

TABLE VI  
 SYMMETRY AND DIMENSIONS OF THE  $\text{Mo}_2\text{Cl}_8^{4-}$  ION IN THREE DIFFERENT CRYSTALS<sup>a</sup>

	In $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}^b$	In $(\text{enH}_2)_2\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$	In $(\text{NH}_4)_5\text{Mo}_2\text{Cl}_8 \cdot \text{H}_2\text{O}$
Crystallographic symmetry	$2/m-C_{2h}$	$\bar{1}-C_1$	$m-C_s$
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 $\text{Cl} \cdots (\text{Mo}) \cdots \text{Cl}$ dist, Å	3.35 (2)	3.35 ± 0.02	3.38 ± 0.02
Mean $\text{Cl} \cdots \text{Cl}$ dist, Å	3.41 ± 0.05	3.41 ± 0.01	3.43 ± 0.09

<sup>a</sup> 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. <sup>b</sup> 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	Caled for		Found, %
	$(\text{NH}_4)_7\text{Mo}_3\text{Cl}_8 \cdot \text{H}_2\text{O}$ , %	$(\text{NH}_4)_5\text{Mo}_2\text{Cl}_8 \cdot \text{H}_2\text{O}$ , %	
N	10.99	11.31	10.6 <sup>a</sup>
H	3.39	3.58	3.62 <sup>a</sup>
Mo	32.23	31.00	31.6 <sup>b</sup>
Cl	51.61	51.54	51.4 <sup>c</sup>
O	1.79	2.58	...

<sup>a</sup> Microanalytical determinations by Galbraith Microanalytical Laboratories, Knoxville, Tenn. <sup>b</sup> Gravimetric as  $\text{PbMoO}_4$ ; a average of four determinations. <sup>c</sup> Gravimetric as  $\text{AgCl}$ ; 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.

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## The Preparation of Some Compounds Containing Multiple Molybdenum-Molybdenum Bonds<sup>1</sup>

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Synthetic procedures for preparing various low-valent molybdenum compounds containing Mo-Mo bonds from  $\text{Mo}_2(\text{O}_2\text{C}-\text{CH}_2)_4$  are discussed. Explicit experimental details are given for the compounds  $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ ,  $\text{K}_4\text{Mo}_2\text{Cl}_8$ ,  $\text{K}_3\text{Mo}_2\text{Cl}_7 \cdot 2\text{H}_2\text{O}$ , and  $\text{Rb}_3\text{Mo}_2\text{Cl}_7 \cdot 2\text{H}_2\text{O}$ . The last three have not yet been structurally characterized, and the last two are new compounds. All compounds are obtained by treatment of  $\text{Mo}_2(\text{O}_2\text{CCH}_2)_4$  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<sup>3,4</sup> provides an excellent starting material for the preparation of halo complexes of molybdenum in oxidation states II

and higher. The isolation<sup>5-10</sup> and characterization<sup>7-10</sup> of compounds containing molybdenum with the oxidation numbers +2 and +2.5 have been reported.  $\text{Mo}_2(\text{O}_2\text{CCH}_2)_4$  also constitutes an excellent starting

(1) Supported by the U. S. Atomic Energy Commission.  
 (2) Fellow of the Samuel Ruben Foundation, 1967-1969.  
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 (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).

material for the preparation of salts of the Mo(III) complexes<sup>11</sup>  $\text{MoCl}_5(\text{H}_2\text{O})^{2-}$  and  $\text{MoCl}_5^{3-}$  and for some compounds of Mo(V).<sup>12</sup> In this report we present detailed procedures, not previously published, for the preparation of several Mo(II) compounds and briefly summarize and discuss the conditions for preparation of all the structurally characterized  $\text{Mo}^{2+}$  and  $\text{Mo}^{2.5+}$  chloro complexes reported from this laboratory.

### Experimental Section

Analyses for Mo and Cl were carried out gravimetrically using  $\text{PbMoO}_4$  and  $\text{AgCl}$ , respectively. Infrared spectra were measured on mineral oil mulls between KBr plates using a Beckman Model 337 grating spectrometer in the range 600–5000  $\text{cm}^{-1}$ .

In the following descriptions of preparative procedures the phrase "dried under vacuum" means that the substance was placed in a desiccator containing KOH pellets and the desiccator was continuously evacuated by a mechanical pump during the stated drying period.

Constant-boiling hydrochloric acid (CBHCl) was prepared by evaporating reagent grade concentrated hydrochloric acid (12 *M*, 37 wt %) at its boiling point and allowing it to cool while prepurified nitrogen was bubbled through it. It is approximately 6 *M*, contains about 20.2 wt % of HCl, and has a boiling point of 108° (760 Torr).

**Tetrapotassium Octachlorodimolybdate(II),  $\text{K}_4\text{Mo}_2\text{Cl}_8$ .**—Two grams of dimolybdenum tetraacetate<sup>3</sup> and 2.8 g of KCl (K:Mo atom ratio  $\approx 4$ ) were placed in an erlenmeyer flask containing 100 ml of concentrated (12 *M*) hydrochloric acid which had been saturated with HCl gas at 0°. The slurry was stirred at 25° for 1 hr. A bright red solid precipitated leaving a yellow solution (probably containing  $\text{Mo}_2\text{Cl}_8^{3-}$  and perhaps other oxidation products). The red solid was separated by filtration at 25° on a glass frit, washed with two 20-ml portions of absolute ethanol, and dried under vacuum at 25° for 8 hr; yield, 2.4 g (80% based on  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ ). *Anal.* Calcd for  $\text{K}_4\text{Mo}_2\text{Cl}_8$ : Mo, 30.37; Cl, 44.88. Found: Mo, 30.0; Cl, 45.4.

The compound appeared to be indefinitely stable in dry air. It dissolved in water to give a red solution but this turned yellow-brown within a few minutes. It was insoluble in  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , dimethyl sulfoxide, and dimethylformamide. The infrared spectrum was blank from 600 to 5000  $\text{cm}^{-1}$ .

**Tetrapotassium Octachlorodimolybdate(II) Dihydrate,  $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ .**—This was prepared from the anhydrous compound by dissolving 400 mg of  $\text{K}_4\text{Mo}_2\text{Cl}_8$  in 20 ml of CBHCl saturated with nitrogen at 25°. To this was added a solution of 1.2 g of potassium chloride dissolved in a second 20-ml portion of CBHCl, and the combined solution was kept in an ice bath for 20 hr in a stoppered flask. The red, diamond-shaped crystals which formed were collected on a filter, washed with two 20-ml portions of absolute ethanol, and dried under vacuum for 8 hr; yield, 210 mg (~50%). *Anal.* Calcd for  $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ : Mo, 28.73; Cl, 42.46. Found: Mo, 28.5; Cl, 41.9.

The compound appeared to be indefinitely stable in dry air. It dissolved in water but the solution decomposed immediately. It was insoluble in methanol or ethanol. The infrared spectrum had bands at 3500, 3440, and 1635  $\text{cm}^{-1}$ , all relatively sharp, indicating the presence of water molecules which are only weakly hydrogen bonded.

**Tripotassium Heptachlorodimolybdate(II) Dihydrate,  $\text{K}_3\text{Mo}_2\text{Cl}_7 \cdot 2\text{H}_2\text{O}$ .** **Method a.**—Six hundred milligrams of  $\text{K}_4\text{Mo}_2\text{Cl}_8$  was dissolved in 40 ml of CBHCl, saturated with nitrogen and previously cooled to 0–10°. Deoxygenated absolute ethanol, 20 ml, was added and the solution, in a stoppered flask, was kept in an ice bath for 1 hr. The violet precipitate was collected on a filter in the air, then washed with two 20-ml portions of absolute ethanol and then two 20-ml portions of anhydrous diethyl ether. It was then dried under vacuum for 4 hr at 25°; yield, 340 mg

(60%). *Anal.* Calcd for  $\text{K}_3\text{Mo}_2\text{Cl}_7 \cdot 2\text{H}_2\text{O}$ : Mo, 32.34; Cl, 41.82. Found: Mo, 32.1; Cl, 42.2.

**Method b.**—Thirty milliliters of CBHCl and 10 ml of 12 *M* hydrochloric acid were mixed in an erlenmeyer flask and deoxygenated by bubbling nitrogen through for 5 min. Dimolybdenum tetraacetate, 430 mg, was added and the mixture was stirred under nitrogen until the acetate had dissolved. This solution was then filtered, under nitrogen, into a deoxygenated solution consisting of 610 mg of KCl dissolved in 15 ml of CBHCl diluted with 5 ml of  $\text{H}_2\text{O}$ . Twenty milliliters of absolute ethanol was added and this entire solution, under nitrogen in a stoppered flask, was left in an ice bath for 20 hr; yield, 350 mg (60%).

This compound was stable in dry air for only a few weeks to perhaps 1 month. It is soluble in water and methanol, but the solutions turned yellow after several minutes. The infrared spectrum of the solid showed a broad band at about 3300  $\text{cm}^{-1}$  and a band at 1600  $\text{cm}^{-1}$ . Crystals of this compound are rod shaped and of adequate size for X-ray crystallography, but always of very poor quality as judged by Weissenberg and precession photographs. Unit cell dimensions are close to those of the rubidium compound described below.

**Trirubidium Heptachlorodimolybdenum(II) Dihydrate,  $\text{Rb}_3\text{Mo}_2\text{Cl}_7 \cdot 2\text{H}_2\text{O}$ .**—One gram of  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  was dissolved with stirring in 80 ml of deoxygenated CBHCl at 5°. This solution was filtered into a solution of 2.26 g of RbCl in 25 ml of deoxygenated CBHCl, and the resulting solution, contained in a stoppered flask from which oxygen had been expelled by a stream of nitrogen, was placed in an ice bath for 16 hr. The precipitate was collected on a filter in the air, washed with two 20-ml portions of absolute ethanol, and dried under vacuum at 25° for 10 hr; yield, 1.2 g (70%). *Anal.* Calcd: Mo, 26.20; Cl, 33.89. Found: Mo, 26.2; Cl, 33.5.

The compound is a red crystalline solid, soluble in water, but the solutions decomposed in about 10 min even when purged of oxygen. The solid appeared to be considerably more stable than the potassium analog. It was kept without evident decomposition in a desiccator over KOH for more than 1 month; visual evidence of decomposition was afforded by a change in color to brown-black. Decomposition was much faster in (moist) laboratory air; a distinct yellow color (presumably due to  $\text{Rb}_2\text{Mo}_2\text{Cl}_6$ ) developed in 3 weeks or less.

The crystals were found to belong to the hexagonal system with unit cell dimensions  $a = 13.01 \pm 0.01 \text{ \AA}$  and  $c = 8.52 \pm 0.01 \text{ \AA}$ . The only observed systematic absence was  $l \neq 3n$  for 00 $l$ . Laue symmetry was  $\bar{3}m1$ . The probable space groups are thus  $\text{P}3_21$  and  $\text{P}3_121$ . From the unit cell volume and reasonable assumptions as to atomic volumes, it would appear that  $Z = 3$ . Intensity data are being collected with a view to solving the structure.

### Discussion

Details of the methods of preparing  $\text{K}_4\text{Mo}_2\text{Cl}_8$ ,  $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ ,  $\text{K}_3\text{Mo}_2\text{Cl}_7 \cdot 2\text{H}_2\text{O}$ , and  $\text{Rb}_3\text{Mo}_2\text{Cl}_7 \cdot 2\text{H}_2\text{O}$  are given in this paper; the methods for preparing  $(\text{enH}_2)_2\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ ,<sup>9</sup>  $(\text{NH}_4)_5\text{Mo}_2\text{Cl}_9 \cdot \text{H}_2\text{O}$ ,<sup>10</sup>  $\text{Rb}_3\text{Mo}_2\text{Cl}_8$ ,<sup>8</sup> and  $\text{Cs}_3\text{Mo}_2\text{Cl}_8$ <sup>8</sup> have previously been reported. While all procedures are based on the reaction of  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  with aqueous hydrochloric acid, the detailed conditions vary from case to case, and, to a considerable extent, the variation in products is in qualitative accord with the law of mass action.

Thus,  $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$  is obtained from constant-boiling (~6 *M*) aqueous HCl, whereas from saturated aqueous HCl, in which the activity of  $\text{H}_2\text{O}$  is greatly reduced due to solvation of the additional protons, the anhydrous compound is obtained.  $(\text{NH}_4)_5\text{Mo}_2\text{Cl}_9 \cdot \text{H}_2\text{O}$ , which consists of the  $\text{Mo}_2\text{Cl}_8^{4-}$  ion, 5  $\text{NH}_4^+$ ,  $\text{Cl}^-$ , and  $\text{H}_2\text{O}$  is also obtained from the more dilute acid but

(11) J. V. Brencic and F. A. Cotton, *Inorg. Syn.*, in press.

(12) J. V. Brencic, unpublished observations.

with a considerable excess of the ammonium salt present in solution.  $(\text{enH}_2)_2\text{Mo}_2\text{Cl}_3 \cdot 2\text{H}_2\text{O}$  is also obtained from dilute acid.

The chloride-deficient compounds,  $\text{M}^{\text{I}}_3\text{Mo}_2\text{Cl}_7 \cdot 2\text{H}_2\text{O}$ , are obtained from dilute acid to which alcohol is added. It is not obvious why the addition of alcohol causes this change in stoichiometry, nor is the structural nature of these new compounds yet known. A reasonable speculation is that they consist of chains of  $\text{Mo}_2\text{Cl}_3$  groups sharing corners, in somewhat the way  $\text{ReCl}_4$  consists of  $\text{Re}_2\text{Cl}_9$  bioctahedra sharing corners.

All of the procedures used to prepare molybdenum(II) chloro complexes from  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  have one thing in common: the solutions are at all times kept at or below  $25^\circ$ . Raising the temperature of such solutions causes oxidation to occur and this, when properly controlled, permits the preparation in good

yield of compounds containing molybdenum in higher oxidation states. The oxidant (possibly  $\text{H}^+$ ) has not been identified. Thus, when  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  is dissolved in 12 *M* hydrochloric acid at  $60^\circ$ , the  $\text{Mo}_2\text{Cl}_8^{3-}$  ion is formed<sup>8</sup> and can be isolated in essentially quantitative yield as the cesium salt or, in somewhat lower yield, as the rubidium salt. When concentrated HCl solutions of  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  are boiled, the Mo(III) species  $\text{MoCl}_5(\text{H}_2\text{O})^{2-}$  and  $\text{MoCl}_6^{3-}$  are formed.<sup>11</sup>

In conclusion we would emphasize that  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  is a uniquely useful starting material for the preparation of many complexes of molybdenum in low or medium oxidation states. Thus, in addition to the  $\text{Mo}_2\text{Cl}_8^{4-}$  ion, it affords excellent yields of  $\text{Mo}_2\text{Cl}_8^{3-}$  which can then be converted essentially quantitatively to  $\text{Mo}_2\text{Cl}_9^{3-}$  by electrolytic oxidation<sup>8</sup> and to species in still higher oxidation states by other oxidizing agents.<sup>12</sup>

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## The Anti- $\text{Th}_3\text{P}_4$ -Type Structure in the Lanthanum-Rhodium System: $\text{La}_4\text{Rh}_{\sim 3}$ <sup>1</sup>

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$\text{La}_4\text{Rh}_{\sim 3}$  has the anti- $\text{Th}_3\text{P}_4$ -type structure, with  $a = 8.922 (\pm 3) \text{ \AA}$ . The space group is  $\bar{I}43d\text{-T}_d^8$ . About  $11\frac{2}{3}$  Rh atoms are randomly distributed in 12(a):  $\frac{2}{3}$ , 0,  $\frac{1}{4}$ . Sixteen La atoms are in 16(c):  $x, x, x$ , where  $x = 0.0570 (\pm 5)$ . The interatomic distances are: Rh-La, 2.851 ( $\pm 5$ ) and 3.357 ( $\pm 4$ )  $\text{ \AA}$ ; La-La, 3.591 ( $\pm 7$ ), 3.863 ( $\pm 2$ ), and 4.122 ( $\pm 6$ )  $\text{ \AA}$ . The Rh atoms are not in contact with each other. The shortened Rh-La bond length, 2.851  $\text{ \AA}$ , indicates some covalent bonding. The causes for the change in stoichiometry from  $\text{A}_3\text{B}_4$  to  $\text{A}_4\text{B}_3$ , where A is always a transition element, and the variations in the positional parameter  $x$  between 0.057 and 0.083 are discussed in terms of the sizes and the chemical nature of the B atoms.

During the course of an investigation in the lanthanum-rhodium system,<sup>2</sup> an intermediate phase with a fairly simple X-ray diffraction pattern was found to exist in the vicinity of 42 atom % Rh. The alloys with 40, 41, and 42 atom % Rh were homogeneous in the as-cast state and consisted only of this phase. Figure 1 shows the microstructure of  $\text{La}_{60}\text{Rh}_{40}$  in the as-cast state. It reveals a fine-grained (ASTM grain size number about 9) single-phase specimen. Similar microstructures were observed in the other alloys in the as-cast state. The alloy corresponding to the formula  $\text{La}_4\text{Rh}_3$  (42.86 atom % Rh) was heterogeneous (two phased) in the as-cast state and was made up mostly of the phase found in the other alloys. The alloys were wrapped in thin molybdenum foils and annealed in evacuated quartz tubes. After annealing for 7 days at  $900^\circ$  under vacuum, the alloys with 40 and 41 atom % Rh also became heterogeneous and contained small

amounts of an additional phase identified as  $\text{La}_5\text{Rh}_3$ .  $\text{La}_{58}\text{Rh}_{42}$  remained single phased while the alloy with 42.86 atom % Rh showed small amounts of the next Rh-rich phase,  $\text{La}_5\text{Rh}_4$ , along with the phase found in the former.

Analysis of the microstructures and X-ray diffraction patterns of the above-mentioned alloys thus showed that an intermediate phase, whose structure is described in this paper, occurs at 42 atom % Rh and has a narrow-phase field, probably between 41.5 and 42.5 atom % Rh at  $900^\circ$  and perhaps between 40 and 42.5 atom % Rh at still higher temperatures. Since the arc-melted alloys were obtained with negligible weight loss (about 2 or 3 mg/g) during melting and there was no weight loss during annealing, a chemical analysis of the alloys was not deemed necessary. The assumed compositions correspond to the starting weights of La and Rh and are considered to be fairly accurate.

The powder X-ray diffraction pattern showed the phase to have a body-centered-cubic structure. The diffraction angles for Ni-filtered Cu  $K\alpha$  radiation were

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(2) P. P. Singh and A. Raman, *Trans. Met. Soc. AIME*, **245**, 1561 (1969).