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2,4,6-Tris((pentafluorothio)methyl)-1,3,5-trioxane

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In our studies of molecular systems containing the pentafluorothio (SF_5) group the synthesis of SF_5CH_2CHO was necessitated because of its potential role as a precursor for pentafluorothio hydrocarbon derivatives. The synthesis of the aldehyde involves dehydration (with phosphorus pentoxide) of its hydrate, $F_5SCH_2CH(OH)_2$, which in turn is obtained by hydrolysis of the vinyl ether $F_5SCH{=}CHOCH_3$ in aqueous hydrochloric acid[1,2] or by treatment of the adduct $F_2SCH_2CHClOAc$ (OAc = CH_3COO)[3] with methanolic potassium hydroxide, respectively. The aldehyde reacts with water, either from the reaction or from the aqueous phase, forming the hydrate, although usually mixtures of the aldehyde and the hydrate are obtained in the above procedures. The intermediate vinyl ether is obtained by several procedures, either by treatment of $F_5SCH_2CHCl_2$ with excess sodium methoxide,[1] by reaction of $F_5SCH{=}CHCl$ with methanolic KOH,[4] or by suspension of sodium methoxide in xylene.[2] These reactions are expressed by the following equations:

$$F_5SCH{=}CHCl + CH_3OH + KOH \rightarrow F_5SCH{=}CHOCH_3 + KCl + H_2O \quad (1)$$

$$F_5SCH{=}CHOCH_3 + HCl(aq) \xrightarrow{\text{reflux}} F_5SCH_2CHO + F_5SCH_2CH(OH)_2 + CH_3Cl \quad (2)$$

$$F_5SCH_2CHClOAc + 2KOH \xrightarrow{CH_3OH} F_5SCH_2CH(OH)_2 + KCl + KOAc \quad (3)$$

$$F_5SCH_2CH(OH)_2 + P_4O_{10} \rightarrow F_5SCH_2CHO + P_4O_{10}{\cdot}H_2O \quad (4)$$

We found that after treatment of the aldehyde hydrate with P_4O_{10} the solid residue contained a product, which was extracted with chloroform. This compound was recrystallized from hexane and exhibited a sharp melting point (110.5-111.5 °C) and an NMR (^1H) pattern consistent with a 1,3,5-trioxane structure. The mass spectrum, however, did not show the molecular ion peak for a trioxane but yielded only the mass of a dimer, even at ionization potentials as low as 15 eV. In order to resolve the actual structure of this material, it was decided to carry out an X-ray determination of the crystal structure, which confirmed the 1,3,5-trioxane structure.

In addition to obtaining the trioxane as a side product in eq 4, it was found that prolonged storage ($\approx$6 weeks) at -5 °C would, upon occasion, give the trimer product. A few tests were carried out in order to find a more dependable method of synthesis. Heating (80 °C) the aldehyde with a drop of 85% phosphoric acid did not produce any change; concentrated H_2SO_4 led to charring at higher temperatures (90-105 °C), but at room temperature the pure aldehyde was quickly converted to the solid trimer in 86% yield. It is thus established that the material can be formed by the usual acid-catalyzed polymerization of aldehydes.

Our synthesis of SF_5CH_2CHO followed a course somewhat different from that reported in the literature[1,2] in that the vinyl ether $F_5SCH{=}CHOCH_3$ was obtained from the compound $F_5SCH{=}CHBr$ by treatment with methanolic sodium methoxide. However, this method is unsatisfactory as formation of the acetal $F_5SCH_2CH(OCH_3)_2$ via nucleophilic addition of the methoxide ion to the vinyl ether $F_5SCH{=}CHOCH_3$ occurred.[4] This acetal cannot be easily separated from the vinyl ether and is almost completely inert to acid hydrolysis. Due to these factors low yields of the desired aldehyde were realized.

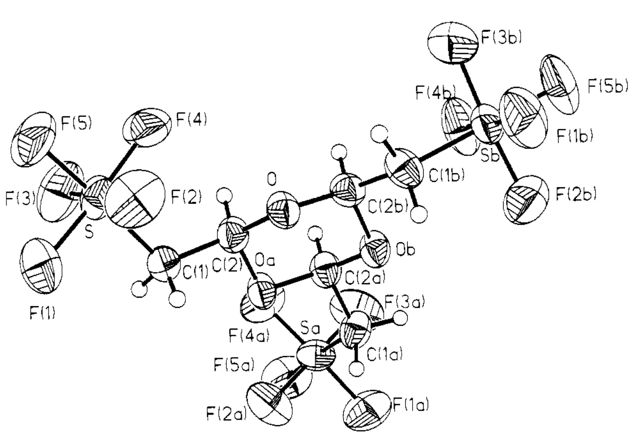
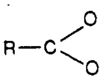


Figure 1. Thermal ellipsoid view of $(SF_5CH_2CHO)_3$ at 50% probability. Hydrogen atom positions are indicated by small spheres. Subscripts a and b denote equivalent atoms generated by rotations of $+2\pi/3$ and $-2\pi/3$ about the 3-fold axis.

Results and Discussion

The ^1H and ^{19}F NMR spectra for monomeric SF_5CH_2CHO and its trimer form were obtained. The ^{19}F NMR spectrum of SF_5CH_2CHO showed for the SF_5 group a normal AB_4 pattern (ϕ_A = +81.5 ppm; ϕ_B = +71.0 ppm) from which the J_{A-B} coupling was found to be 151 Hz. By comparison, the trioxane produced a normal AB_4 pattern in essentially the same region (ϕ_A = +82.0 ppm; ϕ_B = +69.5 ppm; J_{AB} = 152 Hz). The ^1H NMR spectrum for SF_5CH_2CHO contained the aldehyde proton at 9.76 ppm and the methylene protons at 4.36 ppm. The splitting pattern for the methylene protons consisted of a doublet of a pentet with J_{HSF_4} coupling of 8.2 Hz. The chemical shift and coupling values are in line with those found for other SF_5CH_2 systems.[5-8] In the proton NMR spectrum of the symmetrical $(SF_5CH_2CHO)_3$, the resonance due to the aldehyde proton is replaced with the CH resonance of the trioxane ring. In this structure, the CH proton (δ = 5.58 ppm; J_{HH} = 4.7 Hz) is split into a triplet by the neighboring CH_2 protons; for the CH_2 protons, a doublet of a pentet (δ = 3.85 ppm; J_{HH} = 4.7; J_{HSF_4} = 8.0 Hz) is observed.

Symmetrical acetals, R-CH(OR′)$_2$, contain the same structural element as symmetrical trioxanes



The compound $F_5SCH_2CH(OCH_3)_2$ showed, in the ^1H NMR spectrum, a triplet at 5.02 ppm (C-H), a doublet of a pentet at 3.99 ppm (CH_2), and coupling constants of J_{HH} = 4.9 Hz and J_{HSF_4} = 8.4 Hz. The ^{19}F NMR chemical shifts (SF_5, AB_4) for the dimethyl acetal derivative are ϕ_A = +83.5 ppm and ϕ_B = +66.9 ppm.[4,9]

There is no evidence for isomerism in the trimer as is reported for other trioxane compounds (e.g., in parachloral, an α-form and a β-form exist.[10]) The α-form is derived from the cis-trans isomerism of the CCl_3 substituents. The α-trans isomer assumes a tub conformation, apparently stabilized by an intramolecular

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(1) Ray, N. H. British Patent 941392, 1963.
(2) Ray, N. H. *J. Chem. Soc.* **1963**, 1440.
(3) Coffman, D. D.; Chester, W.; Tullock, C. W. U.S. Patent 3,102,903, 1963.
(4) Hoover, F. W.; Coffman, D. D. *J. Org. Chem.* **1964**, *29*, 3567.
(5) Canich, J. M.; Ludvig, M. M.; Paudler, W. W.; Gard, G. L.; Shreeve, J. M. *Inorg. Chem.* **1985**, *24*, 3668.
(6) Steward, J.; Kegley, L.; White, H. F.; Gard, G. L. *J. Org. Chem.* **1969**, *34*, 760.
(7) DeMarco, R. A.; Fox, W. B. *J. Fluorine Chem.* **1978**, *12*, 137.
(8) Mir, Q. C.; DeBuhr, R.; Haug, C.; White, H. F.; Gard, G. L. *J. Fluorine Chem.* **1980**, *16*, 373.
(9) Winter, R.; Gard, G. L. To be submitted for publication.
(10) Archer, S. J.; Irving, A.; Irving, H. M. N. H. *J. Crystallogr. Spectrosc. Res.* **1986**, *16*, 283 and references therein.

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Table I. Crystallographic Data for $(SF_5CH_2CHO)_3$

$C_2H_3OF_5S$	fw 170.1
a = 10.266 (2) Å	space group $R\bar{3}m$
c = 26.336 (8) Å	T = 20 °C
V = 2404 (1) Å^3	ρ_{calcd} = 2.13 g cm^{-3}
Z = 18	μ = 6.16 cm^{-1}
$R_w(F_o)$ = 0.0763	$R(F_o)$ = 0.0572

Table II. Non-Hydrogen Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\times 10^3$) for $(SF_5CH_2CHO)_3$

atom	x	y	z	U^a
S	7331 (1)	6700 (2)	792 (1)	52 (1)
O	3733 (3)	5610 (3)	965 (1)	43 (1)
C(1)	6309 (4)	7569 (5)	1023 (2)	49 (2)
C(2)	4791 (4)	7096 (4)	791 (2)	44 (2)
F(1)	8626 (4)	7648 (5)	1187 (1)	89 (2)
F(2)	6557 (5)	5385 (4)	1183 (1)	89 (2)
F(3)	8151 (4)	7939 (5)	384 (1)	97 (3)
F(4)	6121 (4)	5696 (4)	385 (1)	81 (2)
F(5)	8295 (4)	5992 (5)	604 (1)	93 (3)

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

hydrogen bond. The β-form, or all-cis isomer, has a twisted-chair conformation.[10]

The crystal structure of $(SF_5CH_2CHO)_3$ consists of trimeric units with 3-fold symmetry in which the trioxane ring is situated in a chair-type conformation. The SF_5CH_2 groups lie in an equatorial position (Figure 1). A similar chair-type conformation has been found for α- and β-parabutylchloral, $(CH_3CHClCCl_2CHO)_3$, in which the 1,1,2-trichloropropyl groups are located in a cis,cis arrangement; all $CH_3CHClCCl_2$ groups are in the equatorial positions.[11]

In α-$(CH_3CHClCCl_2CHO)_3$, the C–O bond length varies from 1.396 (7) to 1.425 (8) Å and the C–O–C and O–C–O bond angles for the ring are 109.9 (5) to 110.1 (5)° and 109.6 (5) to 110.5 (5)°, respectively.[11] In $(SF_5CH_2CHO)_3$ a larger alternation of C–O bond lengths of 1.435 and 1.387 Å is found with C–O–C and O–C–O bond angles of 109.6 and 110.4°, respectively. This alternation is undoubtedly due to the steric influence of the CH_2SF_5 groups, which are rotated about the C–C bonds so as to lie closer to the oxygen atom involved in the longer C–O bond.

Experimental Section

The compound $F_5SCH{=}CHBr$ was made according to the literature.[5] Volatile materials were manipulated in a conventional Pyrex glass vacuum line, equipped with a Heise Bourdon tube gauge and a Televac thermocouple unit. Infrared spectra were obtained from neat liquids or solids between KBr and NaCl plates on a Nicolet 20DX spectrometer. The ^{19}F NMR spectra were obtained on a Varian Model EM-390 spectrometer operating at 84.67 MHz. ^1H NMR spectra were obtained either on a Varian EM-390 spectrometer (at 90 MHz) using TMS as an external standard or with a General Electric QE-300 FT NMR spectrometer (at 300 MHz) using TMS as an internal standard. The mass spectrum was obtained witha VG 7070 HS spectrometer at 70 eV. The elemental analysis was performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

An appropriate crystal was chosen and subsequently mounted in a Lindemann glass capillary. X-ray data were collected with a Syntex $P2_1$ four-circle diffractometer upgraded to Nicolet P3 specifications using graphite-monochromated Mo Kα radiation. Accurate unit cell parameters were obtained by centering 25 reflections with 2θ values between 33 and 37°. Pertinent crystallographic parameters are included in Table I.

The crystal structure was solved and refined with Nicolet SHELXTL programs (version 5.1, 1985). Positional parameters and equivalent isotropic thermal parameters are listed in Table II. Table III gives pertinent bond distance and angles.

$F_5SCH{=}CHOCH_3$ from $SF_5CH{=}CHBr$. In a 250-mL round-bottom flask, equipped with a magnetic stirring bar, 11.59 g of sodium (504 mmol) was dissolved in 120 mL of anhydrous methanol. A Claisen head, a dropping funnel, and a Drierite tube were attached. The solution was cooled in an ice bath, and 80.45 g (345.3 mmol) of $F_5SCH{=}CHBr$ was added dropwise to the stirred sodium methoxide solution. The solution became yellow with the formation of sodium bromide precipitate. Addition was complete after 30 min, and the ice bath was removed. Since the solution became warm, it was necessary to use a room-temperature water bath. After 1 h, the Claisen head was replaced by a Drierite tube. Stirring was continued for 96 h at room temperture, until a ^{19}F NMR spectrum of an aliquot indicated that all the olefinic bromide was gone. NaBr was filtered off (25.3 g, 71%), and the reaction mixture was poured into 300 mL of cold water. The lower layer was separated, and a saturated NaCl solution (200 mL) was added to the aqueous layer. After the mixture was allowed to stand overnight, some more product had precipitated. It was washed with a 5-mL saturated NaCl solution and combined with the original product; after drying ($MgSO_4$), 54.7 g (86%) of crude product was obtained. Distillation through a Vigreux column at atmospheric pressure yielded 17.7 g of pure $F_5SCH{=}CHOCH_3$ (bp 114 °C) and 36.2 g of a mixture of vinyl ether and the acetal $F_5SCH_2CH(OCH_3)_2$ in a ratio of about 9:1 (by NMR); boiling range 114–122 °C.

Table III. Non-Hydrogen Bond Lengths (Å) and Angles (deg) for $(SF_5CH_2CHO)_3$

S–C(1)	1.789 (6)	S–F(5)	1.574 (6)
S–F(1)	1.581 (3)	O–C(2)	1.435 (4)
S–F(2)	1.562 (4)	C(1)–C(2)	1.510 (6)
S–F(3)	1.552 (4)	C(2)–O(a)	1.387 (6)
S–F(4)	1.573 (3)		
C(1)–S–F(1)	89.6 (2)	C(1)–S–F(5)	177.3 (2)
C(1)–S–F(2)	92.0 (3)	F(1)–S–F(5)	87.8 (2)
F(1)–S–F(2)	90.4 (2)	F(2)–S–F(5)	88.5 (3)
C(1)–S–F(3)	92.3 (3)	F(3)–S–F(5)	87.2 (3)
F(1)–S–F(3)	90.3 (2)	F(4)–S–F(5)	87.4 (2)
F(2)–S–F(3)	175.7 (3)	C(2)–O–C(2a)	109.6 (4)
C(1)–S–F(4)	95.2 (2)	S–C(1)–C(2)	118.1 (3)
F(1)–S–F(4)	175.3 (3)	O–C(2)–C(1)	108.8 (4)
F(2)–S–F(4)	89.4 (2)	O–C(2)–O(a)	110.4 (4)
F(3)–S–F(4)	89.6 (2)	C(1)–C(2)–O(a)	105.8 (3)

Acid Hydrolysis of $F_5SCH{=}CHOCH_3$ and Preparation of $(SF_5CH_2CHO)_3$. In a 100-mL round-bottom flask fitted with a 30-cm reflux condenser, 53.7 g of a mixture of $F_5SCH{=}CHOCH_3$ and $F_5SCH_2CH(OCH_3)_2$ (ca. 94:6%, by ^{19}F NMR) and 27 mL of concentrated HCl were heated with vigorous stirring to 80–88 °C. After 3 h all starting material appeared to have been consumed (^{19}F NMR), but heating was continued for 1 h; a ^{19}F NMR spectrum indicated a mixture of two compounds in the ratio of 34% F_5SCH_2CHO to 66% $F_5SCH_2CH(OH)_2$; yield 51.6 g. This material was directly used for the preparation of the aldehyde by dehydrating twice with P_4O_{10}. In this fashion 22.1 g of P_4O_{10} was used to dehydrate 39.6 g of the above mixture, leaving a product (29.55 g) that contained dimethyl acetal and some unreacted vinyl ether. The mixture was distilled through a Vigreux column to obtain 20.98 g of a mixture of the vinyl ether (20%) and the aldehyde; boiling range 55–96 °C. This fraction was heated with an excess of concentrated HCl in a 50-mL round-bottom flask with a 30-cm reflux condenser for 15 h to 80–89 °C. A 25%:75% mixture of the aldehyde and the aldehyde hydrate was obtained (19 g); from this mixture the pure aldehyde was prepared in a second treatment as follows:

To 19.0 g of a mixture of F_5SCH_2CHO and $F_5SCH_2CH(OH)_2$ (25%:75% by ^{19}F NMR) was added powdered P_4O_{10} (16.0 g, 56.3 mmol) under cooling in a 50-mL round-bottom flask. The mixture was occasionally swirled, and after ca. 30 min the aldehyde was removed by vacuum transfer (15.6 g).

The residual phosphorus pentoxide was dissolved in 50 mL of distilled water, and the solution was extracted with chloroform (3 × 20 mL); the combined extracts were dried (Na_2SO_4) and brought to dryness, leaving an off-white solid, which was recrystallized (three times) from hexane: yield 0.87 g; mp 110.5–111.5 °C. An analytically pure sample was obtained by sublimation (0.001 Torr, 50 °C).

IR spectrum (KBr plates): 3044 (w), 2988 (vw), 2932 (vw), 1450 (vw), 1423 (m), 1405 (m), 1368 (ms), 1301 (vw), 1227 (m), 1142 (vs), 1068 (s), 1049 (ms), 901 (vs), 867 (s), 838 (vs), 830 (vs, sh), 715 (ms), 651 (s), 607 (ms), 600 (m), 581 (m), 556 (s), 516 (m) cm^{-1}.

Mass spectrum, EI (m/e, %, species): 341, 1.8, $(F_5SCH_2CHO)_2H^+$; 321, 1.1, $((F_5SCH_2CHO)_2H - HF)^+$; 171, 14.0, $F_5SCH_2CHOH^+$; 170, 1.2, $F_5SCH_2CHO^+$; 169, 26.8, $F_5SCH_2CO^+$; 153, 5.7, $F_5SCH_2C^+$; 152, 3.2, $F_5SC_2H^+$; 151, 100.0, $F_5SC_2^+$; 127, 2.9 SF_5^+; 122, 8.6, $C_3H_3FO_2S^+$; 105, 1.4, $C_3H_2FOS^+$; 103, 2.2, C_3FOS^+; 91, 9.6, FSC_2O^+; 89, 40.3, SF_3^+; 77, 1.3, $FSCH_2C^+$; 70, 1.3, SF_2^+; 65, 2.6, CH_2FS^+; 63, 11.5, CFS^+.

Anal. Calc: C, 14.12; H, 1.78; F, 55.9; S, 18.85. Found: C, 14.28; H, 1.78; F, 55.9; S, 19.04.

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(11) Archer, S. J.; Irving, H. M. N. H.; Koch, K. R.; Nassimbeni, L. R. *J. Crystallogr. Spectrosc. Res.* **1985**, *15*, 333.

$F_5SCH_2CHO + H_2SO_4$. 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 ($\approx$2 mL). The volume of the solution was reduced by evaporation to $\approx$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%.

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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

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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

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(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.