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

Stoichiometric and Structural Characterization of the Compound $(NH_4)_5Mo_2Cl_9 \cdot H_2O$[1]

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

Received August 25, 1969

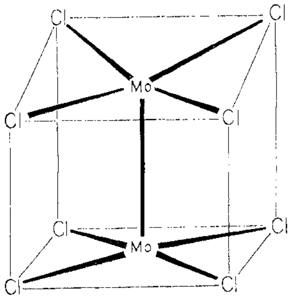
A compound which we believe to be identical with one reported by others as $(NH_4)_7Mo_3Cl_{13} \cdot H_2O$ has been obtained in crystalline form. An X-ray structure determination has allowed an exact stoichiometric and structural characterization, consistent with analytical data which are in themselves inconclusive. The correct formula is $(NH_4)_5Mo_2Cl_9 \cdot H_2O$. The structure consists of NH_4^+ ions, Cl^- ions, H_2O molecules, and $Mo_2Cl_8^{4-}$ ions in the ratio 5:1:1:1. The $Mo_2Cl_8^{4-}$ ion has the same structure as that previously observed in $K_4Mo_2Cl_8 \cdot 2H_2O$ and $(enH_2)_2Mo_2Cl_8 \cdot 2H_2O$. Crystallographic data are: space group, $Cmc2_1$; $a = 10.528$ (4) Å, $b = 13.219$ (5) Å, $c = 13.129$ (5) Å; $Z = 8$; d(calcd) = 2.25 g cm^{-3}, d(measd) = 2.22 ± 0.04 g cm^{-3}. The structure was solved and refined using 534 reflections within a sphere bounded by $\theta = 50°$ for Cu Kα radiation.

Introduction

Several years ago investigations of the reactions of $Mo_2(O_2CCH_3)_4$ with mineral acids, particularly aqueous hydrochloric and hydrobromic acids, were begun in this laboratory and by J. C. Sheldon and his coworkers. With HCl various red to purple solids were obtained depending upon reaction conditions and the cations used. Anderson and Sheldon were the first to describe several of these substances in the literature.[3] Comparable and, in several cases what appeared to be identical, materials had been obtained here but all were relatively insoluble and noncrystalline. Hence, unambiguous chemical and structural characterization was at that time impossible. In view of the structural nature[4] of $Mo_2(O_2CCH_3)_4$ with its strong, quadruple Mo–Mo bond[5] and the known interconvertibility[6,7] of the rhenium species $Re_2(O_2CR)_4X_2$ and $Re_2Y_8^{2-}$, we considered it highly probable that the substances obtained *directly and under mild conditions* from $Mo_2(O_2CCH_3)_4$ would be essentially the products of metathesis, *i.e.*, compounds containing the binuclear cluster, Mo_2, which is present in the starting material. On the other hand, Sheldon, *et al.*,[3,8] proposed only trinuclear structures for the Mo(II) compounds and tetranuclear structures for those which appeared to contain molybdenum in the oxidation state +2.5.

Regardless of one's opinion as to the probabilities of the situation, at this point there were no facts available pertaining to structure, nor did there appear to be any likelihood of resolving the uncertainties on a basis of fact except by obtaining crystalline substances and carrying out X-ray structure analyses on them. Such a program was initiated several years ago in this laboratory.

We have already reported results showing that the compound $K_4Mo_2Cl_8 \cdot 2H_2O$ (which does not seem to be identical with any specific substance described by Sheldon, *et al.*) contains the $Mo_2Cl_8^{4-}$ ion (I) with D_{4h} symmetry and an exceedingly short (2.14 Å) Mo–Mo quadruple bond.[9] It has further been found that a substance with the formula $(enH_2)_2Mo_2Cl_8 \cdot 2H_2O$, which appears certain to be identical with one described as $(enH_2)_3Mo_3Cl_{13}(H_3O)(H_2O)_2$ by Allison, Anderson, and Sheldon,[8] also contains the $Mo_2Cl_8^{4-}$ ion and no trinuclear species.[10] Also, one of the compounds for which a tetranuclear structure had been advocated, $Rb_3Mo_2Cl_8$, has been shown to contain only the binuclear complex anion $Mo_2Cl_8^{3-}$ which is, however, structurally distinct from the $Mo_2Cl_8^{4-}$ ion, consisting essentially of a confacial bioctahedron with one vacant bridge position.[11]



I

On the basis of the accumulating structural data it would thus appear increasingly improbable that species more complex than binuclear ones do in fact arise directly from $Mo_2(O_2CCH_3)_4$. However, one further study of an alleged trinuclear compound appeared worthwhile. Anderson and Sheldon[3] described a substance to which they assigned the stoichiometry $(NH_4)_7Mo_3Cl_{13} \cdot H_2O$. The same substance had been obtained here, also in noncrystalline (or, at best microcrystalline) form, and the analytical data then at

---

(1) Supported by the U. S. Atomic Energy Commission.

(2) Fellow of the Samuel Rubin Foundation, on leave from the University of Ljubljana, Ljubljana, Yugoslavia, 1967–1969.

(3) I. R. Anderson and J. C. Sheldon, *Australian J. Chem.*, **18**, 271 (1965).

(4) D. Lawton and R. Mason, *J. Am. Chem. Soc.*, **87**, 921 (1965).

(5) F. A. Cotton and W. K. Bratton, *ibid.*, **87**, 921 (1965).

(6) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965).

(7) F. A. Cotton, C. Oldham, and W. R. Robinson, *ibid.*, **5**, 1798 (1966).

(8) G. B. Allison, I. R. Anderson, and J. C. Sheldon, *Australian J. Chem.*, **20**, 869 (1967).

(9) J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **8**, 7 (1969).

(10) J. V. Brencic and F. A. Cotton, *ibid.*, **8**, 2698 (1969).

(11) M. J. Bennett, J. V. Brencic, and F. A. Cotton, *ibid.*, **8**, 1060 (1969).

hand could have been considered consistent with this formula, making realistic estimates of error in the analyses. All in all, this substance seemed to us to be perhaps the likliest example of a compound with a trinuclear cluster of molybdenum atoms, *if, indeed, there are any such clusters yet known.* Therefore, when a suitably crystalline sample of this substance was finally obtained, it was immediately subjected to an X-ray structure analysis and to careful chemical analysis. The results of these studies are reported here.

Experimental Section

Preparation.—One gram of freshly prepared dimolybdenum tetraacetate[12] was dissolved in 50 ml of concentrated hydrochloric acid saturated with HCl gas at 0°. To this solution 1 g of solid NH_4Cl was added. The mixture was stirred for about 1 hr as it warmed to room temperature. The violet precipitate was collected on a glass frit at room temperature in the air and was washed with two portions, 20 ml each, of absolute ethanol. The solid was dried under vacuum at room temperature for several hours. The yield, assuming the correct formula to be $(NH_4)_5Mo_2Cl_9 \cdot H_2O$, was 85%.

The compound was recrystallized by dissolving 500 mg of the crude product in 20 ml of constant-boiling HCl at 20° to which 20 ml of the same acid saturated with ammonium chloride was then added. The solution was left in an ice bath for about 1 hr. The precipitate was then filtered, washed with two 20-ml portions of absolute ether, and dried under vacuum at room temperature for 3 hr. The overall yield, including the recrystallization, was about 80%. *Anal.* Found: Mo, 31.6; Cl, 51.4; N, 10.6; H, 3.62.

Crystals suitable for single-crystal X-ray work were prepared in the following way. Recrystallized violet compound (120 mg) was dissolved in 20 ml of constant-boiling hydrochloric acid (~108° (760 Torr)). To this was added a solution of 800 mg of NH_4Cl in 20 ml of constant-boiling HCl. The mixture was placed in an ice bath for 20 hr. The crystals were then separated by rapid filtration through a chilled funnel, so that the solution would not warm appreciably during filtration. The crystals were immediately placed in a vacuum desiccator. In the desiccator they seem to be stable indefinitely at 25° but they are slowly attacked when exposed to laboratory air.

Infrared spectra of the solid compound from 600 to 5000 cm^{-1} were measured employing hexachlorobutadiene mills. In addition to bands attributable to the NH_4^+ ions, there was one sharp band at 3450 cm^{-1} which presumably arises from O–H stretching. However, no band was observed in the 1600–1630-cm^{-1} region as would be expected for the bending mode of H_2O.

The density, measured by flotation in a mixture of 1-iodonaphthalene and CH_2Br_2, was 2.22 ± 0.04 g cm^{-3}.

For the structure analysis a prismatic single crystal bounded by 001, 110, $\bar{1}10$, and the centrically related faces was chosen. This and similar crystals exhibited birefringence in polarized light. The crystal used had dimensions 0.02 × 0.02 × 0.06 mm. The long dimension was in the direction of the c axis; the other two dimensions are the lengths of diagonals across the square basal plane of the prism. The crystal was mounted so the long axis coincided with the ϕ axis of the eucentric goniometer later used to collect intensities.

Weissenberg and precession photographs taken with unfiltered Cu Kα radiation showed that the lattice was orthorhombic with the following systematic extinctions: hkl for $h + k \neq 2n$, $h0l$ for $l \neq 2n$. The three space groups satisfying these observations are $Cmc2_1$ (no. 36), C2cm (no. 40), and Cmcm (no. 63).[13] Unit cell dimensions were determined by least squares from the measured diffraction angles of about 20 reflections in each of the series $h00$, $0k0$, and $00l$, using a manually operated General Electric XRD-5 counter diffractometer equipped with a quarter-circle eucentric goniometer. The dimensions, at 28 ± 2° are: $a = 10.528 \pm 0.004$ Å, $b = 13.219 \times 0.005$ Å, $c = 13.129 \pm 0.005$ Å. Using these cell dimensions and assuming $Z = 4$, a density of 2.25 g cm^{-3} is calculated, in good agreement with the measured value.

Using the counter diffractometer, the intensities of 534 independent reflections bounded by a sphere in reciprocal space with $\theta = 50°$ were collected with Cu Kα radiation, filtered by nickel foil in the reflected beam. 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 at the beginning (B_1) and end (B_2) of each scan. The intensity, I, was then equal to $P - B_1 - B_2$. For four reflections I was calculated as ≤ 0. An estimated value of the intensity, equal to $^1/_2(P + B_1 + B_2)^{1/2}$, was used for these reflections in solving and refining the structure.

Absorption corrections were neglected since $\mu = 234.14$ cm^{-1}. At $\chi = 90°$ the intensities of several $00l$ reflections as a function of ϕ were found to vary by a maximum of 5%. Structure factors were obtained on a relative basis using the expression $|F_o| = (I/Lp)^{1/2}$, where Lp represents the product of the reciprocal Lorentz and polarization corrections. The standard deviation of each reflection, $\sigma(F)$, was taken as $(\sigma^2 + pI^2)^{1/2}/(2Lp|F_o|)$, where σ is the esd based on counting statistics and p was assigned the value 0.002.

Solution and Refinement

A three-dimensional map of the Patterson function was computed.[14] The interpretation of this map was not entirely straightforward. The many Mo–Cl vectors tended to mask the Mo–Mo vector, but a solution in the space group $Cmc2_1$ was obtained by selecting a relatively strong peak ~2.2 Å from the origin as the probable Mo–Mo vector and then assigning plausible coordinates by trial and error to chlorine atoms so as to build up $Mo_2Cl_8^{4-}$ ions with the known structure. This trial structure was supported by a structure factor calculation[15] and five cycles of isotropic least-squares refinement were run on the two independent Mo and six independent Cl atoms leading to a discrepancy factor $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ of 0.18, with equal weights assigned to all structure factors.

A difference Fourier synthesis was then computed and positional parameters were assigned to the remaining atoms. Isotropic refinement was resumed on all atoms and the scale factor with a weight of $[\sigma(F)]^{-2}$ assigned to each reflection. After five cycles the residuals were $R_1 = 0.092$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.113$. Three cycles of anisotropic refinement, using temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ for all (nonhydrogen) atoms led to residuals of $R_1 = 0.065$ and $R_2 = 0.092$. The standard deviation of an observation of unit weight was 2.7, indicating a slight underestimation of error in the data. An empirical

---

[12] T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964).

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

[14] The computer programs used for this and other phases of the work have been cited in many recent publications from this laboratory: *e.g.*, F. A. Cotton and B. H. C. Winquist, *Inorg. Chem.*, **8**, 1304 (1969).

[15] Atomic scattering factors, omitting anomalous dispersion corrections, for neutral Mo, Cl, N, and O atoms were obtained from D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965). The neglect of anomalous dispersion introduces error in the atomic coordinates, but since the dimensions of the $Mo_2Cl_8^{4-}$ ion have been obtained very precisely in previous studies, and the purpose of this work was only to show qualitatively—but conclusively—that it was present here, this aspect has, justifiably, been neglected.

TABLE I

OBSERVED AND FINAL CALCULATED STRUCTURE AMPLITUDES IN UNITS OF 0.1 ELECTRON

H	L	FOBS	FCAL
K = 0**			
0	2	2427	2220
0	4	375	311
0	6	2246	2412
0	8	949	993
0	10	380	309
0	12	226	263
2	0	3096	3339
2	2	1409	1069
2	4	4421	4211
2	8	1780	1656
2	10	954	969
2	12	320	455
4	0	7103	7657
4	2	2048	1825
4	4	287	367
4	6	1957	1868
4	8	988	972
4	10	158	172
4	12	248	195
6	0	2801	2781
6	2	1180	1088
6	4	2207	2233
6	6	607	576
6	8	1384	1285
6	10	686	702
8	0	3815	3904
8	2	1279	1319
8	4	515	485
8	6	1083	1084
8	8	962	892
10	0	2318	2246
10	2	947	1011
K = 1**			
1	0	2150	2446
1	1	2073	2268
1	2	1150	1367
1	3	575	578
1	4	736	860
1	5	481	565
1	6	851	921
1	7	1395	1529
1	8	1017	1164
1	9	687	748
1	10	498	579
1	11	417	569
1	12	299	277
3	0	1167	1337
3	1	1403	1500
3	2	815	923
3	3	370	433
3	4	618	690
3	5	348	385
3	6	511	523
3	7	1080	1145
3	8	1061	1186
3	9	877	961
3	10	526	634
3	11	597	722
3	12	318	354
5	0	2136	2341
5	1	1880	2069
5	2	1156	1245
5	3	678	662
5	4	852	879
5	5	778	808
5	6	1071	1083
5	7	1470	1501
5	8	860	909
5	9	483	473
5	10	506	476
5	11	336	425
7	0	639	653
7	1	763	844
7	2	510	515
7	3	375	361
7	4	583	590
7	5	486	403
7	6	267	304
7	7	814	776
7	8	1006	958
7	9	857	697
9	0	1646	1691
9	1	1427	1456
9	2	864	844
9	3	529	514
9	4	650	699
9	5	687	708
9	6	910	930
K = 2**			
0	0	227	296
0	1	2625	2396
0	2	1949	1988
0	3	623	718
0	4	3935	3594
0	5	1597	1510
0	6	294	327
0	7	3560	3384
0	8	858	867
0	9	590	614
0	10	1221	1178
0	11	590	546
0	12	196	315
2	0	142	166
2	1	1154	919
2	2	156	269
2	3	961	966
2	4	885	829
2	5	282	247
2	6	560	577
2	7	2245	2250
2	8	1488	1599
2	9	1454	1479
2	10	927	872
2	11	1302	1379
2	12	997	1170
4	0	152	190
4	1	1941	1869
4	2	1432	1508
4	3	448	513
4	4	2791	2652
4	5	1228	1182
4	6	180	202
4	7	2875	2829
4	8	573	615
4	9	603	642
4	10	1094	1023
4	11	506	537
6	0	124	194
6	1	956	914
6	2	220	181
6	3	403	418
6	4	1010	903
6	5	223	149
6	6	453	418
6	7	1902	1795
6	8	912	945
6	9	1137	1153
6	10	778	730
8	0	106	107
8	1	1214	1190
8	2	862	807
8	3	244	179
8	4	1634	1514
8	5	709	686
8	6	252	234
8	7	1968	1847
8	8	222	232
10	0	112	165
10	1	818	854
10	2	433	435
10	3	272	144
K = 3**			
1	0	892	817
1	1	571	593
1	2	1083	1120
1	3	2579	2506
1	4	1656	1579
1	5	1482	1476
1	6	1100	1072
1	7	915	922
1	8	970	966
1	9	561	600
1	10	460	506
1	11	803	734
1	12	422	417
3	0	576	558
3	1	460	513
3	2	620	659
3	3	1404	1487
3	4	1001	1038
3	5	1364	1373
3	6	1087	1136
3	7	1131	1195
3	8	1069	1065
3	9	489	523
3	10	314	435
3	11	776	825
3	12	485	612
5	0	853	811
5	1	787	805
5	2	1158	1216
5	3	2356	2440
5	4	1507	1571
5	5	1093	1160
5	6	730	758
5	7	634	655
5	8	822	820
5	9	489	561
5	10	453	511
5	11	508	532
7	0	435	425
7	1	511	466
7	2	366	370
7	3	709	717
7	4	549	568
7	5	976	1020
7	6	922	939
7	7	1133	1123
7	8	980	957
7	9	386	387
9	0	608	583
9	1	648	660
9	2	946	944
9	3	1830	1821
9	4	1148	1189
9	5	778	828
K = 4**			
0	0	1249	1165
0	1	1572	1260
0	2	1142	986
0	3	5694	5424
0	4	1991	1744
0	5	1195	1224
0	6	534	466
0	7	221	175
0	8	258	268
0	9	668	623
0	10	245	270
0	11	1095	1090
0	12	112	39
2	0	3326	3157
2	1	2144	1948
2	2	1386	1254
2	3	1684	1693
2	4	473	443
2	5	2009	1754
2	6	475	508
2	7	1790	1762
2	8	100	83
2	9	184	73
2	10	351	322
2	11	1354	1339
2	12	352	346
4	0	1034	1052
4	1	959	829
4	2	834	801
4	3	4257	4117
4	4	1381	1298
4	5	1175	1112
4	6	372	310
4	7	144	187
4	8	151	219
4	9	544	528
4	10	160	214
4	11	1022	1022
6	0	1867	1886
6	1	778	768
6	2	893	865
6	3	1667	1578
6	4	440	413
6	5	1505	1420
6	6	305	276
6	7	1225	1190
6	8	159	83
6	9	113	76
8	0	857	893
8	1	440	479
8	2	585	620
8	3	2470	2382
8	4	711	702
8	5	1061	988
8	6	196	93
8	7	316	334
K = 5**			
1	0	148	6
1	1	637	669
1	2	1330	1273
1	3	1258	1195
1	4	2492	2367
1	5	1067	1073
1	6	648	610
1	7	662	667
1	8	322	337
1	9	304	311
1	10	1090	1105
1	11	759	778
3	0	482	528
3	1	728	715
3	2	1027	1000
3	3	841	815
3	4	1976	1904
3	5	921	953
3	6	653	619
3	7	473	497
3	8	498	553
3	9	247	324
3	10	986	1059
3	11	754	849
5	0	411	417
5	1	651	672
5	2	1229	1192
5	3	1236	1227
5	4	2176	2183
5	5	1008	981
5	6	576	581
5	7	672	652
5	8	112	264
5	9	358	361
5	10	922	962
7	0	598	550
7	1	687	630
7	2	659	673
7	3	496	472
7	4	1331	1321
7	5	829	746
7	6	608	600
7	7	392	350
7	8	535	578
9	0	392	446
9	1	587	536
9	2	997	958
9	3	960	985
9	4	1641	1626
K = 6**			
0	0	501	433
0	1	2383	2390
0	2	1148	1174
0	3	632	550
0	4	2792	2673
0	5	1017	924
0	6	429	378
0	7	1355	1328
0	8	182	196
0	9	622	673
0	10	1433	1398
0	11	647	750
2	0	109	55
2	1	365	367
2	2	1046	1030
2	3	453	511
2	4	2347	2220
2	5	1608	1514
2	6	421	389
2	7	250	231
2	8	536	517
2	9	787	716
2	10	1446	1366
2	11	2943	1028
4	0	329	328
4	1	1805	1809
4	2	1005	1028
4	3	490	520
4	4	2318	2295
4	5	714	680
4	6	361	368
4	7	1061	1030
4	8	193	166
4	9	493	513
4	10	1314	1263
6	0	102	30
6	1	482	482
6	2	850	870
6	3	409	382
6	4	1800	1755
6	5	866	861
6	6	419	378
6	7	160	95
6	8	298	335
8	0	195	163
8	1	1016	1000
8	2	800	795
8	3	392	367
8	4	1670	1609
8	5	317	291
K = 7**			
1	0	2934	2863
1	1	1166	1155
1	2	1154	1063
1	3	1723	1650
1	4	1026	986
1	5	1192	1081
1	6	832	810
1	7	630	582
1	8	579	552
1	9	275	246
1	10	253	139
3	0	1907	1968
3	1	812	883
3	2	908	912
3	3	1738	1747
3	4	1392	1372
3	5	1239	1198
3	6	574	554
3	7	361	317
3	8	725	683
3	9	423	422
3	10	296	333
5	0	2825	2795
5	1	1070	1144
5	2	970	979
5	3	1150	1212
5	4	583	508
5	5	950	865
5	6	884	879
5	7	696	709
5	8	406	392
5	9	111	89
7	0	1070	1073
7	1	547	599
7	2	691	657
7	3	1422	1456
7	4	113	1248
7	5	1085	1061
7	6	372	315
K = 8**			
0	0	3288	3228
0	1	919	907
0	2	549	477
0	3	410	375
0	4	735	757
0	5	938	963
0	6	1683	1587
0	7	1308	1184
0	8	1201	1159
0	9	340	327
0	10	296	317
2	0	990	914
2	1	854	777
2	2	501	517
2	3	2275	2226
2	4	1005	1012
2	5	717	739
2	6	921	923
2	7	494	470
2	8	1541	1481
2	9	518	519
2	10	752	750
4	0	2619	2655
4	1	617	688
4	2	503	473
4	3	478	460
4	4	512	590
4	5	787	852
4	6	1423	1395
4	7	1042	977
4	8	1147	1081
4	9	271	251
6	0	977	977
6	1	470	516
6	2	294	393
6	3	1504	1524
6	4	586	639
6	5	610	634
6	6	806	836
6	7	385	410
8	0	1660	1660
8	1	354	359
8	2	431	448
K = 9**			
1	0	461	505
1	1	1257	1178
1	2	424	419
1	3	306	299
1	4	377	288
1	5	662	643
1	6	723	688
1	7	2163	2078
1	8	734	728
1	9	889	914
3	0	103	442
3	1	1196	1164
3	2	762	754
3	3	352	346
3	4	531	508
3	5	585	552
3	6	583	570
3	7	2023	1907
3	8	857	741
5	0	468	533
5	1	1027	1039
5	2	314	329
5	3	317	329
5	4	319	155
5	5	610	619
5	6	782	706
5	7	1854	1845
7	0	319	375
7	1	1008	963
7	2	848	833
7	3	386	330
K = 10**			
0	0	664	619
0	1	1328	1340
0	2	837	853
0	3	528	626
0	4	1046	986
0	5	193	128
0	6	338	296
0	7	1481	1411
0	8	681	715
2	0	701	754
2	1	1727	1851
2	2	639	668
2	3	267	220
2	4	293	363
2	5	405	429
2	6	588	516
2	7	1637	1633
2	8	1053	1161
4	0	568	573
4	1	1160	1255
4	2	613	706
4	3	406	515
4	4	831	804
4	5	113	77
4	6	275	305
6	0	564	633
6	1	1372	1450
6	2	405	437
6	3	193	229
K = 11**			
1	0	2238	2325
1	1	702	660
1	2	1144	1140
1	3	1106	1141
1	4	799	788
1	5	320	365
1	6	552	548
1	7	313	208
3	0	2378	2496
3	1	852	785
3	2	1228	1224
3	3	840	834
3	4	518	506
3	5	405	421
3	6	852	807
5	0	1576	1752
5	1	463	493
5	2	917	934
5	3	1162	1178
K = 12**			
0	0	453	433
0	1	423	457
0	2	453	508
0	3	1119	1174
0	4	1013	987
0	5	472	460
2	0	2035	2170
2	1	751	759
2	2	724	846
2	3	637	734
2	4	602	626
4	0	510	518
4	1	416	455
K = 13**			
1	0	157	78
1	1	156	182

TABLE II

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS[a]

Atom	Position[b]	x	y	z	B,[c] Å^2
Mo(1)	4a	0	0.07976 (25)	0	1.59
Mo(2)	4a	0	0.18298 (21)	0.12652 (35)	1.20
Cl(1)	4a	0	0.9055 (6)	0.0712 (9)	2.25
Cl(2)	8b	0.2279 (7)	0.0496 (5)	0.9687 (8)	2.48
Cl(3)	4a	0	0.1894 (8)	0.8529 (10)	2.46
Cl(4)	4a	0	0.3562 (6)	0.0521 (10)	1.95
Cl(5)	8b	0.2292 (6)	0.2099 (5)	0.1636 (8)	2.25
Cl(6)	4a	0	0.0762 (8)	0.2821 (13)	2.75
Cl(7)	4a	0	0.3448 (11)	0.3414 (12)	4.73
O(1)	4a	0	0.5518 (28)	0.3032 (33)	4.44
N(1)	4a	0	0.6309 (25)	0.1081 (23)	2.39
N(2)	8b	0.2514 (23)	0.4508 (17)	0.2181 (23)	2.73
N(3)	8b	0.2274 (22)	0.1957 (18)	0.4222 (26)	2.95

[a] Standard deviations occurring in the last quoted figure of each coordinate are given in parentheses. [b] See ref 13. [c] These are isotropic temperature parameters equivalent to and calculated from the tensor components in Table III.

TABLE III

ANISOTROPIC TEMPERATURE PARAMETERS[a] (×10^4)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	29 (4)	11 (2)	39 (3)	...[b]	...	−8 (2)
Mo(2)	13 (3)	9 (2)	35 (2)	...	...	6 (2)
Cl(1)	51 (9)	10 (5)	49 (8)	...	...	14 (6)
Cl(2)	32 (6)	32 (4)	55 (8)	−2 (4)	6 (6)	−13 (5)
Cl(3)	78 (13)	37 (7)	20 (7)	...	...	5 (5)
Cl(4)	40 (8)	12 (5)	45 (7)	...	...	−1 (6)
Cl(5)	46 (6)	29 (4)	38 (6)	−7 (4)	5 (4)	2 (5)
Cl(6)	33 (12)	22 (7)	75 (11)	...	...	−8 (7)
Cl(7)	110 (14)	68 (10)	65 (11)	...	...	−16 (9)
O(1)	77 (37)	85 (26)	58 (30)	...	...	−27 (28)
N(1)	−69 (18)	98 (29)	48 (26)	...	...	75 (27)
N(2)	76 (27)	41 (14)	27 (19)	−31 (16)	−20 (17)	19 (15)
N(3)	38 (23)	35 (16)	69 (29)	5 (15)	13 (19)	43 (19)

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

expression of the form $\sigma(F)' = \sigma(F)[a - b(c - F_o)]$ with $a = 8.0$, $b = -0.08$, and $c = 60$ was then used for $|F_o| \leq 60$ and the expression $\sigma(F)' = a\sigma(F)$ was used for $F_o > 60$. With this scheme the esd of an observation of unit weight dropped to 1.15, the esd's of the positional and thermal parameters became significantly smaller, and there was essentially no violation of Cruickshank's criterion[16] that $w\Delta^2$ be independent of the magnitude of $|F_o|$ up to $|F_o| = 80$, which includes 519 of the 534 reflections.

A final difference Fourier map had as its largest feature one peak about one-third the height of the average peak due to a nitrogen atom on the previous electron density map. No attempt was made to locate hydrogen atoms. The observed and final calculated structure amplitudes are listed in Table I. For two reflections, 774 and 390, the measured values are evidently grossly incorrect. Unfortunately, this escaped notice until refinement had been completed as described.

Results

The atomic positional parameters and temperature parameters are listed in Tables II and III. Bond lengths, intramolecular angles, and nonbonded contacts for the $Mo_2Cl_8^{4-}$ ion are given in Table IV. The atom-numbering scheme is specified in Figure 1. Table V lists all intermolecular nonbonded contacts less than 4.00 Å.

Discussion

The crystal structure is built from the four entities NH_4^+, Cl^-, H_2O, and $Mo_2Cl_8^{4-}$. The planes at 0, y, z and $^1/_2$, y, z, which are crystallographic mirror planes, contain the Mo atoms and four of the eight Cl atoms of each $Mo_2Cl_8^{4-}$ ion as well as the oxygen atoms of the water molecules, the nitrogen atoms of one-fifth of the ammonium ions, and all of the Cl^- ions which are not part of $Mo_2Cl_5^{4-}$ groups. The arrangement within each of the two sets of planes is identical; the relationship of the contents of the 0, y, z planes to that of the $^1/_2$, y, z planes is specified by the C-centering translation. Figure 2a shows the arrangement in the 0, y, z plane. Interleaving the mirror planes, there are crinkled sheets made up of the rest of the ammonium

---

(16) D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press, Inc., New York, N. Y., 1965, p 113.

TABLE IV

DIMENSIONS[a] OF THE $Mo_2Cl_8^{4-}$ ION

A. Bond Lengths, Å

Mo(1)-Mo(2)	2.150 (5)
Mo(1)-Cl(1)	2.486 (9)
Mo(1)-Cl(2)	2.467 (7)
Mo(1)-Cl(3)	2.415 (13)
Mo(2)-Cl(4)	2.490 (10)
Mo(2)-Cl(5)	2.487 (7)
Mo(2)-Cl(6)	2.483 (16)
Mean	2.47 ± 0.02

B. Bond Angles, Deg

Cl(1)-Mo(1)-Cl(2)	85.0 (2)
Cl(2)-Mo(1)-Cl(3)	87.9 (3)
Cl(4)-Mo(2)-Cl(5)	86.8 (2)
Cl(5)-Mo(2)-Cl(6)	85.4 (3)
Mean	86.3 ± 1.1
Cl(1)-Mo(1)-Cl(3)	149.0 (4)
Cl(2)-Mo(1)-Cl(2)′	153.2 (4)
Cl(4)-Mo(2)-Cl(6)	147.7 (5)
Cl(5)-Mo(2)-Cl(5)′	151.9 (3)
Mean	150.5 ± 2.1
Mo(1)-Mo(2)-Cl(4)	106.3 (3)
Mo(1)-Mo(2)-Cl(5)	104.0 (2)
Mo(1)-Mo(2)-Cl(6)	106.0 (4)
Mo(2)-Mo(1)-Cl(1)	107.3 (2)
Mo(2)-Mo(1)-Cl(2)	103.4 (2)
Mo(2)-Mo(1)-Cl(3)	103.7 (3)
Mean	104.8 ± 1.3

C. Cl···Cl Contacts, Å

Cl(1)-Cl(2)	3.35 (1)
Cl(2)-Cl(3)	3.39 (1)
Cl(4)-Cl(5)	3.42 (1)
Cl(5)-Cl(6)	3.37 (1)
Mean	3.38 ± 0.02
Cl(1)-Cl(6)	3.57 (2)
Cl(2)-Cl(5)	3.32 (2)
Cl(3)-Cl(4)	3.42 (2)
Mean	3.43 ± 0.09

D. Cl···Cl···Cl Angles

The 24 such angles range from 87.2 to 93.2°, with a mean value of 90.0°

[a] Numbers in parentheses are estimated standard deviations occurring in the last significant figure. Numbers following the ± sign are mean deviations from the mean.

TABLE V

NONBONDED INTERMOLECULAR CONTACTS (Å) LESS THAN 4 Å

Mo(1) to:	Cl(6)	$(0, -y, -{}^1/_2 + z)$	3.52
Mo(2) to:	Cl(7)	$(0, y, z)$	3.54
Cl(1) to:	Cl(3)	$(0, 1 - y, -{}^1/_2 + z)$	3.90
	Cl(6)	$(0, -y, -{}^1/_2 + z)$	3.80
	N(1)	$(0, y, z)$	3.66
	N(3)	$(-x, 1 - y, -{}^1/_2 + z)$	3.36
Cl(2) to:	Cl(6)	$(0, -y, -{}^1/_2 + z)$	3.81
	N(3)	$(x, -y, -{}^1/_2 + z)$	3.29
Cl(3) to:	Cl(1)	$(0, 1 - y, {}^1/_2 + z)$	3.90
	Cl(6)	$(0, -y, -{}^1/_2 + z)$	3.63
	O(1)	$(0, 1 - y, {}^1/_2 + z)$	3.48
	N(1)	$(0, 1 - y, {}^1/_2 + z)$	3.99
Cl(4) to:	Cl(7)	$(0, y, z)$	3.80
	O(1)	$(0, 1 - y, {}^1/_2 + z)$	3.48
	N(1)	$(0, y, z)$	3.70
	N(2)	(x, y, z)	3.64
Cl(5) to:	Cl(7)	$(0, y, z)$	3.80
	N(2)	(x, y, z)	3.27
	N(3)	(x, y, z)	3.40
Cl(6) to:	Cl(7)	$(0, y, z)$	3.63
	N(3)	(x, y, z)	3.40
Cl(7) to:	O(1)	$(0, y, z)$	2.78
	N(1)	$(0, 1 - y, {}^1/_2 + z)$	3.51
	N(2)	(x, y, z)	3.40
	N(3)	(x, y, z)	3.27
O(1) to:	N(1)	$(0, y, z)$	2.76
	N(2)	(x, y, z)	3.16
N(1) to:	N(2)	(x, y, z)	3.84

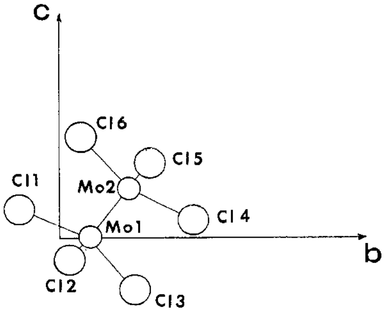


Figure 1.—A projection of the $Mo_2Cl_8^{4-}$ ion on the (100) plane, showing the atom-numbering scheme. All atoms lie in the symmetry plane except atoms Cl(2) and Cl(5).

ions. The nitrogen atoms of these NH_4^+ ions lie near but not in the planes at ${}^1/_4, y, z$ and ${}^3/_4, y, z$. They are relatively far from one another (N···N distances in the range 3.84–4.32 Å) and so placed as to have optimal Coulombic interaction with the $Mo_2Cl_8^{4-}$ and Cl^- ions. Figure 2b shows the arrangement of the N atoms. The crystal structure is a neat and compact one in which the NH_4^+, Cl^-, and H_2O entities beyond those required in the formula $(NH_4)_4Mo_2Cl_8$ evidently play an effective role.

The $Mo_2Cl_8^{4-}$ ion itself, I, has symmetry and dimensions essentially identical with those previously observed, as shown in Table VI. The crystallographic mirror plane passing through it assures that the rotational configuration about the Mo–Mo axis is rigorously eclipsed. The virtual symmetry, as in previous cases, is D_{4h}.

In this crystal structure the $Mo_2Cl_8^{4-}$ ion has neighboring Cl atoms along both extensions of the Mo–Mo axis. One of these is the extra Cl^- ion, which lies 3.54 Å from one Mo atom; the other is a chlorine atom of another $Mo_2Cl_8^{4-}$ ion, which lies 3.53 Å from the other Mo atom. In each case the chlorine atom which approaches a molybdenum atom makes normal contacts with the four chlorine atoms which are bound to that molybdenum atom. Considering the Mo···Cl distances and the other interatomic contacts involved, it is clear that no significant axial Mo–Cl bonds are formed and the $Mo_2Cl_8^{4-}$ ion has a well-defined identity in this substance.

Finally, we may remark on the stoichiometry of the compound. This, of course, can be derived directly and solely from the crystal structure, and it is, indubitably, $(NH_4)_5Mo_2Cl_9\cdot H_2O$. The previously reported formula, $(NH_4)_7Mo_3Cl_{13}\cdot H_2O$, when converted to a basis of two molybdenum atoms, becomes $(NH_4)_{4^2/_3}Mo_2Cl_{8^2/_3}\cdot{}^2/_3H_2O$. The differences, obviously, are small. In fact, the actual differences in analytical

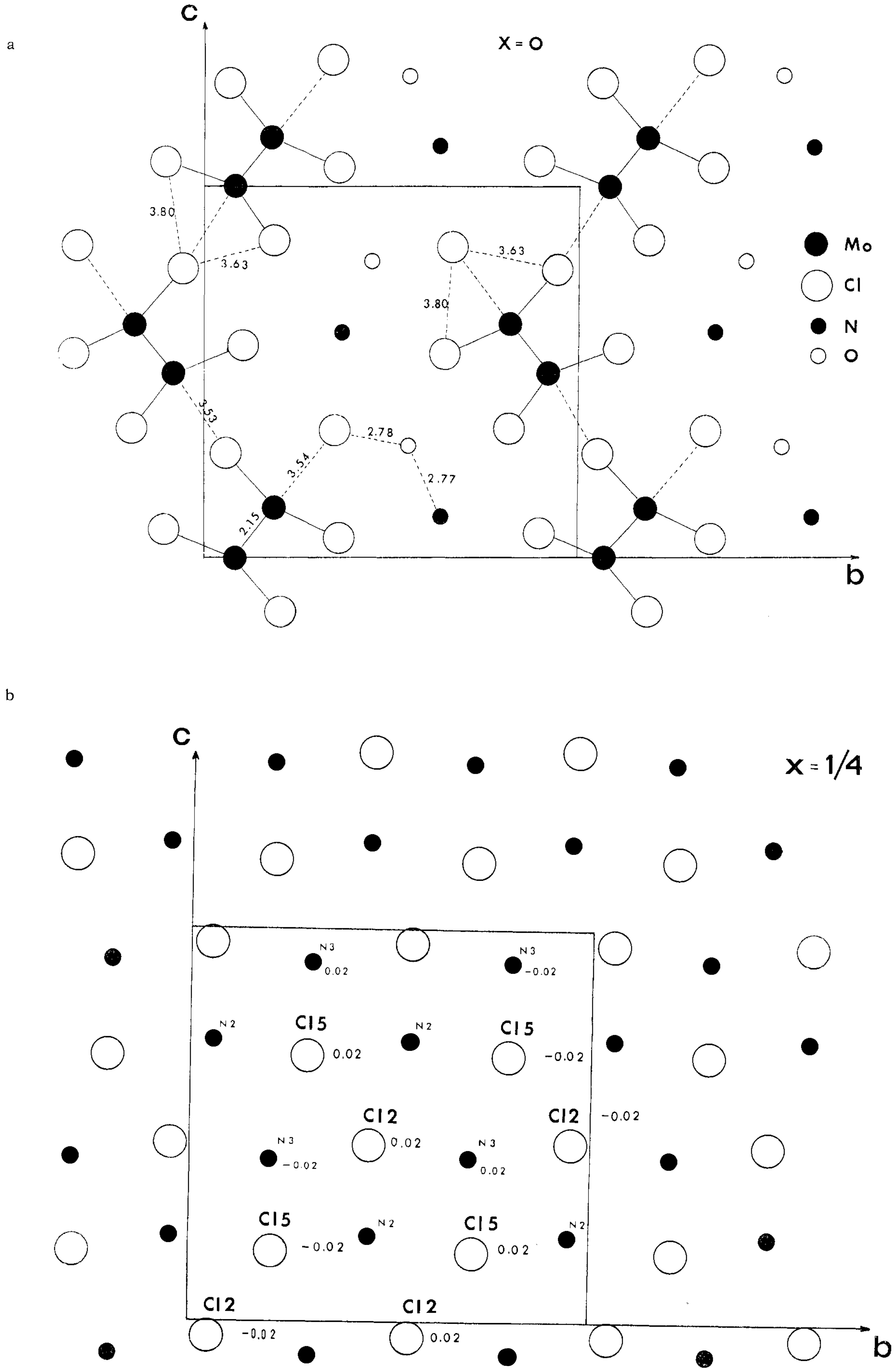


Figure 2.—(a) The 0, y, z plane; selected nonbonded contacts are indicated. (b) The Cl and N atoms near the $^1/_4$, y, z plane; decimal numbers indicate distances above and below the plane as fractional y values.

TABLE VI

SYMMETRY AND DIMENSIONS OF THE $Mo_2Cl_8^{4-}$ ION IN THREE DIFFERENT CRYSTALS[a]

	In $K_4Mo_2Cl_8 \cdot 2H_2O$[b]	In $(enH_2)_2Mo_2Cl_8 \cdot 2H_2O$	In $(NH_4)_5Mo_2Cl_9 \cdot H_2O$
Crystallographic symmetry	$2/m$-C_{2h}	$\bar{1}$-C_i	m-C_s
Virtual symmetry	D_{4h}	D_{4h}	D_{4h}
Mo–Mo dist, Å	2.139 (4)	2.134 (1)	2.150 (5)
Mo–Cl dist (range), Å	2.44–2.46	2.442–2.460	2.415–2.490
Mean Mo–Cl dist, Å	2.45 (2)	2.451 (5)	2.47 ± 0.02
Mo–Mo–Cl angles (range), deg	104.5–105.8	104.58–105.48	103.4–107.3
Mean Mo–Mo–Cl angle, deg	105.1 (7)	105.1 ± 0.4	104.8 ± 1.3
Mean Cl···(Mo)···Cl dist, Å	3.35 (2)	3.35 ± 0.02	3.38 ± 0.02
Mean Cl···Cl dist, Å	3.41 ± 0.05	3.41 ± 0.01	3.43 ± 0.09

[a] Numbers in parentheses are estimated standard deviations (esd's) of either individual or mean values; uncertainty intervals (±) are mean deviations from the average, where these are large enough to make the esd meaningless. [b] Owing to disorder in this case, the quoted esd's are triple those actually calculated in the hope of not seriously underestimating the true uncertainties.

percentages are so small as to make the two formulas indistinguishable in practice. Table VII gives the theoretical figures for the two formulas and the percentages actually found.

TABLE VII

ANALYTICAL FIGURES

Element	Calcd for $(NH_4)_7Mo_3Cl_{13} \cdot H_2O$, %	Calcd for $(NH_4)_5Mo_2Cl_9 \cdot H_2O$, %	Found, %
N	10.99	11.31	10.6[a]
H	3.39	3.58	3.62[a]
Mo	32.23	31.00	31.6[b]
Cl	51.61	51.54	51.4[c]
O	1.79	2.58	...

[a] Microanalytical determinations by Galbraith Microanalytical Laboratories, Knoxville, Tenn. [b] Gravimetric as $PbMoO_4$; average of four determinations. [c] Gravimetric as AgCl; average of four determinations.

It is evident that the differences in calculated analyses for N and H are at best marginal, while for Cl there is no significant difference. There is a substantial difference for oxygen, but lack of convenient and generally satisfactory methods of analysis coupled with the possibility of variation in water content depending on drying conditions, humidity, and temperature nullifies the usefulness of this. For molybdenum, there is a difference of 1.23%, which is in principle, perhaps, exploitable. In our hands, however, no distinction could be drawn. Four analyses all give results lying between the two calculated values and averaging to a figure which is precisely their mean. Thus, the decisive means of establishing the identity of this compound as well as revealing its structure turns out to be the X-ray crystallographic study.

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

The Preparation of Some Compounds Containing Multiple Molybdenum–Molybdenum Bonds[1]

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

Received September 18, 1969

Synthetic procedures for preparing various low-valent molybdenum compounds containing Mo–Mo bonds from $Mo_2(O_2CCH_3)_4$ are discussed. Explicit experimental details are given for the compounds $K_4Mo_2Cl_8 \cdot 2H_2O$, $K_4Mo_2Cl_8$, $K_3Mo_2Cl_7 \cdot 2H_2O$, and $Rb_3Mo_2Cl_7 \cdot 2H_2O$. The last three have not yet been structurally characterized, and the last two are new compounds. All compounds are obtained by treatment of $Mo_2(O_2CCH_3)_4$ with aqueous hydrochloric acid. The particular compound obtained depends on the exact conditions of temperature, acid concentration, and the cation used. All compounds were obtained in crystalline form, and in most though, unfortunately, not all cases crystals were large enough and otherwise suitable for single-crystal X-ray structure studies.

Introduction

The compound dimolybdenum tetraacetate[3,4] provides an excellent starting material for the preparation of halo complexes of molybdenum in oxidation states II and higher. The isolation[5-10] and characterization[7-10] of compounds containing molybdenum with the oxidation numbers +2 and +2.5 have been reported. $Mo_2(O_2CCH_3)_4$ also constitutes an excellent starting

---

[1] Supported by the U. S. Atomic Energy Commission.

[2] Fellow of the Samuel Rubin Foundation, 1967–1969.

[3] T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964).

[4] D. Lawton and R. Mason, *J. Am. Chem. Soc.*, **87**, 921 (1965).

[5] I. R. Anderson and J. C. Sheldon, *Australian J. Chem.*, **18**, 271 (1965).

[6] G. B. Allison, I. R. Anderson, and J. C. Sheldon, *ibid.*, **20**, 869 (1967).

[7] J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **8**, 7 (1969).

[8] M. J. Bennett, J. V. Brencic, and F. A. Cotton, *ibid.*, **8**, 1060 (1969).

[9] J. V. Brencic and F. A. Cotton, *ibid.*, **8**, 2698 (1969).

[10] J. V. Brencic and F. A. Cotton, *ibid.*, **9**, 346 (1970).