–oxygen distance of 2·809 Å compares well with recently reported values.

Hydrogen bonding and infrared spectra

The positions of possible hydrogen bonds were inferred from an examination of the distances between oxygen atoms which do not belong to the same coordination polyhedron of copper or barium. The infrared spectrum of $Ba_2[Cu(OH)_6]$ in the 3μ region consists of a sharp peak at 3520 cm^{-1} and a broader band at

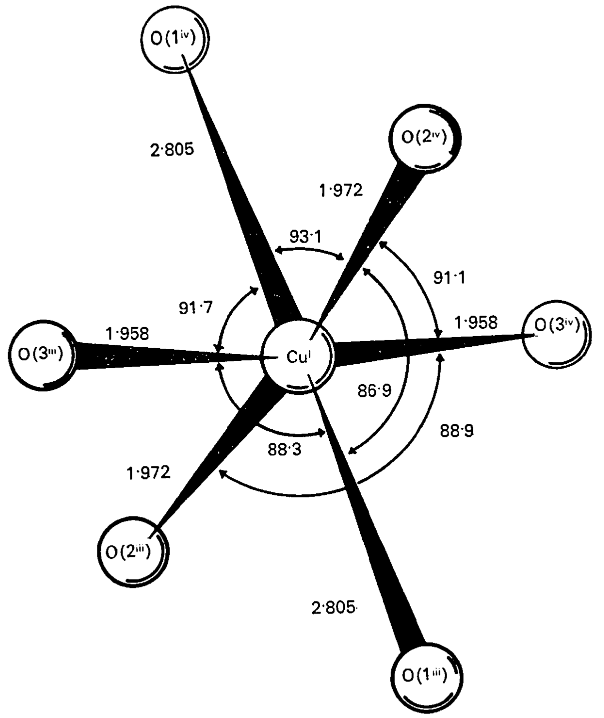

Fig. 3. Interatomic distances (Å) and bond angles (°) of the $[Cu(OH)_6]^{4-}$ polyhedron. The standard deviations σ are 0·004 Å for Cu–O bond lengths and 0·15° for O–Cu–O bond angles.

Table 7. *Mean* Ba–O *distances as a function of coordination number in recently published crystal structures*

Compound	Reference	Central atom	Coordination number	Mean Ba–O distance (Å)
$Ba_3(VO_4)_2$	Süsse & Buerger (1970)	Ba(1)	6	2·760
$BaTeO_3.H_2O$	Nielson, Hazell & Rasmussen (1971)	Ba	7	2·743
$BaFe_2O_4$	Mitsuda, Mori & Okazaki (1971)	Ba(1)	7	2·807
$BaNaP_3O_9$	Martin & Mitschler (1972)	Ba	8	2·801
$Ba_2[Cu(OH)_6]$	This work	Ba	8	2·809
γ-$Ba[AlO(OH)_2]_2$	Glasser & Giovanoli (1972)	Ba	8	2·893
α-$Ba[AlO(OH)_2]_2$	Ahmed & Glasser (1970*a*)	Ba	9	2·912
$Ba_3(VO_4)_2$	Süsse & Buerger (1970)	Ba(2)	10	2·865
$Ba_2[Al_2(OH)_{10}]$	Ahmed & Glasser (1970*b*)	Ba	11	2·911
$Ba_6Ti_{17}O_{40}$	Tillmanns & Baur (1970)	Ba(1)	11	2·937
		Ba(2)	11	2·939
$BaFe_2O_4$	Mitsuda, Mori & Okazaki (1971)	Ba(2)	11	2·968
$Ba_6Ti_{17}O_{40}$	Tillmanns & Baur (1970)	Ba(3)	12	2·925
$BaC_2O_4.H_2C_2O_4.2H_2O$	Dusausoy, Protas, Mutin & Watelle (1970)	Ba	12	2·948
$BaTi_5O_{11}$	Tillmanns (1969)	Ba	12	2·966

3320 cm^{-1}. The sharp peak at 3520 cm^{-1} indicates a practically free OH group, while the peak at 3320 cm^{-1} shows the presence of an OH group which is influenced by a weak hydrogen bond. There is one reasonable hydrogen-bonding distance of 2·902 Å in the structure between $O(1^{i})$ and $O(3^{iii})$. This distance is in reasonable agreement with the hydrogen bonded O–O length of about 2·85 Å which may be deduced from the infrared peak at 3320 cm^{-1} (Schwarzmann 1962). The coordination of O(1) including the hydrogen bonding to O(3) becomes approximately tetrahedral, O(1) being surrounded by three barium atoms and one oxygen atom.

No definite hydrogen bonds seem to exist between O(1)–O(2) and O(2)–O(3).

The authors are indebted to Dr D. Schwarzenbach and Dr W. Petter, Institut für Kristallographie und Petrographie, Eidg. Technische Hochschule Zürich, for the use of computer programs and assistance in the computations. We thank Professor Dr H. G. von Schnering, University of Münster, B.R.D., for valuable discussions. Financial support from the 'Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung' under project Nr. 2.691.72 is gratefully acknowledged.

References

Abrahams, S. C., Bernstein, J. L. & Jamieson, P. B. (1968). *J. Chem. Phys.* **48**, 2619–2629.

Ahmed, A. H. M. & Glasser, L. S. D. (1970*a*). *Acta Cryst.* **B26**, 1686–1690.

Ahmed, A. H. M. & Glasser, L. S. D. (1970*b*). *Acta Cryst.* **B26**, 867–871.

Busing, W. R. (1966). Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Dusausoy, Y., Protas, J., Mutin, J. C. & Watelle, G. (1970). *Acta Cryst.* **B26**, 1567–1574.

Ghose, S., Fehlmann, M. & Sundaralingam, M. (1965). *Acta Cryst.* **18**, 777–787.

Glasser, L. S. D. & Giovanoli, R. (1972). *Acta Cryst.* **B28**, 760–763.

Handlovič, M. (1969). *Acta Cryst.* **B25**, 227–231.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Kierkegaard, P. & Nyberg, B. (1965). *Acta Chem. Scand.* **19**, 2189–2199.

Kihlborg, L. & Gebert, E. (1970). *Acta Cryst.* **B26**, 1020–1026.

Larson, A. C. (1967). *Acta Cryst.* **23**, 664–665.

Laügt, M., Guitel, J. C., Tordjman, I. & Bassi, G. (1972). *Acta Cryst.* **B28**, 201–208.

Martin, C. & Mitschler, A. (1972). *Acta Cryst.* **B28**, 2348–2352.

Mitsuda, H., Mori, S. & Okazaki, C. (1971). *Acta Cryst.* **B27**, 1263–1269.

Nielson, B. R., Hazell, R. G. & Rasmussen, S. E. (1971). *Acta Chem. Scand.* **25**, 3037–3042.

Scholder, R. (1962). *Handbuch der präparativen anorganischen Chemie.* Edited by G. Brauer. Stuttgart: F. Enke.

Schwarzenbach, D. (1972). Institut für Kristallographie und Petrographie, Eidg. Techn. Hochschule, Zürich. Unpublished.

Schwarzmann, E. (1962). *Z. anorg. allgem. Chem.* **317**, 176–185.

Siegel, S. & Hoekstra, H. R. (1968). *Acta Cryst.* **B24**, 967–970.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). Program System XRAY 67, version of July 1970. Computer Science Center, Univ. of Maryland.

Süsse, P. & Buerger, M. J. (1970). *Z. Kristallogr.* **131**, 161–174.

Tillmanns, E. (1969). *Acta Cryst.* **B25**, 1444–1452.

Tillmanns, E. & Baur, W. H. (1970). *Acta Cryst.* **B26**, 1645–1654.

Zahrobsky, R. F. & Baur, W. H. (1968). *Acta Cryst.* **B24**, 508–513.

Åsbrink, S. & Norrby, L.-J. (1970). *Acta Cryst.* **B26**, 8–15.