

capillary tubes were mounted in a 114.6 mm. camera and exposed 24 hours to the K-alpha ( $\lambda$  1.5418 Å.) radiation of copper with an open port and two nickel screens over the film. Samples of different preparations gave identical powder patterns regardless of the capillary size. Lindemann capillaries of 0.5 mm. permitted sample absorption which resulted in line splitting. The observed  $d$ -spacings (Å.) and visually observed intensities are: 6.09(Broad)(VF); 5.57(Broad)(VF); 3.47(M); 3.24(S); 3.07(M); 3.04(M); 2.40(M); 2.36(M); 2.02(M); 1.86(M); 1.83(M); 1.73(M); 1.70(M); 1.67(M); 1.63(M); 1.53(VF); 1.48(VF); 1.37(M); 1.35(F); 1.29(M); 1.28(M); 1.27(M); 1.25(M); 1.23(F); 1.22(F); 1.181(VF); 1.160(VF); 1.137(VF); 1.122(VF); 1.086(VF).

### Discussion

Niobium pentaiodide can be prepared at a lower temperature than reported in the literature. The pentaiodide begins to form from the elements at about 250° and forms rapidly at about 280°. It can be prevented from disproportionating, or being reduced by niobium to lower iodide, by maintaining

a partial pressure of iodine. The niobium completely reacted (and thus eliminated contamination from elemental niobium) to form  $\text{NbI}_5$  which was collected as a compact crystalline mass of low surface area. The excess iodine was easily sublimed away since the pentaiodide is stable and apparently exerts a very low vapor pressure at the melting point of iodine.

The X-ray diffraction patterns from the different preparations were identical. Single crystals of  $\text{NbI}_5$  have not been prepared, and, consequently, there are no data from which reliable lattice parameters can be determined. Therefore, only the observed  $d$ -spacings are reported.

**Acknowledgments.**—I am grateful for the assistance given to me by our X-ray staff and more specifically to Mr. Albert F. Biddle.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF CONNECTICUT]

## Some Ternary Oxides of Tetravalent Molybdenum<sup>1,2</sup>

BY WILLIAM H. MCCARROLL, LEWIS KATZ AND ROLAND WARD

RECEIVED JANUARY 21, 1957

New oxides of tetravalent molybdenum, having formulas of the type  $\text{A}_x\text{M}_2\text{Mo}_3\text{VO}_8$ , have been prepared. The divalent cations which have been used successfully are those of Mg, Mn, Fe, Co, Ni, Zn and Cd. The structure of these compounds has been determined revealing molybdenum to molybdenum bonding and two different coordination numbers for the A cations. Electrical and magnetic properties were examined. Attempts to prepare similar compounds with tetravalent tungsten and rhenium were unsuccessful.

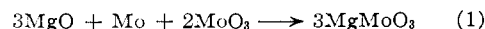
The reported methods for the preparation of molybdenum bronzes analogous to the tungsten bronzes have been examined by Straumanis and Irani<sup>3</sup> who demonstrated that none of the procedures gave a homogeneous product, the only reduced product being  $\text{MoO}_2$ . These attempts to prepare molybdenum bronzes were all based on the premise that the formal oxidation state of molybdenum would lie between 5 and 6 and that the phases would have a composition  $\text{M}_x\text{MoO}_3$  where M is an alkali metal and  $x$  has a value between zero and one. No ternary oxides of tetravalent molybdenum were known until Scholder, Klemm and Brixner<sup>4,5</sup> reported the preparation of the compounds  $\text{BaMoO}_3$ ,  $\text{SrMoO}_3$ ,  $\text{CaMoO}_3$  and  $\text{MgMoO}_3$ . Confirmation of some of these results has been indicated in a recent communication from this Laboratory.<sup>6</sup> However, we were unable to prepare a compound of composition  $\text{MgMoO}_3$ . It was found that by heating molybdenum(IV) oxide with zinc oxide or magnesium oxide, isotypic phases were formed. Chemical analysis of the purified compounds indicated the composition  $\text{Mg}_2\text{Mo}_3\text{O}_8$  and  $\text{Zn}_2\text{Mo}_3\text{O}_8$ . Part of this paper describes the crystal structure determination

of these compounds and the preparation and characterization of other compounds having this structure. In the Discussion, some crystallographic data for  $\text{CaMoO}_3$  are presented also.

### Experimental

**Preparation of Reactants.**—Molybdenum(IV) oxide was prepared by the reduction of reagent grade molybdenum(VI) oxide with hydrogen at 470° for 36 hours. The product was washed successively with 6 *N* hydrochloric acid, distilled water and 6 *N* ammonium hydroxide until the wash solution was colorless. It was then dried at 110°. Analysis gave 75.05% Mo (theor. 74.99). CoO, NiO and MgO were prepared by heating the carbonates in air at 1000 to 1100° while MnO was obtained by the reduction of  $\text{MnO}_2$  at 900° with hydrogen for 36 hours. The other reactants were of C. p. or reagent grade.

**Preparation of  $\text{Mg}_2\text{Mo}_3\text{O}_8$  and  $\text{Zn}_2\text{Mo}_3\text{O}_8$ .**—The synthesis of  $\text{MgMoO}_3$  was attempted by heating in evacuated silica capsules intimate mixtures of reactants according to eq. 1 and 2



The samples were heated for 48 hour periods at 600, 700, 800, 1000, 1100 and 1150°. The brown product obtained at 600° gave an X-ray diffraction pattern of only magnesium oxide and molybdenum(IV) oxide while those formed between 700 and 1000° gave in addition, the pattern of a new phase. At the higher temperatures, products were obtained which gave the pattern of the new phase with only the strongest line of magnesium oxide present. By washing these products with hydrochloric acid, homogeneous black phases were obtained which showed none of the lines of the starting materials in their X-ray patterns. The pattern was indexed on the basis of a hexagonal unit cell. Completely analogous reactions were found using zinc oxide instead of magnesium oxide. The lattice constants and densities are given in Table I (calculated densities in parenthe-

(1) Abstracted in part from the doctoral thesis of William H. McCarroll submitted to the Graduate School of the University of Connecticut, October, 1956.

(2) This work carried out under contract with the Office of Naval Research. Reproduction in whole or part is permitted for any purpose of the United States Government.

(3) M. E. Straumanis and K. Irani, *THIS JOURNAL*, **74**, 2114 (1952).

(4) R. Scholder and W. Klemm, *Angew. Chem.*, **66**, 467 (1954).

(5) R. Scholder and L. Brixner, *Z. Naturforsch.*, **10b**, 178 (1955).

(6) W. H. McCarroll, R. Ward and L. Katz, *THIS JOURNAL*, **78**, 2910 (1956).

ses). These data coupled with chemical analyses establish the general formula  $A_2Mo_3O_8$ . There are two formula weights per unit cell. *Anal.* Calcd. for  $Zn_2Mo_3O_8$ : Zn, 23.92; Mo, 52.66. Found: Zn, 23.99; Mo, 52.89. Calcd. for  $Mg_2Mo_3O_8$ : Mg, 10.47; Mo, 62.01. Found: Mg, 10.44; Mo, 62.21. It might be mentioned in connection with the results in Table I that all X-ray powder diffraction patterns were taken with a North American Philips camera of 57.3 mm. radius and that Cu  $K\alpha$  radiation was used (wave length 1.5418 Å.).

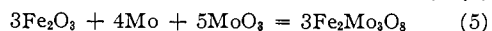
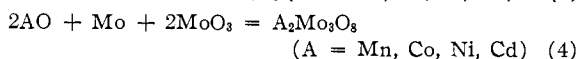
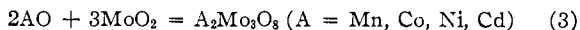
TABLE I

PHYSICAL DATA FOR $A_2Mo_3O_8$ TYPE COMPOUNDS		
Compound	Lattice constant, Å.	Density <sup>a</sup>
$Mg_2Mo_3O_8$	$a = 5.761 \pm 0.002$	5.30
	$c = 9.893 \pm .004$	(5.43)
$Mn_2Mo_3O_8$	$a = 5.795 \pm .005$	5.75
	$c = 10.267 \pm .010$	(5.85)
$Fe_2Mo_3O_8$	$a = 5.782 \pm .005$	6.04
	$c = 10.046 \pm .010$	(6.02)
$Co_2Mo_3O_8$	$a = 5.767 \pm .005$	6.21
	$c = 9.915 \pm .010$	(6.21)
$Ni_2Mo_3O_8$	$a = 5.752 \pm .005$	6.22
	$c = 9.865 \pm .010$	(6.26)
$Zn_2Mo_3O_8$	$a = 5.775 \pm .005$	6.23
	$c = 9.915 \pm .010$	(6.33)
$Cd_2Mo_3O_8$	$a = 5.835 \pm .005$	6.75
	$c = 10.815 \pm .010$	(6.67)

<sup>a</sup> Calculated densities are given in parentheses.

When stoichiometric mixtures of magnesium oxide and molybdenum(IV) oxide were used, small amounts of molybdenum(IV) oxide usually were found in the products. This could be removed by digestion with dilute nitric acid. The compound  $Mg_2Mo_3O_8$  also is formed by the reaction of magnesium with molybdenum(VI) oxide. The equimolar mixture was prepared in pellet form and heated at 400–450° in a Pyrex tube which had been constricted at the open end. This is a procedure which has been given as a method for the preparation of  $Mo_2O_3$ .<sup>7</sup>

**Preparation of Other Compounds of the Type  $A_2Mo_3O_8$ .**—The following methods were found to be successful for the preparation of  $A_2Mo_3O_8$  type compounds. The compositions of the reaction mixture were decided by the equations



The appropriate quantities of reactants were mixed by careful grinding, pressed into pellets and heated in evacuated, sealed, silica capsules for 48 hours. The manganese, cobalt and nickel compounds are best prepared at 1050–1150°. The iron compound was prepared at 1000° since higher temperatures caused appreciable attack of the silica capsule. Danger of an explosion due to the formation of cadmium metal vapor necessitated the use of a maximum temperature of 850° for the preparation of  $Cd_2Mo_3O_8$ . All products except the iron compound were treated with dilute nitric acid to remove any unreacted molybdenum(IV) oxide. The iron compound could not be treated in this manner since it is decomposed rapidly by nitric acid.

The X-ray powder pattern of products of materials treated with nitric acid could be indexed on the basis of hexagonal unit cells similar to those found for  $Mg_2Mo_3O_8$  and  $Zn_2Mo_3O_8$ . The powder pattern of the iron compound contained two lines which could not be indexed. These are believed to be due to an unidentified impurity. In the case of the nickel compound a small amount of a green material, believed to be a nickel molybdate(VI), was also present. No reagent was found to remove this impurity. A partial mechanical separation by decantation can be made which yields a product estimated to be about 99%  $Ni_2Mo_3O_8$ . No chemical analyses of these products were made, X-ray data and densities (Table I) being considered sufficient to establish the general formula  $A_2Mo_3O_8$ .

(7) C. H. Ehrenfeld, *THIS JOURNAL*, 17, 391 (1895).

All of the products are black in the massive form and highly crystalline. When finely powdered, the zinc, cobalt and cadmium compounds are dark green while the manganese compound is brown. Single crystals in the form of hexagonal plates were obtained for all but the magnesium compound. In the latter case a potassium molybdate flux had to be used. The largest crystals were obtained for  $Ni_2Mo_3O_8$ . They were about 1.0–1.5 mm. in largest dimension. Crystals of the other compounds were considerably smaller.

All of the compounds appear to be stable toward hydrochloric acid. Decomposition by dilute nitric acid is appreciable only in the case of the iron compound. Cold, concentrated nitric acid slowly decomposes the manganese and cadmium compounds while the others do not appear to be affected.

Rough estimates of the electrical conductivities of these materials were obtained using the following procedure. The powdered samples were compressed into a hole 5 mm. in diameter in a Lucite block. The resistance of the powder under 15,000 lb. pressure was measured with an electronic voltmeter. All measurements were made at room temperature. All but the iron and manganese compounds were found to be non-conductors of electricity. The conductivity of these two compounds may be due to impurities since measurements made on different preparations of the same compound gave different results (Table II).

TABLE II

CONDUCTIVITY AND MAGNETIC DATA			
Compound	Conductivity (ohm-cm.) <sup>-1</sup>	Magnetic data <sup>a</sup> $X_m$	$\mu_{eff}$
$Mg_2Mo_3O_8$	0	$51 \times 10^{-6}$	0.35
$Mn_2Mo_3O_8$	(1) $4.3 \times 10^{-7}$	$10,300 \times 10^{-6}$	4.93
	(2) $2.7 \times 10^{-5}$	$10,300 \times 10^{-6}$	4.93
$Fe_2Mo_3O_8$	(1) $1.2 \times 10^{-4}$	$9,710 \times 10^{-6}$	4.85
	(2) $1.4 \times 10^{-5}$	.....	..
$Co_2Mo_3O_8$	0	$8,020 \times 10^{-6}$	4.34
$Ni_2Mo_3O_8$	0	$4,860 \times 10^{-6}$	3.39
$Zn_2Mo_3O_8$	0	$48 \times 10^{-6}$	0.34
$Cd_2Mo_3O_8$	0	$42 \times 10^{-6}$	0.32

<sup>a</sup>  $X_m$  and  $\mu_{eff}$  are susceptibility and effective Bohr magnetons per gram atom of A cation, except for the Mg, Zn and Cd compounds for which the values are per gram atom of Mo.

Magnetic susceptibilities of the solid compounds were measured by the Gouy method in an atmosphere of nitrogen at room temperature. The molar susceptibilities were corrected for diamagnetic contribution of the constituent atoms.<sup>8</sup> The results are given in Table II. The molar susceptibilities and effective Bohr magnetons per gram atom of molybdenum are given for magnesium, zinc and cadmium compounds. It is noted that the values are much lower than would be expected for compounds containing tetravalent molybdenum with two unpaired d-orbital electrons. The values of the susceptibilities and effective Bohr magnetons for the manganese, iron, cobalt and nickel compounds are given per gram atom of A cation. The value of  $\mu_{eff}$  has been corrected for the contribution from molybdenum assuming that it is similar to those found for the magnesium, zinc and cadmium compounds. The values would be about 1% higher if this correction were not made. The moments were calculated assuming that the compounds obeyed the Curie law.

### Structure Determination

It was decided to make a critical study of the structure of the  $A_2Mo_3O_8$  compounds, since they appeared to be of a new structure type.  $Zn_2Mo_3O_8$  and  $Mg_2Mo_3O_8$  were studied in particular since they were the first to be prepared. The other members of this series were made during the course of the single crystal studies.

Single crystals of  $Mg_2Mo_3O_8$  were grown by the addition of 3% by weight of potassium molybdate to a mixture of magnesium oxide, molybdenum

(8) P. Selwood, "Magnetochemistry," Interscience Publishers, Inc. New York, N. Y., 1956, p. 78.

metal powder and molybdenum(IV) oxide in the mole ratios  $\text{MgO}:\text{Mo}:\text{MoO}_2 = 3:1:2$ . The sample was pressed into a pellet and heated at  $1150^\circ$  for 48 hours in an evacuated sealed silica capsule. The capsule was cooled slowly over a period of 28 hours to  $675^\circ$  before it was removed from the furnace. Examination of the product under the microscope revealed the presence of small, well-developed crystals in the form of six sided plates which could be separated from the aggregate after leaching with 6 *N* hydrochloric acid and distilled water. A crystal 0.04 mm. in largest dimension was selected for structure studies.

Single crystals of  $\text{Zn}_2\text{Mo}_3\text{O}_8$  were grown in a similar manner but in this case the addition of a flux was not necessary. A crystal 0.18 mm. in largest dimension was used for X-ray analysis.

All X-ray diffraction photographs of both crystals were taken with the rotation or oscillation axis perpendicular to the plate. Weissenberg photographs of the zero, first and second levels of both crystals showed that both are hexagonal and have Laue symmetry  $6/mmm$ . The absence of *hhl* reflections when *l* is odd was the only systematic absence observed. This limited the space group to one of three possibilities:  $P6_3mc$ ,  $P6_2c$  or  $P6_3/mmc$ .

Intensity data for the zinc compound were obtained for the zero, first and second levels, about *c*, by Weissenberg photography and for the *h0l* not by precession photography. Intensity data for the magnesium compound were gathered from the *hk0* and the *hhl* nets only. The multiple film technique was used for Weissenberg photography while several timed exposures were taken for precession work. Copper  $K\alpha$  radiation was used for studies employing the Weissenberg camera. Molybdenum  $K\alpha$  radiation was used for precession photography.

Relative intensities were estimated by comparison with calibrated intensities strips. The usual Lorentz and polarization corrections<sup>9,10</sup> were applied to the observed intensities.

An estimate of the effect of absorption on the intensity of diffraction spots showed that it would be negligible for the magnesium crystal whichever radiation was used. In the case of the larger zinc crystal appreciable absorption effects would be expected when copper  $K\alpha$  radiation was used. Such effects were noted by comparing corresponding reflections appearing on both the Weissenberg and precession photographs. An empirical factor, found by correlation of the Weissenberg and precession data, was used to correct the Weissenberg intensities of the zinc compound. No absorption corrections were made for the magnesium compound.

A first set of atomic position parameters was obtained by trial and error methods. The best fit of observed and calculated structure factors was obtained by placing the atoms in positions of the non-centrosymmetric space group  $P6_3mc$ . The cation locations were checked by computing the projection of the electron density on the *a*-, *b*-plane and on the *c*-axis. For refinement of the *x* parameter of molybdenum it was only necessary to calculate the

electron density projection for the line  $y = 2x$ . The oxygen atoms could not be located accurately because of their relatively low scattering power and the consequent insensitivity of the intensities to small changes in their positions. The positions of the atoms in  $\text{Zn}_2\text{Mo}_3\text{O}_8$  are given in Table III. The positions of the atoms in  $\text{Mg}_2\text{Mo}_3\text{O}_8$  are the same except that  $x_{\text{Mo}} = 0.147$ . Table IV gives the values of the observed and calculated structure factors. The value of the over-all reliability factor (*R*) for  $\text{Zn}_2\text{Mo}_3\text{O}_8$  is 0.118 for 90 reflections of observable intensity. The reliability factor for 16 *hk0* reflections of observable intensity for  $\text{Mg}_2\text{Mo}_3\text{O}_8$  is 0.108. Neither of these values for *R* includes the 220 reflection. The calculated value of the structure factor for this reflection was almost twice as high as the observed value in the case of the zinc compound and about 50% higher in the case of the magnesium compound. This was believed to be the result of secondary extinction effects. In order to check this explanation relative intensities were calculated and compared with observed intensities estimated from diffractometer traces of powders of both compounds. The observed and calculated intensities, including those of the 220 reflection, for the magnesium compound were in excellent agreement with each other. Several anomalous intensities, among them the 220 reflection, were noted in the case of the zinc compound. These are attributed to preferred orientation effects. Indeed, examination of the powdered sample under the microscope clearly showed the presence of minute crystals.

TABLE III

ATOMIC COORDINATES FOR ATOMS IN $\text{Zn}_2\text{Mo}_3\text{O}_8$	
Space group 186	$P6_3mc$
6Mo in 6c with $x = 0.146$	$z = 0.250$
2Zn <sub>I</sub> in 2b with	$z = .0625$
2Zn <sub>II</sub> in 2b with	$z = .500$
2O <sub>I</sub> in 2a with	$z = .385$
2O <sub>II</sub> in 2b with	$z = .133$
6O <sub>III</sub> in 6c with $x = 0.490$	$z = .363$
6O <sub>IV</sub> in 6c with $x = 0.156$	$z = .633$
Position 2a: $0,0,z; 0,0,1/2 + z$	
Position 2b: $1/3, 2/3, z; 2/3, 1/3, 1/2 + z$	
Position 6c: $x, x, z; x, 2x, z; 2\bar{x}, \bar{x}, z; \bar{x}, x, 1/2 + z; \bar{x}, 2\bar{x}, 1/2 + z; 2x, x, 1/2 + z$	

### Discussion

The structure of  $\text{Zn}_2\text{Mo}_3\text{O}_8$  consists of a distorted double-hexagonal closest packing of oxygens (abcb) in which the oxygen layers are held together by alternate layers of zinc and molybdenum atoms. The molybdenum atoms are in octahedral coordination with oxygen. Half of the zinc atoms are in tetrahedral coordination with oxygen while the other half are in octahedral coordination. This coordination scheme results in sums of electrostatic bond strengths from adjacent cations of  $2^{1/2}(\text{O}_{II})$ ,  $2^{1/6}(\text{O}_{III})$ ,  $2(\text{O}_I)$ , and  $1^{2/3}(\text{O}_{IV})$ . Although the value of  $2^{1/2}$  is a pronounced infraction of the electrostatic valence rule,<sup>11</sup> it is not so extreme as those observed for the heteropoly acids of molybdenum and

(9) C. Lu, *Rev. Sci. Instr.*, **14**, 331 (1943).

(10) J. Waser, *ibid.*, **22**, 1567 (1951).

(11) L. Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1940, p. 384.

TABLE IV  
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  $Zn_4Mo_8O_{16}$   
Reliability factor = 0.118 without 220 reflection, 0.132 including 220.

$hk$	A	B	$ F_{\text{calcd.}} $	$ F_{\text{obsd.}} $	$hkl$	A	B	$ F_{\text{calcd.}} $	$ F_{\text{obsd.}} $
100	23	0	23	23	203	128	48	137	124
110	40	0	40	40	303	79	11	80	75
120	-73	0	73	67	403	-68	-29	74	56
130	-6	0	6	<17	503	-115	15	116	108
140	30	0	30	35	604	159	-50	167	125
150	-52	0	52	59	104	34	18	38	36
200	-116	0	116	111	204	-115	29	119	117
220	252	0	252	134	304	-19	-33	38	42
230	70	0	70	73	404	-81	19	83	75
240	-48	0	48	64	504	-56	11	57	58
250	-13	0	13	19	105	2	-52	52	42
300	18	0	18	<23	205	-181	60	191	167
330	64	0	64	70	305	-72	5	72	60
340	-69	0	69	70	405	114	-40	121	144
400	-83	0	83	83	505	75	30	81	68
500	-85	0	85	78	006	-137	-31	140	109
600	123	0	123	100	106	-63	12	64	70
101	32	-4	32	38	206	66	45	80	64
121	-54	-3	54	60	306	57	-22	61	60
131	-1	2	2	13	406	51	31	60	53
141	56	6	56	53	506	38	13	40	<42
151	-2	0	2	<12	107	46	-63	78	75
201	-145	-22	147	146	207	96	42	105	72
231	1	-1	1	<14	307	62	8	63	64
241	64	-5	64	75	407	-62	-19	65	60
251	-81	8	81	90	507	-92	25	95	108
301	-78	-10	79	83	008	179	3	179	155
341	73	-1	73	57	108	46	6	46	46
401	88	19	90	83	208	-54	-10	55	47
501	78	2	78	83	308	-48	4	48	53
601	15	1	15	17	408	43	-7	44	46
002	-136	-37	141	103	508	-47	2	47	44
012	-103	23	106	111	109	-35	-48	59	53
022	47	-45	65	71	209	-80	41	90	99
032	132	-29	135	129	309	-58	-1	58	60
042	29	-18	34	38	409	52	-40	66	82
052	31	3	31	39	509	75	33	86	65
062	-14	-16	21	24	0,0,10	-139	20	136	131
112	141	-34	145	139	1,0,10	39	-8	40	<40
122	-14	10	17	18	2,0,10	50	-26	56	64
132	-58	13	59	67	3,0,10	55	12	56	57
142	75	-18	77	84	4,0,10	52	7	52	60
152	3	4	5	<13	1,0,11	3	-27	27	<40
222	-66	-29	72	81	2,0,11	112	39	118	89
232	-117	17	118	116	3,0,11	54	6	54	60
242	8	-13	15	14	0,0,12	114	-22	116	95
332	34	-15	37	44	1,0,12	23	-17	29	40
342	26	2	26	30	2,0,12	-63	1	63	59
103	77	-24	81	87	3,0,12	21	19	28	44
					1,0,13	-39	-10	40	<40

tungsten.<sup>12</sup> The molybdenum-to-oxygen distances appear to differ in a way which is consistent with the spirit of the electrostatic valence rule in that the longest such bonds (Table V) involve the oxygens with total bond strength of  $2^{1/2}$  and the shortest involve the oxygens with total bond strength of  $1^{2/3}$ . However, although the molybdenum positions have an estimated probable error of  $\pm 0.01$  Å., the zinc positions have an estimated probable error of  $\pm 0.05$  Å. (in  $z$ ) and the oxygen

(12) Ref. 11, p. 395.

positions may be in error by 0.1 Å. or more. It is thus impossible to speak with finality about the cation-to-oxygen distances.

The molybdenum-molybdenum distances for atoms in the same layer are not all the same. The nearest molybdenum-molybdenum approach is 2.53 Å. while the next nearest distance is 3.25 Å. The 2.53 Å. distance is closer than the distance between metal atoms in molybdenum metal itself and hence is indicative of bonding between these atoms.

TABLE V  
BOND LENGTHS IN  $Zn_2Mo_3O_8$ , Å.

Tetrahedral Zn			
Mo-O <sub>I</sub>	1.98	Zn <sub>11</sub> -O <sub>11</sub>	1.94
Mo-O <sub>111</sub>	2.21	Zn <sub>11</sub> -O <sub>111</sub>	1.92
Mo-O <sub>111r</sub>	2.07		
Mo-O <sub>11v</sub>	1.91		
Octahedral Zn			
Mo-Mo	2.53	Zn <sub>11</sub> -O <sub>111</sub>	2.08
Mo-Mo	3.25	Zn <sub>11</sub> -O <sub>11v</sub>	2.21

Figure 1 is a projection of the atoms in  $Zn_2Mo_3O_8$  on the 001 plane. The unit cell contains two "molecules" of  $Zn_2Mo_3O_8$ . Noteworthy is the equilateral triangle of molybdenum atoms, each molybdenum atom having two neighbors at 2.53 Å. An abnormally close approach of 2.48 Å. by molybde-

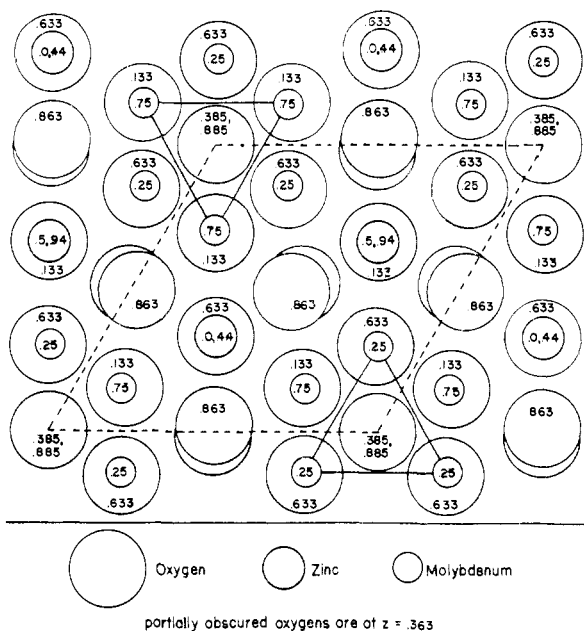


Fig. 1.—Structure of  $Zn_2Mo_3O_8$ , projection on 001 plane.

num atoms in molybdenum(IV) oxide has been observed by Magneli.<sup>13</sup> He attributes this to the formation of an electron pair bond between these atoms.

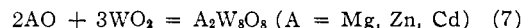
The observed electrical and magnetic properties of  $Zn_2Mo_3O_8$  and its isomorphs can be explained on the basis of the above structure. The data are given in Table II. Five of the seven compounds were found to be non-conductors of electricity. The conductivity of the iron and manganese compounds may be due to impurities since measurements on different preparations of the same compound gave different results. In an isolated molybdenum(IV) ion there are two 4d-orbital electrons which could act as conductors of electricity. If these electrons were localized by the formation of covalent bonds with two other molybdenum(IV) ions, the compounds would not be expected to exhibit conducting properties.

The magnetic data are also in line with this. If such a 3-membered ring of bonded molybdenum(IV) ions exists, then no contribution to the para-

(13) A. Magneli and G. Anderson, *Acta Chem. Scand.*, **9**, 1378 (1955).

magnetic moments by the d-orbital electrons of molybdenum(IV) would be expected. Indeed the magnesium, zinc and cadmium compounds are only very weakly paramagnetic. The observed moments of the iron, cobalt and nickel compounds correspond to those expected if only these ions contribute to the moment and if the d-orbitals of these ions are not used in bonding to the oxide ions. The observed moment of the manganese compound is lower than would be expected and more nearly corresponds to that calculated for Mn(III) instead of Mn(II). An explanation for the anomalous behavior of the manganese compound cannot be given at present. The moments were calculated assuming that the Curie law was obeyed. The weak paramagnetism of the magnesium, zinc and cadmium compounds may be due to deviations from this law. Measurements over a range of temperature will be necessary to answer this question.

Attempts were made using reactions indicated in eq. 7 and 8, to prepare similar compounds of tetra-valent tungsten and rhenium. Both of these ions have the necessary electrons for the formation of the three-membered ring of metal ions found in  $Zn_2Mo_3O_8$ .



The preparative methods were similar to those used for the corresponding molybdenum compound. Preparations made according to reaction 7 were carried out at temperatures ranging from 800–1150°. Rhenium preparations were made at 500–700°. Reactions above 700° were not attempted because of the tendency of  $ReO_2$  to disproportionate into the metal and  $Re_2O_7$  when heated *in vacuo* above this temperature. In no case were any compounds found which appeared to be similar to  $Zn_2Mo_3O_8$ . X-Ray photographs of the products in the case of tungsten showed the presence of the corresponding tungstate(VI) and tungsten metal. Similar results were found by Scholder and Brixner<sup>4,5</sup> in their attempts to prepare  $AWO_3$  type compounds ( $A = Mg, Ca, Sr, Ba$ ). The X-ray powder diffraction pattern of the rhenium preparations showed the presence of the A cation binary oxide and another unidentifiable phase or phases.

Although six of the seven A cations which form the  $A_2Mo_3O_8$  compounds described here have crystal radii shorter than 0.85 Å., the seventh, cadmium, has a crystal radius which is close to that of calcium (0.97 Å. *vs.* 0.99 Å.).<sup>11</sup> Calcium, however, forms  $CaMoO_3$ , which has a distorted perovskite structure<sup>6</sup> and a powder X-ray diffraction pattern which can be indexed on the basis of an orthorhombic cell with  $a = 5.45 \pm 0.01$  Å.,  $b = 5.58 \pm 0.01$  Å., and  $c = 7.80 \pm 0.01$  Å.

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