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Preparation, Structure, and Properties of the Tetramethylammonium Salt of μ_4-Oxo-hexa-μ-chloro-tetra(chlorocuprate(II))

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Received May 19, 1969

The preparation, structure, and properties of a polynuclear copper(II) compound, $[(CH_3)_4N]_4[Cu_4OCl_{10}]$, are reported. The compound crystallizes as red, cubic crystals (a = 19.30 ± 0.02 Å) of space group $P\bar{4}3n$ with eight formula units per unit cell; the calculated density of 1.70 g/cm^3 agrees well with the experimental value of 1.69 ± 0.02 g/cm^3. A total of 310 unique, nonzero reflections were visually estimated from precession camera photographs; least-squares refinement resulted in a conventional R value of 9.0%. The polynuclear anion contains a central oxide ion coordinated tetrahedrally to four copper(II) ions; the copper(II) ions are bridged in pairs by six chloride ions. The remaining four chloride ions complete a trigonal-bipyramidal coordination sphere around each copper(II) ion. Although there are two crystallographically independent anions, the two are virtually identical and undistorted. Average bond distances and angles are: Cu–O, 1.93 ± 0.01 Å; Cu–Cl_{ax}, 2.21 ± 0.04 Å; Cu–Cl_{eq}, 2.41 ± 0.02 Å; Cl_{eq}–Cu–Cl_{eq}, 119 ± 0°; O–Cu–Cl_{ax}, 179 ± 1°.

Introduction

In several recent papers,[2-4] structures have been reported for polynuclear complexes of copper(II) with the general formula $Cu_4OCl_6L_4$. In these complexes, an oxide ion is tetrahedrally coordinated to four copper(II) ions (Cu–O distance of 1.90 Å compared to 1.95 Å in CuO) and coordination about copper is essentially trigonal bipyramidal. The chloride ions, which bridge adjacent copper(II) ions along the six edges of the tetrahedron, form an undistorted octahedron about the central oxygen in the compound with L = triphenylphosphine oxide[2,3] and a distorted octahedron about the central oxygen in the compound with L = pyridine.[4] The conclusion was reached in the case of the pyridine compound that the distortion resulted from intermolecular contacts.

In a preliminary communication,[2] the preparation of an ionic species $Cu_4OCl_{10}^{4-}$ was reported; although it was expected to have a μ_4-oxo type of structure ($Cu_4OCl_6L_4$ with L = Cl^-), the structure was of interest because of (1) its ionic nature, (2) the possibility of obtaining further information about the nature of the distortion of the chloride octahedron, and (3) the possibility of comparing the coordination of copper to that reported[5,6] for the $CuCl_5^{3-}$ ion. In this paper, we report the structure of the tetramethylammonium salt of $Cu_4OCl_{10}^{4-}$.

Experimental Section

Preparation.—A methanol solution of anhydrous $CuCl_2$ was refluxed with CuO for 24 hr; a stoichiometric amount of $(CH_3)_4NCl$ was added to the hot solution. Deep red octahedral-shaped crystals deposited over a period of about 24 hr; the crystals were filtered and dried in a vacuum desiccator over sulfuric acid. *Anal.* Calcd for $Cu_4OCl_{10}N_4C_{16}H_{48}$: Cu, 27.58; Cl, 38.48; C, 20.85; H, 5.26. Found: Cu, 27.77; Cl, 38.10; C, 21.00; H, 5.22.

Magnetic Susceptibility Measurement.—The magnetic susceptibility of the compound, 2162 × 10^{-6} cgsu/g-atom of Cu, was determined by the Gouy method at 25° using $HgCo(CNS)_4$ as a calibrant. A correction for diamagnetism (133 × 10^{-6} cgsu/g-atom of Cu) was made, using published atomic values.[7] The value of μ_{eff} was found to be 2.2 ± 0.1 BM.

Collection and Reduction of X-Ray Data.—The crystal chosen for space group determination was octahedral shaped with an average trigonal face to trigonal face distance of 0.3 mm. Precession photographs, using Zr-filtered Mo Kα (λ 0.7107 Å) radiation, indicated that the crystal was cubic with a unit cell dimension, a, of 19.30 ± 0.02 Å; the Laue symmetry was m3m and the *hhl* reflections were systematically absent for l odd. Although space groups Pm3n and $P\bar{4}3n$ were possible, only the latter was consistent with the presence of eight anions per unit cell and the successful refinement confirmed $P\bar{4}3n$ as the correct space group. The calculated density of 1.70 g/cm^3 agrees well with the experimental value of 1.69 ± 0.02 g/cm^3 obtained by the flotation method using carbon tetrachloride and methylene iodide.

Intensity data were collected using the same crystal as used for the space group determination; a precession camera and Zr-filtered Mo Kα radiation (λ 0.7107 Å) were used to collect a total of 310 unique, nonzero reflections (visually estimated) from the *hkL* layers (L = 0–4). Lorentz and polarization (Lp) corrections were computed; for unobserved reflections, F_{min} values were obtained by multiplying I_{min} of the standard series by the Lp factor for the reflection and then taking the square root of the product. No corrections for absorption were made; the calculated absorption coefficient, μ, is 32 cm^{-1}.

Solution of the Structure.—From a three-dimensional Patterson synthesis and the assumption that the basic structural unit would be similar to that found in other $Cu_4OCl_6L_4$ structures, coordinates were assigned to all atoms except those of the tetramethylammonium ions. The eight oxygens occupied a 2a set[8] (site symmetry 23) and a 6c set (site symmetry $\bar{4}$); the copper ions coordinated to the oxygens of the 2a set (origin anion) occupied an 8e set and the copper ions coordinated to the oxygens of the 6c set (nonorigin anion) occupied general positions 24i. The bridging chlorides of the origin anion were placed in a 12f set and the bridging chlorides of the nonorigin anion required 12g and 24i sets (since the bridging chlorides occupy equatorial positions in the coordination sphere of copper, they will be designated Cl_{eq}; primed symbols will be used throughout for the nonorigin anion). The terminal chlorides (designated Cl_{ax}) were placed in an 8e set for the origin anion and a general, 24i, set for the nonorigin anion.

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[1] Alfred P. Sloan Research Fellow, 1966–1968.

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[7] B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 403.

[8] "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965.

Two cycles of full-matrix least-squares refinement of coordinates resulted in a conventional R value $(\Sigma/||F_o| - |F_c||/\Sigma|F_o|)$ of 0.17; a Fourier synthesis was then computed, using the phases calculated for the known part of the structure, and the remaining nonhydrogen atoms were located. Least-squares refinement of all atom coordinates not defined by symmetry, individual isotropic temperature factors, and individual scale factors for the five layers of data was continued until successive cycles gave no appreciable change in any parameter; the final R value (conventional) was 0.090. Structure factors were calculated for unobserved reflections; none of the calculated values exceeded $2F_{\min}$. Table I lists the final structural parameters and Table II lists observed and calculated structure factors.

TABLE I

POSITIONAL AND THERMAL PARAMETERS FOR $[(CH_3)_4N]_4[Cu_4OCl_{10}]$

Atom	x	y	z	B, Å^2
O	0	0	0	2.4 (2.3)[a]
O′	$^1/_4$	$^1/_2$	0	8.7 (3.0)
Cu	0.0582 (5)	0.0582 (5)	0.0582 (5)	4.3 (3)
Cu′	0.1922 (5)	0.5501 (4)	0.0637 (4)	3.6 (2)
Cl_{eq}	0.1537 (20)	0	0	7.2 (8)
Cl_{eq}' (1)	0.0980 (14)	$^1/_2$	0	4.8 (5)
Cl_{eq}' (2)	0.2457 (8)	0.6511 (8)	0.0178 (8)	3.7 (3)
Cl_{ax}	0.1231 (13)	0.1231	0.1231	8.2 (1.4)
Cl_{ax}'	0.1295 (9)	0.6100 (9)	0.1417 (10)	5.5 (5)
N	0.3401 (34)	0.3401	0.3401	5.1 (2.4)
N′	0.8549 (39)	0.9243 (42)	0.3459 (40)	7.3 (1.9)
C(1)	0.2955 (60)	0.2955	0.2955	12.9 (5.9)
C(2)	0.3365 (68)	0.4060 (49)	0.3251 (61)	9.9 (3.2)
C′(1)	0.8046 (48)	0.9532 (47)	0.2916 (48)	9.1 (2.3)
C′(2)	0.8490 (41)	0.8449 (41)	0.3276 (40)	7.1 (1.8)
C′(3)	0.9284 (43)	0.9246 (43)	0.3371 (50)	8.3 (2.0)
C′(4)	0.8418 (41)	0.9242 (36)	0.4108 (40)	5.3 (1.5)

[a] Numbers in parentheses here and elsewhere are the estimated standard deviations occurring in the last digitslisted. None is given for parameters fixed by symmetry.

Computations were carried out on the Burroughs 5500 computer and on the Univac 1108 computer; programs employed included modified versions of Zalkin's FORDAP Fourier summation program, the Busing–Martin–Levy ORFLS and ORFFE least-squares and function and error programs, and various locally written programs. In structure factor calculations, the scattering factors tabulated by Ibers[9] were employed for all atoms. No corrections were made for anomalous dispersion.

Description of the Structure

The structure consists of two independent polynuclear units of $Cu_4OCl_{10}^{4-}$; the basic structural unit, Figure 1, is analogous to that found for $Cu_4OCl_6(OP(C_6H_5)_3)_4$,[2,3] $Cu_4OCl_6(py)_4$,[4] and $Mg_4OBr_6(C_4H_{10}O)_4$.[10] Interatomic distances and angles are given in Table III.

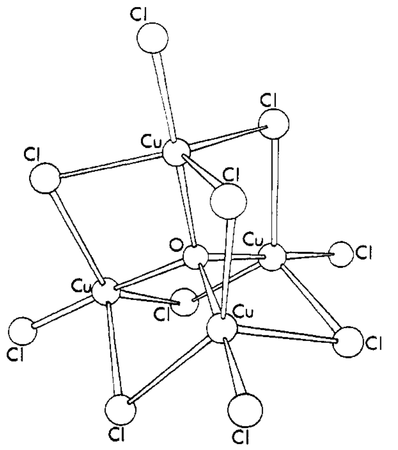

Figure 1.—A perspective drawing of the structure of the $Cu_4OCl_{10}^{4-}$ anion.

Although crystallographically independent, the only significant difference in the two anions is the Cu–Cl_{ax} distance, 2.17 (2) Å in the origin anion and 2.25 (2) Å in the nonorigin anion. The Cu–O distances, 1.95 (1) and 1.92 (1) Å, agree well with the values from the previous structures, 1.88–1.92 (2) Å, and with the value for copper(II) oxide, 1.95 Å. The octahedron of bridging chlorides for the origin anion is, because of symmetry, undistorted with a Cu–Cl_{eq} distance of 2.43 (3) Å; that the chloride octahedron of the nonorigin anion is not significantly distorted is indicated by the agreement between Cu–Cl_{eq} distances, 2.38 (2)–2.45 (2) Å, and the agreement between Cl_{eq}–Cu–Cl_{eq} angles,118.0 (5)–120.5 (5)°. As in previous structures, the copper is displaced out of the equatorial plane and away from the oxygen to give Cl_{eq}–Cu–O angles of 85 (1)° for both anions; the O–Cu–Cl_{ax} arrangement is linear because of symmetry

TABLE II

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES FOR $[(CH_3)_4N]_4[Cu_4OCl_{10}]$

H	K	FO	FC
L=0			
H	K	FO	FC
3	3	733	731
4	0	3493	3175
4	2	550	595
4	3	423	463
4	4	4950	4724
6	0	2422	2244
6	1	1719	1779
6	5	828	981
7	3	462	480
7	6	3105	3131
8	0	1967	1511
8	2	1121	1085
8	4	1516	1598
8	6	2298	2434
8	8	6932	7013
9	2	1984	1970
9	4	601	530
9	6	1856	1962
10	0	2582	2687
10	1	2184	2126
10	3	1527	1443
10	5	1270	1394
10	7	1459	1516
10	8	1623	1716
10	9	1168	1235
11	2	1293	1270
11	6	1053	992
11	7	674	724
11	10	703	753
12	4	1172	780
12	5	340	400
12	6	1537	1413
12	7	347	181
12	8	1403	1338
12	10	359	352
12	12	1383	1519
13	2	775	774
13	3	491	526
13	4	349	557
13	5	496	557
13	6	1224	1052
13	12	375	517
14	0	1423	1479
14	1	1744	1595
14	4	507	200
14	5	882	831
15	1	365	409
15	2	517	466
15	3	732	844
15	10	536	539
15	15	551	559
16	0	2237	2381
16	2	1180	1133
16	5	531	439
16	6	376	287
16	8	1316	1234
16	10	542	493
16	11	385	311
16	12	774	690
16	16	669	492
17	2	536	601
17	4	380	460
17	6	540	471
17	10	669	730
17	16	380	168
18	1	941	1022
18	3	544	640
18	7	386	388
18	8	547	551
18	9	671	647
19	2	548	556
20	0	1739	1367
20	2	777	677
20	4	673	468
24	0	625	447
L=1			
H	K	FO	FC
3	2	1239	1050
4	3	2124	2137
4	1	2233	2098
4	2	2172	2004
5	2	570	487
6	2	626	584
6	1	601	656
6	4	1502	1647
6	5	2441	2413
7	2	720	764
7	3	421	592
7	4	303	310
7	5	1158	1102
7	6	2242	2385
8	2	1405	1519
8	4	1017	941
8	5	1601	1535
8	6	2355	2408
8	7	1075	1223
9	2	1761	1867
9	4	830	840
9	5	767	770
9	6	1707	1647
9	8	1021	782
10	1	1395	1235
10	3	2228	2089
10	4	502	614
10	7	2179	2336
10	8	1296	1249
10	9	1076	1260
11	2	1157	1031
11	4	1171	975
11	5	1181	1181
11	6	1306	1274
11	10	398	360
12	1	537	500
12	2	538	546
12	5	948	807
12	6	1460	1374
12	7	557	480
12	11	585	827
13	2	394	332
13	3	791	782
13	4	889	922
13	5	399	418
13	6	697	736
13	10	418	382
14	1	704	636
14	2	575	579
14	3	1527	1274
14	4	409	357
14	6	413	325
14	11	431	484
14	12	616	703
14	13	440	583
15	2	1025	916
15	3	419	421
15	10	615	672
15	11	438	495
15	12	442	297
15	13	445	534
16	1	741	810
16	2	428	591
16	3	607	536
16	5	431	289
16	6	612	560
16	10	765	867
16	13	450	443
17	2	757	784
17	3	619	609
17	6	623	461
17	10	775	844
18	1	1406	1470
18	4	446	289
18	5	446	393
18	6	447	338
18	7	634	379
18	8	636	633
18	9	780	629
18	11	453	453
19	2	637	545
20	2	643	547
22	4	455	294
L=2			
H	K	FO	FC
3	3	1805	1812
4	1	1994	2004
4	2	2267	2325
4	3	2588	2872
4	4	1621	1745
5	1	555	487
5	3	807	821
5	4	2529	2561
5	5	1189	1191
6	1	582	584
6	2	1454	988
6	4	1785	1901
6	6	5256	4925
7	3	1031	990
7	4	1363	1244
7	5	1083	1041
7	7	2565	2506
8	3	1696	1817
8	4	460	665
8	5	1151	1069
8	6	339	410
8	7	1702	1635
8	8	1884	1861
9	3	1672	1769
9	4	977	1054
9	6	356	390
9	7	1360	1325
9	8	1173	1246
9	9	1515	1623
10	2	2264	2557
10	4	728	960
10	5	521	643
10	6	2362	2326
10	10	565	730
11	3	1311	1321
11	4	1525	1429
11	6	550	449
11	7	788	816
11	8	692	741
11	11	592	556
12	3	1478	1428
12	5	693	717
12	6	700	782
12	7	913	1011
12	8	584	614
12	9	418	489
12	12	436	575
13	3	410	269
13	4	922	895
13	5	1245	1161
13	8	425	358
13	12	631	782
13	13	639	748
14	2	2395	2376
14	4	953	893
14	6	862	759
14	8	437	315
14	10	445	659
14	12	455	581
14	14	806	833
15	8	448	453
15	9	639	592
15	12	655	554
16	5	639	687
16	6	454	302
16	7	456	560
16	8	794	791
16	9	799	853
16	11	810	702
17	7	658	668
17	8	661	694
17	9	664	602
18	1	468	323
19	3	477	446
L=3			
H	K	FO	FC
5	4	1865	1777
6	3	1879	1844
6	4	1996	1968
7	4	2193	2174
7	6	1421	1527
10	8	435	582
11	4	1135	1180
11	5	434	280
11	6	439	478
11	8	784	664
11	9	651	644
10	6	420	564
9	5	874	872
9	8	723	685
9	7	816	788
10	3	1138	1033
10	4	1995	2021
10	5	584	648
9	6	1056	946
9	4	542	598
8	4	506	559
8	6	1068	1010
8	7	549	704
12	3	1180	1097
12	5	2028	2159
12	6	794	825
12	7	927	823
12	11	850	1087
13	4	1623	1385
13	6	476	380
13	7	480	430
13	12	722	645
14	4	1086	1081
14	7	496	255
14	11	730	699
14	12	522	551
15	4	710	735
15	12	754	752
16	3	515	534
16	10	927	933
20	3	795	791
L=4			
H	K	FO	FC
5	5	2941	3275
6	6	1574	1917
7	5	1819	1673
7	6	1468	1493
7	7	603	524
8	4	1523	1357
8	6	437	388
9	5	785	603
9	6	465	529
9	7	478	533
10	4	1161	1190
10	5	1366	1364
10	6	697	697
11	5	1251	1413
11	6	734	744
11	7	1180	1134
11	11	569	653
12	4	2124	1943
12	8	969	939
13	5	1374	1413
13	6	1267	1237
13	7	573	698
13	11	604	740
13	13	622	678
14	5	1167	1097
14	6	832	1142
14	7	840	973
14	13	637	771
14	14	645	641
15	5	1209	1169
15	6	608	847
15	11	637	794
16	4	1076	935
16	6	627	357
16	8	899	840
17	6	645	357
19	7	677	638

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TABLE III

INTERATOMIC DISTANCES AND ANGLES WITHIN THE $\mathrm{Cu_4OCl_{10}}^{4-}$ ANIONS

Atoms	Distance, Å	Atoms	Angle, deg	Atoms	Angle, deg
Cu–O	1.95 (1)	Cu–O–Cu	109.5	Cl$_{eq}$′(1)–Cu′–Cl$_{eq}$′(2)	118.0 (5)
Cu′–O′	1.92 (1)	Cu′–O′–Cu′	109.0 (5)		120.5 (5)
Cu–Cu	3.18 (1)		109.7 (3)	Cl$_{eq}$′(2)–Cu′–Cl$_{eq}$′ (2)	118.9 (4)
Cu′–Cu′	3.14 (1)	O–Cu–Cl$_{ax}$	180.0	Cl$_{ax}$–Cu–Cl$_{eq}$	95.5 (8)
Cu–Cl$_{eq}$	2.43 (3)	O′–Cu′–Cl$_{ax}$′	177.0 (7)	Cl$_{ax}$′–Cu′–Cl$_{eq}$′ (1)	98.2 (7)
Cu′–Cl$_{eq}$′(1)	2.40 (2)	O–Cu–Cl$_{eq}$	84.5 (6)	Cl$_{ax}$′–Cu′–Cl$_{eq}$′(2)	93.5 (7)
Cu′–Cl$_{eq}$′(2)	2.38 (2)	O′–Cu′–Cl$_{eq}$′(1)	84.8 (5)		94.4 (7)
	2.45 (2)	O′–Cu′–Cl$_{eq}$′(2)	85.6 (5)	Cu–Cl$_{eq}$–Cu	81.5 (1.2)
Cu–Cl$_{ax}$	2.17 (2)		83.5 (5)	Cu′–Cl$_{eq}$′(1)–Cu′	81.4 (9)
Cu′–Cl$_{ax}$′	2.25 (2)	Cl$_{eq}$–Cu–Cl$_{eq}$	119.1 (2)	Cu′–Cl$_{oq}$′(2)–Cu′	81.2 (6)

requirements in the origin anion and only slightly bent, 177.0 (7)°, in the nonorigin anion.

The bond distances and bond angles of the tetramethylammonium ions are given in Table IV. The high temperature factor for C(1) suggests the possibility of disorder; however, no unusual features were noted in the final difference Fourier map in the vicinity of this group. The temperature factor of O′ is also high; the high value probably results from inaccuracies in the data and the fact that the motion of the copper atoms was treated as isotropic rather than anisotropic.

TABLE IV

INTERATOMIC DISTANCES AND ANGLES WITHIN THE TETRAMETHYLAMMONIUM CATIONS

Atoms	Distance, Å	Atoms	Angle, deg
N–C(1)	1.49 (7)	C(1)–N–C(2)	113.8 (7.2)
N–C(2)	1.31 (9)	C(2)–N–C(2)	104.8 (6.7)
N′–C′(1)	1.53 (9)	C′(1)–N′–C′(2)	98.8 (6.0)
N′–C′(2)	1.58 (11)	C′(1)–N′–C′(3)	123.0 (7.7)
N′–C′(3)	1.43 (10)	C′(1)–N′–C′(4)	123.1 (8.1)
N′–C′(4)	1.28 (10)	C′(2)–N′–C′(3)	92.7 (6 6)
		C′(2)–N′–C′(4)	101.8 (8.4)
		C′(3)–N′–C′(4)	108.2 (8.0)

Discussion

The complex anion can be thought of as a member of the series of compounds with the general formula $\mathrm{Cu_4OCl_6L_4}$; the basic $\mathrm{Cu_4OCl_6}$ unit in the two independent anions and in the previously reported structure for the compound with L = triphenylphosphine oxide[2,3] are all essentially identical; the compound with L = pyridine[4] is very similar but shows a significant distortion of the chloride octahedron (Cu–Cl distances vary from 2.36 to 2.49 Å; Cl–Cu–Cl angles vary from 108 to 138°). Since none of the other complexes shows such distortion, it appears that intramolecular contacts between pyridine carbons and the chlorides are responsible.

One of the interesting features of the structure of the triphenylphosphine oxide complex was the linear P–O–Cu arrangement; it was suggested that such an arrangement could be a result of π bonding, with back-donation from copper to the phosphine oxide, and that this factor would strengthen the bond between copper and the oxygen of the phosphine oxide. A similar effect in the present complex, involving back-donation from the copper to the vacant 3d orbitals of the chloride, should result in a shortening of the Cu–Cl$_{ax}$ distance; the Cu–Cl$_{ax}$ distances (2.17 (2), 2.25 (2) Å) are considerably shorter than the Cu–Cl$_{eq}$ distances (2.38 (2)–2.45 (2) Å).

Comparison of the coordination sphere of copper in the polynuclear anions and in the $\mathrm{CuCl_5}^{3-}$ ion[5,6] shows good agreement; in both cases, the Cu–Cl$_{ax}$ distances are considerably less than the Cu–Cl$_{eq}$ distances. The Cu–Cl$_{eq}$ distances in the polynuclear anions (2.38 (2)–2.45 (2) Å) and in the $\mathrm{CuCl_5}^{3-}$ ion (2.39 Å) are identical even though the Cl$_{eq}$ atoms in the polynuclear anion are bridging groups; comparison of the Cu–Cl$_{eq}$ distances of the polynuclear anions (2.17 (2), 2.25 (2) Å) with that of $\mathrm{CuCl_5}^{3-}$ (2.30 Å) shows a significant shortening only in the case of the origin anion. The shorter distance for Cu–Cl$_{ax}$ than for Cu–Cl$_{eq}$ is consistent with the π-bonding argument; a shorter Cu–Cl$_{ax}$ distance in the polynuclear anion than in $\mathrm{CuCl_5}^{3-}$ is also consistent since in the $\mathrm{CuCl_5}^{3-}$ ion two axial chlorides would compete for the copper electrons in the same manner that *trans*-carbonyl groups compete for metal electrons (and weaken bonds) in metal carbonyl complexes.

The normal magnetic moment, 2.2 BM, observed for $\mathrm{[(CH_3)_4N]_4[Cu_4OCl_{10}]}$ at room temperature is similar to the moments reported for the other $\mathrm{Cu_4OCl_6L_4}$ compounds. Although normal, these moments are nevertheless unusual since most copper(II) complexes with oxygen bridges exhibit subnormal moments at room temperature owing to superexchange. The explanation for this different behavior may be related to the fact that the oxygen atom in the μ_4-oxo complexes has no low-energy orbitals available for superexchange through a π-type interaction. In this respect, it is significant that the copper complex of the Schiff's base of acetylacetone and 2-aminoethanol has a normal moment of 1.84 BM and a recent structure determination[11] indicates that the alkoxide oxygens form μ_3 bridges; all outer orbitals of the bridging oxygens are, thus, involved in σ bonding (to three copper ions and one carbon atom) and there are no low-energy orbitals available for a π-type interaction. Studies of other polynuclear copper(II) complexes with normal moments are in progress.

It is interesting that the copper(II) tetrahedra in the Schiff's base complex, which has a cubane-type structure,[11] and in the μ_4-oxo complexes are almost identical (Cu–Cu distances of 3.01 and 3.26 Å in the cubane-type structure and 3.09–3.17 Å in the μ_4-oxo comples). In

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the cubane-type structure alkoxide oxygens are above the faces of the copper(II) tetrahedron and in the μ_4-oxo structure there is an oxygen at the center of the tetrahedron and a chloride above each edge; the close relationship between the bonding in these two types of structures has been discussed.[12]

Acknowledgments.—This work was supported by NSF Grant GP-7406. The help of the Rich Electronic Computer Center of Georgia Institute of Technology with computations is gratefully acknowledged.

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The C Rare Earth Oxide–Corundum Transition and Crystal Chemistry of Oxides Having the Corundum Structure

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Received December 2, 1968

Syntheses of new corundum-type phases at a pressure of 65 kbars show that complete solid solubility exists in the systems In_2O_3–Tl_2O_3, In_2O_3–Fe_2O_3, and Fe_2O_3–Ga_2O_3. Sc_2O_3 is soluble in In_2O_3 up to a ratio of about 1:1. A structure refinement of In_2O_3 II resulted in average interatomic distances essentially the same as those found for In_2O_3 I. Attempts to refine the structure of Tl_2O_3 II were not successful. Consideration of the structural relationships among corundum, B rare earth oxides, and C rare earth oxides and comparison of electronegativity differences between In_2O_3 and the rare earth oxides suggests why In_2O_3 and Tl_2O_3 transform to the corundum structure whereas Sc_2O_3, Y_2O_3, Lu_2O_3, and Tm_2O_3 transform to the B rare earth oxide structure at high pressure. Plots of effective cationic volume *vs.* unit cell volume, normalized *c/a* ratios *vs.* d-electron configuration, and metal–metal distances *vs.* effective ionic radii for all corundum-type phases provide a better understanding of the crystal chemistry of corundum-type oxides. Interatomic distances and *c/a* ratios are shown to be consistent with the Goodenough model which correlates electrical properties with metal–metal interactions. In addition, these correlations have been used to predict individual interatomic distances in the Rh_2O_3 structure.

Introduction

Several simple oxides are known to occur with the corundum (α-Al_2O_3) structure, including Al_2O_3, Ti_2O_3, V_2O_3, Cr_2O_3, Fe_2O_3, Ga_2O_3, and Rh_2O_3.[1] Recently, high-pressure transformations of In_2O_3 and Tl_2O_3, which normally have a C rare earth oxide structure, to a modification with the corundum structure[2] have been reported.[3,4] The corundum modification at high pressure was unexpected in that the usual high-pressure transformation observed for compositions with the C rare earth oxide structure is to the B rare earth oxide form. Hoekstra[5] found that even at intermediate pressures corundum structures are not formed for any of the rare earth oxides. Since density increases in the order C → corundum → B, it was not clear why the rare earth oxides are never found in a corundum modification, while In_2O_3 apparently never adopts the B form.[6] In order to attempt resolution of this problem, we have investigated the effects of pressure on the simple oxides Sc_2O_3, Y_2O_3, Lu_2O_3, Tm_2O_3, and Mn_2O_3 and on the ternary systems In_2O_3–Tl_2O_3, Fe_2O_3–Ga_2O_3, In_2O_3–Fe_2O_3, and In_2O_3–Sc_2O_3. We have also refined the structure of In_2O_3 II. Consideration of the results of this work in relation to the structures of the three available modifications provides a reasonable explanation for the high-pressure stabilization of the particular oxide phases in question.

Least-squares refinements of the structures of the following oxides have been reported: Al_2O_3,[7] Ti_2O_3,[7,8] V_2O_3,[7] Cr_2O_3,[7] Fe_2O_3,[7,9] Ga_2O_3,[10] and In_2O_3.[4] The availability of new crystallographic data for In_2O_3 II and Tl_2O_3 II, whose existence considerably broadens the stability field of known corundum phases, now provides a basis for considering the general crystal chemistry of corundum-type oxides. Such a consideration is also facilitated by the recent derivation of a set of ionic radii,[11] which appear to permit more reliable generalization. Accordingly, we present in the discussion of our work an attempt to correlate systematically the relations between observed structural parameters, chemistry of the various cations, ionic radii, and physical properties for the oxides that are known to have the corundum structure. Finally, the correlation of struc-

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