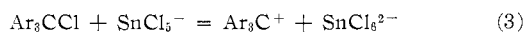
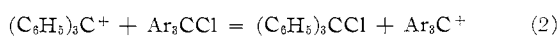


(IV) ion has a negative enthalpy (-11.9 kcal/mol). The entropy term for the ionization, however, is also large and negative (-48.8 eu); above about -25° the contribution of the $T\Delta S$ term overcomes the favorable enthalpy term, and the free energy of ionization becomes positive. Thus the stability of triphenylcarbonium pentachlorostannate(IV) arises from a rather delicate balance of factors; the energy required to ionize triphenylmethyl chloride reduces the enthalpy of hexahalostannate(IV) formation, and the negative entropy of the ionogenic reaction becomes dominant. With a simple halide—such as a tetraalkylammonium halide—there is no comparable ionization energy; entropy comparisons are harder to make, but if we consider the *reverse* reaction of formation of halide and pentachlorostannate(IV) from the hexachlorostannate(IV), it is likely that the molecule-forming reaction in the triarylcarbonium case would have the more positive entropy.⁴⁶

Consideration of the equations



(46) This discussion is based on solution measurements; however, the use of these data to predict successfully the stability of other salts (*vide infra*) makes extension to the solid state reasonable.

shows that (3) is the summation of (1) and (2), and thus $\Delta G^\circ(3) = \Delta G^\circ(1) + \Delta G^\circ(2)$. For a triarylmethyl chloride (Ar_3CCl) to react with stannic chloride to form a stable hexachlorostannate(IV) salt, $\Delta G^\circ(2)$ must be negative and at least as large numerically as $\Delta G^\circ(1)$, which from this work is $+1.85$ kcal/mol. Young, Sandel, and Freedman⁴⁷ have determined $\Delta G^\circ(2)$ for a variety of triarylmethyl chlorides. Their values of $\Delta G^\circ(2)$ for *p*-tolylidiphenylmethyl chloride (-1.6 kcal/mol), di-*p*-tolylphenylmethyl chloride (-3.2 kcal/mol), and tri-*p*-tolylmethyl chloride (-4.6 kcal/mol) suggest that the former would not react with stannic chloride to form a stable hexachlorostannate(IV) salt even in the presence of excess *p*-tolylidiphenylmethyl chloride, while the latter two chlorides should form stable hexachlorostannate(IV) salts. These predictions are confirmed by experiment. In addition, it is clear why 1,2-dichloro-1,2,3,4-tetraphenylcyclobutene ($\Delta G^\circ(2) = 1.8$ kcal/mol) forms a stable pentachlorostannate(IV) salt.^{48,49}

Acknowledgment.—We wish to thank Sharon Alderman and Alan A. MacDonald, who carried out many of these reactions.

(47) A. E. Young, V. R. Sandel, and H. H. Freedman, *J. Am. Chem. Soc.*, **88**, 4532 (1966).

(48) There is a tacit assumption in this discussion that $\Delta H^\circ(L)$ ⁴⁹ for the formation of these complexes is similar; since structural differences are small, this would appear to be reasonable.

(49) K. M. Harmon, S. D. Alderman, K. E. Benker, D. J. Diestler, and P. A. Gebauer, *ibid.*, **87**, 1700 (1965).

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The Preparation and Structural Characterization of Trirubidium Octachlorodimolybdenum. A Binuclear Structure with Strong Metal–Metal Bonding¹

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The compounds $\text{Rb}_3\text{Mo}_2\text{Cl}_8$ and $\text{Cs}_3\text{Mo}_2\text{Cl}_8$ have been isolated and structurally characterized. The green-yellow crystals in solids are obtained by treatment of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ with deoxygenated 12 *N* HCl at 60° , followed by addition of RbCl or CsCl and cooling to 0° . The cesium compound is obtained in practically quantitative yield. These compounds can be converted electrochemically into $\text{Rb}_3\text{Mo}_2\text{Cl}_9$ and $\text{Cs}_3\text{Mo}_2\text{Cl}_9$ in excellent yields; we believe this is the best way to prepare the latter compounds. $\text{Rb}_3\text{Mo}_2\text{Cl}_8$ and $\text{Cs}_3\text{Mo}_2\text{Cl}_8$ appear virtually certain to be isostructural. The structure of $\text{Rb}_3\text{Mo}_2\text{Cl}_8$ has been solved and refined: space group $P62c$; $a = 7.190$ (5) Å, $c = 16.662$ (10) Å at 24° ; $d_{\text{calcd}}(Z = 2) = 3.26$ g cm⁻³; $d_{\text{obsd}} = 3.23 \pm 0.04$ g cm⁻³. The structure consists of Rb^+ ions and discrete $\text{Mo}_2\text{Cl}_8^{3-}$ ions. The latter are not related structurally to the $\text{Mo}_2\text{Cl}_8^{4-}$ ion but may be described as Mo_2Cl_8 groups of the biocahedron ($\text{W}_2\text{Cl}_8^{3-}$) type in which one-third of the bridging Cl atoms are missing. These defective binuclear entities are then rotationally disordered in the crystal. The Mo–Mo distance, 2.38 (1) Å, as well as the squashing together of the two octahedra, shows that there is strong metal–metal bonding, though not so strong as in $\text{Mo}_2\text{Cl}_8^{4-}$ (Mo–Mo = 2.14 Å).

Introduction

In this paper we present the second of a series of reports on the chemical and structural properties of low-valent molybdenum compounds which can be obtained

by treatment of dimolybdenum tetraacetate with mineral acids. The previous paper³ described the structural characterization of $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$, a compound containing the $\text{Mo}_2\text{Cl}_8^{4-}$ ion, which has a D_{4h} non-bridged structure (Mo–Mo = 2.14 Å), comparable to that of $\text{Re}_2\text{Cl}_8^{2-}$, with which it is isoelectronic.

(1) Supported by the U. S. Atomic Energy Commission.
(2) Fellow of the Samuel Ruben Foundation. On leave from The University of Ljubljana, Ljubljana, Yugoslavia.

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

Studies of the reactions of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ with aqueous HCl and HBr were undertaken several years ago in this laboratory and also, independently, by Sheldon and his coworkers;^{4,5} roughly similar results were obtained initially in both laboratories and several products have been described by Sheldon, *et al.* Until recently we have issued no reports because only materials unsuitable for structural characterization by single-crystal X-ray work were obtained, and we were reluctant to speculate upon the actual molecular formulas and structures. More recently, however, techniques have been devised for obtaining usable, albeit small, single crystals of several of the compounds.

The materials dealt with in this report are those of empirical formulas $\text{Rb}_3\text{Mo}_2\text{Cl}_9$ and $\text{Cs}_3\text{Mo}_2\text{Cl}_9$. The latter was reported by Anderson and Sheldon,⁴ who gave it the formula $\text{Cs}_8\text{Mo}_4\text{Cl}_{16}$ and assigned to it an esthetically pleasing structure based upon a regular tetrahedron of molybdenum atoms. So far as we can see, however, there was no evidence to support anything beyond a statement of the empirical formula, $\text{Cs}_3\text{Mo}_2\text{Cl}_9$, and we show here that this is, in fact, also the molecular formula. The detailed structure of $\text{Rb}_3\text{Mo}_2\text{Cl}_9$, isomorphous with $\text{Cs}_3\text{Mo}_2\text{Cl}_9$, which is described here is highly novel, involving an incomplete bioctahedron ($\text{W}_2\text{Cl}_9^{3-}$) type of binuclear anion in which one bridging Cl atom is absent. It also involves a strong metal-to-metal bond ($\text{Mo-Mo} = 2.38 \text{ \AA}$).

Experimental Section

Preparation of Compounds. $\text{Rb}_3\text{Mo}_2\text{Cl}_9$.—Freshly prepared⁶ dimolybdenum tetraacetate (0.40 g) was dissolved in 50 ml of warm ($\sim 60^\circ$), deoxygenated 12 *N* hydrochloric acid. Solid RbCl (0.34 g) was then added and the solution was cooled in an ice bath. Within a few hours a green-yellow solid precipitated. The product was filtered, washed with several portions of absolute ethanol and then ether, and dried for 2 hr under vacuum at 25° . Chlorine was determined by Volhard titration and molybdenum was determined as the oxinate. The same method was used for chlorine analyses in the other compounds discussed below. *Anal.* Calcd for $\text{Rb}_3\text{Mo}_2\text{Cl}_9$: Cl, 38.75; Mo, 26.22. Found: Cl, 38.6; Mo, 25.8.

$\text{Cs}_3\text{Mo}_2\text{Cl}_9$.—To 100 ml of the warm HCl solution of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ (2.0 g) described above was added 3.0 g of CsCl. Precipitation of the green-yellow product occurred immediately. This was washed and dried in the same way as its Rb analog. The yield was virtually quantitative. Like the Rb analog, the compound crystallized in the form of hexagonal plates. *Anal.* Calcd for $\text{Cs}_3\text{Mo}_2\text{Cl}_9$: Cl, 32.44. Found: Cl, 32.0.

$\text{Rb}_3\text{Mo}_2\text{Cl}_9$.—Concentrated hydrochloric acid (200 ml) was boiled for 15 min and cooled in a nitrogen atmosphere. $\text{Rb}_3\text{Mo}_2\text{Cl}_9$ (2.0 g) was dissolved therein and the solution was placed in the anode compartment of an electrolytic cell, the construction of which is described elsewhere.⁷ The anode was a platinum plate of approximately 1 cm^2 surface and a graphite rod served as a cathode. A direct current of 1 A at a voltage of 5 V was passed through the solution for 5 min. During this time the color of the solution changed from yellow to reddish brown and a reddish brown crystalline solid precipitated. This solid was separated by filtration, washed with ether, and dried under vacuum at 25° ; yield, 45%. Continuation of the electrolysis leads to formation

of higher-valent molybdenum compounds. *Anal.* Calcd for $\text{Rb}_3\text{Mo}_2\text{Cl}_9$: Cl, 41.58. Found: Cl, 40.8.

$\text{Cs}_3\text{Mo}_2\text{Cl}_9$.—Proceeding in an analogous way, this compound was prepared in virtually quantitative yield from 1.0 g of $\text{Cs}_3\text{Mo}_2\text{Cl}_9$ in 200 ml of HCl. *Anal.* Calcd for $\text{Cs}_3\text{Mo}_2\text{Cl}_9$: Cl, 35.07. Found: 35.0.

Physical Measurements. Infrared Spectra.—All four compounds were examined as Nujol mulls in the range 2.5–16 μ using a Beckman 337 recording infrared spectrometer. No absorption bands were found in any case.

Magnetic Measurements.—A Gouy balance was used and measurements were made at $\sim 20^\circ$. $\text{Rb}_3\text{Mo}_2\text{Cl}_9$ and $\text{Cs}_3\text{Mo}_2\text{Cl}_9$ have magnetic susceptibilities of approximately zero. Hence, if allowance is made for diamagnetic corrections, they have small, effective magnetic moments of $\sim 0.5 \text{ BM}$ (per dinuclear formula unit). $\text{Rb}_3\text{Mo}_2\text{Cl}_9$ is paramagnetic and μ_{eff} at 300° (with diamagnetic correction of 309×10^{-6} cgsu applied to χ_{mol} of 293×10^{-6} cgsu) is $1.2 \pm 0.1 \text{ BM}$ (per dinuclear formula unit).

Lattice Parameters from Powder Photographs.—The lattice parameters for $\text{Rb}_3\text{Mo}_2\text{Cl}_9$, $\text{Cs}_3\text{Mo}_2\text{Cl}_9$, and $\text{Cs}_3\text{Mo}_2\text{Cl}_9$ were determined using a Debye-Scherrer camera with a diameter of 114.6 mm. Samples were diluted with starch to avoid absorption errors and sealed in glass capillaries. Cu $K\alpha$ radiation ($\lambda(K\alpha_1) 1.5405 \text{ \AA}$; $\lambda(K\alpha_2) 1.5443 \text{ \AA}$) filtered by nickel foil was used. All lines observed for each compound could be indexed on the basis of hexagonal symmetry, and in each case $00l$ reflections for $l = 2n + 1$ were absent. While no definite suggestion can be made as to the space group for $\text{Rb}_3\text{Mo}_2\text{Cl}_9$ and $\text{Cs}_3\text{Mo}_2\text{Cl}_9$, the presence of the 111 reflection for each indicates that they do not have the same space group as $\text{Rb}_3\text{Mo}_2\text{Cl}_9$. The powder data for $\text{Cs}_3\text{Mo}_2\text{Cl}_9$ are consistent with this compound having the same space group as $\text{Rb}_3\text{Mo}_2\text{Cl}_9$.

Lattice parameters were refined by least squares, using an average of about 20 lines in each case and assigning each observation a weight of $(\sin 2\theta)^{-2}$, where θ equals arc $\sin(\lambda/2d_{hkl})$. The lattice parameters a and c (\AA) and their standard deviations (with $\text{Rb}_3\text{Mo}_2\text{Cl}_9$ parameters for comparison) are, respectively: $\text{Rb}_3\text{Mo}_2\text{Cl}_9$, 7.190 (5), 16.662 (10); $\text{Rb}_3\text{Mo}_2\text{Cl}_9$, 7.18 (1), 16.90 (2); $\text{Cs}_3\text{Mo}_2\text{Cl}_9$, 7.27 (3), 16.97 (8); $\text{Cs}_3\text{Mo}_2\text{Cl}_9$, 7.33 (4), 17.23 (10).

The method was checked by determining the lattice constant of sodium chloride. A value of $5.63 \pm 0.02 \text{ \AA}$ was obtained; the reported value is⁸ 5.63 at 24° .

The previously reported values⁹ for $\text{Cs}_3\text{Mo}_2\text{Cl}_9$ are $a = 7.352$ and $c = 17.55 \text{ \AA}$. From the data of Anderson and Sheldon⁴ for $\text{Cs}_8\text{Mo}_4\text{Cl}_{16}$ we calculate, using the same least-squares procedure, $a = 7.37$ (3) and $c = 17.06$ (4) \AA .

Solution and Refinement of the $\text{Rb}_3\text{Mo}_2\text{Cl}_9$ Structure

The best crystals obtainable had the shape of very thin hexagonal plates. Approximately half of one such plate was used for the structural study; its approximate dimensions were $0.16 \times 0.07 \times 0.005 \text{ mm}$. These hexagonal plates were examined in polarized light and no deviation from uniaxial extinction was observed, thus ruling out the possibility of pseudo-hexagonal rather than real hexagonal symmetry or twinning of ordinary type. Precession photographs taken with unfiltered molybdenum radiation showed 6/mm symmetry for the $hk0$ level. Because of the thinness of the crystal in the c direction, Weissenberg photographs taken with Ni-filtered Cu radiation were used subsequently for the determination of the correct Laue group and space group. Zero, first, and second levels that contained reciprocal lattice rows coincident with or parallel to the c^* and a^* directions were obtained. Upper levels

(4) I. R. Anderson and J. C. Sheldon, *Australian J. Chem.*, **8**, 271 (1965).

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

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

(7) K. H. Lohmann and R. C. Young, *Inorg. Syn.*, **4**, 97 (1953).

(8) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1965, p 122.

(9) D. J. W. Ijdo, Thesis, Leiden, 1960, as quoted by P. W. Smith, Ph.D. Thesis, London, 1962.

showed two mirror planes, one perpendicular to the c^* axis and the second perpendicular to the a^* axis. These features unequivocally establish 6/mmm Laue symmetry. The only systematic absences were for $hh\bar{2}hl$ reflections with $l \neq 2n$. Therefore, three space groups¹⁰ were possible, *viz.*, $P6_3mc$ (no. 186), $P\bar{6}2c$ (no. 190), and $P6_3/mmc$ (no. 194).

Unit cell dimensions were determined by measuring the positions of $h00$ and $00l$ series of reflections using a manually operated General Electric XRD-5 counter diffractometer equipped with a quarter-circle eucentric goniometer. The measurements were extrapolated to $\theta = 90^\circ$ by a method previously described.¹¹ Using copper radiation ($\lambda(K\alpha_1)$ 1.5405 Å; $\lambda(K\alpha_2)$ 1.5443 Å) the dimensions obtained at $24 \pm 1^\circ$ are: $a = 7.190 \pm 0.005$ Å; $c = 16.662 \pm 0.010$ Å. With these dimensions and $Z = 2$ (for the formula $Rb_3Mo_2Cl_8$; mol wt, 731.91) the density is calculated to be 3.26 g cm^{-3} . The density determined by flotation in a mixture of bromoform and diiodomethane was $3.23 \pm 0.04 \text{ g cm}^{-3}$.

Intensities were measured with the same crystal on the diffractometer, using nickel-filtered Cu $K\alpha$ radiation. The crystal was mounted with its 110 axis coincident with the ϕ axis of the goniometer. One hundred and eighty independent reflections were measured within the range of $\theta = 50^\circ$. Each peak was scanned from $2\theta(\text{calcd}) - 1.33^\circ$ to $2\theta(\text{calcd}) + 1.33^\circ$ at the scan rate of $4^\circ/\text{min}$, giving P counts. Background was counted for 20 sec each at the beginning (B_1) and the end (B_2) of each scan. The intensity was then taken as $I = P - B_1 - B_2$. The standard deviation, D , of each intensity was taken as $D = (P + B_1 + B_2)^{1/2}$. For 36 reflections $I < 2D$; these were omitted in solving and refining the structure. These 36 reflections included those for which $I \leq 0$.

Because of the plate shape of the crystal, absorption corrections were both necessary ($\mu = 401.6 \text{ cm}^{-1}$) and difficult. By carefully measuring the crystal dimensions, six facial planes were identified. The thickness of the plate, however, could not be accurately determined by direct measurement. Therefore, the angle χ was set at 90° and several reflections were measured at frequent intervals as ϕ was varied from 0 to 360° . Curves could be calculated in best agreement with all such sets of points using a thickness of $5.0 \times 10^{-4} \text{ cm}$. After applying absorption corrections using this value together with the other measured dimensions of the crystal, the maximum variation in any ϕ scan was $\pm 5\%$. All intensities were then corrected for absorption and the L_p factor. Transmission factors varied from 0.30 to 0.82 for all the data.

A Patterson function was computed in the vector set space group $P6/mmm$ which is common to the three possible crystal space groups. This function had a very high peak at $u = 1/3$, $v = 2/3$, and $w = 1/2$. This, together with the observation that all reflections for which $h - k = 3n$ and $l = 2n$ were of relatively high

intensity, suggested that the heavy atoms (Mo, Rb) should be found at positions of the type $\pm(1/3, 2/3, z; 2/3, 1/3, z + 1/2)$, namely, the 2b positions of $P6_3mc$ or the 4f positions of $P\bar{6}2c$ and $P6_3/mmc$. These locations for cations are analogous to those reported for $K_3W_2Cl_9$ ^{12a} and $Cs_3Cr_2Cl_9$.^{12b} On this basis a Patterson peak on the Harker line 0, 0, w at $w = 0.14$ could be assigned to an Mo-Mo pair separated by ~ 2.4 Å. Assuming for the moment the centrosymmetric space group $P6_3/mmc$, the Mo atoms were placed on a 4f equipoint with $z \approx 0.18$ and four Rb atoms were placed on another 4f equipoint with $z \approx 0.58$. The two remaining Rb atoms were assigned to the 2b positions. Three cycles of least-squares refinement of z coordinates and isotropic temperature factors for Mo and Rb atoms lead to a discrepancy index, $R_1 = ||F_o| - ||F_c|/|F_o| = 0.32$. Using structure factor signs from the last of these refinement cycles, a difference electron density map was computed. From this map chlorine atoms were assigned to the 12k and 6h positions (of $P6_3/mmc$). It was apparent, however, that the peaks for the 12-fold position were denser (peak density $18 \text{ e}^-/\text{Å}^3$) than those for the 6-fold position ($14 \text{ e}^-/\text{Å}^3$), suggesting that the normal requirement of the space group (18 Cl atoms per cell) and the analytical data (16 Cl atoms per cell) might be reconciled by assuming vacancies in the 6h set.

Refinement was begun in the space group $P6_3/mmc$. The atomic scattering factors of Cromer and Waber¹³ for neutral atoms of Mo, Rb, and Cl were used. Calculated structure factors included corrections for the real and imaginary parts of anomalous scattering¹⁴ for all atoms. Weighting factors, w , were assigned equal to $[\sigma(F)]^{-2}$. $\sigma(F)$ is given by $[D + \rho I^2]^{1/2}/2A(L_p)|F_o|$, where D is as defined above, $A(L_p)$ is the product of the transmission factor and the Lorentz-polarization factor, and ρ is an uncertainty factor¹⁵ to which the value 0.002 was assigned. The refinement program¹⁶ was used to minimize $\sum w(|F_o| - |F_c|)^2$. The weighted discrepancy index is defined as $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

After three cycles, refinement of all positional parameters and isotropic temperature parameters converged with $R_1 = 0.18$ and $R_2 = 0.23$. In these cycles the occupancy factor for the 6h position was 1.0. Reducing this to 0.67 made no appreciable improvement in the discrepancy indices. We then switched from $P6_3/mmc$ to the noncentric space groups.

Refinement in the space group $P6_3mc$ was next tried. This converged to $R_1 = 0.14$ and $R_2 = 0.18$ but the standard deviations were relatively high. Turning then to $P\bar{6}2c$, satisfactory refinement was accomplished. Six cycles of isotropic refinement converged with $R_1 = 0.086$ and $R_2 = 0.11$. In these cycles the occupation

(12) (a) W. H. Watson, Jr., and J. Waser, *Acta Cryst.*, **11**, 689 (1958); (b) G. J. Wessel and D. J. W. Ijdo, *ibid.*, **10**, 466 (1957). Note that the direct comparison of the $K_3W_2Cl_9$ and $Cs_3Cr_2Cl_9$ structures requires a shift in origin of $z/2$ in one or the other.

(13) D. T. Cromer and J. T. Waber, *ibid.*, **18**, 104 (1965).

(14) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(15) Cf. R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).

(16) C. T. Prewitt, "SPR5, A Full-Matrix Crystallographic Program for the IBM 360" (modified by B. M. Foxman).

(10) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965.

(11) M. J. Bennett, F. A. Cotton, and J. Takats, *J. Am. Chem. Soc.*, **90**, 903 (1968).

TABLE I
OBSERVED AND FINAL CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS $\times 10^{-1}$)

H	L	FCBS	FCAL	H	L	FCBS	FCAL	H	L	FCBS	FCAL	H	L	FCBS	FCAL	H	L	FCBS	FCAL	H	L	FCBS	FCAL																																																																																																																																																												
0	2	879	858	1	6	595	597	2	6	535	537	3	10	256	259	4	6	346	356	5	1	407	417	6	10	256	259	7	12	757	841	8	5	472	222	9	14	235	218	10	16	818	828	11	2	171	167	12	3	593	589	13	5	622	623	14	7	880	633	15	8	1020	567	16	11	777	369	17	13	809	759	18	4	623	194	19	7	203	122	20	8	819	820	21	1	444	420	22	3	331	323	23	4	459	463	24	6	245	246	25	7	610	513	26	8	717	706	27	10	239	238	28	3	393	328	29	4	1	400	30	1	171	158	31	2	286	330	32	3	749	756	33	0	490	509	34	4	630	584	35	4	573	530	36	6	302	298	37	7	762	729	38	8	649	625	39	8	1001	997	40	3	2	436	41	3	6	225	42	8	637	743	43	1	4	400	44	3	351	389

factor of the 6h equipoint was left at 1.0. The temperature parameter of the 6h chlorine atoms was much higher (6.9 \AA^2) than that of the 12i chlorine atoms (4.4 \AA^2). This is contrary to expectation (and the results of other studies) since the former are in bridging positions and the latter in terminal positions of a bioctahedron ($\text{W}_2\text{Cl}_9^{3-}$) type of structure. The occupation factor for the 6h chlorine atoms was now reduced to 0.67 and left hereafter as a variable parameter. In the first cycle of isotropic refinement it did not change, but the discrepancy indices dropped significantly, to $R_1 = 0.079$ and $R_2 = 0.092$.

Anisotropic refinement was then commenced. At convergence (no parameter change $> \sigma/4$) the residuals were $R_1 = 0.061$ and $R_2 = 0.075$ and the standard deviation of an observation of unit weight was 1.96. A difference Fourier map had no peak of density above $1 \text{ e}^-/\text{\AA}^3$. An empirical weighting scheme was tested. It reduced the standard deviation of an observation of unit weight to nearly 1.0 but did not significantly alter any positional parameters or lessen their standard deviations. The final value of the occupation factor for the 6h chlorine atoms was 0.67 with an esd of 0.01. The observed and final calculated structure factors, in units of 0.1 electron, are listed in Table I.

Results

The final positional and thermal parameters of all atoms are listed in Table II. Figure 1 gives a sketch of the Mo_2Cl_8 unit and shows some of its principal dimensions; others are listed in Table III.

The structure consists of discrete $\text{Mo}_2\text{Cl}_8^{3-}$ entities, which are crystallographically identified as Mo_2Cl_8 ($2/3\text{Cl}$) $_8^{3-}$ entities, packed together with Rb^+ ions in essentially the same way as the $\text{W}_2\text{Cl}_9^{3-}$ and K^+ ions are packed in $\text{K}_3\text{W}_2\text{Cl}_9$. There are slight differences in detail owing to the slightly different dimensions and the different symmetry constraints imposed by the different space groups, but the two compounds may be considered isostructural in an inexact but meaningful sense.

Discussion

The Structure of $\text{Rb}_3\text{Mo}_2\text{Cl}_9$.—As the structure of this substance was being solved, the question of its stoichiometry had to be reopened. Prior to any X-ray work, analytical data, both here and in Sheldon's laboratory, had consistently agreed with the $\text{M}_3^{\text{I}}\text{Mo}_2\text{Cl}_9$ stoichiometry ($\text{M} = \text{Rb}, \text{Cs}$) and differed significantly from the figures calculated for $\text{M}_3\text{Mo}_2\text{Cl}_9$. Moreover, the properties of compounds which had been reported to have the 3:2:9 stoichiometry were different from the properties of the $\text{M}_3\text{Mo}_2\text{Cl}_9$ compounds; this was par-

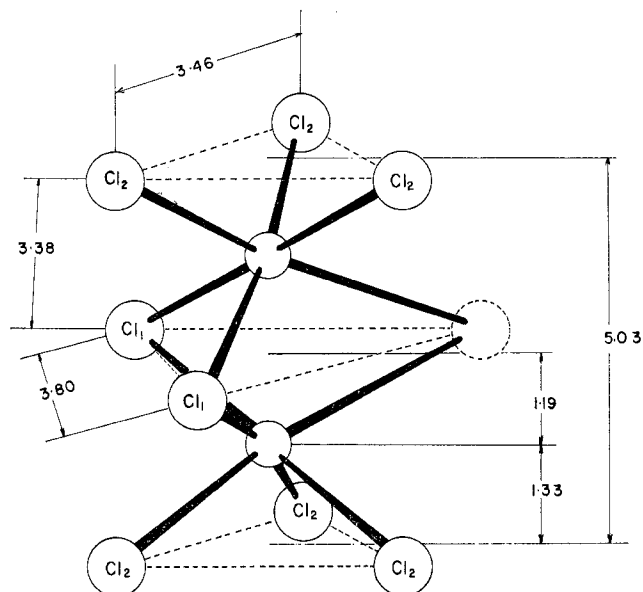


Figure 1.—A sketch of the $\text{Mo}_2\text{Cl}_8^{3-}$ ion emphasizing its relation to a bioctahedron.

TABLE II
FINAL POSITIONAL AND THERMAL PARAMETERS^{a, b}

Position	Atom				
	Mo 4f	Rb(1) 4f	Rb(2) 2b	Cl(1) 6h	Cl(2) 12i
x	$1/3$	$1/3$	0	0.4740 (42)	0.1805 (49)
y	$2/3$	$2/3$	0	0.0166 (41)	0.3491 (15)
z	0.1786 (3)	0.5721 (4)	$1/4$	$1/4$	0.0987 (6)
$10^4\beta_{11}$	52 (20)	156 (34)	96 (44)	48 (100)	343 (85)
$10^4\beta_{22}$	52 (20)	156 (34)	96 (44)	154 (61)	219 (31)
$10^4\beta_{33}$	15 (2)	19 (3)	22 (5)	22 (7)	42 (4)
$10^4\beta_{12}$	26 (10)	78 (17)	48 (22)	69 (63)	72 (80)
$10^4\beta_{13}$	21 (39)
$10^4\beta_{23}$	-36 (14)
$B, \text{ \AA}^2$	1.10 (10)	2.32 (30)	1.82 (20)	1.30 (40)	4.93 (50)

^a Standard deviations occurring in the last quoted figure of each parameter are given in parentheses. ^b Anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^c Isotropic temperature factors equivalent to and computed from the tensors. ^d Required by symmetry to be zero.

TABLE III
DIMENSIONS OF THE $\text{Mo}_2\text{Cl}_8^{3-}$ ION

—Bond lengths, \AA —		—Bond angles, deg—		—Nonbonded contacts, \AA —	
Mo—Mo	2.38 (1)	Cl ₁ —Mo—Cl ₁ '	99.2 (15)	Cl ₁ —Cl ₁ '	3.80 (6)
Mo—Cl ₂	2.38 (1)	Cl ₂ —Mo—Cl ₂ '	93.1 (14)	Cl ₂ —Cl ₂ '	3.46 (5)
Mo—Cl ₁	2.50 (2)	Cl ₁ —Mo—Cl ₂	87.7 (9)	Cl ₁ —Cl ₂	3.38 (3)
		Mo—Cl ₁ —Mo	56.8 (9)		

ticularly true of the colors: red-purple for $\text{M}_3^{\text{I}}\text{Mo}_2\text{Cl}_9$ vs. yellow for $\text{M}_3\text{Mo}_2\text{Cl}_9$. Nevertheless, in the early stages of solving the structure, when it appeared that with four Mo atoms in the unit cell, chlorine atoms occupied one 12-fold and one 6-fold position (making an 18:4 or

9:2 ratio for Cl:Mo), it was natural that at least some skepticism was aroused about the formula. However, the entire course of the refinement, with a final occupation factor of 0.67 ± 0.01 at the 6h chlorine site, leaves no doubt that the correct formula is indeed $\text{Rb}_3\text{Mo}_2\text{Cl}_8$.

The structure of $\text{Rb}_3\text{Mo}_2\text{Cl}_8$ seems to be very unusual. It may be considered to consist of two square-pyramidal MoCl_5 groups sharing a basal edge, with the open square faces *cis* to each other and drawn together by Mo–Mo bonding. We know of no close precedent for such a structure among halo complexes.^{17,18}

The immediately preceding description of the structure imposes few restraints regarding equalities of bond distances and angles, whereas, in the crystal, the $\text{Mo}_2\text{Cl}_8^{3-}$ ion appears to have all of the bond length and bond angle equalities characteristic of a bioctahedron, namely, those required by D_{3h} symmetry.¹⁹ Thus, the $\text{Mo}_2\text{Cl}_8^{3-}$ ion can be regarded as a Cl-defective M_2X_9 type of structure in which one bridging X atom is absent, although this may be a valid description only when the anion is in the crystalline environment.

Metal–Metal Bonding in $\text{Mo}_2\text{Cl}_8^{3-}$.—The dimensions of the $\text{Mo}_2\text{Cl}_8^{3-}$ ion show that there is a strong Mo–Mo bond. The over-all shape of the $\text{Mo}_2\text{Cl}_8^{3-}$ ion argues strongly for direct Mo–Mo bonding when examined according to criteria previously described.²⁰ Thus there are marked distortions indicative of the squashing together of the component (incomplete) octahedra of the (incomplete) bioctahedron. The shared triangular face is splayed out, the parallel, outer triangular faces are pinched in, and the metal atoms are displaced well off the approximate centers of the octahedra toward each other. There is an extremely small angle, 57° , at the bridging chlorine atoms. The similarity to the squashing distortion in $\text{W}_2\text{Cl}_9^{3-}$ is very evident.

The Mo–Mo distance itself, 2.38 Å, affords convincing evidence of direct Mo–Mo bonding when comparisons are made with other Mo–Mo distances. In metallic molybdenum, the distance²¹ is 2.73 Å; the structure of the metal is body-centered cubic so that each Mo atom is forming eight bonds. Since there are only six valence electrons per Mo atom, the Mo–Mo bond order in the metal has an upper limit of $6/8$. In dimolybdenum tetracetate²² and the octachlorodimolybdenum ion,³ $\text{Mo}_2\text{Cl}_8^{4-}$, where there are quadruple bonds, the Mo–Mo distances are 2.11 and 2.14 Å, respectively.

(17) With simple ligands like halide ions, there is only the somewhat remote similarity of the $\text{Bi}_2\text{Cl}_8^{2-}$ ion found^{18a} in Bi_2Cl_8 . This consists of two square-pyramidal BiCl_5 groups sharing a basal edge; however, the configuration is transoid and the pyramidal bases are coplanar. In $\text{Co}_2(\text{CO})_8$ the geometry is quite similar^{18b} to that of $\text{Mo}_2\text{Cl}_8^{3-}$, but the crystal packing is very different, and there is, of course, no chemical similarity.

(18) (a) A. Hershaft and J. D. Corbett, *Inorg. Chem.*, **2**, 979 (1963); (b) G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Cryst.*, **17**, 732 (1964).

(19) It must be kept in mind that in each individual $\text{Mo}_2\text{Cl}_8^{3-}$ ion bond length and bond angle inequalities may possibly occur, but they are sufficiently small that (1) they do not interfere with the packing of randomly oriented anions in the hexagonal crystal and (2) they do not lead to displacements which cause temperature parameters to appear unreasonably large. The isotropic temperature parameters, 4.9 and 1.3 Å², for terminal and bridge chlorine atoms in $\text{Mo}_2\text{Cl}_8^{3-}$ are not larger than those reported¹¹ for $\text{W}_2\text{Cl}_9^{3-}$, namely, 5.2 and 3.6 Å².

(20) F. A. Cotton, *Rev. Pure Appl. Chem.*, **17**, 25 (1967).

(21) W. B. Pearson, "Lattice Spacings and Structures of Metals and Alloys," Pergamon Press Ltd., London, 1957.

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

On the basis of these data, one might be tempted to estimate that the Mo–Mo bond order is in the neighborhood of 2. However, such an estimate is very likely to be meaningless, since the Mo–Mo distance is doubtless strongly influenced by the bonding and packing requirements of the surrounding chlorine atoms, as the following discussion will indicate.

After allowance is made for the formation of Mo–Cl bonds and the charge, the pair of Mo atoms has a total of seven electrons and each Mo atom has four valence-shell orbitals remaining. The magnetic moment at room temperature suggests that only one of the seven electrons remains unpaired. One way to account for these facts is to assume that four Mo–Mo bonding orbitals (and four corresponding antibonding orbitals) are formed and that three of these are occupied by electron pairs while the fourth one is occupied by the unpaired electron. It would then be further postulated that the tendency of these 3.5 bonding interactions to draw the Mo atoms very close together is counteracted by the $\text{Cl}\cdots\text{Cl}$ repulsions, by the resistance of Mo–Cl bonds to stretching, and by the resistance of the Mo–Cl–Mo angles to excessive compression. Thus, an equilibrium situation is reached in which electron spin pairing is achieved by four *interatomic* overlaps although none of them can reach its potential maximum value because the close Mo–Mo approach required for this would be incompatible with maintaining Mo–Cl bond strength, retaining sufficiently large Mo–Cl–Mo bond angles, and avoiding excessive $\text{Cl}\cdots\text{Cl}$ nonbonded contacts. This description requires us to abandon any attempt to find a direct correlation of Mo–Mo distance with bond order in this type of structure. For metal atom clusters, in general, the more extensive the superstructure of ligand atoms, especially bridging ones, the more we may expect the closeness of metal–metal approach to be more severely limited by the steric requirements of these ligand atom configurations than by the intrinsic character of the metal–metal bonding.

The preceding formulation of the electronic structure is entirely equivalent to assuming that we begin with a complete bioctahedron, $\text{Mo}_2\text{Cl}_9^{3-}$, in which there are assumed to be three Mo–Mo bonding interactions, one σ and two π . We then remove one bridging chlorine atom, to give $\text{Mo}_2\text{Cl}_8^{3-}$. One unpaired electron then remains in a symmetrical MO formed from the Mo orbitals previously used to bind the chlorine atom which is now missing. Of course, some degree of reorganization of all of the other orbitals will occur, but this need not be very great.

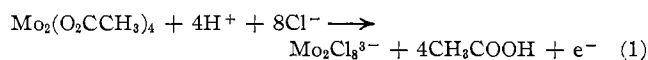
Other ways of formulating the electronic structure of $\text{Mo}_2\text{Cl}_8^{3-}$ seem less probable or less useful. It could, for example, be assumed that, of the seven electrons to be considered, four exist in the form of two localized pairs with *intraionically* coupled spins and only three occupy two-center, bonding MO's. On this assumption, one valence-shell orbital on each molybdenum atom would remain vacant and unused. This seems improbable.

It is necessary to examine also the possibility that

some interatomic spin pairing takes place by means of superexchange coupling across the bridging chlorine atoms. Since this process does not generate any substantial attractive force between the metal atoms, whereas direct Mo-Mo bonding is indicated by the structure, it alone cannot account for all of the spin pairing, but the possibility that at least some of the spin pairing is accomplished in this way cannot be ruled out. However, if substantial direct overlap of metal atom orbitals is possible, it seems reasonable to suppose that this form of interaction will take precedence since it can make a significant contribution to the stability of the molecule. Thus we feel that the concept of a multiple interaction, consisting of at least three and probably four separate though submacimal overlaps of metal orbitals, is an acceptable and useful way to formulate the M-M bonding in this case, and *mutatis mutandis*, in $W_2Cl_9^{3-}$.

Under comparable conditions molybdenum would be expected to show a lesser tendency to M-M bond formation than tungsten. The fact that the Mo-Mo distance in $Mo_2Cl_8^{3-}$ is slightly shorter than the W-W distance in $W_2Cl_9^{3-}$ is presumably due to the three principal differences between these species. First, in $Mo_2Cl_8^{3-}$ there are only two instead of three bridging chlorine atoms to resist the approach of the metal atoms. This may well be the principal factor. Second, the Mo atoms are in a lower valence state (2.5) than the tungsten atoms (3.0), and in general the tendency to M-M bond formation increases with decreasing oxidation state. Third, in $Mo_2Cl_8^{3-}$ there is an additional electron which may enhance the M-M interaction by occupying a more-or-less bonding orbital.

Chemical Properties of $Mo_2Cl_8^{3-}$.—The reaction by which the $Mo_2Cl_8^{3-}$ compounds are produced may be written as



When the cation used is one such as Cs^+ which forms a product, $Cs_3Mo_2Cl_8$, of very low solubility, the yield is nearly quantitative in the sense of eq 1. Thus, disproportionation cannot be the means of generating the $Mo^{2.5+}$ product from the Mo^{2+} starting material. However, the identity of the oxidizing agent has not yet been established. The reaction proceeds most cleanly when the warm HCl solution in which the $Mo_2(O_2CCH_3)_4$ is dissolved has been deoxygenated; when this is not done, various species containing molybdenum in higher oxidation states are produced. This does not

necessarily permit us to dismiss the possibility that oxygen at low concentration is the oxidizing agent in the above reaction. The only other likely oxidizing agent appears to be H^+ . Experiments are in progress to identify the oxidizing agent with certainty.

We wish to emphasize that under the specified experimental conditions of concentration, temperature, and time, the $Mo_2Cl_8^{3-}$ ion (or a solution species from which it is directly obtainable in precipitation reactions) is produced in high purity and good yield; its rubidium and, particularly, cesium salts can be easily isolated.

A useful chemical relationship we have discovered is that the $Mo_2Cl_8^{3-}$ ion in aqueous HCl solution may be electrolytically oxidized to $Mo_2Cl_9^{3-}$ in a clean and virtually quantitative manner. Using Cs^+ the $Mo_2Cl_9^{3-}$ ion can be isolated almost quantitatively. With Rb^+ the yield was only $\sim 50\%$, but we believe that this could be substantially improved under optimum conditions (which we did not systematically seek) of concentration and temperature.

Three methods for the preparation of $Mo_2Cl_9^{3-}$ compounds have previously been described: (1) a high-temperature reaction²³ between MCl ($M =$ alkali metal) and $MoCl_3$, (2) the disproportionation of K_2MoCl_6 in liquid ammonia²⁴ to give $K_3Mo_2Cl_9$ as the residue, and (3) the addition of alkali cations to the molybdenum(III) solution obtained by electrolytic reduction of MoO_3 dissolved in concentrated hydrochloric acid.²⁵ The first method, though it affords a pure product, is time consuming and gives low yields. The second method has apparently been used only in one instance, and no data on yield or purity were reported. The third method seems to give satisfactory yields, but because highly concentrated solutions are employed, impurities are difficult to avoid. The method described here provides both purity and a high yield; it is also relatively fast. The entire reaction sequence, beginning with the preparation of $Mo_2(O_2CCH_3)_4$, takes only about 12 hr, most of the time being required to prepare the $Mo_2(O_2CCH_3)_4$.

A more comprehensive discussion of the chemical properties of this and other halo compounds of low-valent molybdenum will be given later after structural studies have clarified the nature of still other products of the reaction of $Mo_2(O_2CCH_3)_4$ with mineral acids.

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