Inorg. Chem. **1992**, *31*, 3891-3896

Synthesis, Structure, and Characterization of the Diimido-Bridged, Bimetallic Molybdenum(V) Complex Bis(diethyldithiocarbamato)bis(μ-2-aminothiophenolato)oxodimolybdenum(V)-Bis(dichloromethane), (dtc)MoO(μ-NC_6H_4S)$_2$Mo(dtc)·$2CH_2Cl_2$, and of the Precursor in the Formation of this Bimetallic Molybdenum(V) Complex, Bis(diethyldithiocarbamato)(2-aminothiophenolato)(methoxy)molybdenum(VI), Mo(NC_6H_4S)(OCH_3)(dtc)$_2$[1]

Martin Minelli,*,† Roger L. Kuhlman,† Steven J. Shaffer,† and Michael Y. Chiang‡

Departments of Chemistry, Grinnell College, Grinnell, Iowa 50112, and Washington University, One Brookings Drive, St. Louis, Missouri 63130

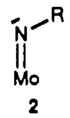
Received December 13, 1991

As previously reported, the reaction of $MoOCl_2(dtc)_2$ (dtc = diethyldithiocarbamate) with 2-aminothiophenol yields the imido complex $Mo(NC_6H_4S)Cl(dtc)_2$. When $MoOX_2(dtc)_2$ (X = F, Br; X_2 = dtc, O) and $Mo_2O_3(dtc)_4$ are reacted with 2-aminothiophenol, a common product, the bimetallic, diimido-bridged Mo(V) complex (dtc)MoO(μ-NC_6H_4S)$_2$Mo(dtc) (**I**) is formed. The structure of **I** has been determined by X-ray crystallography at −100 °C. The crystals are orthorhombic, space group *Pbca* with a = 13.579 (3) Å, b = 19.669 (6) Å, c = 26.001 (8) Å, and Z = 8. The structure was refined to $R = 4.20\%/R_w = 4.47\%$ using 4547 independent reflections. Excluding the Mo–Mo bond, Mo(1) is six-coordinate with a distorted octahedral symmetry; Mo(2) is five-coordinate. The Mo–Mo distance is 2.659 (1) Å, indicating a bond between the molybdenum atoms. The molybdenum atoms and the two bridging imido nitrogens are not coplanar, but are in a "butterfly" arrangement. The Mo–N distances are slightly shorter toward Mo(1) (1.927 (5) and 1.917 (5) Å) than toward Mo(2) (1.992 (5) and 2.018 (5) Å). The molybdenum–sulfur distances range from 2.413 to 2.521 Å. The 2-aminothiophenol sulfurs are slightly closer to Mo(1) than the dithiocarbamate sulfurs. The Mo(2)–O distance is 1.679 Å. The bond corresponds to a band at 956 cm^{-1} in the infrared spectrum. **I** has a quasi-reversible two-electron reduction peak in the cyclic voltammogram at −0.91 V. An intermediate, $Mo(NC_6H_4S)(OCH_3)(dtc)_2$ (**II**) was observed during the reaction of all of the Mo(VI) starting materials with 2-aminothiophenol in methanol. When **II** is heated under vacuum, **I** is formed. The structure of **II** has been determined by X-ray crystallography at room temperature. The crystals are monoclinic, space group *C2/c* with a = 35.287 (8) Å, b = 9.896 (4) Å, c = 14.179 (3) Å, β = 112.20 (2)°, and Z = 8. The structure was refined to $R = 3.56\%/R_w = 5.71\%$ using 4039 independent reflections. The geometry of the complex is distorted pentagonal bipyramidal. The molybdenum–imido nitrogen distance is 1.772 (4) Å and the imido linkage (Mo–N(3)–C(11)) has an angle of 136.4 (4)°. The O–Mo–N(3) angle is 160.7 (2)°. The complex has a ^{95}Mo NMR signal at 200 ppm. The imido nitrogen absorbs at 70 ppm in the ^{14}N NMR spectrum.

Introduction

Relatively few Mo(VI) and Mo(V) imido complexes have been synthesized and characterized by X-ray crystallography.[2-16] Although the most common method for the synthesis of organoimido complexes is via deprotonation of primary amines, Mo(VI) and Mo(V) complexes have been mainly synthesized by oxo/imido exchange reactions using phosphinimines, sulfinylamines, arylazides and isocyanates.[2-14] Two Lewis structures have been proposed for the metal nitrogen bond in imido complexes.[5] In structure **1**, the nitrogen acts as a four π-electron donor and a Mo–N–R angle close to 180° is expected; in structure **2**, the nitrogen acts as a two π-electron donor and the Mo–N–R linkage is bent. The majority of the known Mo(VI) imido compounds have linear imido linkages. We have reacted $MoOCl_2(dtc)_2$ with substituted anilines to synthesize Mo(VI) imido complexes with linear and bent imido linkages.[15,16] Aniline itself will not form imido compounds under the same experimental conditions. The reaction of 2-aminothiophenol with $MoOCl_2(dtc)_2$ yields $Mo(NC_6H_4S)Cl(dtc)_2$,[16] a compound with a bent imido linkage. We tried to synthesize two related $Mo(NC_6H_4S)X$-

1



2

---

† Grinnell College.

‡ Washington University.

(1) This work was presented at the 26th ACS Midwest Regional Meeting, Omaha, NE, Nov. 6–8, 1991.

(2) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123 and references therein.

(3) Maatta, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 2409.

(4) Haymore, B. L.; Maatta, E. A.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1979**, *101*, 2063.

(5) Maatta, E. A.; Haymore, B. L.; Wentworth, R. A. D. *Inorg. Chem.* **1980**, *19*, 1055.

(6) Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Neaves, B. D.; Dahlstrom, P.; Hyde, J.; Zubieta, J. *J. Organomet. Chem.* **1981**, *213*, 109.

(7) Chou, C. Y.; Devore, D. D.; Huckett, S. C.; Maatta, E. A.; Huffman, J. C.; Takusagawa, F. *Polyhedron* **1986**, *5*, 301.

(8) Chou, C. Y.; Huffman, J. C.; Maatta, E. A. *Inorg. Chem.* **1986**, *25*, 822.

(9) Green, M. L. H.; Moynihan, K. J. *Polyhedron* **1986**, *5*, 921.

(10) Hogarth, G.; Konidaris, P. C. *J. Organomet. Chem.* **1990**, *399*, 149.

(11) Green, M. L. H.; Hogarth, G.; Konidaris, P. C.; Mountford, P. *J. Organomet. Chem.* **1990**, *394*, C9.

(12) Green, M. L. H.; Hogarth, G.; Konidaris, P. C.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1990**, 3781.

(13) Fletcher, J.; Hogarth, G.; Tocher, D. A. *J. Organomet. Chem.* **1991**, *403*, 345.

(14) Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 186.

(15) Minelli, M; Carson, M. R.; Whisenhunt, D. W., Jr.; Hubbard, J. L. *Inorg. Chem.* **1990**, *29*, 442.

(16) Minelli, M; Carson, M. R.; Whisenhunt, D. W., Jr.; Imhof, W.; Huttner, G. *Inorg. Chem.* **1990**, *29*, 4801.

0020-1669/92/1331-3891$03.00/0

Table I. Crystallographic Data for I and II

chem formula	$Mo_2S_6ON_4C_{22}H_{28}{\cdot}2CH_2Cl_2$	$MoS_5ON_3C_{17}H_{27}$
fw	918.6	545.7
space group	*Pbca*	*C*2/*c*
unit cell dimens		
a, Å	13.579 (3)	35.287 (8)
b, Å	19.669 (6)	9.896 (4)
c, Å	26.001 (8)	14.179 (3)
β, deg		112.20 (2)
vol, Å^3	6944 (3)	4584 (2)
Z	8	8
T, °C	−100	22
λ, Å	0.710 73	0.710 73
ρ_{calc}, g/cm^3	1.757	1.581
μ, cm^{-1}	13.9	10.09
final *R* indices (obs)	*R* = 4.20% R_w = 4.47%	*R* = 3.56% R_w = 5.71%

$(dtc)_2$ (X = F, Br) compounds by reacting $MoOX_2(dtc)_2$ (X = F, Br) with 2-aminothiophenol to study the changes in the structural and physical properties due to halogen replacement. The final products of these reactions were not the expected mononuclear analogues, but a novel bimetallic Mo(V) compound whose structure and properties are described in this paper.

Experimental Part

All reactions were performed under an argon atmosphere using standard Schlenk techniques unless otherwise mentioned. The solvents were dried and distilled prior to use. $MoOBr_2(dtc)_2$,[17] $[MoO(dtc)_3]BF_4$,[18] $MoO_2(dtc)_2$,[19] and $Mo_2O_3(dtc)_4$[20] were synthesized according to the literature. 2-Aminothiophenol and HF (70% in pyridine) were purchased from Aldrich and used without further purification. The elemental analyses were carried out by Atlantic Microlab, Inc., Norcross, GA.

Preparation of $MoOF_2(dtc)_2$. The compound was prepared by an adaptation of the method described by Weiss, et al.[17] A suspension of $MoO_2(dtc)_2$ (3.0 g, 7.1 mmol) in a 4:1 mixture of hexanes/ether (about 70 mL) was stirred in a 500-mL polyethylene bottle, equipped with a screwtop lid. To the suspension was added excess HF (70% in pyridine, 3.0 mL) and the cap was screwed on tightly. The reaction was allowed to stir for 18 h, and the solvent was decanted. The sticky yellow solid was washed with 4:1 hexanes/ether to remove any residual HF and transferred to a Schlenk flask for reaction with 2-aminothiophenol. The yellow product is quite unstable after separation from the suspension and turns purple when allowed to stand in air. The presence of fluorine was confirmed by ^{19}F NMR spectroscopy. An Mo=O stretch in the IR spectrum at 942 cm^{-1} (lit.[17] value: 945 cm^{-1}) was observed. Anal. Calcd for $MoOF_2S_4N_2C_{10}H_{20}$: C, 26.90; H, 4.52, N, 6.27; S, 28.72. Found: C, 26.28; H, 4.18; N, 5.78; S, 28.11.

Preparation of $(dtc)MoO(\mu\text{-}NC_6H_4S)_2Mo(dtc)$ (I). A 2.0-g sample of $MoOBr_2(dtc)_2$ (3.6 × 10^{-3} mol) was suspended in 40 mL of methanol. Then 0.40 mL (3.7 × 10^{-3} mol) of 2-aminothiophenol was added dropwise with a gastight syringe, followed by 1.2 mL (8.6 × 10^{-3} mol) of triethylamine. The suspension was then refluxed for 7 h, cooled to room temperature, and filtered. A black-brown solid was isolated and recrystallized from CH_2Cl_2/hexanes; yield 0.6 g (40%).

To grow crystals for X-ray crystallography, the compound was dissolved in CH_2Cl_2 and a layer of hexanes was added to the top. After 2–3 weeks, crystals suitable for X-ray crystallography had formed. The crystals contain two molecules of CH_2Cl_2 per complex. After filtration and drying in vacuo, the crystals lose one molecule of CH_2Cl_2. Anal. Calcd for $Mo_2S_6ON_4C_{22}H_{28}{\cdot}CH_2Cl_2$: C, 33.14; H, 3.63; N, 6.72; S, 23.07. Found: C, 33.13; H, 3.72; N, 6.78; S, 23.09.

The complex can also be synthesized, using different reaction times, from other Mo(VI) starting materials such as $[MoO(dtc)_3]BF_4$ (16 h), $MoO_2(dtc)_2$ (24 h), and $MoOF_2(dtc)_2$ (4 days).

When $Mo_2O_3(dtc)_4$ is reacted with 2 equiv. of 2-aminothiophenol in the absence of triethylamine, I is formed after 2 $^1/_2$ h. Another route to obtain I is by heating $Mo(NC_6H_4S)(OCH_3)(dtc)_2$ (II) for 18 h under vacuum at 180 °C. The yield is quantitative.

Table II. Atomic Coordinates (×10^5) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^4) for I

	x	*y*	*z*	*U*(eq)[a]
Mo(1)	17368 (4)	8897 (3)	13472 (2)	149 (1)
Mo(2)	4367 (4)	18940 (3)	14368 (2)	142 (1)
S(1)	6164 (12)	30758 (8)	11620 (6)	231 (5)
S(2)	911 (12)	26366 (8)	21759 (6)	194 (5)
S(3)	4467 (13)	2837 (8)	8674 (6)	242 (5)
S(4)	19680 (12)	−3779 (8)	14253 (6)	230 (5)
S(5)	32237 (12)	9384 (9)	8305 (6)	250 (5)
S(6)	29596 (11)	8459 (9)	20199 (6)	235 (5)
O(1)	−6549 (30)	16178 (22)	12175 (16)	237 (13)
N(1)	155 (41)	39516 (26)	18809 (18)	213 (16)
N(2)	6896 (39)	−10586 (24)	8176 (19)	205 (16)
N(3)	10014 (34)	12046 (24)	19300 (18)	145 (15)
N(4)	15047 (36)	16884 (24)	9351 (19)	186 (15)
C(1)	2089 (43)	33265 (31)	17626 (24)	192 (18)
C(2)	803 (62)	44925 (34)	14843 (26)	377 (25)
C(3)	−8502 (66)	45259 (39)	11757 (31)	535 (32)
C(4)	−3397 (48)	41531 (33)	23959 (23)	260 (20)
C(5)	4770 (58)	44431 (39)	27239 (26)	413 (26)
C(6)	9838 (46)	−4813 (31)	10112 (23)	199 (19)
C(7)	11850 (55)	−17092 (30)	9296 (27)	315 (23)
C(8)	5308 (60)	−22155 (36)	12045 (29)	417 (26)
C(9)	−1559 (53)	−10811 (34)	4634 (25)	319 (23)
C(10)	−11529 (51)	−10529 (36)	7275 (30)	391 (26)
C(11)	21983 (45)	9556 (31)	25530 (24)	213 (19)
C(12)	25206 (53)	9211 (36)	30649 (24)	287 (21)
C(13)	18866 (55)	10727 (34)	34588 (24)	309 (22)
C(14)	9188 (55)	12523 (33)	33528 (26)	295 (22)
C(15)	5768 (48)	13031 (30)	28506 (23)	215 (19)
C(16)	12286 (43)	11601 (29)	24507 (23)	176 (18)
C(17)	28978 (47)	15923 (31)	4057 (23)	208 (19)
C(18)	20003 (44)	19181 (29)	5019 (22)	172 (17)
C(19)	16568 (51)	24197 (31)	1639 (22)	229 (19)
C(20)	22249 (51)	26076 (34)	−2554 (24)	264 (21)
C(21)	31440 (55)	23022 (34)	−3327 (25)	312 (23)
C(22)	34780 (51)	17947 (34)	−58 (25)	301 (22)
Cl(1)	79099 (17)	6016 (13)	2310 (8)	598 (8)
Cl(2)	57985 (17)	8262 (12)	1330 (9)	571 (8)
Cl(3)	76346 (18)	31888 (15)	17160 (9)	735 (10)
Cl(4)	76136 (17)	30202 (18)	28121 (9)	845 (12)
C(23)	69045 (68)	7066 (42)	−1904 (29)	556 (33)
C(24)	75027 (57)	26200 (38)	22212 (26)	361 (25)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Preparation of $Mo(NC_6H_4S)(OCH_3)(dtc)_2$ (II). The same quantities and conditions described for I were used. The suspension was refluxed for 4 h using $MoOBr_2(dtc)_2$. After cooling, a red-brown solid was filtered off and recrystallized from CH_2Cl_2/hexanes; yield 1.4 g (70%). Crystals for X-ray crystallography were grown by dissolving the compound in CH_2Cl_2 and adding a layer of hexanes to the solution. Suitable crystals had formed after 1 week.

Anal. Calcd for $MoS_5ON_3C_{17}H_{27}$: C, 37.42; H, 4.99; N, 7.70; S, 29.38. Found: C, 36.82; H, 4.78; N, 7.53; S, 28.75.

II has also been observed as an intermediate in the reactions of $MoOF_2(dtc)_2$, $MoO_2(dtc)_2$, and $MoO(dtc)_3{}^+$ with 2-aminothiophenol.

Preparation of $Mo(NC_6H_4S)F(dtc)_2$ (III). When the synthesis of I was carried out with $MoOF_2(dtc)_2$ as starting material, a red-brown solid, III, was isolated after 18 h of refluxing. The compound was recrystallized in CH_2Cl_2/hexanes; yield 0.7 g (28%). The presence of fluorine in the compound was confirmed by ^{19}F NMR spectroscopy (Table VI). Anal. Calcd for $MoS_5FN_3C_{16}H_{24}{\cdot}1CH_2Cl_2$: C, 31.66; H 4.07; N, 6.52; S, 24.86. Found: C, 32.12; H, 4.07; N, 6.97; S, 24.54.

X-ray Structure Determination. Diffraction data for both compounds were collected with ω scan mode on a Siemens R3m/V diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Space group determinations were based on systematic absences and photographic evidence. All computations used the SHELXTL PLUS package of programs (SHELXTL PLUS, G. Sheldrick, Universität Göttingen, Göttingen, West Germany, 1988).

---

(17) Dirand, J.; Ricard, L.; Weiss, R. *J. Chem. Soc., Dalton Trans.* **1976**, 278.

(18) Young, C. G.; Broomhead, J. A.; Boreham, C. J. *J. Chem. Soc., Dalton Trans.* **1983**, 2135.

(19) Moore, F. N.; Larson, M. L. *Inorg. Chem.* **1967**, *6*, 998.

(20) Newton, W. E.; Corbin, J. L.; Bravard, D. C.; Searles, J. E.; McDonald, J. W. *Inorg. Chem.* **1974**, *13*, 1100.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for I

Mo(1)–Mo(2)	2.659 (1)	Mo(1)–S(3)	2.459 (2)
Mo(1)–S(4)	2.521 (2)	Mo(1)–S(5)	2.427 (2)
Mo(1)–S(6)	2.413 (2)	Mo(1)–N(3)	1.917 (5)
Mo(1)–N(4)	1.927 (5)	Mo(2)–S(1)	2.444 (2)
Mo(2)–S(2)	2.459 (2)	Mo(2)–O(1)	1.679 (4)
Mo(2)–N(3)	2.018 (5)	Mo(2)–N(4)	1.992 (5)
S(5)–C(17)	1.752 (6)	S(6)–C(11)	1.742 (6)
N(3)–C(16)	1.391 (8)	N(4)–C(18)	1.388 (8)
Mo(2)–Mo(1)–S(3)	86.1 (1)	Mo(2)–Mo(1)–S(4)	144.1 (1)
S(3)–Mo(1)–S(4)	69.5 (1)	Mo(2)–Mo(1)–S(5)	124.8 (1)
S(3)–Mo(1)–S(5)	109.3 (1)	S(4)–Mo(1)–S(5)	88.9 (1)
Mo(2)–Mo(1)–S(6)	114.8 (1)	S(3)–Mo(1)–S(6)	147.2 (1)
S(4)–Mo(1)–S(6)	79.7 (1)	S(5)–Mo(1)–S(6)	80.2 (1)
Mo(2)–Mo(1)–N(3)	49.1 (1)	S(3)–Mo(1)–N(3)	100.7 (1)
S(4)–Mo(1)–N(3)	108.7 (1)	S(5)–Mo(1)–N(3)	149.1 (1)
S(6)–Mo(1)–N(3)	78.3 (1)	Mo(2)–Mo(1)–N(4)	48.3 (1)
S(3)–Mo(1)–N(4)	89.8 (2)	S(4)–Mo(1)–N(4)	150.6 (2)
S(5)–Mo(1)–N(4)	78.2 (2)	S(6)–Mo(1)–N(4)	123.0 (2)
N(3)–Mo(1)–N(4)	95.2 (2)	Mo(1)–Mo(2)–S(1)	127.9 (1)
Mo(1)–Mo(2)–S(2)	129.5 (1)	S(1)–Mo(2)–S(2)	71.5 (1)
Mo(1)–Mo(2)–O(1)	108.4 (1)	S(1)–Mo(2)–O(1)	107.3 (2)
S(2)–Mo(2)–O(1)	106.8 (2)	Mo(1)–Mo(2)–N(3)	45.9 (1)
S(1)–Mo(2)–N(3)	141.9 (1)	S(2)–Mo(2)–N(3)	88.6 (1)
O(1)–Mo(2)–N(3)	109.5 (2)	Mo(1)–Mo(2)–N(4)	46.3 (1)
Mo(1)–N(3)–Mo(2)	85.0 (2)	Mo(1)–N(3)–C(16)	129.3 (4)
Mo(2)–N(3)–C(16)	138.2 (4)	Mo(1)–N(4)–Mo(2)	85.4 (2)
Mo(1)–N(4)–C(18)	129.6 (4)	Mo(2)–N(4)–C(18)	144.9 (4)

Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for II

	x	y	z	U(eq)[a]
Mo	1154 (1)	2004 (1)	6920 (1)	31 (1)
S(1)	1876 (1)	1314 (1)	8012 (1)	41 (1)
S(2)	1484 (1)	650 (1)	5937 (1)	42 (1)
S(3)	461 (1)	2846 (1)	6782 (1)	41 (1)
S(4)	616 (1)	1602 (1)	5174 (1)	44 (1)
S(5)	1281 (1)	3104 (1)	8626 (1)	43 (1)
O(1)	1003 (1)	433 (3)	7531 (2)	40 (1)
N(1)	2228 (1)	−325 (4)	7062 (3)	41 (1)
N(2)	−146 (1)	2297 (4)	4993 (3)	44 (1)
N(3)	1291 (1)	3681 (3)	6746 (3)	36 (1)
C(1)	1915 (1)	430 (4)	7016 (3)	36 (1)
C(2)	2586 (1)	−477 (5)	8020 (4)	50 (2)
C(3)	2562 (2)	−1711 (6)	8598 (4)	65 (2)
C(4)	2234 (2)	−1085 (5)	6178 (4)	52 (2)
C(5)	2491 (2)	−420 (8)	5699 (4)	77 (3)
C(6)	251 (1)	2261 (4)	5565 (3)	41 (2)
C(7)	−437 (1)	2858 (5)	5404 (4)	52 (2)
C(8)	−479 (2)	4361 (6)	5342 (5)	62 (2)
C(9)	−302 (2)	1796 (6)	3929 (4)	57 (2)
C(10)	−346 (2)	2925 (6)	3188 (4)	72 (3)
C(11)	1365 (1)	4862 (4)	7290 (3)	42 (2)
C(12)	1428 (1)	6131 (5)	6930 (4)	52 (2)
C(13)	1484 (2)	7251 (5)	7561 (6)	70 (3)
C(14)	1483 (2)	7099 (6)	8535 (6)	72 (3)
C(15)	1427 (2)	5875 (5)	8884 (4)	58 (2)
C(16)	1364 (1)	4732 (5)	8282 (3)	42 (2)
C(17)	870 (2)	157 (5)	8268 (4)	60 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Selected Bond Lengths (Å) and Bond Angles (deg) for II

Mo–S(1)	2.524 (1)	Mo–S(2)	2.514 (2)
Mo–S(3)	2.520 (2)	Mo–S(4)	2.518 (1)
Mo–S(5)	2.533 (2)	Mo–O(1)	1.948 (3)
Mo–N(3)	1.772 (4)	S(1)–C(1)	1.711 (5)
S(2)–C(1)	1.716 (4)	S(3)–C(6)	1.701 (5)
S(4)–C(6)	1.711 (6)	S(5)–C(16)	1.740 (5)
O(1)–C(17)	1.325 (8)	N(1)–C(1)	1.313 (6)
N(2)–C(6)	1.329 (5)	N(3)–C(11)	1.370 (6)
S(1)–Mo–S(2)	67.9 (1)	S(1)–Mo–S(3)	149.6 (1)
S(2)–Mo–S(3)	140.5 (1)	S(1)–Mo–S(4)	140.5 (1)
S(2)–Mo–S(4)	72.9 (1)	S(3)–Mo–S(4)	68.1 (1)
S(1)–Mo–S(5)	75.9 (1)	S(2)–Mo–S(5)	143.7 (1)
S(3)–Mo–S(5)	75.5 (1)	S(4)–Mo–S(5)	143.4 (1)
S(1)–Mo–O(1)	83.8 (1)	S(2)–Mo–O(1)	94.7 (1)
S(3)–Mo–O(1)	83.1 (1)	S(4)–Mo–O(1)	94.6 (1)
S(5)–Mo–O(1)	84.2 (1)	S(1)–Mo–N(3)	94.2 (1)
S(2)–Mo–N(3)	102.3 (1)	S(3)–Mo–N(3)	89.3 (1)
S(4)–Mo–N(3)	98.9 (1)	S(5)–Mo–N(3)	76.8 (1)
O(1)–Mo–N(3)	160.7 (2)	Mo–S(1)–C(1)	90.6 (1)
Mo–O(1)–C(17)	138.8 (3)	C(1)–N(1)–C(2)	121.1 (4)
C(7)–N(2)–C(9)	119.0 (4)	Mo–N(3)–C(11)	136.4 (4)

The data collection on compound I was carried out at −100 °C, and the structure was solved using the heavy atom method. The data for compound II were collected at ambient temperature, and the structure was solved by direct methods. Both structures were completed by successive full-matrix least-squares refinements and difference electron density map calculations. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed at idealized positions, riding upon their respective carbon atoms. Table I provides the crystallographic data. Fractional atomic coordinates and equivalent isotropic displacement parameters (Tables II and IV), selected bond lengths and bond angles (Table III and V) are also provided. Complete lists of the crystallographic data, anisotropic displacement parameters, bond lengths, bond angles, isotropic parameters, and structure factors are available as supplementary material.

NMR Spectra. The NMR spectra were measured on a Bruker AC 300-MHz NMR spectrometer. For the ^{1}H and ^{13}C NMR spectra a 5-mm dual ^{1}H/^{13}C probehead was used. ^{14}N and ^{95}Mo NMR spectra were measured on a 10-mm broadband probehead (^{109}Ag–^{31}P) with digital tuning. For the ^{1}H and ^{13}C NMR spectra the residual solvent was used as an internal reference. For the other nuclei external standards were used: nitromethane, neat (^{14}N NMR); 2 M Na_2MoO_4 in D_2O, basic (^{95}Mo NMR); CF_3COOD (^{19}F NMR). The ^{19}F NMR spectra were measured on a Bruker 500-MHz NMR spectrometer.

Electronic Spectra. The electronic spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer using 1.0-cm quartz cells.

IR Spectra. The infrared spectra were measured on a Nicolet 5SXB FT-IR spectrometer using KBr pellets.

Electrochemistry. The cyclic voltammograms were recorded using a PAR 175 universal programmer and a PAR 173 potentiostat. The three-electrode electrochemical cell consisted of a platinum-disk working electrode, a platinum-wire auxiliary electrode, and a silver electrode as a reference electrode. The potentials were corrected to potentials vs SCE using ferrocene as an internal standard. The complexes were dissolved (5 × 10^{-4} M) in acetonitrile in the presence of 0.1 M tetrabutylammonium tetrafluoroborate as electrolyte. The chronocoulometry experiment was performed using a PAR 273 potentiostat/galvanostat and PAR Electrochemical Analysis System software.

Results and Discussion

The compounds $MoOX_2(dtc)_2$ (X = F, Br; X_2 = dtc, O) react with 2-aminothiophenol in methanol to form the bimetallic Mo(V) complex $(dtc)MoO(\mu\text{-}NC_6H_4S)_2Mo(dtc)$ (**I**). During all reactions, the precursor $Mo(NC_6H_4S)(OCH_3)(dtc)_2$ (**II**) can be isolated. **II** can be converted to I quantitatively by heating the solid under vacuum at 180 °C. This shows that the terminal oxygen in I comes from the methoxy ligand. Two intermediates have been isolated and identified in the reaction of $MoOF_2(dtc)_2$ with 2-aminothiophenol, $Mo(NC_6H_4S)F(dtc)_2$ (**III**) and **II**. The sequential formation of these two products is consistent with the overall reaction sequence shown in Figure 1. We also heated **III** under vacuum, and as expected, I was not formed. There was no evidence for the formation of $Mo(NC_6H_4S)Br(dtc)_2$ during the reaction with $MoOBr_2(dtc)_2$; only **II** was observed. The same reaction with $MoOCl_2(dtc)_2$, even after 5 days of refluxing, produces only a small amount of I; the main product is still $Mo(NC_6H_4S)Cl(dtc)_2$.

I can also be synthesized from the Mo(V) dimer $Mo_2O_3(dtc)_4$ and two equivalents of 2-aminothiophenol.[21] No intermediates were observed during this reaction.

Structures. The structures of I and **II** have been determined by X-ray crystallography.

An ORTEP diagram of I is shown in Figure 2. Selected bond lengths and bond angles are listed in Table III.

---

[21] Coghill, A. L.; Minelli, M. Unpublished results.

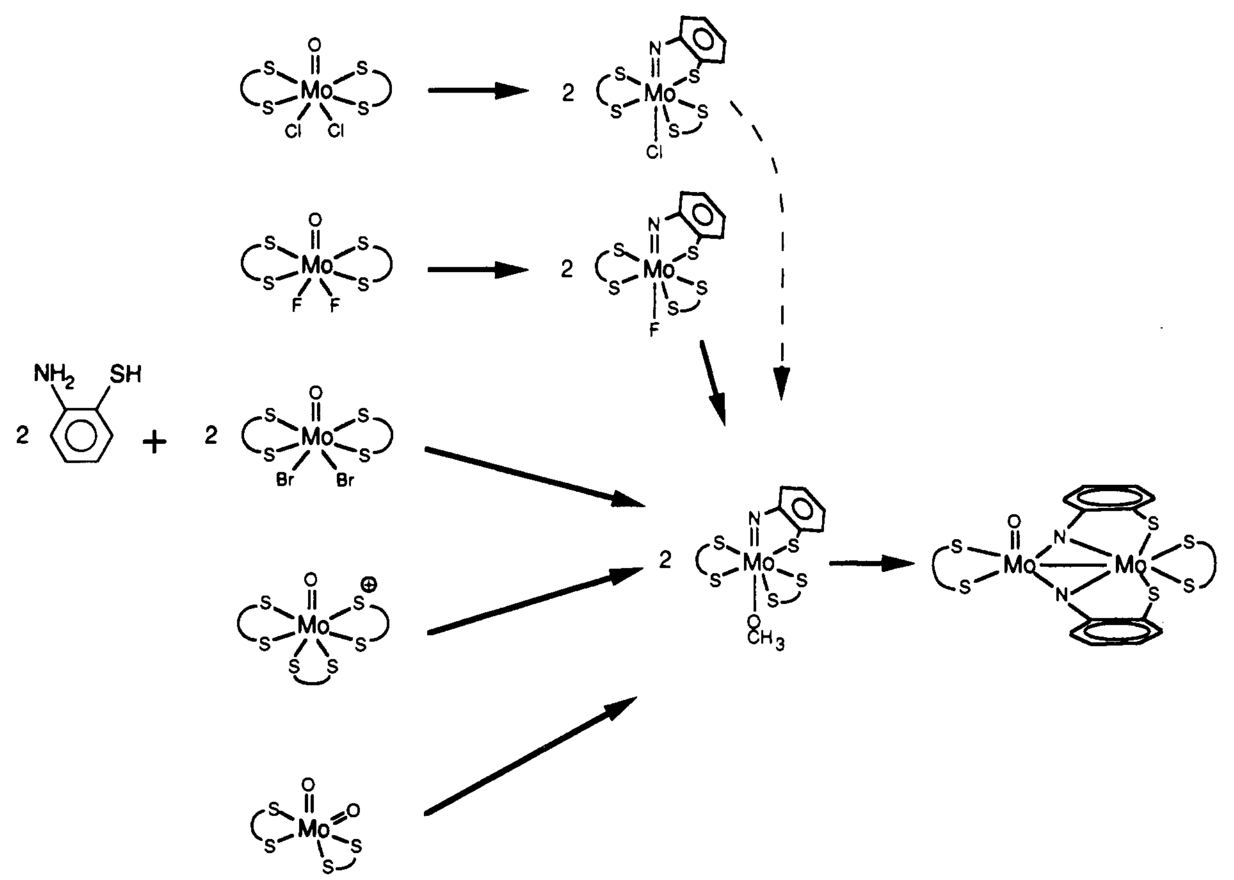


Figure 1. Formation of (dtc)MoO(μ-NC_6H_4S)$_2$Mo(dtc) from different Mo(VI) starting materials in MeOH in the presence of 2 equiv of NEt_3. SS = diethyldithiocarbamate.

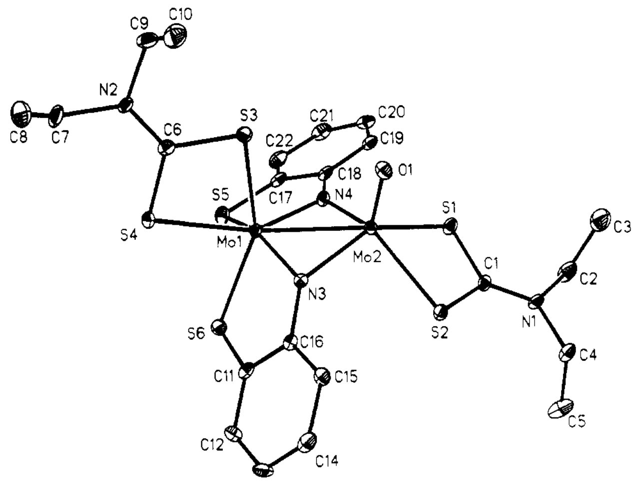


Figure 2. Structure of (dtc)MoO(μ-NC_6H_4S)$_2$Mo(dtc) (I).

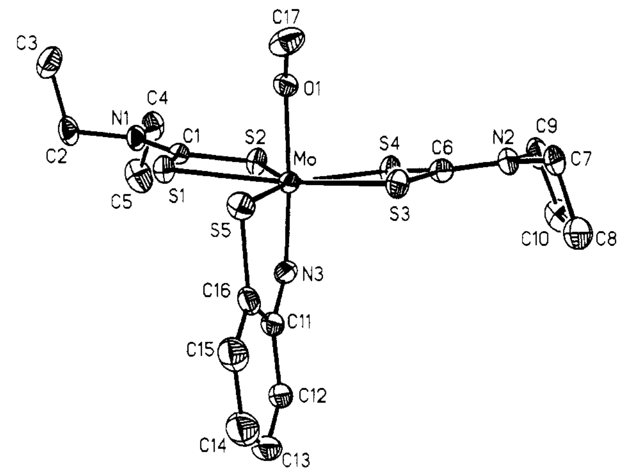
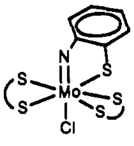
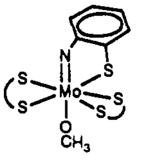
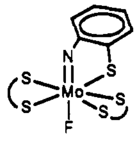
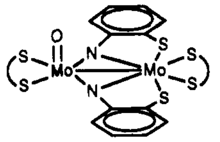


Figure 3. Structure of Mo(NC_6H_4S)(OCH_3)(dtc)$_2$ (II).

Not taking into account the Mo–Mo bond, Mo(1) is six-coordinate with distorted octahedral geometry due to the presence of three bidentate ligands. Mo(2) is five-coordinate with the molybdenum sitting above the basal plane of a square pyramid, formed by two dtc sulfurs and the two bridging nitrogens. The terminal oxygen atom tops the pyramid. The Mo–Mo distance of 2.659 (1) Å indicates a Mo–Mo bond. The Mo–Mo distance in I is slightly shorter than the Mo–Mo distance in the two known diimido bridged Mo(V) dimers, [Mo($C_5H_4CH_3$)O(μ-NC_6H_5)]$_2$[11] (2.691 (1) Å) and [Mo($C_5H_4CH_3$)(NC_6H_5)(μ-NC_6H_5)]$_2$[12] (2.717 (5) Å). While the two Mo atoms and the two briding nitrogens are coplanar in [Mo($C_5H_4CH_3$)O(μ-NC_6H_5)]$_2$[11] and [Mo($C_5H_4CH_3$)(NC_6H_5)(μ-NC_6H_5)]$_2$,[12] they are not coplanar in I, but instead assume a "butterfly" arrangement. The Mo–N distances are slightly shorter toward Mo(1) (1.927 (5) and 1.917 (5) Å) than to Mo(2) (1.992 (5) and 2.018 (5) Å). The molybdenum–sulfur distances range from 2.413 to 2.521 Å. The 2-aminothiophenol sulfurs are slightly closer to Mo(1) than the dithiocarbamate sulfurs. The Mo(2)–O distance is 1.679 (4) Å, typical for Mo–terminal oxygen bonds. There is a pseudo mirror plane in the molecule through N(1), C(1), Mo(2), Mo(1), O(1), C(6), and N(2), responsible for the simplicity of the NMR spectra (see below). The structure of the molecule resembles an airplane, which is our laboratory name for the compound.

The geometry of II is distorted pentagonal bipyramidal, similar to the previously reported Mo(NC_6H_4S)Cl(dtc)$_2$[16] with five sulfurs in the equatorial plane and the nitrogen and the oxygen in the axial positions. The O–Mo–N(3) angle is 160.7 (2)°. The deviation from the ideal angle of 180° is due to the fixed ring system Mo–S(5)–C(11)–C(16)–N(3). An ORTEP diagram of

Table VI. NMR Data[a]

					
^{95}Mo		292 (300)	200 (2100)	–335 (2100)	
^{14}N		70 (500)	70 (450)	65 (600)	35 (350)
^{1}H	NS	7.42 (d, 1 H), 6.97 (t, 1 H), 6.79 (t, 1 H), 6.48 (d, 1 H)	7.36 (d, 1 H), 6.80 (t, 1 H), 6.72 (t, 1 H), 6.23 (d, 1 H)	7.43 (d, 1 H), 6.90 (t, 1 H), 6.76 (t, 1 H), 6.39 (d, 1 H)	7.82 (d, 1 H), 7.66 (d, 1 H), 7.20 (t, 1 H), 7.10 (t, 1 H)
	dtc	3.79–3.61 (m, 8 H), 1.29 (t, 6 H), 1.23 (t, 6 H)	3.79–3.60 (m, 8 H), 1.25 (t, 6 H), 1.19 (t, 6 H)	3.82–3.63 (m, 8 H), 1.28 (t, 6 H), 1.23 (t, 6 H)	3.82 (q, 2 H), 3.50 (q, 2 H), 1.28 (t, 3 H), 1.05 (t, 3 H)
	OCH_3		4.05 (s, 3 H)		
^{13}C	dtc	194.9, 43.6, 42.7, 12.7, 12.4	196.6, 43.5, 42.6, 12.6, 12.2	195.7, 43.5, 42.8, 12.6, 12.3	203.7, 194.5, 46.2, 45.0, 12.6, 12.5
	NS	170.3, 150.2, 128.7, 128.1, 121.8, 116.7	166.0, 155.4, 127.2, 126.8, 121.3, 114.0	170.8, 128.0, 127.5, 121.4, 116.3	163.2, 154.4, 128.6, 124.6, 122.9, 118.9
	OCH_3		61.1		
^{19}F				–46	

[a] The chemical shifts are given in ppm, line widths in Hz in parentheses. Key: d = doublet, t = triplet, s = singlet, m = multiplet, and q = quartet. The ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$, all others in CH_2Cl_2. The NMR data for the chloro complex are from ref 16.

complex **II** is shown in Figure 3. Selected bond lengths and bond angles are listed in Table V.

The imido linkage in **II** is bent with an angle of 136.4 (4)°. The nitrogen acts as a two-π-electron donor according to structure **2** in the Introduction. The corresponding angle in $Mo(NC_6H_4S)Cl(dtc)_2$ is 137.7 (7)°.[16] The molybdenum–imido nitrogen distance is 1.772 (4) Å, slightly longer than in the chloro analog (1.744 (6) Å). The Mo–methoxy oxygen distance is 1.948 (3) Å. The Mo–sulfur distances range from 2.514 (2) to 2.533 (2) Å. The longest bond is between the molybdenum and the 2-aminothiophenol sulfur. The same trend was observed for $Mo(NC_6H_4S)Cl(dtc)_2$.

NMR Data. The multinuclear NMR data for **I**, **II**, **III**, and $Mo(NC_6H_4S)Cl(dtc)_2$ are listed in Table VI. We were not able to obtain a ^{95}Mo NMR spectrum for **I**. Dioxo-bridged Mo(V) dimers can be observed by ^{95}Mo NMR spectroscopy,[21] but so far no ^{95}Mo NMR chemical shifts have been reported for bimetallic Mo(V) imido compounds. A combination of low solubility and fast relaxation times may be the reason why we were not able to obtain a ^{95}Mo NMR signal for **I**.

The ^{95}Mo nucleus in **II** has a signal at 200 ppm, shielded by 92 ppm compared to the chloro analog. It has been shown previously for Mo(VI) oxo complexes that replacement of a chloro with a methoxy ligand in an otherwise identical Mo(VI) complex causes a shielding of about 100 ppm.[23] The ^{95}Mo nucleus of the fluoro complex is shielded by over 600 ppm compared to the ^{95}Mo nucleus in the chloro complex. Mo(VI)–oxo complexes exhibit an inverse halogen dependence;[22,23] i.e., one would expect the ^{95}Mo nucleus to be more shielded if the Mo(VI) imido compounds follow the same trend as Mo(VI) oxo compounds. Typically, chemical shift changes from 50 to 300 ppm are observed when one halogen is replaced by another in analogous compounds.[22] The large amount of shielding for **III** could be due to a structural difference. Perhaps the fluorine is in an equatorial rather than an axial position. We are currently trying to grow crystals of **III** suitable for an X-ray structure determination to see where the fluorine is located. Due to the broad line width of the ^{95}Mo NMR signal, no ^{95}Mo–^{19}F coupling was observed.

The imido nitrogens of **II** and $Mo(NC_6H_4S)Cl(dtc)_2$ both show a signal at 70 ppm in the ^{14}N NMR spectrum. The imido nitrogen in the fluoro complex is shielded by 5 ppm. These nitrogens in bent imido linkages are more deshielded than the nitrogens in linear imido linkages, which have been observed between +12 and –20 ppm.[15,24] The bridging imido nitrogens in **I** absorb at 35 ppm, between the chemical shifts for bent and linear imido nitrogens. In bridging imido ligands, the lone electron pair on the imido nitrogen participates in the π-bonding.[25] The shielding of the nitrogen from the bent via the bridging to the linear imido linkage could be a measure of the involvement of the lone electron pair in the bonding to the metal atoms.

The carbons bound to the imido nitrogens, the second most deshielded carbon of the 2-aminothiophenol ligand, do not follow the same trend as the ^{14}N nuclei. No systematic trends are obvious in the ^{13}C NMR chemical shifts.

In **I**, the aromatic protons next to the S and N in the coordinated 2-aminothiophenol are the most deshielded, resulting in a doublet–doublet, triplet–triplet pattern for the aromatic protons. In the $Mo(NC_6H_4S)X(dtc)_2$ compounds, a doublet–triplet, triplet–doublet pattern is observed. The proton next to the imido nitrogen becomes more deshielded when **I** is formed from **II**. The aromatic protons in **I** are generally more deshielded than the aromatic protons in the Mo(VI) complexes. **II** can be easily identified in the ^{1}H NMR spectrum through the methyl peak of the methoxy group at 4.05 ppm.

Infrared, UV–Visible, and Electrochemical Data. Selected IR UV–vis, and electrochemical data are listed in Table VII. The cyclic voltammogram of **I** shows a quasi-reversible two-electron reduction. The number of electrons was determined by chronocoulometry. Several attempts to reduce **I** by bulk electrolysis failed. The current did not drop after more than three electrons had been added, indicating a side reaction with the solvent. **II** has an irreversible reduction peak at –0.91 V, compared to the chloro and fluoro analogs which have two one-electron reduction peaks. The first is irreversible for the reduction from Mo(VI) to Mo(V). The irreversibility is due to the loss of a ligand from the coordination sphere of the molybdenum. The second, quasi-reversible reduction is due to the reduction of this Mo(V) species to Mo(IV).[16]

Conclusions. The bimetallic Mo(V) complex **I** is formed from the reaction of $MoOX_2(dtc)_2$ (X = F, Br; X_2 = dtc, O) with 2-aminothiophenol. One of the molybdenum centers in this compound has an open coordination site which may allow coordination of redox-active substrates. We have shown that the oxygen from the terminal oxo group in **I** comes from the methoxy group of **II**. Two intermediates, $Mo(NC_6H_4S)F(dtc)_2$ and $Mo(NC_6H_4S)(OCH_3)(dtc)_2$, have been isolated. A comparison of

---

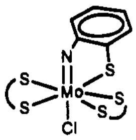
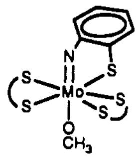
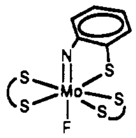
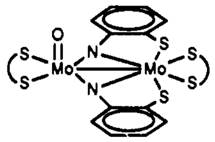
(22) Minelli, M; Enemark, J. H.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Coord. Chem. Rev.* **1985**, *68*, 169.

(23) Minelli, M.; Yamanouchi, K.; Enemark, J. H.; Subramanian, P.; Kaul, B. B.; Spence, J. T. *Inorg. Chem.* **1984**, *23*, 2554.

(24) Timm, N.; Minelli, M. Unpublished results.

(25) Schofield, M. H.; Kee, T. P.; Anhaus, J. T.; Schrock, R. R.; Johnson, K. H.; Davis, W. M. *Inorg. Chem.* **1991**, *30*, 3595.

Table VII. Selected IR, UV–Vis, and Electrochemical Data[a]

				
IR		O—CH$_3$: 1095 (s)		Mo=O: 956 (s)
UV–vis		232 (4.7 × 10^4)	230 (3.3 × 10^4)	246 (5.0 × 10^5)
		258 (5.7 × 10^4)	254 (4.1 × 10^4)	412 (6.9 × 10^4)
	530 (4 × 10^3)	460 (2.1 × 10^3)	330 (8.1 × 10^3)	554 (3.2 × 10^4)
E_{pc}	–0.64, –0.87	–0.91	–0.71, –0.87	–0.91

[a] The IR stretches are given in cm^{-1}; the λ_{max} values are given in nm with the ϵ values (M^{-1} cm^{-1}) in parentheses; the electrochemical data are given in V vs SCE; E_{pc} = cathodic peak.

the reactivity of the Mo(NC$_6$H$_4$S)X(dtc)$_2$ complexes shows that the stability of the Mo–X bond decreases in the order Cl > F > Br. The ^{95}Mo NMR chemical shifts of the Mo(NC$_6$H$_4$S)X(dtc)$_2$ compounds follow the same trends as the corresponding oxo complexes, i.e., they show an inverse halogen dependence. The imido ^{14}N nuclei become more shielded the more the lone electron pair on the nitrogen becomes involved in π-bonding to the Mo.

Acknowledgment. We thank the Research Corp. for supporting this work and the PEW Midstates Science and Mathematics Consortium for funding of the X-ray structure determinations and ^{19}F NMR measurements. We are grateful to Prof. J. H. Enemark at the University of Arizona for helpful discussions, Dr. Andre d'Avignon at Washington University for measuring the ^{19}F NMR spectra, John Marshall at Grinnell College for his help in preparing the manuscript, and Andrew L. Coghill for preliminary results of his research.

Supplementary Material Available: Tables listing the complete structure determination summary, atomic coordinates and equivalent isotropic and anisotropic displacement coefficients for all atoms including H atoms, bond lengths, and bond angles for I and II (16 pages). Ordering information is given on any current masthead page.