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Preparation of the Oxotetrabromo- and Oxotetraiodomolybdenum(V) Ions from Dimolybdenum Tetraacetate. Structures by X-ray Crystallography

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The $[MoOBr_4(H_2O)]^-$ ion has long been known, but its structure has been determined only roughly. We have found that a number of compounds containing this ion are formed when $Mo_2(O_2CCH_3)_4$ reacts in the presence of oxygen with aqueous HBr. These preparative reactions are reported in detail and the crystal structures of two compounds, one of which contains two crystallographically independent $[MoOBr_4(H_2O)]^-$ ions, reported. The structurally characterized compounds and their crystallographic properties are as follows. **1**, $(C_5H_5NH)_5[MoOBr_4(H_2O)]_3Br_2$: space group *Pmma*; a = 21.875 (3), b = 8.487 (1), c = 13.724 (2) Å; V = 2547.9 (1) Å^3; the unit cell contains six $[MoOBr_4(H_2O)]^-$ ions, four with *m* symmetry and two with *mm* symmetry. **2**, $(Et_4N)[MoOBr_4(H_2O)]$: space group *Pnma*; a = 11.202 (2), b = 12.957 (3), c = 11.523 (2) Å; V = 1672.5 (1) Å^3; Z = 4. The compound $(Et_4N)[MoOI_4(H_2O)]$ (**3**), the first reported compound containing the oxoiodo ion, is prepared in a similar way. It is isomorphous with **2** with a = 11.592 (3) Å, b = 13.623 (3) Å, c = 11.898 (3) Å, and V = 1879 (1) Å^3. The Mo=O distances in **1** are 1.61 (2) and 1.62 (2) Å, while those in **2** and **3** are 1.65 (1) and 1.65 (1) Å.

Introduction

Oxomolybdenum(V) complexes are the dominant type for that oxidation state and an enormous number of both mono- and binuclear ones are known.[1] Among the mononuclear ones the $[MoOCl_4]^-$, $[MoOCl_5]^{2-}$, and $[MoOCl_4(H_2O)]^-$ ions have been extensively studied chemically and structurally. The bromo analogues to these have long been known but have not been studied nearly so thoroughly. In fact, there has not previously been an accurate structural study reported for a bromo ion. The one reported X-ray crystallographic investigation,[2] of $(Ph_4As)[MoOBr_4(H_2O)]$, gave an Mo=O distance of 1.78 (7) Å, clearly inaccurate and likely to be much too high. So far as we can determine, no type of oxoiodomolybdenum(V) compound has ever appeared in the literature.

Our previous studies[3] of the reaction of $Mo_2(O_2CCH_3)_4$ with aqueous HCl lead to the isolation of a compound containing, inter alia, the $[MoOCl_4(H_2O)]^-$ ion. We have now found that the reaction of $Mo_2(O_2CCH_3)_4$ with aqueous HBr and HI (the latter contaminated with considerable I_2) affords crystalline products containing the $[MoOBr_4(H_2O)]^-$ and $[MoOI_4(H_2O)]^-$ ions. We report here the preparations and the crystal structure determinations of three of these compounds.

Experimental Section

Preparations. $(C_5NH_6)_5[MoOBr_4(H_2O)]_3Br_2$ (1). $Mo_2(O_2CCH_3)_4$ (0.1 g), prepared by a literature method,[4] was dissolved in 25 mL of 8 M HBr. The solution was stirred and heated to ca. 80 °C. Pyridine hydrochloride, $(C_5NH_6)Cl$ (0.1 g), was added and the solution was left to stand in an open beaker. After 8 days the yellow crystals that had formed were collected; yield 85 mg. These crystals appear to be stable in the normal laboratory atmosphere indefinitely.

$(C_2H_5)_4N[MoOBr_4(H_2O)]$ (2). This compound was prepared in a way analogous to **1**. $(C_2H_5)_4NCl$ (0.1 g) was added and the yield was 70 mg.

$(C_2H_5)_4N[MoOI_4(H_2O)]$ (3). This compound was prepared in a way analogous to that used for **2**. $Mo_2(O_2CCH_3)_4$ was dissolved in aqueous HI (45%), taken directly from the shelf and doubtless contaminated with iodine.

X-ray Crystallography. Collection of Data. Data were collected for all compounds on a Syntex $P\bar{1}$ automated four-circle diffractometer using Mo (λ 0.71073 Å) radiation with a graphite crystal monochromator in the incident beam. Rotation photographs and ω scans

Table I. Crystallographic Data

formula	1	2	3
space group	*Pmma*	*Pnma*	*Pnma*
a, Å	21.875 (3)	11.202 (2)	11.592 (3)
b, Å	8.487 (1)	12.957 (3)	13.623 (3)
c, Å	13.724 (2)	11.523 (2)	11.898 (3)
V, Å^3	2548 (1)	1672 (1)	1879 (1)
d, g/cm^3	2.567	2.303	2.714
Z	6	4	4
cryst size, mm	0.1 × 0.15 × 0.2	0.1 × 0.1 × 0.2	0.08 × 0.08 × 0.1
μ, cm^{-1}	123.9	108.9	73.2
range of 2θ, deg	1 → 45	1 → 45	1 → 50
no. of unique data	1273	906	749
data with $F_o^2 > 3\sigma(F_o^2)$	854	683	693
R_1	0.052	0.065	0.037
R_2	0.063	0.078	0.049
goodness of fit	1.27	1.48	1.01

of several strong reflections indicated in each case that the crystals were of satisfactory quality. The unit cell dimensions were obtained by a least-squares fit of 15 strong reflections in the range $25° < 2\theta < 45°$. Data were collected at 22 ± 3° by using the θ–2θ scan technique with a variable scan rate from 4.0 to 24.0°/min. General procedures for data collection have been reported elsewhere.[5] Crystallographic data and other pertinent information are given in Table I. For each crystal, Lorentz and polarization corrections were applied. Intensity data for **1**, **2**, and **3** were corrected for absorption by the empirical ψ-scan method. This was deemed necessary because of the shape and the size of the crystals.

Solution and Refinement of the Structures.[6] The heavy-atom positions in **1** and **2** were obtained by direct methods by using the MULTAN program. The structure of **1** was refined in space group *Pmma* to convergence by using anisotropic thermal parameters for all molybdenum and bromine atoms and isotropic ones for all nonhydrogen atoms. The structure of **2** was refined in space group *Pnma* to convergence by using anisotropic thermal parameters for all molybdenum, bromine, and oxygen atoms and isotropic ones for the rest of the nonhydrogen atoms. The positions of all the atoms of **3** were taken from **2**. Anisotropic thermal parameters were used for all molybdenum, bromine, iodine, oxygen, and nitrogen atoms and isotropic ones for all carbon atoms. The discrepancy indices

$$R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|]^{1/2}$$

are listed in Table I. The final difference maps showed no peaks of structural significance. Lists of all observed and calculated structure factors are available as supplementary material.

Results

Tables II–IV give the atomic positional and thermal parameters for the three compounds.

Compound 1. The unit cell contains two formula units and there are two crystallographically distinct $[MoOBr_4(H_2O)]^-$ ions. One of them, containing Mo(1), lies at the intersection of two mirror planes, with the Br atoms in the planes and Mo(1) on a twofold axis. The imposed symmetry is C_{2v}. The other type, containing Mo(2), has only one crystallographic mirror plane, with two of the Br atoms lying in it. The four uncoordinated Br^- ions lie in mirror planes and the pyridinium ions are of three types, all of which have a mirror plane

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $(C_5NH_6)_5[MoOBr_4(H_2O)]_3Br_2$, **1**[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.2500 (0)	0.0000 (0)	0.2769 (3)	4.6 (2)	2.6 (2)	2.9 (2)	0	0	0
Mo(2)	0.5711 (1)	0.0000 (0)	0.2108 (2)	3.8 (1)	3.0 (1)	3.5 (1)	0	−0.1 (1)	0
Br(1)	0.2500 (0)	0.2932 (4)	0.3071 (2)	5.6 (2)	2.8 (1)	6.6 (2)	0	0	1.0 (2)
Br(2)	0.5868 (1)	0.2940 (3)	0.2228 (2)	7.5 (1)	2.45 (9)	5.7 (1)	1.0 (1)	0.8 (1)	0.4 (1)
Br(3)	0.3646 (2)	0.0000 (0)	0.2969 (4)	3.7 (2)	3.9 (2)	14.2 (3)	0	−1.0 (2)	0
Br(4)	0.6309 (2)	0.0000 (0)	0.0502 (3)	11.2 (3)	4.4 (2)	5.1 (2)	0	3.4 (2)	0
Br(5)	0.5411 (2)	0.0000 (0)	0.3864 (2)	8.0 (2)	4.0 (2)	4.6 (1)	0	2.3 (2)	0
Br(6)	0.7500 (0)	0.2714 (4)	0.3809 (2)	5.0 (1)	2.9 (1)	4.2 (1)	0	0	−0.3 (1)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O(1)	0.2500 (0)	0.0000 (0)	0.444 (2)	4.6 (7)	C(1)	0.615 (1)	0.364 (3)	0.514 (2)	5.9 (6)
O(2)	0.2500 (0)	0.0000 (0)	0.159 (3)	7.8 (9)	C(2)	0.563 (1)	0.363 (3)	0.575 (2)	6.0 (6)
O(3)	0.6691 (9)	0.0000 (0)	0.274 (1)	4.8 (5)	C(3)	0.537 (1)	0.500 (0)	0.607 (2)	4.3 (7)
O(4)	0.5038 (11)	0.0000 (0)	0.161 (2)	7.2 (6)	C(4)	0.750 (0)	0.376 (5)	0.124 (3)	7.2 (10)
N(1)	0.636 (1)	0.5000 (0)	0.486 (2)	7.4 (8)	C(5)	0.750 (0)	0.362 (5)	0.016 (3)	7.0 (9)
N(2)	0.750 (0)	0.5000 (0)	0.165 (3)	7.1 (11)	C(6)	0.750 (0)	0.500 (0)	−0.030 (3)	4.3 (10)
N(3)	0.385 (2)	0.5000 (0)	0.190 (3)	12.5 (13)	C(7)	0.392 (1)	0.362 (4)	0.149 (2)	9.2 (8)
					C(8)	0.415 (1)	0.374 (4)	0.054 (2)	9.0 (8)
					C(9)	0.428 (2)	0.500 (0)	0.007 (3)	10.4 (13)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for $(Et_4N)[MoOBr_4(H_2O)]$, **2**[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0.2313 (2)	0.2500 (0)	0.0939 (2)	1.14 (7)	3.3 (1)	2.37 (9)	0	−0.1 (1)	0
Br(1)	0.3611 (2)	0.3870 (2)	0.0027 (2)	3.23 (8)	3.9 (1)	4.7 (1)	−0.50 (9)	1.29 (9)	0.7 (1)
Br(2)	0.1436 (2)	0.1141 (2)	0.2272 (2)	3.05 (8)	3.34 (9)	4.42 (9)	−0.10 (9)	1.12 (8)	0.48 (9)
O(1)	0.125 (2)	0.2500 (0)	−0.006 (2)	2.1 (8)	6 (1)	3.2 (9)	0	−0.9 (7)	0
O(2)	0.385 (1)	0.2500 (0)	0.231 (2)	1.5 (7)	5 (1)	2.4 (8)	0	−0.3 (7)	0

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
N(1)	0.757 (2)	0.7500 (0)	0.384 (2)	2.8 (5)	C(4)	0.640 (3)	0.683 (3)	0.372 (3)	3.6 (9)
C(1)	0.638 (2)	0.616 (2)	0.498 (2)	5.3 (6)	C(5)	0.865 (3)	0.816 (3)	0.394 (3)	3.2 (8)
C(2)	0.877 (2)	0.885 (2)	0.270 (2)	5.0 (5)	C(6)	0.757 (3)	0.821 (3)	0.273 (3)	2.9 (8)
C(3)	0.760 (3)	0.687 (3)	0.493 (3)	2.5 (7)					

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for $(Et_4N)[MoOI_4(H_2O)]$, **3**[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I(1)	0.6351 (1)	0.60744 (10)	0.0016 (1)	3.92 (5)	3.72 (5)	4.00 (5)	−0.53 (6)	0.99 (5)	0.78 (6)
I(2)	0.8672 (1)	0.60876 (9)	−0.2318 (1)	3.97 (5)	2.84 (4)	4.09 (5)	−0.02 (6)	1.15 (5)	−0.50 (5)
Mo	0.7731 (2)	0.7500 (0)	−0.0920 (2)	2.01 (8)	2.68 (9)	2.23 (8)	0	0.04 (8)	0
O(1)	0.875 (1)	0.7500 (0)	0.005 (1)	2.3 (6)	4.5 (9)	2.8 (7)	0	−0.4 (7)	0
O(2)	0.623 (1)	0.7500 (0)	−0.230 (1)	2.8 (7)	4.9 (9)	2.3 (7)	0	−1.7 (7)	0
N	0.747 (1)	0.7500 (0)	0.381 (1)	2.3 (8)	3.6 (9)	1.1 (7)	0	0.4 (6)	0

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(1)	0.631 (2)	0.621 (2)	0.489 (2)	5.9 (5)	C(4)	0.642 (3)	0.694 (2)	0.376 (3)	2.8 (6)
C(2)	0.863 (2)	0.880 (2)	0.275 (2)	4.8 (4)	C(5)	0.857 (3)	0.813 (3)	0.389 (3)	3.0 (7)
C(3)	0.754 (3)	0.687 (3)	0.492 (3)	4.0 (8)	C(6)	0.744 (3)	0.810 (3)	0.273 (3)	3.5 (8)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table V. Bond Distances and Bond Angles for $(C_5NH_6)_5(MoOBr_4(H_2O)]_3Br_2$, 1

	Bond Distances, Å		
Mo(1)-Br(1)	2.523 (3)	Mo(2)-Br(2)	2.524 (2)
Br(3)	2.522 (3)	Br(4)	2.563 (4)
		Br(5)	2.498 (4)
O(1)	2.29 (2)	O(3)	2.31 (1)
O(2)	1.61 (2)	O(4)	1.62 (2)
N(1)-C(1)	1.30 (2)	N(3)-C(7)	1.31 (3)
C(1)-C(2)	1.42 (4)	C(7)-C(8)	1.39 (3)
C(2)-C(3)	1.36 (2)	C(8)-C(9)	1.28 (3)
N(2)-C(4)	1.20 (4)		
C(4)-C(5)	1.48 (5)		
C(5)-C(6)	1.33 (3)		
	Bond Angles, Deg		
Br(1)-Mo(1)-Br(1)′	161.0 (2)	Br(2)′-Mo(2)-Br(2)	162.7 (2)
Br(3)	88.97 (3)	Br(4)	89.24 (8)
O(1)	80.5 (1)	Br(5)	88.45 (8)
O(2)	99.5 (1)	O(3)	81.35 (8)
Br(3)-Mo(1)-Br(3)′	167.5 (3)	Br(2)′-Mo(2)-O(4)	98.67 (8)
O(1)	83.7 (1)	Br(4)-Mo(2)-Br(5)	164.6 (2)
O(2)	96.3 (1)	O(3)	81.5 (8)
		O(4)	95.7 (8)
		Br(5)-Mo(2)-O(3)	83.1 (8)
		O(4)	99.7 (8)
		O(3)-Mo(2)-O(4)	177 (1)
C(1)-N(1)-C(1)′	125 (3)	C(4)-N(2)-C(4)′	124 (3)
N(1)-C(1)-C(2)	118 (2)	N(2)-C(4)-C(5)	122 (3)
C(1)-C(2)-C(3)	121 (1)	C(4)-C(5)-C(6)	114 (3)
C(2)-C(3)-C(2)′	117 (2)	C(5)-C(6)-C(5)′	124 (4)
C(7)-N(3)-C(7)′	126 (3)		
N(3)-C(7)-C(8)	113 (3)		
C(7)-C(8)-C(9)	127 (4)		
C(8)-C(9)-C(8)′	113 (5)		

Table VI. Bond Distances and Bond Angles for $(C_2H_5)_4N[MoOBr_4(H_2O)]$, **2**

	Bond Distances, Å		
Mo-Br(1)	2.524 (2)		
Br(2)	2.535 (2)		
O(1)	1.65 (1)		
O(2)	2.34 (1)		
N(1)-C(3)	1.49 (3)	C(1)-C(3)	1.65 (3)
C(4)	1.58 (4)	C(4)	1.69 (4)
C(5)	1.49 (3)	C(2)-C(5)	1.68 (4)
C(6)	1.57 (3)	C(6)	1.58 (4)
	Bond Angles, Deg		
Br(1)-Mo-Br(1)′	89.4 (1)	C(3)-N(1)-C(4)	113 (2)
Br(2)′	164.6 (1)	C(5)	103 (2)
Br(2)	89.25 (6)	C(6)	111 (2)
O(1)	97.2 (4)	C(4)-N(1)-C(5)	111 (2)
O(2)	81.7 (3)	C(6)	105 (2)
Br(2)-Mo-Br(2)′	88.0 (1)	C(5)-N(1)-C(6)	113 (2)
O(1)	98.2 (4)	N(1)-C(3)-C(1)	108 (2)
O(2)	83.0 (3)	C(4)-C(1)	103 (2)
O(1)-Mo-O(2)	178.4 (6)	C(5)-C(2)	108 (2)
		C(6)-C(2)	109 (2)

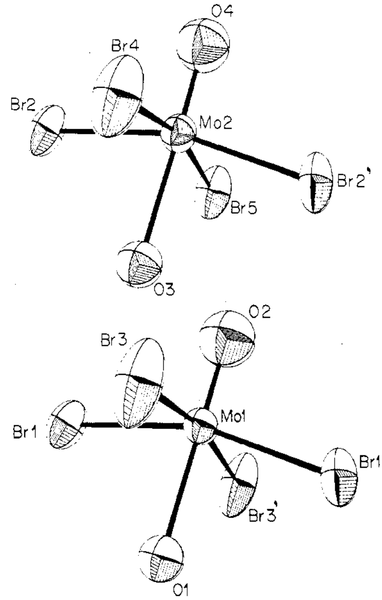

Figure 1. Two crystallographically independent $[MoOBr_4(H_2O)]^-$ ions found in compound **1**. Each atom is represented by its thermal vibration ellipsoid scaled to enclose 50% of its electron density and the atomic numbering used in the tables is defined.

Table VII. Bond Distances and Bond Angles for $(C_2H_5)_4N[MoOI_4(H_2O)]$, **3**

	Bond Distances, Å		
Mo-I(1)	2.752 (2)		
I(2)	2.768 (2)		
O(1)	1.65 (1)		
O(2)	2.40 (1)		
N-C(3)	1.57 (4)	C(1)-C(3)	1.70 (4)
C(4)	1.43 (3)	C(4)	1.67 (4)
C(5)	1.55 (4)	C(2)-C(5)	1.63 (4)
C(6)	1.53 (4)	C(6)	1.67 (4)
	Bond Angles, Deg		
I(1)-Mo-I(1)′	89.78 (9)	C(3)-N-C(4)	112 (2)
I(2)	88.95 (4)	C(5)	102 (2)
I(2)′	164.4 (1)	C(6)	114 (2)
O(1)	97.5 (4)	C(4)-N-C(5)	114 (2)
O(2)	81.6 (3)	C(6)	104 (2)
I(2)-Mo-I(2)′	88.09 (8)	C(5)-N-C(6)	111 (2)
O(1)	98.1 (4)	N-C(3)-C(1)	103 (2)
O(2)	82.8 (3)	C(4)-C(1)	111 (2)
O(1)-Mo-O(2)	178.7 (7)	C(5)-C(2)	107 (2)
		C(6)-C(2)	106 (2)

perpendicular to the ring. Table V lists all the bond distances and angles in this structure. Figure 1 depicts the two independent $[MoOBr_4(H_2O)]^-$ ions and defines the atomic numbering scheme.

Compounds 2 and 3. These two compounds form isomorphous crystals. The four $[MoOX_4(H_2O)]^-$ ions in each cell are equivalent and have mirror symmetry, with the mirror plane bisecting a pair of opposite Br–Mo–Br angles. The bond lengths and angles are listed in Tables VI and VII for the

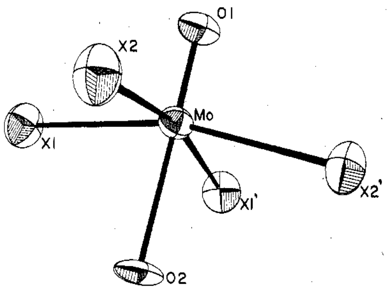

Figure 2. The $[MoOX_4(H_2O)]^-$ ions occurring in **2** (X = Br) and **3** (X = I), showing the numbering scheme. The thermal vibration ellipsoids used are those for **2** and are scaled to enclose 50% of the electron density.

Table VIII. Average Values of Distances and Angles in $[MoOX_4(H_2O)]^-$ Ions

	X		
	Cl[a]	Br	I
Mo=O, Å	1.66 ± 0.01	1.62 ± 0.02	1.65 (1)
Mo–X, Å	2.364 ± 0.005	2.53 ± 0.01	2.76 (1)
Mo–OH$_2$, Å	2.36 ± 0.03	2.32 ± 0.02	2.40 (1)
O=Mo–X, deg	98.2 ± 0.8	97.9 ± 1.1	97.8 ± 0.3
X–Mo–X, deg	89.0 ± 0.3	89.4 ± 0.4	88.9 ± 0.4

[a] See ref 3 for sources.

bromo and iodo compounds, respectively. Figure 2 shows the $[MoOX_4(H_2O)]^-$ ions.

Comparison of Structures. We now have two accurate structure determinations for the $[MoOCl_4(H_2O)]^-$ ion, three for the $[MoOBr_4(H_2O)]^-$ ion (counting the occurrence of two independent ions in compound **1**), and one for the $[MoOI_4(H_2O)]^-$ ion and it is interesting to compare the structures of the three homologous ions. In Table VIII we list the values of the important distances and angles. In each case we have averaged over all available values counting each distance or angle as many times as it actually occurs even when a given pair were required to be equal by symmetry. For the Mo=O distances in the chloro and bromo compounds the averages were calculated by weighting each individual measurement by the inverse of its own esd; in all other cases each value was given the same weight. The mean deviations from the averages are indicated by the ± interval, while figures in parentheses for the iodo compound are esd's for the single determination of that parameter.

There is a remarkable degree of regularity in the three structures. The Mo=O distance is invariant within experimental error. A value of 1.64 ± 0.02 Å can be taken as characteristic for all three compounds. Similarly, the weakly bonded water molecules are at essentially the same distance, 2.36 ± 0.04 Å in each case. What is perhaps more remarkable is the essential constancy of the O=Mo—X and X—Mo—X angles from one case to another, despite the changing size of the X atoms. There appears to be a natural explanation for this, however. The increasing van der Waals radii are accompanied by increasing Mo–X distances so that nonbonded repulsions tend to retain about the same influence on bond angles. The increasing Mo–X distances run nearly parallel to the increases in the accepted single bond radii of the halogen atoms, though not entirely. Thus, while the atomic bond radii increase by 0.15 and 0.19 Å from Cl to Br and Br to I, respectively, the bond lengths in the anions increase by 0.17 and 0.23 Å for the corresponding steps. This may be due to an overall increase in nonbonded repulsions or it may reflect a decreasing contribution from π bonding as the halogen orbitals grow too large to overlap well with the metal atom d orbitals.

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Registry No. **1**, 71096-99-6; **2**, 52729-41-6; **3**, 71097-01-3; $Mo_2(O_2CCH_3)_4$, 14221-06-8.

Supplementary Material Available: Tables of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

References and Notes

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Tetrakis(dimethylphosphoniumdimethylido)dichromium and -dimolybdenum. 1. Crystal and Molecular Structures

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The title compounds, $[(CH_3)_2P(CH_2)_2]_4Cr_2$ (**1**) and $[(CH_3)_2P(CH_2)_2]_4Mo_2$ (**2**), have been investigated crystallographically, shown to be isomorphous, and shown to have extremely short bonds between the metal atoms. Compound **1** crystallized in space group *Pccn* with $a = 13.036$ (5) Å, $b = 13.037$ (5) Å, $c = 13.096$ (5) Å, and $Z = 4$. The structure consists of discrete molecules residing on crystallographic inversion centers but having effectively C_{4h} symmetry. The Cr–Cr distance is 1.895 (3) Å. Average values of some other molecular dimensions are as follows: Cr–C, 2.22 (1) Å; P–C, 1.80 (3) Å; ∠Cr–Cr–C, 103.3 (4)°; ∠C–Cr–C, 87.0 (6)°. Compound **2** also crystallizes in space group *Pccn* with $a = 13.122$ (3) Å, $b = 13.238$ (2) Å, $c = 13.244$ (2) Å, and $Z = 4$. The Mo–Mo distance is 2.082 (2) Å, and the average values of the other molecular dimensions are as follows: Mo–C, 2.31 (2) Å; P–C, 1.78 (2) Å; ∠Mo–Mo–C, 101.5 (8)°; ∠C–Mo–C, 88 (1)°.

Introduction

Several years ago Kurras et al. reported the preparations of the compounds $[(CH_3)_2P(CH_2)_2]_4Cr_2$[1] (**1**) and $[(CH_3)_2P(CH_2)_2]_4Mo_2$[2] (**2**). In connection with our recent discoveries of many compounds[3] containing "supershort" Cr–Cr quadruple bonds (i.e., those shorter than ca. 1.90 Å), we found it of interest to determine the bond length in **1**. As noted in a preliminary report,[4] this bond length is in the supershort range.

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