$F_5SCH_2CHO + H_2SO_4$. Into a 2.5-mL tube was added 0.5180 g (3.05 mmol) of F_5SCH_2CHO (purified by GC, 30% SE on Chromosorb W, 80 °C). Four drops of 96% H_2SO_4 were added at room temperature, and an immediate formation of a white compound was observed. The tube was capped and gently shaken. During this time heat was liberated, and within 5 min a white solid remained in the tube; the typical odor of the aldehyde was gone after 20 min. After the sample was kept at room temperature overnight, the product was dissolved in acetone (≈2 mL). The volume of the solution was reduced by evaporation to ≈0.5 mL, CH_2Cl_2 (3 mL) was added, and the solution was treated with a saturated $NaHCO_3$ solution dropwise with swirling until CO_2 formation ceased. The lower layer was removed, and the remaining aqueous layer was extracted with methylene chloride (1 mL). The two solutions were combined, and the resultant mixture was dried (Na_2SO_4). The solution was then filtered through a filter pipet, the Na_2SO_4 was rinsed with CH_2Cl_2 (1 mL), and the rinse solution was combined with the filtrate; after evaporation of the solvent in a stream of air and drying in an oven (120 °C, 15 min), an off-white product (solidified melt) was obtained. The IR spectrum of this material was identical with the spectra of the products obtained either by the extraction of the P_4O_{10} residue from the dehydration procedure or from the precipitate collected from the aldehyde after storage at −5 °C (6 weeks); yield 0.4460 g (0.87 mmol), 86%.

Acknowledgment. We express our appreciation to the Gas Research Institute (Contract No. 5084-260-1085) and the U.S. Department of Energy (Grant No. DE-FG21-88MC25142) for support of this work. Dr. G. D. Knerr at the University of Idaho obtained the mass spectra. The X-ray diffraction facility was established through funds from the NSF (Grant No. CHE-8408407) and the Boeing Co.

Supplementary Material Available: Figure SI, showing the stereographic pair illustrating the unit cell, Tables SI–SIII, listing crystal data, thermal parameters, and hydrogen atom coordinates (4 pages); a table of calculated and observed structure factors (6 pages). Ordering information is given on any current masthead page.

Contribution from the Exxon Research & Engineering Company,
Route 22 East, Annandale, New Jersey 08801

$Mo_2(C_6H_4S_2)_5$, the Purple Product in Molybdenum–Dithiol Reactions: A Novel Molybdenum(V) Dimer Dithiolate Structure

Thomas R. Halbert* and Edward I. Stiefel*

Received October 12, 1988

Dithiolene (unsaturated 1,2-dithiolate) complexes have attracted considerable attention in view of their intense colors and rich spectra,[1,2] their ability to be isolated in multiple oxidation states,[1,2] their unusual coordination geometries,[1,2] and the novel photochemical and conductivity behavior of their molecular and ionic solids.[3-5] Of late, interest in molybdenum dithiolate species has heightened due to the postulation of a molybdenum 1,2-dithiolate as a key linkage in the molybdenum cofactor[6,7] common to over 12 enzymes.[8] In order to provide evidence of potential linkage modes of dithiolate ligands to Mo centers, we have reinvestigated some of the chemistry of molybdenum with the benzene- and toluenedithiolate ligands.

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement Parameters for $Mo_2(C_6H_4S_2)_5\cdot 2C_4H_8O$

formula	$C_{30}H_{20}S_{10}Mo_2\cdot 2C_4H_8O$	fw	1037.23
a, Å	12.370 (7)	space group	$P\bar{1}$
b, Å	16.625 (7)	temp, °C	23
c, Å	10.878 (5)	ρ_{obsd}, g cm^{-3}	1.7250
α, deg	101.53 (5)	λ, Å	0.701 69
β, deg	106.62 (4)	μ, cm^{-1}	11.5
γ, deg	103.51 (5)	$R(F_o)$	5.2
V, Å^3	1997.12	$R_w(F_o)$	6.7
Z	2		

The ligand toluene-3,4-dithiolate (tdt) has been used extensively in analytical chemistry. The standard "dithiol" analysis for molybdenum involves formation of the green complex $Mo(tdt)_3$, whose visible spectrum is used for quantitation. In early work a second complex of Mo and tdt having a red or red-purple color was reported. This complex was originally formulated[9] as $Mo(Htdt)(tdt)_2$ or $Mo(H_2tdt)(tdt)_2$ and later reformulated[10,11] as $Mo_2(tdt)_5$. No structural information was given, and the detailed formulation based on elemental analysis might be questioned in light of the report of an EPR signal in the later work.[11] Since NMR showed the material to be nominally diamagnetic, the EPR signal was likely the result of an impurity. In order to establish unequivocally the nature of this complex, we have prepared the analogous compound with benzene-1,2-dithiolate (bdt) ligands. While the tdt complex has proven impossible to crystallize (presumably due to the myriad of possible isomers), the bdt complex is readily crystallized, permitting full structural characterization.

Experimental Section

Benzene-1,2-dithiol, prepared by following published procedures,[12] was a gift from Dr. J. L. Corbin of the Charles F. Kettering Research Lab. $MoCl_4(THF)_2$ was also prepared by literature procedures.[13] Toluene-3,4-dithiol (Aldrich Chemical) was used as received. Tetrahydrofuran (THF) was distilled from Na/benzophenone under Ar; $CHCl_3$ and hexane (Burdick & Jackson) were used as received. Electronic spectra were recorded on a Hewlett-Packard 8451A diode array spectrophotometer; infrared spectra were recorded on a Perkin-Elmer 683 spectrophotometer.

$Mo_2(bdt)_5$. A sample of $MoCl_4(THF)_2$ (0.66 g, 1.73 mmol) was stirred under inert atmosphere with 10 mL of THF. Benzene-1,2-dithiol (0.74 g, 5.2 mmol) was added, and the mixture was stirred for 16 h under a slow Ar purge. Filtration yielded 350 mg of dark microcrystalline solid. Thin-layer chromatography (silica gel, 1:1 $CHCl_3$/hexane) revealed a mixture containing a small amount of green $Mo(bdt)_3$ and a larger proportion of an unidentified purple product. Shorter reaction times gave larger proportions of the $Mo(bdt)_3$, with this green species being the predominant product (>90%) when the reaction was stopped after only 10 min.

Pure $Mo_2(bdt)_5$ can be readily isolated from the mixture by dry column chromatography as follows. The solid mixture was stirred with 50 mL of $CHCl_3$ for 1 h and then filtered. The filtrate was mixed with 50 cm^3 of dry silica gel (60–200 mesh) and the solvent evaporated under reduced pressure. The impregnated silica gel was then poured on top of a column of dry silica gel (40 × 3 cm) and eluted with 1:1 $CHCl_3$/hexane. An initial green band of $Mo(bdt)_3$ was eluted off the column. The following purple band was collected and solvent allowed to evaporate slowly in air, yielding up to 300 mg of pure $Mo_2(bdt)_5$ (depending on the relative concentrations of the monomer and dimer in the starting solid). UV–vis spectra (THF) λ, nm (ε, L mol^{-1} cm^{-1}): 358 (15 400), 500 (13 700), 640 (sh).

$Mo_2(tdt)_5$. This material was prepared for comparison to the bdt complex as follows. Toluene-3,4-dithiol (5.9 g, 0.038 mol) was dissolved in a solution containing 15 mL of 5% aqueous sulfuric acid and 135 mL

---

(1) McCleverty, J. A. *Prog. Inorg. Chem.* **1969**, *10*, 49.
(2) Burns, R. P.; McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 303.
(3) Miller, J. S.; Epstein, A. J. *J. Coord. Chem.* **1979**, *8*, 191.
(4) Ahmed, M. M.; Underhill, A. E. *J. Chem. Soc., Dalton Trans.* **1983**, 165.
(5) Valade, L.; Legros, J. P.; Bousseau, M.; Cassoux, P.; Garbanskas, M.; Interrante, L. Y. *J. Chem. Soc., Dalton Trans.* **1985**, 783.
(6) Cramer, S. P.; Stiefel, E. I. In *Molybdenum Enzymes*; Spiro, T. G., Ed.; J. Wiley & Sons: New York, 1985; p 411.
(7) Cramer, S. P.; Johnson, J. L.; Ribeiro, A. A.; Millington, D. S.; Rajagopalan, K. V. *J. Biol. Chem.* **1987**, *262*, 16,357.
(8) Burgmayer, S. J. N.; Stiefel, E. I. *J. Chem. Educ.* **1986**, *62*, 943.
(9) Gilbert, T. W.; Sandell, E. B. *J. Am. Chem. Soc.* **1960**, *82*, 1087.
(10) Butcher, A.; Mitchell, P. C. H. *J. Chem. Soc., Chem. Commun.* **1967**, 176.
(11) Koyama, M.; Emoto, K.; Kawashima, M.; Fujinaga, T. *Chem. Anal. (Warsaw)* **1972**, *17*, 679.
(12) Hunig, S.; Fleckenstein, E. *Liebigs Ann. Chim.* **1970**, 738, 192.
(13) Anker, M. W.; Chatt, J.; Leigh, G. J.; Wedd, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 2639.

Table II. Positional Parameters

atom	x	y	z	B,[a] Å^2
Mo1	0.3996 (1)	0.15057 (8)	0.1823 (1)	2.209 (3)
Mo2	0.4754 (1)	0.23890 (8)	0.0191 (1)	2.14 (3)
S1	0.5699 (3)	0.2875 (2)	0.2694 (4)	2.66 (9)
S2	0.5499 (3)	0.1197 (2)	0.0823 (4)	2.49 (9)
S3	0.3260 (3)	0.0980 (2)	−0.0760 (3)	2.28 (9)
S4	0.3419 (3)	0.2653 (3)	−0.1683 (4)	3.3 (1)
S5	0.3393 (3)	0.2764 (2)	0.1466 (4)	2.53 (9)
S6	0.1917 (3)	0.0977 (2)	0.1565 (4)	3.0 (1)
S7	0.5567 (3)	0.3902 (2)	0.0493 (4)	3.2 (1)
S8	0.6100 (3)	0.2292 (2)	−0.0962 (4)	3.0 (1)
S9	0.3761 (3)	0.0044 (2)	0.1912 (4)	2.78 (9)
S10	0.4531 (3)	0.1775 (3)	0.4152 (4)	3.1 (1)
C1	0.697 (1)	0.2527 (9)	0.297 (1)	2.5 (3)*
C2	0.686 (1)	0.1760 (8)	0.213 (1)	2.3 (3)*
C3	0.784 (1)	0.1446 (9)	0.223 (1)	2.9 (3)*
C4	0.895 (1)	0.195 (1)	0.328 (2)	3.8 (4)*
C5	0.900 (1)	0.270 (1)	0.417 (2)	4.2 (4)*
C6	0.802 (1)	0.3003 (9)	0.407 (1)	3.2 (3)*
C7	0.196 (1)	0.1088 (8)	−0.181 (1)	2.2 (3)*
C8	0.209 (1)	0.1811 (9)	−0.227 (1)	2.9 (3)*
C9	0.109 (1)	0.188 (1)	−0.327 (1)	3.6 (4)*
C10	0.005 (1)	0.119 (1)	−0.376 (2)	4.5 (4)*
C11	−0.009 (1)	0.046 (1)	−0.331 (2)	4.1 (4)*
C12	0.089 (1)	0.0398 (9)	−0.229 (1)	3.2 (3)*
C13	0.183 (1)	0.2398 (9)	0.068 (1)	2.8 (3)*
C14	0.118 (1)	0.1628 (8)	0.079 (1)	2.4 (3)*
C15	−0.005 (1)	0.1363 (9)	0.028 (1)	3.2 (3)*
C16	−0.061 (1)	0.190 (1)	−0.029 (2)	3.8 (4)*
C17	0.000 (1)	0.267 (1)	−0.037 (2)	4.4 (4)*
C18	0.126 (1)	0.2942 (9)	0.008 (1)	3.2 (3)*
C19	0.605 (1)	0.3923 (9)	−0.088 (1)	2.8 (3)*
C20	0.633 (1)	0.3214 (9)	−0.145 (1)	2.7 (3)*
C21	0.681 (1)	0.326 (1)	−0.250 (2)	3.9 (4)*
C22	0.704 (1)	0.404 (1)	−0.284 (2)	3.8 (4)*
C23	0.680 (1)	0.475 (1)	−0.222 (2)	4.3 (4)*
C24	0.629 (1)	0.472 (1)	−0.119 (1)	3.6 (4)*
C25	0.354 (1)	0.0046 (9)	0.339 (1)	2.8 (3)*
C26	0.390 (1)	0.0816 (9)	0.442 (1)	2.9 (3)*
C27	0.385 (1)	0.0837 (9)	0.570 (1)	3.3 (3)*
C28	0.342 (1)	0.002 (1)	0.596 (1)	3.7 (4)*
C29	0.306 (1)	−0.076 (1)	0.490 (2)	3.7 (4)*
C30	0.312 (1)	−0.076 (1)	0.369 (1)	3.6 (4)*
O1	0.807 (1)	0.6473 (9)	0.466 (1)	8.2 (4)*
C31	0.744 (2)	0.686 (1)	0.539 (2)	7.5 (6)*
C32	0.622 (2)	0.626 (1)	0.487 (2)	7.6 (6)*
C33	0.634 (2)	0.538 (1)	0.424 (2)	7.8 (6)*
C34	0.735 (2)	0.562 (2)	0.377 (2)	9.7 (8)*
O2	0.031 (1)	0.540 (1)	0.339 (2)	9.9 (5)*
C35	0.005 (3)	0.445 (2)	0.306 (3)	12.2 (9)*
C36	−0.098 (2)	0.410 (2)	0.188 (3)	11.3 (9)*
C37	−0.083 (3)	0.481 (2)	0.124 (3)	14 (1)*
C38	−0.023 (2)	0.564 (2)	0.221 (3)	11.1 (9)*

[a] Starred values are for atoms refined isotropically. Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Selected Interatomic Distances and Angles

Distances (Å)			
Mo1–S1	2.504 (4)	Mo1–S2	2.507 (4)
Mo1–S3	2.583 (3)	Mo1–S5	2.444 (3)
Mo1–S6	2.429 (3)	Mo1–S9	2.404 (3)
Mo1–S10	2.347 (4)	Mo2–S1	2.508 (4)
Mo2–S2	2.506 (4)	Mo2–S3	2.426 (3)
Mo2–S4	2.418 (4)	Mo2–S5	2.575 (4)
Mo2–S7	2.397 (4)	Mo2–S8	2.368 (4)
S–C$_{av}$	1.75	Mo1–Mo2	2.746 (2)
Angles (deg)			
S1–Mo1–S2	74.0 (1)	S1–Mo2–S2	74.0 (1)
S3–Mo2–S4	80.3 (1)	S5–Mo1–S6	80.3 (1)
S7–Mo2–S8	82.4 (1)	S9–Mo1–S10	82.0 (1)
Mo1–S1–Mo2	66.4 (1)	Mo1–S2–Mo2	66.4 (1)
Mo1–S3–Mo2	66.5 (1)	Mo1–S5–Mo2	66.4 (1)

of 95% EtOH. A solution of Na_2MoO_4 (2.59 g, 0.0126 mol) in 150 mL of water was added rapidly with strong stirring. After being stirred for 40 min, the mixture was extracted with 2 × 250 mL of $CHCl_3$. The extracts were washed with water and dried over anhydrous $MgSO_4$. The chloroform solution was mixed with 200 cm^3 of dry silica gel, and solvent was removed under reduced pressure. The resulting mixture was poured onto a column of dry silica (60 × 7 cm). Elution with 2:1 hexane/$CHCl_3$ gave 1.85 g of pure Mo(tdt)$_3$; continued elution with pure $CHCl_3$ gave 1.6 g of Mo$_2$(tdt)$_5$. UV–vis spectra (THF) λ, nm (ε, L mol^{-1} cm^{-1}): 360 (7800), 512 (6500), 640 (sh).

X-ray Crystallography. An irregular dark violet crystal of Mo$_2$(bdt)$_5$·2THF was grown by slow evaporation of a THF/hexane solution. The crystal was glued onto the end of a glass fiber with epoxy. Preliminary examination and data collection were performed on an Enraf-Nonius CAD-4 diffractometer. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I. Table II lists the positional and thermal parameters, while Table III lists selected bond angles and bond lengths. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement by using the setting angles of 25 reflections in the range $8° < 2\theta < 28°$, measured by the computer-controlled diagonal slit method of centering. As a check on crystal quality, ω scans of several intense reflections were measured, showing an acceptable width at half-height of 0.4°. The reduced cell dimensions indicated the crystal belonged to the triclinic system, and successful refinement was carried out in the space group $P\bar{1}$. The data were collected by using the ω–2θ scan technique. The scan rate varied from 1 to 7°/min.

As a check on crystal stability, two representative standards were measured every 60 min. Instrumental problems which occurred after collection of two-thirds of the data led to the collection of the remaining data after a 2-week delay. A loss of intensity in the standards of about 11% in the last one-third of the data was corrected by using the nonlinear decay correction routine CHORT (part of the Enraf-Nonius SDP package of software). Lorentz and polarization corrections were also applied to the data. No absorption correction was applied. The positions of the Mo atoms were determined by heavy-atom (Patterson) techniques; the remaining atoms were located by successive cycles of difference Fourier synthesis and least-squares refinement using the VAX-SDP programs. Refinement was carried out by using full-matrix least-squares techniques on F, minimizing the function $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2F_o^2$. Because of the limited amount of data, only the Mo and S atoms were refined anisotropically.

Results and Discussion

Sellman and co-workers recently reported[14] a new synthesis of the well-known benzene-1,2-dithiolate (bdt) complex Mo(bdt)$_3$, involving the reaction of $MoCl_4(THF)_2$ with $C_6H_4(SH)_2$ in tetrahydrofuran (THF) under inert atmosphere. We find that if the reaction mixture is allowed to stand for periods of time exceeding the 15 min reported by Sellman, the yields of green Mo(bdt)$_3$ are reduced at the expense of formation of a purple product we have characterized as the dimer Mo$_2$(bdt)$_5$. After 16 h, thin-layer chromatography on silica gel with $CHCl_3$/hexane (1:1) eluent shows the predominant product to be this purple dimer. Column chromatography gives first a green band of Mo(bdt)$_3$ and then a dark purple band of the dimer. Removal of solvent from the purple band yields pure Mo$_2$(bdt)$_5$ in up to 40% yield. Comparison of electronic and infrared spectra clearly show that the Mo$_2$(bdt)$_5$ dimer is homologous with the previously reported purple tdt complex.

Slow evaporation of a THF/hexane solution produced small irregular dark purple crystals of Mo$_2$(bdt)$_5$·2THF that proved suitable for the single-crystal x-ray diffraction study. The structure, illustrated in Figure 1, consists of discrete Mo$_2$(bdt)$_5$ and THF molecules with no intermolecular contacts shorter than van der Waals distances. The distance between the two Mo atoms of 2.746 (2) Å is consistent with the presence of a single bond, as expected for a diamagnetic d^1–d^1 Mo(V) dimer. The dimer has approximate C_2 symmetry with the five bdt ligands adopting three distinct coordination modes. One ligand on each Mo is a simple bidentate chelate. A second ligand chelates each Mo and bridges to the second Mo through one S atom. A single symmetrically bridging ligand completes the coordination. The overall

---

[14] Sellmann, D.; Zapf, L. *Z. Naturforsch.* **1985**, 40b, 380.

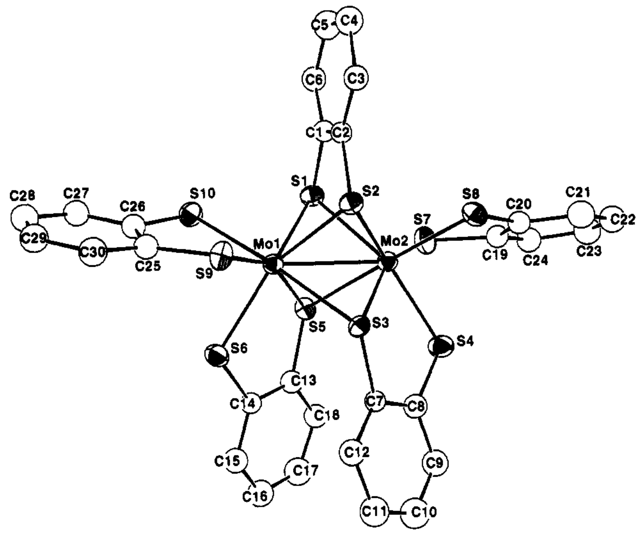

Figure 1. ORTEP drawing of the structure of the $Mo_2(bdt)_5$ molecule, showing the atom-labeling scheme.

structure is closely related to the structure[15] of $Mo_2(S_2)[S_2C_2(C_6H_5)_2]_4$, the primary difference being replacement of the symmetrically bridging S_2 ligand in the earlier structure by the bridging dithiolene containing S1 and S2 in the present structure. The two simple bidentate bdt ligands have mean Mo–S bond lengths of 2.38 Å. This compares closely to the mean Mo–S length of 2.37 Å observed[16] for $Mo(bdt)_3$ and for the corresponding terminal dithiolene ligands in $Mo_2(S_2)[S_2C_2(C_6H_5)_2]_4$. The ligand planes are also tipped from their respective Mo–S–S planes by 29.4 and 21.5°, much like the corresponding bdt ligands in $Mo(bdt)_3$, which are tipped between 13 and 30°. The two "half-bridging" bdt ligands act as simple chelating ligands to one Mo, with slightly elongated Mo–S bonds (mean 2.429 Å) and with the addition of a longer bridging bond (mean 2.579 Å) crossing over to the other Mo atom. The ligand planes of these bdt's are also tipped with respect to the Mo–S–S planes of the Mo atoms to which they chelate, by 14.8 and 18.5°. The fifth bdt ligand has both sulfur atoms (S1 and S2) located in symmetrical bridging positions, with the mean of the four Mo–S distances being 2.506 Å. The ligand plane of this bdt ligand is inclined a slight 2.6° from the vector connecting the two Mo atoms. Rather short S–S distances are observed between S1 and S5 (2.73 Å) and between S2 and S3 (2.71 Å). These distances are significantly longer than an S–S single bond ($\sim$2.05 Å) but much shorter than the sum of the van der Waals radii for nonbonded sulfurs (3.7 Å). A similar short S–S interaction (2.74 Å) was observed between the bridging sulfurs from the dithiolenes in $Mo_2(S_2)[S_2C_2(C_6H_5)_2]_4$ and between thiolate sulfur donor atoms bound to a single Mo center.[17,18]

The coordination geometry of the seven sulfur atoms bonded to each Mo has been compared to typical 7-coordination polyhedra (capped octahedron, CO; capped trigonal prism, CTP; pentagonal bipyramid, PB) by the method of Dollase[19] as implemented in a computer program written by Drew.[20] This program calculates the root-mean-square deviation of the observed coordinates from the ideal coordination polyhedra. For Mo1 the root-mean-square deviations from CTP, CO, and PB are 0.126, 0.132, and 0.239 Å, respectively. Thus, the geometry about Mo1 can be described equally well as a slightly distorted CTP, with S6 capping a rectangular face, or as a slightly distorted CO, with S1 capping a triangular face. An even more useful description of the geometry is the 3:4:3 arrangement of four donor atoms (S1, S2, S3, S5) parallel to a plane of three donor atoms (S6, S9, S10). As shown by Drew,[21] this geometry typically gives root-mean-square fits to CTP and CO similar to those observed in this case. If the geometry about Mo2 is combined with that about Mo1, it seems that the best overall description of the structure is a 3:4:3 double-decker sandwich. This structure is interestingly related to a number of $(CpMo)_2$"S_4" structures discussed by Rakowski DuBois and co-workers,[22] wherein the outer sets of three donors in the 3:4:3 arrangement are provided by the Cp ligands and the inner four sulfurs are provided by any of several combinations of sulfido, 1,1-alkanedithiolato, and 1,2-alkene- or 1,2-alkanedithiolato ligands.

The present structure reveals the versatility of "dithiolene" type ligands, confirms the proclivity of Mo(V) complexes to be dinuclear, and establishes unequivocally the stoichiometric and structural nature of the additional product of reactions which form tris(dithiolene)molybdenum complexes.

Supplementary Material Available: Tables SI–SV, listing bond distances, bond angles, and anisotropic thermal parameters for $Mo_2(bdt)_5$ and bond distances and angles for the THF solvate (8 pages); a table of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

---

(15) Bravard, D. C.; Newton, W. E.; Huneke, J. T.; Yamanouchi, K.; Enemark, J. H. *Inorg. Chem.* **1982**, *21*, 3795.

(16) Cowie, M.; Bennett, M. J. *Inorg. Chem.* **1976**, *15*, 1584.

(17) Berg, J. M.; Spira, D. J.; Hodgson, K. O.; Bruce, A. E.; Miller, K. F.; Corbin, J. L.; Stiefel, E. I. *Inorg. Chem.* **1984**, *23*, 3412.

(18) Stiefel, E. I.; Miller, K. F.; Bruce, A. E.; Corbin, J. L.; Berg, J. M.; Hodgson, K. O. *J. Am. Chem. Soc.* **1980**, *102*, 3624.

(19) Dollase, W. A. *Acta Cryst.* **1974**, *A30*, 513.

(20) A copy of the FORTRAN program and numerous helpful comments were provided by Prof. M. G. B. Drew, Department of Chemistry, The University, Whiteknights, Reading, England.

(21) Drew, M. G. B. *Prog. Inorg. Chem.* **1977**, *23*, 78.

(22) Laurie, J. C. V.; Duncan, L.; Haltiwanger, R. C.; Weberg, R. T.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6234 and references therein.

Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Isolation and Characterization of the Redox Pair $[Re_2H_5(PMe_3)_6](PF_6)_n$ (*n* = 1 or 2)

Dawn R. Root, Karen E. Meyer, and Richard A. Walton*

Received February 8, 1989

The dirhenium octahydride complexes of general stoichiometry $Re_2H_8(PR_3)_4$[1,2] are the most hydrogen rich of the known neutral dirhenium polyhydrides.[3] For two of these derivatives (PR_3 = PPh_3 and PMe_2Ph), studies of their chemistry have included various aspects of their redox[4] and protonation[5] behavior, as well as their reactions with certain nucleophiles (nitrile and isocyanide ligands)[4,6] and with copper(I),[7] gold(I),[8] and tin(II)[9] reagents; the latter lead to mixed Cu–Re, Au–Re, and Sn–Re clusters. With our development of a convenient synthetic route to a much wider range of complexes of the type $Re_2H_8(PR_3)_4$ (PR_3 represents a

---

(1) Chatt, J.; Coffey, R. A. *J. Chem. Soc. A* **1969**, 1963.

(2) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872.

(3) Conner, K. A.; Walton, R. A. In *Comprehensive Coordination Chemistry*; Pergamon: Oxford, England 1987; Chapter 43, pp 125–213.

(4) (a) Allison, J. D.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1983**, 401. (b) Allison, J. D.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 163.

(5) Moehring, G. A.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 1861.

(6) Allison, J. D.; Cotton, F. A.; Powell, G. L.; Walton, R. A. *Inorg. Chem.* **1984**, *23*, 159.

(7) Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 5137.

(8) Mueting, A. M.; Bos, W.; Alexander, B. D.; Boyle, P. D.; Casalnuovo, J. A.; Balaban, S.; Ito, L. N.; Johnson, S. M.; Pignolet, L. H. *New. J. Chem.* **1988**, *12*, 505.

(9) Westerberg, D. E.; Sutherland, B. R.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1988**, *110*, 1642.