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Registry No. $[Cr_2(O_2CH)_4(H_2O)_2]_3(H_2O)_{10}$, 65366-48-5.

Supplementary Material Available: Tables of structure factors and a table of atom parameters for the false minimum (11 pages). Ordering information is given on any current masthead page.

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(7) We are especially grateful to Dr. Jan Troup for helpful discussions on this matter.
(8) Supplementary material.

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Reactions and Reaction Products of Bromine and Iodine with Tetrakis(ethyl xanthato)dimolybdenum(*4° Mo-Mo*)

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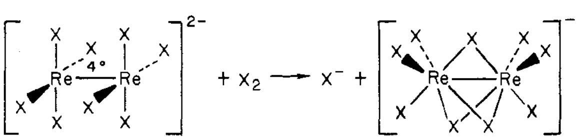
The reactions of Br_2 and I_2 with $Mo_2(S_2COC_2H_5)_4$ produce crystalline solids with the composition $Mo_2(S_2COC_2H_5)_4X_2$, both of which have been fully characterized by x-ray crystallography. They are isomorphous, crystallizing in space group $P2_1/c$ with the following unit cell dimensions, where the two figures refer first to the bromide and second to the iodide: a = 12.355 (3), 12.538 (2) Å; b = 8.885 (2), 8.897 (1) Å; c = 12.835 (3), 13.279 (3) Å; β = 115.18 (1), 115.71 (1)°; V = 1275.1 (8), 1334.6 (4) Å^3; Z = 2. The structures were solved and refined to residuals (R_1, R_2) of 0.038, 0.050 for the bromide and 0.025, 0.038 for the iodide. Each half of the centrosymmetric dinuclear molecule consists of a nearly planar $Mo(S_2COEt)_2$ unit with a halogen atom bonded perpendicular to the mean MoS_4 plane. These halves are then joined with each molybdenum atom lying over one of the S_2C groups of the other half so that it is bonded to both S atoms (mean Mo-S, 2.44 Å) and the C atom (2.302 Å). The S_2C group plane is approximately prependicular to the extension of the X-Mo line so that the coordination of Mo can be described as roughly octahedral, provided the "side-on" S_2C group is considered to occupy one coordination site. In addition, there is a metal-metal bond (Mo-Mo, 2.720 (3) Å) which can be thought of as a single bond that completes an 18-electron configuration about each Mo atom. The Mo-Br and Mo-I bonds are unusually long (2.627 (2) and 2.852 (1) Å, respectively). The bridging S_2COR groups, forming a total of five bonds, are unprecedented for either xanthato or dithiocarbamato ligands. The reactivity of the $Mo_2(S_2COC_2H_5)_4X_2$ compounds with a variety of reagents has been examined.

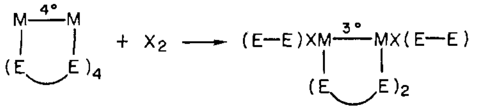
Introduction

The first attempts to oxidize species containing metal-to-metal quadruple (4°M-M) bonds with halogens, namely, by the action of X_2 (X = Cl, Br) on the $Re_2X_8^{2-}$ ions, were reported some 10 years ago.[1] These reactions resulted in extensive structural rearrangement accompanied by considerable reduction in the M-M bond strength as indicated in eq 1. The $Re_2Cl_9^-$ anion has been shown[2] to have an Re-Re distance of 2.70 Å, indicative of only a weak bond between the rhenium atoms. The reaction can be thought of formally as a combination of an oxidative addition and a rearrangement that includes expulsion of one X^- ligand.



(1)

We have recently taken a renewed interest in oxidative addition reactions as possible ways of preparing triple M-M bonds from quadruple M-M bonds. This is particularly pertinent in view of the discovery that certain compounds, e.g., $W_2(O_2CNR_2)_2(\mu\text{-}O_2CNR_2)_2X_2$, with triple W-W bonds have five-coordinated metal atoms. This suggests the possibility that reactions of the type (2) might provide a method, conceivably a fairly general one, for conversion of quadruple M-M to triple M-M. We are presently testing this idea with a variety of compounds.



(2)

In the case where the bidentate, uninegative ligand, EE, is ethyl xanthate, $EtOCS_2^-$, and M = Mo, the reaction does not follow the simple course shown in eq 2 in the structural sense although the stoichiometry is as shown. We describe in detail here the chemical and x-ray crystallographic investigation of the reactions in which X_2 represents Br_2 and I_2. The starting material, $Mo_2(S_2COC_2H_5)_4$, is already a well-characterized compound.[3]

Experimental Section

Materials and Methods. $Mo_2(O_2CCH_3)_4$ was prepared according to an established procedure.[4] $KS_2COC_2H_5$ and $KS_2COCH(CH_3)_2$ were prepared by adding CS_2 to an alcoholic solution of KOH. All other compounds and solvents were of reagent grade or better, from commercial sources.

Carbon and hydrogen analyses were performed at the Center for Trace Characterization, Texas A&M University.

All reactions involving molybdenum compounds were performed under nitrogen using air-tight glassware. All solvents were dried over molecular sieves and deoxygenated prior to use.

Preparation of $Mo_2(xan)_4$. The reported procedure[3] calls for the addition of a large excess of potassium ethyl xanthate to dimolybdenum tetraacetate in ethanol. Using this method, a considerable amount of a green impurity was always present. However, if only an equivalent amount of the xanthate is used, the reaction produces no noticeable amount of this impurity. In a typical reaction, $Mo_2(O_2CCH_3)_4$ (3.30 g, 7.5 mmol) was added to 350 mL of absolute ethanol. To this was added $KS_2COC_2H_5$ (4.8 g, 30 mmol). The mixture was stirred for 6–12 h at room temperature. The product was then filtered, washed

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Table I. Crystallographic Data for $Mo_2(S_2COC_2H_5)_4I_2$ and $Mo_2(S_2COC_2H_5)_4Br_2$

Parameter	$Mo_2(S_2COC_2H_5)_4I_2$	$Mo_2(S_2COC_2H_5)_4Br_2$
Space group	$P2_1/c$	$P2_1/c$
a, Å	12.538 (2)	12.355 (3)
b, Å	8.897 (1)	8.885 (2)
c, Å	13.279 (3)	12.835 (3)
β, deg	115.71 (1)	115.18 (1)
V, Å^3	1334.6 (4)	1275.1 (8)
Z	2	2
Crystal size, mm	0.15 × 0.15 × 0.21	0,10 × 0.12 × 0.15
μ, cm^{-1}	38.7	49.3
2θ range (Mo Kα), deg	0–45	0–45
No. of unique data	1761	1679
No. of unique $\lvert F_o\rvert^2 > 3\sigma(\lvert F_o\rvert^2)$	1461	1162
No. of variables	127	127
R_1	0.025	0.038
R_2	0.038	0.050
Esd of an obsn of unit weight	0.924	1.031

with three 20-mL portions of ethanol, and vacuum dried (10^{-3} Torr) for 4 h at room temperature. The isopropyl derivative, $Mo_2(S_2COCH(CH_3)_2)_4$ was prepared in a similar manner using $KS_2COCH(CH_3)_2$. Its appearance and properties are much the same as those of the ethyl xanthate.

Preparation of $Mo_2(xan)_4X_2$. The reaction of iodine or bromine with $Mo_2(xan)_4$ can be carried out in $CHCl_3$, CH_2Cl_2, $ClCH_2CH_2Cl$, or C_4H_8O(THF). Addition of a stoichiometric amount of the halogen results in an immediate color change and in most cases a completely homogeneous reaction mixture. In a typical reaction $Mo_2(S_2COC_2H_5)_4$ (0.85 g, 1.75 mmol) was added to 40 mL of CH_2Cl_2. To this suspension was added I_2 (0.32 g, 1.75 mmol). The resulting solution was stirred for 3–4 h at room temperature. The solution was then filtered using a medium frit. To the filtrate was added 40 mL of hexane all at once and with rapid stirring. In a few seconds a crystalline precipitate appeared which was stirred for an additional hour. The product was then filtered, washed with two 20-mL portions of hexane, and vacuum dried (10^{-3} Torr) for 3 h at room temperature. Yield 0.78 g (67% based on Mo). Anal. Calcd for $Mo_2(S_2COC_2H_5)_4I_2$: C, 15.48; H, 2.15. Found: C, 15.11; H, 2.00.

The preparation of the bromide followed the same general procedure with the exception that the bromine was dissolved in a small amount of solvent prior to its addition to the xanthate. Anal. Calcd for $Mo_2(S_2COC_2H_5)_4Br_2$: C, 17.22; H, 2.39. Found: C, 16.97; H, 2.31.

To ensure that the reaction was general for this class of compound, $Mo_2(S_2COCH(CH_3)_2)_4$ was also reacted with iodine in a similar manner and gave a product similar in appearance. Anal. Calcd for $Mo_2(S_2COCH(CH_3)_2)_4I_2$: C, 19.47; H, 2.83. Found: C, 19.39; H, 2.64.

Products from THF are apparently solvated and elemental analyses were not consistent. Crystals of $Mo_2(S_2COC_2H_5)_4I_2$ and $Mo_2(S_2COC_2H_5)_4Br_2$ suitable for x-ray analysis were obtained by slow evaporation under nitrogen using chlorinated solvents. Methylene chloride was preferable for the iodide whereas dichloroethane was found to be better for the more soluble bromide.

X-Ray Crystallography. Considerable difficulty was encountered in finding good single crystals of $Mo_2(S_2COC_2H_5)_4I_2$ and $Mo_2(S_2COC_2H_5)_4Br_2$. Several batches of crystals were examined before satisfactory crystals were found. The crystals were mounted, wedged in thin-walled glass capillaries. In both cases, ω scans of intense low-angle reflections had peak widths at half-height of ca. 0.15°. Cell constants and axial photographs indicated that the crystals belonged to the monoclinic system. All constants are given in Table I.

Data were collected at 22 ± 2 °C on a Syntex $P\bar{1}$ autodiffractometer using Mo Kα (λ 0.710730 Å) radiation with a graphite crystal monochromator. The θ–2θ scan technique was used with scans ranging from 1.0° above and 1.0° below the calculated Kα_1, Kα_2 doublet, with variable scan speeds from 4.0 to 24.0°/min and with a scan to background time ratio of 0.5. The intensities of three standard reflections were monitored throughout data collection and remained constant.

Since the crystals were small and nearly equidimensional, it was considered that an absorption correction would probably be unnecessary. This was verified by ψ scans of several reflections of $Mo_2(S_2COC_2H_5)_4I_2$ which showed only slight (ca. 4%) variations in intensity as a function of ϕ, suggesting that the maximum errors in the structure factors due to absorption were ca. 2%. Additional information concerning data collection is given in Table I.

Following data collection the intensities were reduced[5] to a set of relative $\lvert F_o\rvert^2$. Those data having $\lvert F_o\rvert^2 > 3\sigma(\lvert F_o\rvert^2)$ were used in structure solution and refinement. The structure of $Mo_2(S_2COC_2H_5)_4I_2$ was solved using conventional heavy-atom methods.[5] The atomic positional parameters of $Mo_2(S_2COC_2H_5)_4I_2$ were used as starting values for the refinement of the $Mo_2(S_2COC_2H_5)_4Br_2$ structure. Both structures were refined to convergence in several cycles of full-matrix least-squares refinement utilizing anisotropic thermal parameters. The final residuals are given in Table I and are defined as follows:

$$R_1 = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$$

$$R_2 = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$$

A value of 0.07 was used for p in the calculation of the weights, w. Final difference Fourier maps showed no peaks of structural significance.

Results

Structural. The atomic positional and thermal parameters are listed in Tables II and III and the bond distances and angles for both compounds are given in Table IV. Figure 1 is a ORTEP drawing of the dinuclear molecule of the iodine compound, showing the atom numbering scheme used in the tables.

The molecule has a crystallographically imposed center of symmetry midway between the metal atoms. Because of the orientations of the OEt groups there are no other symmetry elements, not even approximate ones. However, if the ethyl groups are omitted from consideration, the remaining central portion of the molecule has virtual C_{2h} $(2/m)$ symmetry, with the virtual symmetry plane defined as the mean plane of the atoms C(1), C(4), Mo, and I.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2(S_2COC_2H_5)_4Br_2$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.09250 (6)	0.0108 (1)	0.10645 (6)	0.00396 (5)	0.0060 (1)	0.00348 (5)	−0.0001 (1)	0.00407 (7)	−0.0000 (1)
Br	0.12524 (9)	0.2231 (1)	0.25950 (9)	0.00690 (8)	0.0128 (2)	0.00580 (7)	0.0003 (2)	0.0057 (1)	−0.0066 (2)
S1	0.1192 (2)	−0.0508 (3)	−0.0671 (2)	0.0049 (2)	0.0083 (4)	0.0041 (1)	0.0011 (4)	0.0053 (2)	0.0007 (4)
S2	−0.0116 (2)	−0.2239 (3)	0.0272 (2)	0.0048 (2)	0.0063 (3)	0.0050 (2)	−0.0003 (4)	0.0052 (2)	0.0006 (4)
S3	0.3178 (2)	0.0223 (3)	0.1884 (2)	0.0045 (2)	0.0087 (4)	0.0058 (2)	−0.0014 (4)	0.0054 (2)	0.0014 (5)
S4	0.1852 (2)	−0.1491 (3)	0.2839 (2)	0.0050 (2)	0.0117 (4)	0.0049 (2)	−0.0007 (5)	0.0050 (2)	0.0036 (5)
O1	0.2177 (5)	−0.2953 (7)	0.0618 (5)	0.0048 (4)	0.007 (1)	0.0075 (5)	0.004 (1)	0.0062 (7)	0.003 (1)
O2	0.4236 (6)	−0.1428 (9)	0.3706 (6)	0.0045 (5)	0.015 (1)	0.0065 (5)	0.002 (1)	0.0024 (8)	0.005 (1)
C1	0.1251 (8)	−0.201 (1)	0.0201 (8)	0.0050 (6)	0.010 (2)	0.0048 (6)	−0.001 (2)	0.0057 (9)	−0.001 (2)
C2	0.1971 (10)	−0.446 (1)	0.0935 (11)	0.0093 (9)	0.007 (2)	0.0134 (10)	0.006 (2)	0.0122 (14)	0.008 (2)
C3	0.3082 (11)	−0.534 (2)	0.1276 (13)	0.0121 (10)	0.014 (2)	0.0212 (14)	0.016 (2)	0.0207 (16)	0.020 (3)
C4	0.3190 (8)	−0.097 (1)	0.2910 (8)	0.0040 (7)	0.008 (1)	0.0047 (7)	−0.001 (2)	0.0016 (11)	−0.002 (2)
C5	0.4236 (10)	−0.254 (2)	0.4586 (9)	0.0080 (9)	0.020 (2)	0.0073 (8)	0.008 (3)	0.0059 (13)	0.015 (2)
C6	0.5502 (11)	−0.292 (2)	0.5312 (12)	0.0083 (11)	0.022 (3)	0.0108 (12)	0.003 (3)	0.0002 (19)	0.013 (3)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2(S_2COC_2H_5)_4I_2$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I	0.13046 (4)	0.23156 (5)	0.26814 (3)	0.00676 (3)	0.01283 (6)	0.00495 (3)	0.00068 (7)	0.00443 (4)	−0.00624 (6)
Mo	0.09233 (4)	0.00629 (5)	0.10322 (3)	0.00385 (3)	0.00621 (6)	0.00320 (3)	−0.00023 (7)	0.00350 (4)	−0.00008 (7)
S1	0.1164 (1)	−0.0457 (2)	−0.0671 (1)	0.00485 (8)	0.0078 (2)	0.00385 (7)	0.0005 (2)	0.0051 (1)	0.0007 (2)
S2	−0.0122 (1)	−0.2252 (2)	0.0200 (1)	0.00466 (9)	0.0065 (2)	0.00458 (8)	−0.0004 (2)	0.0046 (1)	0.0004 (2)
S3	0.3153 (1)	0.0168 (2)	0.1861 (1)	0.00447 (9)	0.0097 (2)	0.00547 (9)	−0.0012 (2)	0.0044 (1)	0.0007 (2)
S4	0.1821 (1)	−0.1596 (2)	0.2722 (1)	0.00505 (9)	0.0115 (2)	0.00414 (8)	−0.0001 (3)	0.0036 (1)	0.0041 (2)
O1	0.2147 (3)	−0.2940 (4)	0.0534 (3)	0.0050 (2)	0.0069 (5)	0.0063 (2)	0.0019 (6)	0.0057 (4)	0.0008 (6)
O2	0.4182 (3)	−0.1511 (6)	0.3616 (4)	0.0050 (3)	0.0182 (8)	0.0065 (3)	0.0023 (9)	0.0013 (5)	0.0071 (9)
C1	0.1222 (4)	−0.1999 (6)	0.0138 (4)	0.0047 (4)	0.0069 (7)	0.0042 (3)	0.0008 (9)	0.0042 (5)	−0.0010 (8)
C2	0.1956 (6)	−0.4460 (7)	0.0791 (6)	0.0080 (5)	0.0062 (8)	0.0134 (6)	0.0030 (11)	0.0100 (8)	0.0057 (12)
C3	0.3111 (7)	−0.5277 (8)	0.1179 (8)	0.0099 (6)	0.0111 (10)	0.0180 (9)	0.0097 (13)	0.0120 (11)	0.0128 (15)
C4	0.3159 (5)	−0.1062 (7)	0.2832 (5)	0.0050 (4)	0.0113 (9)	0.0046 (4)	0.0009 (10)	0.0026 (6)	0.0019 (10)
C5	0.4182 (7)	−0.2646 (10)	0.4445 (7)	0.0075 (6)	0.0244 (14)	0.0081 (5)	0.0043 (15)	0.0028 (9)	0.0160 (14)
C6	0.5388 (8)	−0.2814 (10)	0.5287 (8)	0.0099 (8)	0.0227 (15)	0.0105 (8)	0.0023 (19)	−0.0022 (14)	0.0147 (17)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table IV. Bond Distances (A) and Angles (deg) in $Mo_2(S_2COC_2H_5)_4X_2$; X = I, Br[a]

Atoms	X = I	X = Br	Atoms	X = I	X = Br
			Distances		
Mo-Mo	2.717 (1)	2.723 (2)	C1-S1	1.724 (6)	1.72 (1)
-X	2.852 (1)	2.627 (2)	-S2	1.737 (6)	1.74 (1)
-S1	2.452 (2)	2.448 (3)	-O1	1.340 (7)	1.33 (1)
-S1′	2.472 (2)	2.469 (3)	C2-O1	1.440 (8)	1.46 (1)
-S2	2.434 (2)	2.434 (3)	-C3	1.50 (1)	1.47 (2)
-S2′	2.460 (2)	2.463 (3)	C4-S3	1.689 (7)	1.68 (1)
-S3	2.523 (2)	2.525 (3)	-S4	1.688 (7)	1.68 (1)
-S4	2.508 (2)	2.510 (3)	-O2	1.315 (8)	1.33 (1)
-C1	2.302 (6)	2.307 (11)	C5-O2	1.49 (1)	1.50 (1)
			-C6	1.45 (1)	1.48 (2)
			Angles		
Mo′-Mo-X	126.11 (3)	126.70 (6)	S2′-Mo-S3	108.43 (5)	107.94 (9)
-S1	56.87 (4)	56.75 (6)	-S4	162.97 (6)	163.8 (1)
-S2	56.75 (4)	56.74 (7)	-C1	113.5 (2)	113.3 (3)
-S3	137.70 (5)	136.63 (8)	S3-Mo-S4	69.45 (5)	69.40 (9)
-S4	137.22 (5)	137.29 (8)	-C1	81.8 (2)	81.1 (3)
-S1′	56.16 (4)	56.02 (6)	S4-Mo-C1	83.3 (2)	82.4 (3)
-S2′	55.83 (4)	55.72 (7)	Mo-S1-Mo	66.97 (4)	67.24 (7)
-C1	72.8 (2)	72.8 (3)	-C1	64.2 (2)	64.4 (3)
X-Mo-S1	142.58 (4)	143.44 (8)	Mo′-S1-C1	89.4 (2)	89.6 (3)
-S2	145.20 (4)	144.42 (7)	Mo-S2-Mo	67.43 (4)	67.54 (7)
-S3	81.61 (4)	82.40 (7)	-C1	64.5 (2)	64.6 (4)
-S4	82.28 (4)	82.08 (8)	Mo′-S2-C1	89.4 (2)	89.4 (4)
-S1′	81.95 (4)	82.10 (7)	Mo-C1-S1	73.5 (2)	73.2 (4)
-S2′	80.70 (4)	81.77 (7)	-S2	72.6 (2)	72.4 (4)
-C1	161.0 (2)	160.5 (3)	-O1	127.0 (4)	128.0 (7)
S1-Mo-S2	71.29 (5)	71.34 (9)	S1-C1-S2	110.7 (3)	110.5 (6)
-S3	81.55 (6)	80.60 (9)	-O1	122.5 (4)	122.7 (7)
-S4	121.83 (6)	120.9 (1)	S2-C1-O1	126.3 (5)	126.3 (8)
-S1′	113.03 (4)	112.76 (7)	C1-O1-C2	118.4 (5)	118.0 (8)
-S2′	73.38 (5)	73.15 (9)	O1-C2-C3	107.6 (6)	109 (1)
-C1	42.4 (2)	42.4 (3)	Mo-S3-C4	86.9 (2)	86.6 (3)
S1′-Mo-S2	73.48 (5)	73.29 (9)	Mo-S4-C4	87.5 (2)	87.2 (4)
-S3	163.46 (6)	164.5 (1)	S3-C4-S4	116.2 (4)	116.8 (6)
-S4	106.47 (5)	107.56 (9)	-O2	118.7 (5)	118.5 (8)
-S2′	70.52 (5)	70.51 (8)	S4-C4-O2	125.1 (5)	124.7 (8)
-C1	114.1 (2)	113.9 (3)	C4-O2-C5	118.4 (6)	118.1 (8)
S2-Mo-S3	120.39 (6)	120.1 (1)	O2-C5-C6	107.8 (8)	107 (1)
-S4	81.53 (6)	81.36 (9)			
-S2′	112.57 (4)	112.46 (7)			
-C1	42.9 (2)	43.0 (2)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Chemical. The oxidative addition of Br_2 and I_2 to $Mo_2(S_2COR)_4$, where R is ethyl or propyl in the cases we have studied but may presumably be any other alkyl group, occurs smoothly and essentially quantitatively at room temperature in slightly polar solvents. The products are easy to isolate in crystalline form and appear to be stable indefinitely in laboratory air. The reactivity of the iodide toward a variety of reagents has been examined.

With excess Et_4NCl or NaO_2CCH_3 the iodide was recovered unchanged. With LiMe and with C_3H_5MgBr the iodide reacted rapidly but we have not been able to characterize any product. With diethyldithiocarbamate a yellow-green product was formed but its elemental analysis does not suggest to us any discrete formula. Similarly, reactions with KCN and with pyridine occur but appear to be complex and no product compositions have been defined. Reaction of the iodide with an excess of $KS_2COC_2H_5$ gives a compound whose analysis is approximately that expected for $Mo_2(S_2COC_2H_5)_6$. The bromide will react with additional bromine but no identifiable product has been obtained.

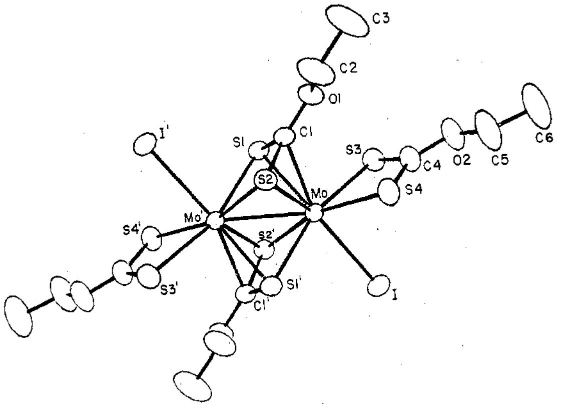

Figure 1. An ORTEP drawing of the molecule of $Mo_2(S_2COC_2H_5)_4I_2$. Each atom is represented by a sphere or ellipsoid of thermal vibration scaled to enclose 50% of its electron density.

The addition of X_2 to $Mo_2(S_2COC_2H_5)_4$ is not thermally reversible, at least in the solid state. Thus, even at 100 °C under vacuum the iodide does not evolve I_2. This behavior is in interesting contrast to that of the $Mo_2(O_2CR)_4$ compounds, which also react smoothly with iodine to give $Mo_2(O_2CR)_4I_3$ from which $Mo_2(O_2CR)_4$ and I_2 may be regenerated upon heating.[6]

Discussion

The difference in reactivity of $Mo_2(S_2COR)_4$ as compared to $Mo_2(O_2CR)_4$ with I_2 presumably has its origin in the very different electronic properties of the S_2COR ligand as compared to O_2CR, since structurally the starting compounds are quite similar. The greater ability of xanthates (like dithiocarbamates) to stabilize higher oxidation states is bound to be a factor in promoting the oxidation of Mo(II) to Mo(III). Moreover, the extraordinary way in which two of the xanthato groups are coordinated in the products doubtless has much to do with stabilizing the product molecules.

There is no precedent in the literature for the structural features involving the bridging xanthato groups, i.e., those containing S(1), S(2), and C(1). The bridging xanthato group is bonded to one molybdenum atom in a way that differs little from the ordinary form of coordination, a model for which is provided by the other type of xanthato group also present, i.e., the one containing S(3), S(4), and C(4). In both cases the $Mo(S_2CO)$ atoms are essentially planar and the Mo–S distances are nearly the same although those involving the bridging xanthato group are shorter by about 0.05 Å. This shortening may result primarily from a tendency of the Mo–Mo bond (see later) to compress the Mo–S bonds in the bridging system. The bridging xanthato group is thus a bidentate, three-electron donor to one Mo atom.

At the same time the bridging xanthato group is a tridentate, four-electron donor to the other Mo atom. It is noteworthy that the two Mo–S bonds formed by each bridging S atom, despite their great difference in direction relative to the rest of the ligand, are not significantly different in length; the mean values of the two types are 2.466 ± 0.006 and 2.443 ± 0.009 Å. Moreover, the Mo–C distance, 2.302 (6) Å, is indicative of strong bonding when compared with the mean Mo–C distances observed in $Mo_2(CH_2SiMe_3)_6$ and $Mo_2(CH_3)_8^{4-}$ which are 2.13[7] and 2.29 Å,[8] respectively. From a molecular orbital point of view, the π system of the S–C–S part of the xanthato ligand consists of a filled, symmetric bonding orbital, a filled, antisymmetric nonbonding orbital, and an empty, symmetric antibonding orbital. It appears likely that both of the filled π orbitals participate in the bonding to the metal atom that lies over the S_2CO plane. The fact that the S–C distances in the bridging xanthato group are but slightly longer (the apparent difference is only about equal to 3σ) would be in accord with the loss of π-electron density mainly from the nonbonding orbital.

It appears reasonable to conclude that the Mo–Mo bond order is 1. If each metal atom and the ligands are taken as neutral for purposes of electron counting, we have 6 electrons from Mo itself, 1 from Br or I, 3 from the terminal xanthato ligand, and 7 from the two bridging xanthato ligands, for a total of 17 electrons. The formation of a single bond between the metal atoms allows each one to have an 18-electron configuration and accounts for the diamagnetism of the compounds. Any higher Mo–Mo bond order would violate the 18-electron rule (unless we modify our assumption about the number of electrons contributed by the bridging xanthato groups, which does not seem justified). The observed Mo–Mo distances, 2.723 (2) and 2.717 (1) Å, are within the normal range for Mo–Mo single bonds.[9]

Another feature of these structures is the abnormal length of the Mo–Br and Mo–I bonds. For comparison, we note that in the $Mo_2Br_9^{3-}$ ion[10] and the $Mo_2Br_8H^{3-}$ ion[11] the Mo–Br(terminal) distances are 2.54 and 2.55 Å, respectively, and in $Mo_2Br_8^{4-}$ the mean value is 2.60 Å.[12] The present Mo–Br distance, 2.63 Å, is ca. 0.08 Å longer than those in the two Mo(III) complexes and is even longer than that in the Mo(II) complex. Another slightly less direct but valid comparison can be made with the Mo(III) complexes of the $M_2(NR_2)_4X_2$ type.[13] For the isomorphous compounds with $R = CH_3$, $X = Cl$, and M = Mo and W, we have Mo–Cl = 2.35 Å and W–Cl = 2.33 Å, which indicates that the bond radius for Mo is essentially the same as that for W. We can then compare the present Mo–Br and Mo–I distances with the W–Br and W–I distances in the $W_2(NEt_2)_4X_2$ compounds, whereupon we find that the Mo–Br and Mo–I distances are about 0.15 and 0.17 Å "too long", respectively. In summary, then, the present Mo–X distances are somewhere between 0.08 and 0.17 Å longer than would have been expected from the available comparisons. One possible explanation might be that in the $Mo_2(S_2COC_2H_5)_4X_2$ molecules the Mo atoms have 18-electron configurations whereas in the molecules with which they are being compared the configurations are >12 but <18. Alternatively, or in addition, the Mo–X bonds may be lengthened by a trans effect since they are opposite to the π-bonded, bridging xanthato group which is formally a four-electron donor.

In conclusion, we return to our opening point, namely, that oxidative addition of halogens to species with quadruple M–M bonds usually entails extensive structural rearrangement and considerably more weakening of the quadruple M–M bond than a mere decrease from quadruple to triple. The reactions, and reaction products, described here provide further examples of this. While there are differences in detail, the general behavior of these molybdenum systems is not unlike that of the rhenium systems mentioned at the outset.

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Registry No. $Mo_2(S_2COCH(CH_3)_2)_4$, 65102-00-3; $Mo(S_2COCH(CH_3)_2)_2$, 65102-09-2; $Mo_2(S_2COC_2H_5)_4$, 50284-10-1; $Mo(S_2COC_2H_5)_2$, 14582-06-0; $Mo_2(S_2COC_2H_5)_4Br_2$, 65138-62-7; $Mo_2(S_2COC_2H_5)_4I_2$, 65138-63-8; $Mo_2(S_2COCH(CH_3)_2)_4I_2$, 65138-61-6.

Supplementary Material Available: Tables of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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Detailed Structure of Bis(μ-trimethylsilylmethylidyne)-tetrakis(trimethylsilylmethyl)ditungsten(*W–W*)

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The crystal and molecular structures of a compound of composition $W_2(CSiMe_3)_2(CH_2SiMe_3)_4$ have been determined. The compound consists of dinuclear molecules which contain bridging alkylidyne groups, $CSiMe_3$, which, along with the tungsten atoms, form planar, rhombic rings, $\overline{\text{W–C–W–C}}$. Two alkyl groups, CH_2SiMe_3, are attached to each metal atom to form distorted tetrahedra about the metal atoms. There are two crystallographically independent molecules, each residing on a crystallographic inversion center. The two crystallographically independent W–W distances, 2.521 (2) and 2.549 (2) Å, are consistent with the presence of W–W single bonds. The basic crystallographic data are as follows: space group $P2_1/a$; unit cell dimensions a = 11.976 (4), b = 18.989 (5), c = 18.111 (5) Å; β = 101.02 (2)°; V = 4043 (2) Å^3; Z = 4.

Introduction

In a previous study[2] we attempted to prepare $W_2(CH_2SiMe_3)_6$[3] from the reaction between WCl_4 and Me_3SiCH_2MgCl (1:4 mole ratio) and fortuitously isolated a new compound which we formulated,[2] on the basis of noncrystallographic evidence, as bis(μ-trimethylsilylmethylidyne)-tetrakis(trimethylsilylmethyl)ditungsten, $W_2(CSiMe_3)_2(CH_2SiMe_3)_4$, I. We proposed this structure by analogy to that found[4] for $Nb_2(CSiMe_3)_2(CH_2SiMe_3)_4$ but explicitly noted that the ditungsten compound should contain a metal-to-metal bond. $W_2(CSiMe_3)_2(CH_2SiMe_3)_4$ has also been prepared independently,[5] and the same structure has been proposed.

We report here the results of a single-crystal x-ray study on I that confirms the structure proposed for it.

Experimental Section

The method we used for the preparation of I has been described previously.[2] Crystals of I were grown from pentane at ca. −78 °C. Reactions of I with C_2H_2, MeCCMe, PhCCH, $MeO_2CC_2CO_2Me$, C_3H_4, C_2H_4, 1,3-butadiene, and CO_2 were carried out in 5-mm NMR tubes in toluene-d_8. Gaseous reagents were added to solutions of I using vacuum-line techniques. Other reagents were added to the NMR tubes by syringe. The progress of the reactions was monitored via ^{1}H NMR spectroscopy. No attempt was made to isolate any of the products of these reactions.

X-Ray Crystallography. Crystal Selection and Data Collection. Considerable difficulty was encountered (i) in mounting crystals of $W_2(CSiMe_3)_2(CH_2SiMe_3)_4$ in such a manner that they did not decompose and (ii) once they were mounted, in finding a crystal of suitable quality. Finally, a platelike crystal measuring ca. 0.17 × 0.34 × 0.56 mm was mounted by wedging it into a nitrogen-filled capillary in a glovebox. The ends of the capillary were sealed with a small hand torch. The crystal was mounted with its longest dimension nearly coincident with the ϕ axis. ω scans of several intense low-angle reflections had peak widths at half-height of ca. 0.2°. Lattice constants and axial photographs indicated that the crystal belonged to the monoclinic system. The unit cell constants, determined from the setting angles of 15 reflections having $21° < 2\theta(\text{Mo K}\alpha) < 27°$, are a = 11.976 (4) Å, b = 18.989 (5) Å, c = 18.111 (5) Å, β = 101.02 (2)°, and V = 4043 (2) Å^3. The observed volume was consistent with that expected for $Z = 4$. The systematic absences observed during data collection, $0k0$ ($k = 2n + 1$) and $h0l$ ($h = 2n + 1$), uniquely determined the space group to be $P2_1/a$ (equivalent positions $\pm\{x, y, z; {}^1/_2 - x, {}^1/_2 + y, -z\}$, a nonstandard setting of $P2_1/c$ (No. 14).

The data were collected at 25 °C with a Syntex $P\bar{1}$ autodiffractometer equipped with a graphite crystal monochromator and using Mo Kα (λ 0.710 730 Å) radiation. Variable scan rates from 4.0 to 24.0°/min were used for symmetric $\theta/2\theta$ scans ranging from 1.0° below to 1.0° above the calculated Mo Kα_1–Kα_2 doublet. The ratio of scan to background time was 2.0. A total of 5313 unique, nonsystematically absent reflections having $0° < 2\theta_{\text{MoK}\alpha} < 45.0°$ were recorded. The intensities of three standard reflections were monitored frequently throughout data collection and showed no decrease in intensity. The data were reduced to a set of relative $|F_o|^2$ values.[6] The intensities were corrected for absorption effects (μ = 62.1 cm^{-1}); transmission coefficients ranged from 0.160 to 0.394 with an average of 0.285. The 2396 data having $I > 3\sigma(I)$ were retained as observed and used in subsequent structure solution and refinement.

Structure Solution and Refinement.[6] The positions of the 32 unique nonhydrogen atoms were determined by standard heavy-atom methods. The structure was refined to convergence using anisotropic thermal parameters for the tungsten and silicon atoms and isotropic thermal parameters for the carbon atoms. The final discrepancy indices were

$$R_1 = \Sigma||F_o| - |F_c||/|F_o| = 0.070$$
$$R_2 = (\Sigma w||F_o| - |F_c||^2/\Sigma|F_o|^2)^{1/2} = 0.083$$

The estimated standard deviation of an observation of unit weight was 1.48. A final difference Fourier map showed no peaks of chemical significance. The largest seven peaks in the map were within ca. 1 Å of the tungsten atoms and presumably reflect the inadequacies of the absorption correction. The large thermal parameters for some methyl carbon atoms are due mainly to librational motion.

A table of observed and calculated structure factors is available as supplementary material.

Results and Discussion

Reactivity. I is a highly reactive, air-sensitive compound. It reacts in solution at room temperature with acetylene, dimethylacetylene, phenylacetylene, dimethylacetylenedicarboxylate, allene, ethylene, and 1,3-butadiene. No reaction was observed with CO_2. The above reactions were carried out

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