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Two New Molybdenum Complexes and Their Structures

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The reaction of dimolybdenum tetraacetate with the sodium salt of 2-mercaptopyridine in the presence of oxygen gives the deep red compound $Mo_2O_3(C_5H_4NS)_4$ in excellent yield. X-ray crystallography shows that the molecule is centrosymmetric with a trans, planar O═Mo—O—Mo═O central unit. Principal crystallographic data are space group $P\bar{1}$, $a = 9.010$ (2) Å, $b = 10.872$ (2) Å, $c = 7.316$ (2) Å, $\alpha = 104.48$ (1)°, $\beta = 106.26$ (1)°, $\gamma = 70.16$ (1)°, $V = 637.5$ (8) Å^3, and $Z = 1$. Quadruple-bond-containing compounds of the type $Mo_2Cl_4(RSCH_2CH_2SR)_2$ undergo slow decomposition in methylene chloride solution to deposit brown crystals of compounds with the formula $Mo_2Cl_6L_2$, where L is the same dithiaalkane ligand. A crystallographic study of the compound in which $R = C_2H_5$ shows it to consist of binuclear molecules in which octahedrally coordinated molybdenum atoms are united by a planar $Mo(\mu\text{-}Cl)_2Mo$ bridge system with Mo–Mo = 2.735 (2) Å. The principal crystallographic data are space group $P2_1/c$, $a = 10.642$ (7) Å, $b = 7.391$ (5) Å, $c = 16.097$ (9) Å, $\beta = 108.17$ (1)°, $V = 1203$ (2) Å^3, and $Z = 2$.

The chemistry of molybdenum is as broad and diverse as that of any transition element, and it is currently the subject of extensive research in part because of its recently recognized biochemical importance. Stiefel has recently provided an excellent and timely review.[1] In the course of research on several aspects of molybdenum chemistry, we have prepared and characterized two new compounds, one of Mo^V and the other of Mo^{III}. These compounds were prepared from two different Mo^{II} quadruply bonded dimers. This suggests that such dimers might be useful precursors to higher oxidation state complexes of molybdenum with unusual geometries. Therefore, though these compounds are not related directly to each other, we describe them both here because of commonality in certain experimental procedures used and for economy of space.

Results and Discussion

$Mo_2O_3(C_5H_4NS)_4$. The formation of this molybdenum(V) compound from $Na(C_5H_4NS)$ and molybdenum(II) acetate is caused by atmospheric oxygen. The reaction mixture can, in fact, be described as an avid "getter" for even traces of oxygen. Even when reasonable precautions are taken to exclude oxygen, the reaction mixtures promptly develop a red color. The compound is thermally stable and can be handled in air.

The crystals are triclinic with only one molecule in the unit cell. The space group $P\bar{1}$ allowed satisfactory refinement and, thus, the molecule lies on a center of inversion and the asymmetric unit is half of the molecule. The molecular structure is shown in Figure 1. The atomic positional and thermal parameters are listed in Table II and the bond distances and angles in Table III.

Each molybdenum atom is at the center of a distorted octahedron of ligand atoms provided by two chelating 2-mercaptopyridine anions and two mutually cis oxygen atoms. These two octahedral units share one oxygen atom, O(1), which constitutes a crystallographically rigorous center of inversion. Therefore, the entire central O═Mo—O—Mo═O unit is rigorously trans planar.

Only three structures in this general class have heretofore been described, though other compounds are known,[2] and they are of two symmetry types.[1] The first such structure investigated, that of $Mo_2O_3(Etxan)_4$, where Etxan represents $EtOCS_2$, and $Mo_2O_3(S_2CNPr_2)_4$ have a cis configuration in the essentially planar O═Mo—O—Mo═O unit; the Mo–O–Mo chain is practically but not rigorously linear. The third compound, $Mo_2O_3[S_2P(OEt)_2]_4$, resembles our mercaptopyridine compound in having a trans O═Mo—O—Mo═O chain with rigorous inversion symmetry. The discovery of a second trans system is significant in showing that both the cis and trans arrangements may be of general occurrence.

Table I. Crystallographic Data

parameter	$Mo_2O_3(C_5H_4NS)_4$	$Mo_2Cl_6(C_6H_{14}S_2)_2$
a, Å	9.010 (2)	10.642 (7)
b, Å	10.872 (2)	7.391 (5)
c, Å	7.316 (2)	16.097 (9)
α, deg	104.48 (1)	90.0
β, deg	106.26 (1)	108.17 (1)
γ, deg	70.16 (1)	90.0
V, Å^3	637.5 (8)	1203 (2)
Z	1	2
formula wt	680.41	705.21
approx crystal size, mm	0.6 × 0.2 × 0.1	0.2 × 0.1 × 0.1
absorption coeff, cm^{-1}	12.976	20.103
range of 2θ, deg	0-45	0-45
no. of observns with $F^2 > 3\sigma(F^2)$	1339	886
unweighted R factor	0.037	0.047
weighted R factor	0.053	0.058
error in an observn of unit wt	1.273	1.120
space group	$P\bar{1}$	$P2_1/c$
density calculated	1.689	1.883
temp, °C	22	22

One of the notable properties of the present compound is that it is, at present, unique among $Mo_2O_3(LL)_4$ molecules in having atoms other than sulfur among the donor atoms in the LL ligands.

$Mo_2Cl_6(EtSCH_2CH_2SEt)_2$. This red-brown compound has been obtained from a dichloromethane solution of the quadruply bonded dimolybdenum(II) species[3] $Mo_2Cl_4(EtSCH_2CH_2SEt)_2$ only in small quantities, insufficient for elemental analysis or other physical methods. However, the procedure is entirely reproducible and was repeated several times. Also, the reaction involved appears to be general for $Mo_2Cl_4(RSCH_2CH_2SR)_2$ compounds since it occurs also for the case where $R = C_4H_9$ We believe that the CH_2Cl_2 solvent is the source of additional chlorine atoms, but this is speculative, and we have not attempted to develop a synthetic method that is capable of providing larger quantities of product. With two molecules in a unit cell belonging to space group $P2_1/c$, each molecule lies on a crystallographic center of symmetry. The atomic coordinates for the atoms of the asymmetric unit, half of the molecule, are listed in Table IV. An ORTEP drawing of the molecule is presented in Figure 2, and the important interatomic distances and angles are listed in Table V. The numbering scheme is defined in Figure 2

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2O_3(C_5H_4NS)_4$[a,b]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	−0.07074 (6)	0.18131 (5)	−0.08483 (7)	3.00 (2)	4.55 (2)	3.95 (2)	−0.33 (2)	0.83 (2)	1.48 (2)
S(1)	0.0782 (2)	0.1694 (2)	0.4164 (2)	3.96 (7)	4.43 (6)	4.86 (7)	−0.30 (5)	−0.06 (6)	1.84 (5)
S(2)	−0.3327 (2)	0.2275 (2)	−0.1520 (2)	4.85 (8)	6.71 (9)	3.96 (7)	−0.57 (7)	−0.19 (6)	1.64 (6)
O(1)	0.0000 (0)	0.0000 (0)	0.0000 (0)	3.6 (2)	5.5 (3)	4.3 (2)	0.6 (2)	1.2 (2)	0.6 (2)
O(2)	0.0211 (6)	0.2498 (5)	−0.0150 (7)	5.6 (2)	9.4 (2)	6.5 (2)	−2.1 (2)	1.6 (1)	3.8 (2)
N(1)	−0.1578 (6)	0.3584 (4)	0.2907 (7)	3.5 (2)	3.8 (2)	4.6 (2)	−1.1 (2)	0.0 (2)	1.2 (2)
N(2)	−0.2816 (5)	0.1440 (4)	0.1610 (7)	3.2 (2)	3.2 (2)	4.2 (2)	−0.8 (1)	0.8 (2)	−0.0 (2)
C(1)	−0.0603 (7)	0.3250 (5)	0.4587 (9)	3.9 (2)	3.7 (2)	4.5 (3)	−1.2 (2)	0.0 (2)	1.5 (2)
C(2)	−0.0786 (9)	0.4066 (7)	0.6345 (10)	6.1 (3)	4.7 (3)	4.9 (3)	−1.5 (2)	0.9 (2)	0.7 (2)
C(3)	−0.2053 (10)	0.5256 (7)	0.6329 (12)	7.8 (4)	5.2 (3)	6.6 (4)	−1.5 (3)	1.9 (3)	0.1 (3)
C(4)	−0.3037 (10)	0.5596 (7)	0.4564 (13)	6.5 (4)	4.1 (3)	7.4 (4)	−0.3 (3)	0.3 (3)	0.3 (3)
C(5)	−0.2794 (8)	0.4728 (6)	0.2857 (10)	4.2 (3)	3.1 (2)	6.1 (3)	−0.3 (2)	−0.2 (3)	1.2 (2)
C(11)	−0.4006 (7)	0.1830 (6)	0.0135 (9)	3.1 (2)	3.5 (2)	4.5 (3)	−0.2 (2)	0.4 (2)	0.1 (2)
C(12)	−0.5602 (8)	0.1858 (7)	0.0038 (12)	3.9 (3)	4.5 (3)	7.7 (4)	−1.0 (2)	1.3 (3)	−0.8 (3)
C(13)	−0.5865 (8)	0.1461 (7)	0.1536 (13)	4.1 (2)	5.3 (3)	9.8 (5)	−2.0 (2)	2.3 (3)	−1.7 (3)
C(14)	−0.4625 (8)	0.1080 (6)	0.3086 (11)	6.3 (3)	4.5 (3)	8.0 (4)	−2.3 (2)	4.0 (2)	−1.0 (3)
C(15)	−0.3072 (8)	0.1073 (6)	0.3123 (9)	5.6 (3)	3.9 (2)	5.0 (3)	−1.8 (2)	2.3 (2)	0.0 (2)

[a] Numbers in parentheses are esd's occurring in least significant digit. [b] 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. Distances (Å) and Angles (deg) in the $Mo_2O_3(C_5H_4NS)_4$ Molecule[a]

Bond Distances

Mo(1)-S(1)	2.433 (2)	N(2)-C(11)	1.329 (7)
-S(2)	2.483 (2)	-C(15)	1.365 (7)
-O(1)	1.853 (1)	C(1)-C(2)	1.384 (9)
-O(2)	1.673 (4)	C(2)-C(3)	1.41 (1)
-N(1)	2.185 (5)	C(3)-C(4)	1.40 (1)
-N(2)	2.305 (5)	C(4)-C(5)	1.39 (1)
S(1)-C(1)	1.742 (6)	C(11)-C(12)	1.410 (9)
S(2)-C(11)	1.727 (7)	C(12)-C(13)	1.38 (1)
N(1)-C(1)	1.348 (7)	C(13)-C(14)	1.38 (1)
-C(5)	1.351 (7)	C(14)-C(15)	1.39 (1)

Bond Angles

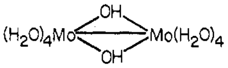
S(1)-Mo(1)-S(2)	149.6 (1)	S(1)-C(1)-N(1)	110.2 (4)
-O(1)	94.4 (1)	S(1)-C(1)-C(2)	128.0 (5)
-O(2)	107.4 (2)	N(1)-C(1)-C(2)	121.8 (5)
-N(1)	66.6 (1)	C(1)-C(2)-C(3)	117.6 (6)
-N(2)	89.0 (1)	C(2)-C(3)-C(4)	119.7 (7)
S(2)-Mo(1)-O(1)	97.6 (1)	C(3)-C(4)-C(5)	119.7 (6)
-O(2)	96.0 (2)	N(1)-C(5)-C(4)	119.6 (6)
-N(1)	92.2 (1)	C(11)-N(2)-C(15)	122.2 (5)
-N(2)	63.9 (1)	S(2)-C(11)-N(2)	111.7 (4)
O(1)-Mo(1)-O(2)	105.9 (2)	S(2)-C(11)-C(12)	127.0 (6)
-N(1)	154.4 (1)	N(2)-C(11)-C(12)	121.3 (6)
-N(2)	87.2 (1)	C(11)-C(12)-C(13)	116.9 (7)
O(2)-Mo(1)-N(1)	96.4 (2)	C(12)-C(13)-C(14)	121.4 (7)
-N(2)	157.8 (2)	C(13)-C(14)-C(15)	119.6 (7)
N(1)-Mo(1)-N(2)	76.0 (2)	N(2)-C(15)-C(14)	118.6 (6)
C(1)-N(1)-C(5)	121.5 (5)		

[a] Figures in parentheses are the esd's occurring in the least significant digit.

except for the ethyl carbon atoms since the ethyl groups are omitted in the interest of clarity. The numbering of these is S(1)–C(11)–C(12) and S(2)–C(21)–C(22).

Each molybdenum atom is at the center of a distorted octahedron and the two octahedra share an edge defined by the Cl(1) and Cl(1)′ ligands. The Mo(μ-Cl)$_2$Mo ring is strictly planar since there is a crystallographic inversion center at its midpoint.

There appear to be very few other examples of doubly bridged molybdenum(III) species. The only ones we have found are the complexes of the type



$$(H_2O)_4Mo\overset{OH}{\underset{OH}{\langle\rangle}}Mo(H_2O)_4$$

first reported by Ardon and Pernick.[4] The crystal structure of the related complex $K[Mo_2(O_2CCH_3)(OH)_2(edta)]$ was reported.[5] While these dihydroxy-bridged species have the same basic geometry as the complex reported here, the bonding between the metals is quite different. These complexes are green and diamagnetic and have an Mo–Mo distance of only 2.430 (3) Å. This is substantially shorter than the 2.735 Å distance for the dichloro-bridged compound and is indicative of a metal–metal triple bond.

A more pertinent comparison may be made with the ion $Mo_2Cl_9^{3-}$ even though it has a different geometry. The important distances and angles in the two compounds are listed in Table VI. The metal–metal distance in $Mo_2Cl_6(DTO)_2$ (DTO = 3,6-dithiaoctane) is somewhat longer than that[6] in $Mo_2Cl_9^{3-}$ but shorter than that[7] in $Mo_2Br_9^{3-}$ where it is 2.82 Å. The reported magnetic susceptibilities for the two $Mo_6X_9^{3-}$ ions are 0.6 and 0.8 μ_B, for the chloride and bromide, respectively. It is quite possible, considering the similarities in the Mo–Mo distances that $Mo_2Cl_6(DTO)_2$ has a similar low magnetic moment indicative of appreciable but incomplete

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2Cl_6(EtSCH_2CH_2SEt)_2$[a,b]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.3669 (1)	0.4673 (2)	−0.02620 (7)	2.24 (4)	2.14 (5)	1.86 (4)	0.06 (5)	0.71 (3)	0.01 (5)
Cl(1)	0.5348 (3)	0.2412 (5)	0.9926 (2)	2.9 (1)	2.0 (2)	3.0 (1)	0.2 (1)	0.9 (1)	0.1 (1)
Cl(2)	0.6756 (3)	0.5263 (6)	0.1812 (2)	3.4 (1)	3.8 (2)	2.0 (1)	−0.2 (2)	0.5 (1)	0.2 (2)
Cl(3)	0.1635 (3)	0.6322 (6)	0.9587 (2)	2.7 (1)	3.7 (2)	4.3 (2)	0.7 (2)	1.0 (1)	0.3 (2)
S(1)	0.2318 (3)	0.1779 (6)	0.9414 (2)	2.8 (1)	3.7 (2)	2.7 (1)	0.8 (2)	1.1 (1)	0.5 (1)
S(2)	0.3740 (3)	0.3920 (5)	1.1262 (2)	2.7 (1)	2.5 (2)	2.0 (1)	−0.1 (1)	1.0 (1)	0.0 (1)
C(1)	0.228 (2)	0.106 (2)	1.0496 (9)	6.7 (8)	2.5 (7)	2.6 (6)	1.4 (7)	1.9 (5)	0.3 (6)
C(2)	0.224 (1)	0.265 (2)	1.1089 (9)	3.4 (5)	4.2 (8)	4.0 (6)	−0.6 (6)	2.7 (4)	0.0 (6)
C(11)	0.945 (1)	0.769 (2)	0.1149 (11)	1.9 (7)	5.2 (9)	6.0 (9)	0.4 (7)	−0.9 (6)	−0.7 (8)
C(12)	−0.002 (2)	0.093 (4)	0.8236 (17)	4 (1)	13 (2)	12 (2)	−0 (1)	−3 (1)	8 (1)
C(21)	0.340 (1)	0.593 (2)	1.1829 (8)	5.0 (7)	3.3 (7)	2.6 (5)	0.1 (6)	2.2 (4)	−1.5 (5)
C(22)	0.341 (2)	0.541 (2)	1.2751 (9)	9.6 (9)	3.9 (8)	4.1 (6)	−1.2 (8)	4.4 (5)	−0.9 (7)

[a] Numbers in parentheses are esd's occurring in least significant digit. [b] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4B_{11}\cdot h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

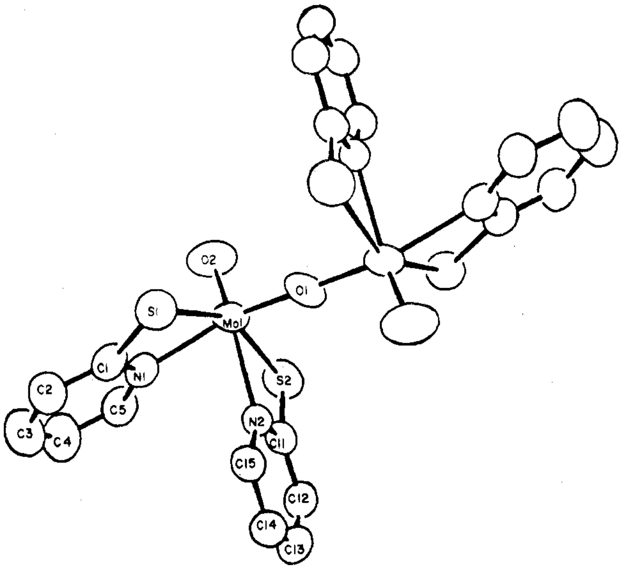


Figure 1. ORTEP drawing of the $Mo_2O_3(C_5H_4NS)_4$ molecule. Unlabeled atoms are related to those with labels by a center of inversion at O(1). Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 50% of its electron density.

Table V. Distances (Å) and Angles (deg) in the $Mo_2Cl_6(EtSCH_2CH_2SEt)_2$ Molecule[a,b]

	Bond Distances		
Mo(1)-Mo(1)′	2.735 (2)	S(1)-C(1)	1.83 (1)
Mo(1)-Cl(1)	2.396 (4)	S(2)-C(2)	1.80 (2)
Mo(1)-Cl(1)′	2.383 (4)	C(1)-C(2)	1.52 (2)
Mo(1)-Cl(2)	2.393 (3)	S(1)-C(11)	1.85 (2)
Mo(1)-Cl(3)	2.429 (4)	S(2)-C(21)	1.84 (1)
Mo(1)-S(1)	2.538 (4)	C(11)-C(12)	1.42 (3)
Mo(1)-S(2)	2.493 (4)	C(21)-C(22)	1.53 (2)
	Bond Angles		
Mo(1)′-Mo(1)-Cl(1)	54.86 (9)	Cl(2)-Mo(1)-Cl(3)	90.7 (1)
-Cl(1)′	55.31 (9)	-S(1)	83.8 (1)
-Cl(2)	99.1 (1)	-S(2)	165.4 (1)
-Cl(3)	138.3 (1)	Cl(3)-Mo(1)-S(1)	88.4 (1)
-S(1)	132.7 (1)	-S(2)	87.9 (1)
-S(2)	91.5 (1)	-S(2)	81.7 (1)
Cl(1)-Mo(1)-Cl(1)′	110.2 (1)	C(1)-S(1)-C(11)	101.8 (8)
-Cl(2)	92.1 (1)	C(2)-S(2)-C(21)	101.4 (7)
-Cl(3)	165.6 (1)	S(1)-C(1)-C(2)	112 (1)
-S(1)	77.9 (1)	S(2)-C(2)-C(1)	107 (1)
-S(2)	85.8 (1)	S(1)-C(11)-C(12)	110 (1)
Cl(1)′-Mo(1)-Cl(2)	98.4 (1)	S(2)-C(21)-C(22)	110 (1)
-Cl(3)	83.3 (1)		
-S(1)	171.5 (1)		
-S(2)	95.9 (1)		

[a] Figures in parentheses are the esd's occurring in the least significant digit. [b] Primed atoms are related by the inversion center to unprimed ones with the same numbers.

metal–metal interaction.

One feature of the $Mo_2Cl_6(DTO)_2$ structure that especially merits comment is the fact that the Mo–Cl(bridge) bonds are *not* longer than the Mo–Cl(terminal) bonds. This is a situation for which we know of no precedent. The situation prevailing in the $Mo_2Cl_9{}^{3-}$ ion (Table VI) is the typical one, with the bridge bonds being distinctly (say, 0.1 Å) longer. We cannot say for certain why this should be so but suggest that there may be appreciable π bonding through the Mo–Cl–Mo chains which both lowers the magnetic moment and shortens the bridge bonds.

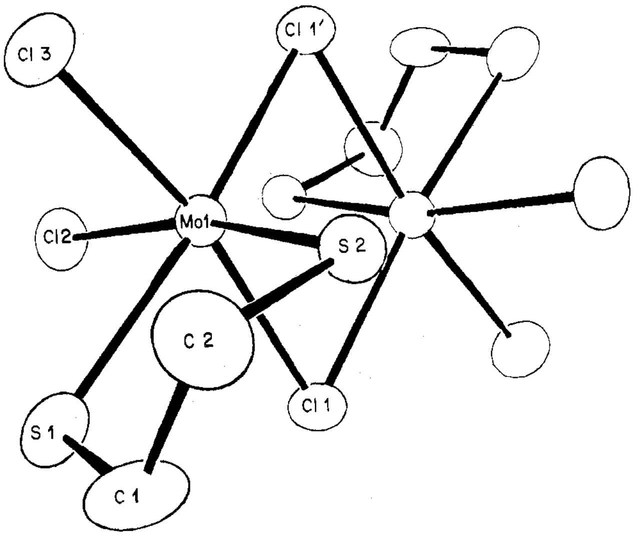


Figure 2. ORTEP drawing of the $Mo_2Cl_6(DTO)_2$ molecule. The ethyl groups attached to the sulfur atoms have been omitted. Each atom is represented by its ellipsoid of thermal motion scaled to enclose 50% of the electron density. Unlabeled atoms are related by the inversion center to labeled ones

Table VI. Comparison of Important Bond Distances (Å) and Angles (deg) for $Cs_3Mo_2Cl_9$ and $Mo_2Cl_6(EtSCH_2SEt)_2$

	$Cs_3Mo_2Cl_9$[a]	$Mo_2Cl_6(DTO)_2$
Mo-Mo	2.655	2.735
$Mo–Cl_b$[b]	2.487	2.396, 2.383
$Mo-Cl_t$	2.384	2.393, 2.429
$Mo-Cl_b-Mo$	64.52	69.8
$Cl_b-Mo-Cl_b$	94.2	110.2

[a] From ref 6. [b] Cl_b is the bridging chloride while Cl_t is the terminal one.

Experimental Section

Preparation of $Mo_2O_3(C_5H_4NS)_4$. 2-Mercaptopyridine (1.02 g, 9.2 mmol) is added to an ethanolic solution of sodium ethoxide (prepared by dissolving 0.20 g (8.6 mmol) of Na in 25 mL of absolute ethanol) under a nitrogen atmosphere. $Mo_2(O_2CCH_3)_4$ (0.20 g, 0.5 mmol) is added to this solution and a dark green precipitate forms. This initially formed solid is then isolated by filtration in air after which it is washed with ethanol (2 × 15 mL) and then with ether (15 mL). Oxidation of the solid reaction product (yield 0.28 g) is then effected by pulling air through it for about 10 min. Anal. Calcd for $C_{20}H_{16}Mo_2N_4O_3S_4$: C, 35.3; H, 2.35. Found: C, 34.5; H, 2.44. The compound may be further purified by recrystallization from dry chloroform or methylene chloride to yield dark red crystals. Solutions of the compound are burgundy by transmitted light and show a green fluorescence.

Crystallographic Study of $Mo_2O_3(C_5H_4NS)_4$. Suitable crystals were grown by slow evaporation in a stream of nitrogen of a methylene chloride solution of the compound. The crystal selected for study was cemented to a glass fiber and was coated with epoxy resin.

The crystal was examined using a Syntex $P\bar{1}$ four-circle automated diffractometer. After rotation photographs and ω scans indicated that the crystal was of good quality, lattice parameters were obtained by a least-squares fit of 15 strong reflections. Data were measured by θ–2θ scans and procedures were, in general, the same as those routinely used.[8] The discrepancy indices used were

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

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

Data reduction and structure refinement were carried out using the Enraf-Nonius Structure Determination Package on the PDP 11/45 computer owned by Molecular Structure Corp. The structure was solved by conventional heavy-atom methods. A final difference map had no peaks with intensity greater than 1 e/Å^3. Crystallographic data are listed in Table I. No absorption correction was applied.

Preparation of $Mo_2Cl_6(EtSCH_2CH_2SEt)_2$. 3,6-Dithiaoctane (DTO) was obtained from Pflatz and Bauer. Tetrachlorobis(3,6-dithiaoctane)dimolybdenum(II) was prepared by a procedure analogous to that of San Filippo et al. for the preparation of tetrachlorobis(2,5-dithiahexane)dimolybdenum(II).[3] The compound was dissolved in methylene chloride, and a layer of hexane was floated above this solution. After about 7 days, the hexane layer was bronze colored and began depositing red-brown crystals of $Mo_2Cl_6(DTO)_2$. The compound is air-stable and insoluble in most organic solvents and water.

Crystallographic Study of $Mo_2Cl_6(DTO)_2$. Suitable crystals were obtained by the above procedure. The crystal selected was mounted on the end of a glass fiber. The crystal was examined, data were collected, and the structure was refined following essentially the procedure described above for the other compound. The largest peak in the final difference Fourier was 0.83 e/Å^3. Crystallographic data are listed in Table I. No absorption correction was applied.

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Registry No. $Mo_2O_3(C_5H_4NS)_4$, 67583-97-5; $Mo_2Cl_6(DTO)_2$, 67584-20-7; $Mo_2(O_2CCH_3)_4$, 14221-06-8; $Mo_2Cl_4(EtSCH_2CH_2SEt)_2$, 67598-73-6.

Supplementary Material Available: Tables of structure factors for both compounds (10 pages). Ordering information is given on any current masthead page.

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Syntheses and Molecular Structures of Two Metalloindene Complexes: 1,1-Bis(η^5-cyclopentadienyl)-2,3-bis(pentafluorophenyl)benzotitanole and 1,1-Bis(η^5-cyclopentadienyl)-2-trimethylsilyl-3-phenylbenzotitanole

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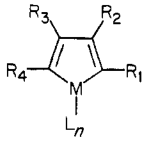
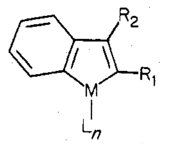
The thermally induced reactions of bis(η^5-cyclopentadienyl)diphenyltitanium with several symmetrical and unsymmetrical acetylenes have been investigated. Two of the products, derived from bis(pentafluorophenyl)acetylene and phenyltrimethylsilylacetylene, have been shown to be 1,1-bis(η^5-cyclopentadienyl)-2,3-bis(pentafluorophenyl)benzotitanole (**7**) and 1,1-bis(η^5-cyclopentadienyl)-2-trimethylsilyl-3-phenylbenzotitanole (**8**), respectively. Their unique metalloindene structures have been unequivocally established (by means of single-crystal X-ray diffraction techniques) with three-dimensional data gathered by counter methods. Orange-red crystals of $(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6F_5)_2$ (**7**) belong to the monoclinic space group $C2/c$ with unit cell constants $a = 27.953$ (7) Å, $b = 14.912$ (5) Å, $c = 15.783$ (5) Å, and $\beta = 119.14$ (2)°. The calculated density of 1.52 g·cm^{-3}, assuming eight molecules of **7** and four molecules of hexane of crystallization per unit cell, agrees well with the measured value of 1.50 (3) g·cm^{-3}. Full-matrix least-squares refinement converged with a conventional R factor of 0.070 based on 1993 observed reflections. The Ti–C (σ) bond lengths are 2.132 (10) and 2.219 (9) Å. Crystals of $(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6H_5)[Si(CH_3)_3]$ (**8**) form in the orthorhombic space group $Pbca$ with $a = 10.521$ (7) Å, $b = 15.207$ (7) Å, $c = 28.636$ (7) Å, and $\rho_{calcd} = 1.25$ g·cm^{-3} for eight molecules in the unit cell. The final R value was 0.032 for 2198 observed reflections. The Ti–C (σ) bond lengths are 2.161 (3) and 2.170 (3) Å.

Introduction

Metallocyclic derivatives of the transition metals have been the subject of considerable research in recent years, both from their possible intermediacy in various homogeneous catalytic processes such as acetylene oligomerization, olefin disproportionation, etc., and from the potential aromaticity of various unsaturated analogues. As part of our continuing research program in metallocycle chemistry, we have recently been able to isolate and carry out X-ray diffraction studies on a variety of metallocyclopentadienes (metalloles) (**1**) containing Ti,[2] Hf,[2] Co,[3] and Rh.[4]



1



2

The present study was undertaken in order to gain analogous structural information on a related series of organometallic compounds, the metalloindenes (**2**), which formally are metallocyclopentadienes containing an unsymmetrically fused benzene ring. Compared to the metallocyclopentadienes **1**, metalloindenes **2** have been considerably less investigated. In the case of transition-metal analogues, the known metalloindenes are presently limited to examples in which the heteroatom is either Ti[5,6] or Mn[7] and a variety of binuclear complexes of Fe,[8-12] Ru,[12] and Os[12] in which the metalloindene ring system is simultaneously coordinated to a $M(CO)_3$ fragment of the same respective metal.

The only X-ray crystallographic investigations on metalloindenes have thus far been conducted on these latter types of complexes containing either Fe (**3**, **4**)[11,13] or Os (**5**).[12] These studies would not necessarily be expected to provide useful structural information relative to the molecular parameters of *non*coordinated metalloindenes, however, since it is known that coordination of a metallocyclic ring to a transition metal considerably perturbs the ring system.[14]

In the present paper, we report on the synthesis, properties,

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