CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS 02139

The Octachlorodimolybdate(II) Ion. A New Species with a Quadruple Metal–Metal Bond[1]

BY JURIJ V. BRENCIC[2] AND F. A. COTTON

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The compound $K_4Mo_2Cl_8 \cdot 2H_2O$ has been prepared as a red, crystalline solid and definitively characterized by X-ray crystallography as a compound containing the $Mo_2Cl_8^{4-}$ ion, isostructural with the $Re_2Cl_8^{2-}$ and $Tc_2Cl_8^{3-}$ ions. The $Mo_2Cl_8^{4-}$ ion consists of an approximately cubic array of eight chlorine atoms, within which a pair of molybdenum atoms is centered along one fourfold axis. The Mo–Mo distance is 2.138 (4) Å while the mean Mo–Cl bond length is 2.45 Å. The water molecules are bound to the K^+ ions and not to the $Mo_2Cl_8^{4-}$ ions. The eclipsed configuration, the short Mo–Mo bond (*cf.* $Mo_2(O_2CCH_3)_4$, Mo–Mo = 2.11 Å), and the fact that $Mo_2Cl_8^{4-}$ is isoelectronic as well as isostructural with $Re_2Cl_8^{2-}$ leave no doubt that it has the type of quadruple bond (σ, 2π, δ) previously discussed for $Re_2X_8^{2-}$ compounds and their derivatives. The principal crystallographic data are as follows: space group, Pbam; unit cell edges: $a = 8.005 \pm 0.004$ Å, $b = 13.267 \pm 0.006$ Å, $c = 8.059 \pm 0.004$ Å; measured density, 2.54 ± 0.05 g cm^{-3}; density calculated for $Z = 2$, 2.60 g cm^{-3}. The structure was solved and refined using 510 statistically significant nonzero reflections measured with a counter diffractometer. Absorption corrections were applied and anisotropic refinement was carried out to final unweighted and weighted residuals of 0.055 and 0.076, respectively.

Introduction

The existence of a quadruple bond was first recognized[3] in 1965 with the preparation[4,5] and structural characterization[6,7] of the $Re_2Cl_8^{2-}$ ion. Since then, other studies have revealed the existence of additional compounds, for example, $Re_2Cl_6(PR_3)_2$,[8,9] $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$,[10,11] $Mo_2(O_2CCH_3)_4$,[12,13] $Re_2(O_2CR)_4X_2$,[14-16] $Re_2Br_8^{2-}$,[5,17] $Re_2(SCN)_8^{2-}$,[18] which we believe to contain quadruple metal–metal bonds, as well as related compounds, such as $Re_2Cl_5(DTH)_2$[19] and $Ru_2(O_2CR)_4Cl$,[20,21] which are relevant to an understanding of the quadruple and other multiple metal–metal bonds. The nature of the quadruple bond in $Re_2Cl_8^{2-}$ has also been considered in more detail from a theoretical point of view.[22]

The ready interconvertibility of the $Re_2X_8^{2-}$ and $Re_2(O_2CR)_4X_2$ species was established several years ago.[5] By analogy, then, the possibility of converting $Mo_2(O_2CR)_4$ species into $Mo_2X_8^{4-}$ species was apparent to us immediately when the structural nature of $Mo_2(O_2CCH_3)_4$ was reported,[13] and a study of the reactions of $Mo_2(O_2CCH_3)_4$ with hydrohalic acids was undertaken. A variety of products was obtained but none, initially, in crystalline condition. All were relatively insoluble and thus difficult to characterize. In the meantime, Sheldon and his coworkers published several reports upon such reactions and offered detailed though quite unsubstantiated structural proposals.[23,24]

During the past year, we have succeeded in preparing in crystalline form a number of compounds by the action of aqueous hydrochloric acid on $Mo_2(O_2CCH_3)_4$, all of them having a formula of the type $M^I_xMo_yCl_z \cdot w(H_2O)$. The chemical properties and structural characterization of these compounds will be reported in a series of papers of which this is the first. In this first paper we describe the structural investigation of a compound, $K_4Mo_2Cl_8 \cdot 2H_2O$, containing the $Mo_2Cl_8^{4-}$ ion, which was the earliest goal in studying the reactions of $Mo_2(O_2CCH_3)_4$ with hydrohalic acids.

Experimental Procedure

Red crystals of $K_4Mo_2Cl_8 \cdot 2H_2O$ were obtained from cold HCl solution. The compound was identified initially by analysis, infrared spectrum, unit cell volume, and density, and, ultimately, by solving the crystal structure.

Anal. Calcd for $K_4Mo_2Cl_8 \cdot 2H_2O$: Mo, 28.73; Cl, 42.46. Found: Mo, 28.50; Cl, 41.93.

The infrared spectrum, recorded (Beckman 337 spectrometer) from 2.5 to 20.0 μ using a Nujol mull between KBr plates, contained only three bands, at 3500, 3440, and 1635 cm^{-1}, due to

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[2] Fellow of the Samuel Rubin Foundation. On leave from The University of Ljubljana, Ljubljana, Yugoslavia.

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the water of hydration. Their positions and their sharpness indicate that there are no hydrogen bonds of strongly directional character.

The compound appears to be indefinitely stable in air at 25°.

A single, well-formed crystal was selected and used for the entire crystallographic study. This crystal, which differed from a number of others only in being more regular, had six well-developed faces. Two (001, 00$\bar{1}$) were the rhombic bases and four (110, $\bar{1}$10, 1$\bar{1}$0, $\bar{1}\bar{1}$0) were the rectangular sides of a rhombic parallelepiped. Examination under the polarizing microscope showed pronounced birefringence and revealed a set of three mutually perpendicular twofold axes. Thus all morphological and optical evidence indicated mmm point symmetry. The approximate dimensions of the crystal were 0.055 × 0.033 × 0.056 mm.

With the crystal mounted on the c axis, Weissenberg photographs of the hk0, hk1, and hk2 levels were taken with Cu Kα radiation. The suspected mmm symmetry was confirmed and the following systematic absences were observed: 0kl for $k \neq 2n$; h0l for $h \neq 2n$. These observations require that the space group[25] be either Pbam (no. 55) which is centric or Pba2 (no. 32) which is not centric.

Accurate values of the unit cell dimensions were determined by measuring the positions of the h00, 0k0, and 00l series of reflections using a manually operated General Electric XRD-5 counter diffractometer equipped with a quarter-circle eucentric goniometer and extrapolating these to $\theta = 90°$ by a method previously described.[26] Cu Kα radiation ($\lambda(\text{K}\alpha_1)$ 1.5405 Å, $\lambda(\text{K}\alpha_2)$ 1.5443 Å) was used. The uncertainties are based on the results of calibrations with NaCl crystals and represent estimated accuracy rather than merely precision. The dimensions at 24.0 ± 0.5° are $a = 8.005 \pm 0.004$ Å, $b = 13.267 \pm 0.006$ Å, and $c = 8.059 \pm 0.004$ Å.

The density, measured by flotation, is 2.54 ± 0.05 g cm^{-3}. The density calculated using the unit cell dimensions and assuming $Z = 2$ for the formula $K_4Mo_2Cl_8 \cdot 2H_2O$ is 2.60 g cm^{-3}.

The intensities were measured on the XRD-5 diffractometer using nickel-filtered Cu Kα radiation. The crystal was mounted with its c axis coincident with the ϕ axis of the goniometer. Within the range $\theta < 60°$, 709 independent reflections were measured. Each peak was scanned from 2θ(calcd) $-1.33°$ to 2θ(calcd) $+1.33°$ at a scan rate of 4°/min, giving P counts. Background was counted for 20 sec each at the beginning (B_1) and end (B_2) of each scan. The intensity, I, was then taken as $I = P - B_1 - B_2$.

The standard deviation, D, of an I value was taken as $D^2 = P + B_1 + B_2$. Reflections (199) for which $I < 3D$ (including $I \leq 0$) were omitted in solving and refining the structure.

The 00l reflections showed approximately a 30% variation in intensity during rotation about the ϕ axis with $\chi = 90°$. The crystal dimensions were therefore measured and absorption corrections ($\mu = 316.2$ cm^{-1}) were applied. The accuracy of these absorption corrections was confirmed by calculating absorption as a function of ϕ for some 00l reflections and correcting the ϕ-scan curves. The variations with ϕ were reduced to about ±2% in the worst case. The transmission factors, A, were in the range 0.35–0.53.

Structure amplitudes were obtained by applying absorption and Lp corrections to the I's, *viz.*

$$|F_o| = [I/A(\text{Lp})]^{1/2}$$

The standard deviation, $\sigma(F)$, applicable to each observed structure amplitude was taken as

$$\sigma(F) = [D^2 + pI^2]^{1/2}/2A(\text{Lp})|F_o|$$

where $p = 0.002$.

Choice of Space Group.—For Pbam (centric) we have

$$F_{hkl}^2 = F_{\bar{h}\bar{k}l}^2 = F_{\bar{h}\bar{k}\bar{l}}^2$$

whereas, for Pba2 we have

$$F_{hkl}^2 = F_{hkl}^2 \neq F_{\bar{h}\bar{k}\bar{l}}^2$$

For a number of hkl, $\bar{h}\bar{k}\bar{l}$, and $\bar{h}\bar{k}l$ sets, essential equality of F^2's was observed. Anomalous dispersion effects would have produced detectable differences for Pba2. The space group Pbam was therefore assumed. Success in solving the structure and refining it without anomalies to a low discrepancy factor confirms this choice.

Solution and Refinement of the Structure[27]

Solution.—A three-dimensional map of the Patterson function suggested placing the molybdenum atoms on the 4e positions (0, 0, 0.132). By image seeking about the Mo–Mo vector it was possible to identify two sets of chlorine atoms each occupying the general (8i) position. The positions of the four Mo and sixteen Cl atoms, together with their temperature factors and an over-all scale factor, were then refined by least squares for three cycles, giving a residual $R_1 = \Sigma||F_o| - |F_c||/|F_o|$ of 0.28. A difference electron density map was then calculated and potassium atoms were found on 4g and 4h positions. Refinement of the potassium atom coordinates led to $R_1 = 0.114$. From a new difference Fourier map a set of 4h positions was found for the oxygen atoms.

Refinement.—The atomic scattering factors of Cromer and Waber[28] for the neutral atoms Mo, K, Cl, and O were used. Calculated structure factors included corrections for the real and imaginary parts of anomalous scattering[29] by the Mo, K, and Cl atoms. Weighting factors w were equal to $[\sigma(F)]^{-2}$, $\sigma(F)$ being defined earlier. The weighted residual, R_2, is defined as $[\Sigma w \cdot [|F_o| - |F_c|]^2/\Sigma w|F_o|^2]^{1/2}$. Anisotropic temperature factors are expressed as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Using the coordinates available from the previously mentioned Patterson and difference Fourier maps two cycles of isotropic and then two cycles of anisotropic refinement were run, giving the residuals $R_1 = 0.074$ and $R_2 = 0.092$. A difference Fourier map was then computed and peaks of approximate density 7 e/Å^3 were found on a 4g equipoint with coordinates (0.072, 0.064, 0). We believe that these peaks are due to a form of disorder, in which about 7% of the Mo–Mo pairs lie along a fourfold axis of their own Cl_8 cube which is perpendicular to the crystallographic z axis, while the majority (93%) lie parallel to the z axis.

The figure of 7% was selected by trial and error to give the second set of Mo atoms (the Mo*'s) isotropic temperature factors equal to those of the main set of Mo's. Later, the occupancy number was held fixed and the two B values diverged somewhat.

Since some of the Cl_8 groups are occupied by Mo–Mo

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TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10, IN ELECTRONS) FOR $K_4Mo_2Cl_8 \cdot 2H_2O$

H	L	FOBS	FCAL
K = 0**			
2	0	1042	930
4	0	1574	1524
6	0	348	362
8	0	199	226
0	1	1332	1429
2	1	1659	1612
4	1	229	159
6	1	509	470
0	2	504	544
2	2	256	114
4	2	355	386
6	2	356	315
8	2	447	429
0	3	2239	2365
2	3	191	59
4	3	1514	1504
6	3	386	338
8	3	385	386
0	4	956	993
2	4	1107	1120
4	4	620	629
6	4	1489	1488
8	4	731	716
0	5	615	620
2	5	223	157
4	5	595	562
6	5	661	637
0	6	782	746
4	6	287	198
0	7	276	261
2	7	1017	1000
0	8	800	804
2	8	598	601
0	9	712	647
K = 1**			
1	0	1231	1281
2	0	185	181
3	0	2012	2010
5	0	467	419
6	0	433	434
7	0	1086	1113
1	1	959	914
3	1	1042	1037
5	1	447	491
6	1	202	178
7	1	574	600
9	1	188	233
1	2	671	690
2	2	1306	1280
3	2	657	669
4	2	794	763
5	2	771	751
6	2	335	348
7	2	273	245
8	2	355	344
9	2	283	271
1	3	1047	1063
2	3	663	654
3	3	1223	1198
4	3	481	455
5	3	256	168
7	3	556	715
8	3	185	199
1	4	1053	1131
3	4	650	631
5	4	928	898
7	4	455	461
1	5	402	428
2	5	291	244
5	5	839	829
6	5	272	326
2	6	406	343
4	6	311	274
5	6	303	298
1	7	516	518
2	7	225	436
3	7	314	319
4	7	368	366
5	7	886	912
1	8	551	528
3	8	391	438
1	9	279	250
K = 2**			
0	0	1208	1137
2	0	496	445
3	0	1988	2001
4	0	1287	1248
5	0	279	226
6	0	1267	1250
8	0	614	550
0	1	1414	1431
1	1	485	510
3	1	223	124
4	1	1233	1201
5	1	354	296
6	1	470	444
7	1	300	249
8	1	515	536
0	2	944	986
2	2	1295	1247
4	2	650	666
5	2	347	361
8	2	274	260
0	3	915	896
1	3	544	569
2	3	614	636
3	3	666	608
4	3	684	656
6	3	819	836
7	3	270	220
8	3	399	378
0	4	1357	1399
2	4	1113	1153
3	4	1004	1048
4	4	869	840
6	4	461	422
8	4	578	598
1	5	222	217
2	5	1321	1361
3	5	415	496
5	5	352	344
6	5	363	322
7	5	186	155
2	6	527	482
3	6	304	299
6	6	296	322
0	7	632	675
1	7	275	244
2	7	876	902
3	7	489	462
4	7	498	527
0	8	295	294
2	8	809	822
4	8	378	342
K = 3**			
1	0	827	786
2	0	186	117
3	0	1323	1280
4	0	825	804
5	0	387	311
6	0	373	347
7	0	1272	1301
1	1	1011	1012
3	1	737	733
4	1	212	188
5	1	391	339
7	1	458	481
1	2	1464	1444
2	2	479	451
4	2	198	172
5	2	369	353
6	2	317	256
7	2	877	857
8	2	273	301
2	3	206	193
3	3	1001	988
4	3	260	274
5	3	719	731
6	3	300	242
7	3	1150	1106
8	3	235	228
1	4	1024	1063
3	4	901	894
4	4	381	367
5	4	1131	1100
7	4	382	368
1	5	821	824
3	5	417	358
4	5	324	370
5	5	671	612
6	5	293	211
7	5	183	94
3	6	327	259
1	7	1167	1217
3	7	499	489
1	8	663	792
2	8	209	132
3	8	460	440
K = 4**			
0	0	945	916
1	0	909	917
2	0	200	159
3	0	991	1031
4	0	1562	1552
5	0	506	471
6	0	1146	1118
7	0	244	223
8	0	731	722
0	1	685	603
1	1	1056	1101
2	1	628	646
4	1	754	755
5	1	568	547
6	1	716	717
8	1	354	402
0	2	787	794
1	2	1237	1258
3	2	529	557
5	2	756	768
0	3	1293	1287
2	3	477	496
4	3	765	798
6	3	506	476
8	3	434	451
0	4	1238	1289
1	4	201	207
2	4	1384	1426
3	4	691	712
4	4	494	465
5	4	245	179
6	4	440	440
0	5	508	520
1	5	1069	1095
2	5	741	780
4	5	274	201
5	5	669	665
7	5	339	144
1	6	229	193
3	6	303	320
4	6	350	323
5	6	206	231
6	6	302	280
0	7	401	399
2	7	834	849
4	7	436	440
0	8	354	349
1	8	287	268
2	8	472	490
3	8	311	320
K = 5**			
1	0	1789	1785
2	0	377	389
3	0	1362	1354
4	0	703	717
5	0	591	523
6	0	244	213
7	0	517	515
8	0	502	502
1	1	674	684
2	1	260	254
3	1	814	813
5	1	594	551
7	1	516	513
8	1	217	199
1	2	465	480
2	2	529	526
3	2	358	394
5	2	286	253
6	2	300	282
8	2	1067	1079
1	3	1233	1240
3	3	897	865
4	3	691	700
5	3	434	346
6	3	301	268
7	3	401	355
1	4	670	647
2	4	202	215
3	4	704	687
4	4	265	228
5	4	781	831
7	4	637	671
1	5	100	266
3	5	578	537
4	5	551	516
6	5	198	176
1	6	233	151
2	6	294	284
4	6	212	202
5	6	259	224
1	7	319	289
2	7	273	150
3	7	417	413
4	7	529	542
1	8	484	500
2	8	197	64
3	8	459	467
K = 6**			
0	0	2559	2621
1	0	1312	1354
2	0	1390	1415
3	0	662	676
4	0	847	862
5	0	454	441
6	0	247	126
7	0	240	216
8	0	364	351
0	1	1032	1028
1	1	207	174
2	1	1087	1132
3	1	255	260
4	1	263	247
5	1	204	167
6	1	392	367
8	1	254	255
0	2	358	334
2	2	524	580
3	2	605	592
5	2	338	273
7	2	234	239
8	2	299	292
0	3	1151	1137
1	3	676	692
2	3	701	699
3	3	804	775
4	3	905	893
5	3	244	205
6	3	387	388
1	4	680	685
2	4	717	697
3	4	305	288
4	4	746	725
5	4	350	305
6	4	1023	1000
7	4	256	235
1	5	246	200
3	5	272	162
4	5	592	606
6	5	565	547
0	6	355	308
1	7	431	431
2	7	464	475
3	7	560	555
4	7	323	373
0	8	642	663
2	8	406	428
K = 7**			
1	0	742	716
2	0	727	743
3	0	900	929
5	0	1047	1079
6	0	682	704
7	0	684	694
8	0	342	325
1	1	397	426
3	1	632	591
5	1	725	763
6	1	277	222
7	1	508	500
1	2	626	660
2	2	763	771
5	2	244	172
6	2	563	588
7	2	298	257
1	3	1024	1040
2	3	544	645
3	3	636	623
5	3	371	397
6	3	362	340
7	3	284	276
1	4	1064	1058
2	4	293	295
3	4	713	708
5	4	491	456
6	4	399	354
1	5	498	492
2	5	372	386
3	5	444	399
6	5	536	530
5	6	397	353
1	7	371	340
2	7	466	490
3	7	535	522
K = 8**			
2	0	1149	1181
3	0	943	940
4	0	470	398
5	0	247	242
6	0	1040	1082
8	0	615	658
0	1	666	670
2	1	224	216
3	1	394	580
4	1	797	811
6	1	387	374
8	1	527	554
0	2	368	363
1	2	587	613
2	2	360	390
3	2	421	446
4	2	316	269
6	2	241	167
7	2	185	179
1	3	316	308
2	3	538	548
4	3	299	258
6	3	600	775
0	4	1324	1325
1	4	531	520
2	4	567	566
4	4	547	941
6	4	329	310
0	5	774	740
2	5	700	674
3	5	770	752
4	5	240	160
1	6	206	152
2	6	446	458
0	7	1020	1047
1	7	196	204
2	7	370	406
3	7	208	196
K = 9**			
1	0	506	508
3	0	417	391
4	0	700	711
5	0	1062	1059
7	0	469	618
1	1	740	703
3	1	384	403
5	1	455	419
7	1	231	324
1	2	355	379
2	2	272	190
4	2	300	269
5	2	506	512
1	3	317	253
3	3	420	405
4	3	326	287
5	3	903	930
6	3	191	129
1	4	915	923
3	4	857	865
4	4	344	346
1	5	509	495
2	5	365	383
3	5	594	599
1	6	351	327
1	7	774	816
K = 10**			
0	0	402	363
1	0	387	401
2	0	702	735
3	0	297	300
4	0	669	855
5	0	368	328
6	0	509	678
0	1	223	148
1	1	295	273
2	1	720	752
4	1	349	343
6	1	538	761
0	2	228	291
1	2	560	581
2	2	674	706
3	2	273	227
4	2	408	428
5	2	477	507
0	3	818	840
1	3	263	174
2	3	710	686
4	3	467	463
5	3	230	196
0	4	689	873
2	4	832	852
4	4	389	399
0	5	1017	1022
1	5	447	444
4	5	459	492
0	6	229	194
1	6	225	142
K = 11**			
1	0	1380	1400
3	0	598	563
1	1	689	661
2	1	244	257
3	1	411	437
1	2	396	390
2	2	296	264
4	2	510	458
5	2	274	246
1	3	830	811
2	3	344	296
3	3	385	397
4	3	350	350
5	3	624	615
1	4	269	287
2	4	610	617
3	5	390	380
K = 12**			
0	0	689	648
1	0	274	234
2	0	1392	1423
3	0	327	310
4	0	237	230
6	0	354	382
0	1	757	739
2	1	547	547
3	1	244	254
4	1	330	348
5	1	185	140
0	2	212	140
2	2	454	461
3	2	208	157
5	2	307	298
0	3	244	207
2	3	830	892
3	3	403	406
4	3	265	307
0	4	556	563
1	4	261	217
3	4	188	203
2	5	182	94
K = 13**			
1	0	614	589
2	0	322	353
3	0	372	397
4	0	437	434
1	1	296	285
3	1	732	746
1	2	238	157
1	3	624	622
3	3	281	279
1	4	598	596
2	4	210	229
K = 14**			
1	0	704	709
2	0	688	695
0	1	383	414
2	1	476	437
3	1	313	302
0	2	652	629
K = 15**			
3	0	257	263
3	1	249	291

pairs lying in a different direction from the majority, additional uncertainty, beyond that assessed by the calculated esd's, is introduced into the Cl positional parameters; this is because the Cl_8 groups are not perfect cubes independent of the orientation of the Mo–Mo pairs within them. One is looking at nearly but not exactly overlapping distorted Cl_8 cubes.

Anisotropic refinement was resumed with 93% of the Mo atoms assigned to the 4e positions and 7% to the 4g positions. All atoms except O and the Mo atoms on 4g positions were refined anisotropically. After three cycles the residuals fell to $R_1 = 0.055$ and $R_2 = 0.076$. In the final cycle the standard deviation of an observation of unit weight was 1.27 and no positional parameter changed by more than one-tenth of its esd. A final difference Fourier function had no peak higher than 1.3 e$^-$/Å^3 and there were few in this range.

A list of observed and final calculated structure amplitudes is given in Table I.

Results

The final fractional coordinates of the atoms are given in Table II. The anisotropic temperature factors are listed in Table III. The $Mo_2Cl_8^{4-}$ ion is depicted in Figure 1, and the numbering scheme shown here is used in Table IV which lists the dimensions of the $Mo_2Cl_8^{4-}$ ion.

Discussion

The chemical significance of this compound lies in the existence and structure of the $Mo_2Cl_8^{4-}$ ion. The crystallographic symmetry of the ion as it resides in crystals of this compound is C_{2h}, but for all practical purposes it has D_{4h} symmetry. It consists of two $MoCl_4$ groups bound together through a very short Mo–Mo bond so as to give an *eclipsed* configuration. The Mo–Cl bonds have an average length of 2.45 Å. Although no direct comparison with any other Mo(II) to nonbridging halogen bond can be made, on comparison with the Re–Cl distances in $Re_2Cl_8^{2-}$ and $Re_2Cl_6[P(C_2H_5)_3]_2$ (~2.30 Å), the Tc–Cl distances in $Tc_2Cl_8^{3-}$ (~2.35 Å), the $Mo^{2.5+}$–Cl distances in $Mo_2Cl_8^{3-}$ (~2.50 Å),[30] and the Mo^{IV}–Cl distances in $MoCl_6^{2-}$ (~2.31 Å),[31] this bond length seems reasonable though perhaps slightly longer than such comparisons might have suggested. However, it is important to realize that this structure is a very sterically crowded one, where nonbonded repulsions may have significant effects on bond lengths.

The structure can, in fact, be alternatively described by stating that the chlorine atoms lie at the vertices of a nearly perfect cube. The eight edges of the type Cl_1–Cl_2 and Cl_1'–Cl_2 have an average length (3.35 Å) which is only slightly less than that of the other four

TABLE II

FRACTIONAL ATOM COORDINATES[a]

Atom	Position[b]	x	y	z	B,[d] Å^2
Mo[c]	4e	0	0	0.13269 (25)	0.98 (5)
Mo*[c]	4g	0.0763 (35)	0.0680 (20)	0	1.50 (5)
Cl_1[e]	8i	−0.0659 (5)	0.1741 (3)	0.2157 (6)	1.92 (8)
Cl_2[e]	8i	0.2883 (4)	0.0397 (3)	0.2084 (6)	1.94 (8)
K_1	4g	0.0895 (7)	0.3472 (4)	0	2.57 (12)
K_2	4h	0.2456 (8)	0.1944 (4)	1/2	2.27 (11)
O	4h	0.0851 (24)	0.3764 (14)	1/2	3.1 (4)

[a] Standard deviations occurring in the last quoted figure of each coordinate are given in parentheses. [b] See ref 25, p 143. [c] Mo refers to the 93% of the Mo atoms at the 4e sites; Mo* refers to the 7% of Mo atoms at the 4g sites. [d] For all but Mo* and O these are derived from the anisotropic temperature factors given in Table III. [e] Owing to disordering (see refinement section), Cl positional parameters must be less reliable than indicated by the calculated esd's. All molecular parameters (Table IV) were calculated using esd's three times larger than those above.

TABLE III

ANISOTROPIC TEMPERATURE PARAMETERS[a] (×10^5)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	353 (26)	138 (10)	405 (28)	25 (16)	. . .[b]	. . .
Cl_1	911 (59)	191 (22)	809 (71)	17 (32)	132 (65)	−98 (35)
Cl_2	502 (55)	308 (24)	913 (71)	−28 (29)	−137 (56)	−105 (37)
K_1	855 (94)	368 (35)	1126 (105)	−123 (46)	. . .	. . .
K_2	1015 (89)	280 (32)	880 (94)	−2 (46)	. . .	. . .

[a] Standard deviations occurring in the last quoted figure are given in parentheses. [b] Required by symmetry to be zero.

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(30) M. J. Bennett, J. V. Brencic, and F. A. Cotton, submitted for publication.

(31) A. G. Edwards, R. D. Peacock, and A. Said, *J. Chem. Soc.*, 4643 (1962).

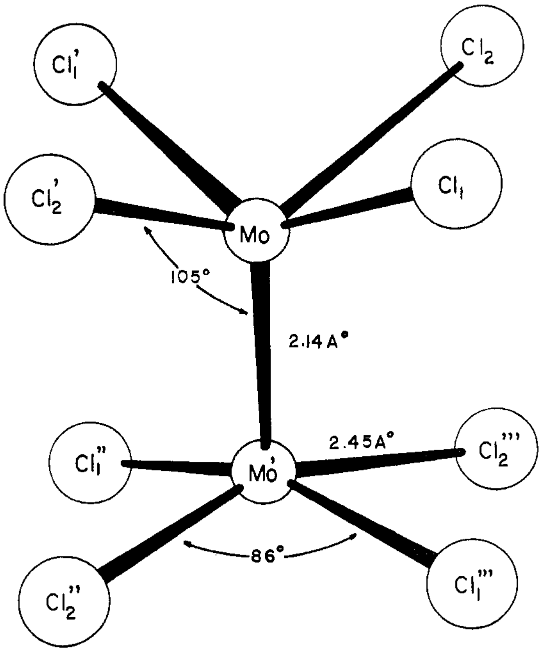

Figure 1.—A perspective view of the $Mo_2Cl_8^{4-}$ ion showing the atom-numbering scheme. Mean values of the principal dimensions are shown.

Table IV

Dimensions of the $Mo_2Cl_8^{4-}$ Ion[a]

Bond lengths, Å		Bond angles, deg	
Mo–Mo'	2.139 (4)	Cl_1–Mo–Cl_2	86.1 (6)
Mo*–Mo*'	2.18 (8)	Cl_1'–Mo–Cl_2	86.1 (3)
Mo–Cl_1	2.46 (1)	Mo'–Mo–Cl_2	105.8 (6)
Mo–Cl_2	2.44 (1)	Mo'–Mo–Cl_1	104.5 (6)
Nonbonded contacts, Å		**Nonbonded angles, deg**	
Cl_1–Cl_2	3.35 (2)	Cl_1–Cl_2–Cl_1'	89.9 (6)
Cl_2–Cl_1'	3.35 (2)	Cl_2–Cl_1–Cl_2'	90.1 (6)
Cl_2–Cl_2'''	3.47 (3)		
Cl_1–Cl_1'''	3.36 (3)		

[a] Standard deviations occurring in the last quoted figure are given in parentheses. See footnote *e* of Table II regarding magnitude of esd's where Cl atoms are involved.

edges of the types Cl_1–Cl_1''' and Cl_2–Cl_2''' (3.41 Å). Clearly Cl–Cl repulsions play a prominant role and the dimensions of the cube are mainly determined by the van der Waals radii of the chlorine atoms. The 24 Cl–Cl–Cl angles are all very close to 90°. Within this Cl_8 cube an Mo–Mo pair lies centered on a fourfold axis.

The $Mo_2Cl_8^{4-}$ structure is comparable in all essentials to the $Re_2Cl_8^{2-}$ and $Tc_2Cl_8^{3-}$ structures.[6,7,11] The ion is isoelectronic with $Re_2Cl_8^{2-}$, and, in view of its eclipsed structure and the exceedingly short Mo–Mo distance (2.139 Å), the presence of a quadruple bond (σ, π, π, δ components) between the metal atoms is postulated, exactly as for $Re_2Cl_8^{2-}$.

It is particularly appropriate to compare the Mo–Mo distances in $Mo_2Cl_8^{4-}$ and $Mo_2(O_2CCH_3)_4$, these being, respectively, 2.139 and 2.11 Å. While the difference, ~0.03 Å, is certainly real at a better than 99.5% confidence level according to the reported standard deviations, it is a relatively small difference and the assumption that there is essentially similar Mo–Mo bonding in the two compounds seems plausible. In all likelihood, the combined requirements of minimizing Cl···Cl repulsions and preserving Cl–Mo–Cl bond angles near 90° may provide an explanation for the slight lengthening of the Mo–Mo bond in $Mo_2Cl_8^{4-}$ as compared to that in $Mo_2(O_2CCH_3)_4$. A similar comparison exists between the Re–Re bond lengths in $Re_2(O_2CC_6H_5)_4Cl_2$ and $Re_2Cl_8^{2-}$, although here the two metal–metal distances are even more nearly equal. If, then, the essential similarity of the bonds in the two compounds is accepted, we may consider that further strong support has been given for the postulate of a quadruple bond in $Mo_2(O_2CCH_3)_4$, for, although the eclipsed structure in $Mo_2(O_2CCH_3)_4$ could be attributed solely to the rigidity of the bridging carboxylate structure, the only reasonable explanation which we can suggest in the $Mo_2Cl_8^{4-}$ case is, as for $Re_2Cl_8^{2-}$, the presence of the quadruple bond with its δ component.

Finally, we may note that packing of the potassium ions and water molecules together with the $Mo_2Cl_8^{4-}$ ions gives rise to reasonable coordination numbers and distances. The K_1 ions (on 4g positions) are surrounded by eight Cl atoms in a very distorted cubic array. Four Cl's lie on the vertical face of one $Mo_2Cl_8^{4-}$ ion, two are on the edge of another, and two more are on the edge of still a third. The K–Cl distances (each twice) are 3.137 (6), 3.210 (7), 3.272 (6), and 3.299 (6) Å. The K_2 ions (on 4h positions) are surrounded by six Cl atoms and two O atoms in the form of a distorted bicapped trigonal prism. The prism is defined by the six Cl atoms, with K–Cl distances (each twice) of 3.138 (6), 3.250 (6), and 3.397 (6) Å. The K–O distances are 2.74 (2) and 2.88 (2) Å. The K_2 and O atoms form zigzag chains running parallel to the *a* axis at $z = {}^1/_2$.