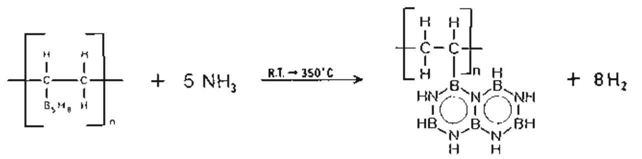
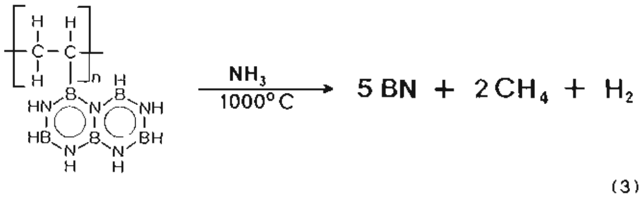


(2)

of a borazine polymer intermediate (eq 2), followed by a second decomposition reaction at higher temperatures to form BN as shown in eq 3. Indeed, it was also found that further treatment



(3)

of a pure sample of II under ammonia at higher temperatures resulted in formation of BN.

In summary, the results described herein demonstrate that poly(2-vinylpentaborane) oligomers are useful soluble ceramic precursors that can be readily converted to boron nitride in high yields. The potential applications for the processing of BN in this manner are numerous and include synthesis of composite materials[20] and the generation of thin films or coatings.[21] Furthermore, owing to the highly reactive nature of the pentaborane cage, these polymers may well serve as precursors to a wide variety of other important boron-containing ceramics and work exploring these possibilities is currently in progress.

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Synthesis of Thiomolybdenyl Complexes with $[Mo_2(S)_2(O)_2]^{2+}$ Cores and Substitutionally Labile Ligands. Crystal and Molecular Structure of the $[Mo_2O_2S_4(DMF)_3]$ Complex

Sir:

The reactivity characteristics of the Mo-coordinated S^{2-}, S_2^{2-}, and S_4^{2-} terminal ligands (L^{2-}) in the $[L_2Mo_2(\mu\text{-}S)_2S_nO_{2-n}]^{2-}$ complexes (n = 0-2) are greatly affected by the nature of the neighboring terminal ligands on the Mo atom.[1] A detailed study of neighbor-ligand effects in the relative nucleophilic properties of coordinated S^{2-}, S_2^{2-}, or S_4^{2-} ligands is expected to be useful in the evaluation of specific features that may be important in the catalysis of the hydrodesulfurization (HDS) reaction.[2] Among these features are included (a) the presence of proximal terminal oxo groups on the Mo atoms and (b) the interactions of the Mo atoms with oxides or hydroxides on the surface of the supporting γ-Al_2O_3 matrix.

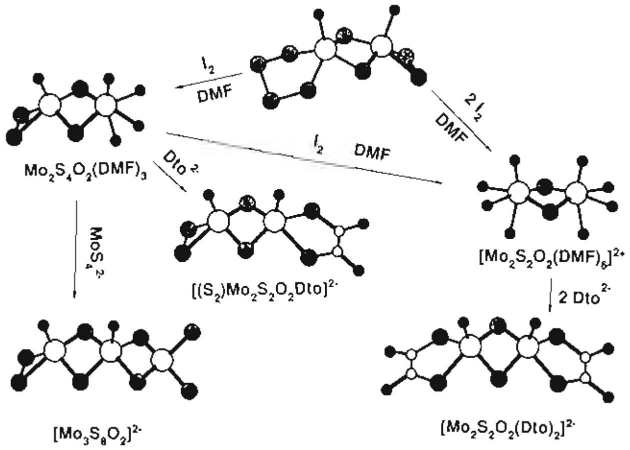

Figure 1. Synthesis and derivatives of the $[Mo_2O_2S_4(DMF)_3]$ and $[Mo_2O_2S_2(DMF)_6]^{2+}$ complexes.

The systematic synthesis of thiomolybdates with specific functional groups, and reactivity studies of such groups depend on the facile synthesis of simple derivatives of the $[Mo_2(\mu\text{-}S)_2S_nO_{2-n}]^{2+}$ cores, with substitution-labile terminal ligands. In the past, oxidative desulfurization reactions have been effective in the removal of coordinated S_x^{2-} ligands and their replacement by substitutionally labile ligands. Such reactions are exemplified in the synthesis of the $[Cp_2Fe_2(CH_3CN)_2(SEt)_2]^{2+}$ and $Os(I)_2(CO)_2(PPh_3)_2$ complexes. The former was obtained[3] by air oxidation of $[Cp_2Fe_2(S_2)(SEt)_2]^{0,+}$ in CH_3CN solution and the latter[4] by the I_2 oxidation of the $Os(\eta^2\text{-}S_2)(CO)_2(PPh_3)_2$ complex in CH_2Cl_2.

The reactions of $(Et_4N)_2[Mo_2O_2S_8]$[5] (I) with I_2 in dimethylformamide (DMF) are shown in Figure 1. The reaction of I with an equimolar amount of I_2 proceeds readily at ambient temperature and following unexceptional workup affords the orange crystalline $[Mo_2O_2S_4(DMF)_3]$ product[6] (II) in 70% yield. A similar reaction of I with 2 equiv of I_2 or the reaction of II with an equimolar amount of I_2 results in the formation of the $[Mo_2O_2S_2(DMF)_6]^{2+}$ cation in high yields. The latter can be isolated in crystalline form as the diiodide salt III.[6] The infrared spectra of the complexes show the Mo-O vibrations at 948 and 954 cm^{-1} for II and at 928 and 947 cm^{-1} for III. The C-O stretching vibrations of the coordinated DMF molecules appear as doublets at 1641, 1657 and 1647, 1664 cm^{-1} for II and III, respectively. The Mo-η^2-S_2 and Mo-S_b vibrations in II are found at 527 and 469 cm^{-1}, and the Mo-S_b stretching vibration in III occurs at 474 cm^{-1}. The conductivity of III in DMF solution (Λ

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(5) Hadjikyriacou, A.; Coucouvanis, D., manuscript in preparation. The synthesis of $[Mo_2O_2S_8]^{2-}$ is carried out, under aqueous aerobic conditions, by the reaction of $(NH_4)_2Mo_7O_{24}\cdot4H_2O$ (8.1 mmol in 400 mL of H_2O) with a sulfur-enriched, aqueous $(NH_4)_2S$ solution. The latter was obtained by the addition of 0.47 mmol of elemental sulfur to 65 mL of 22% $(NH_4)_2S$ solution obtained from Fisher Scientific. After a brief stirring at ambient temperature and standing for 24 h in air, the reaction mixture was treated with a solution of 50 mmol of Et_4NCl in 150 mL of water. The suspension of $(Et_4N)_2[Mo_2O_2S_8]$ that formed upon standing for 30 min was isolated, washed with ethanol, CS_2, and diethyl ether, and dried. The compound was recrystallized from 200 mL of DMF by the addition of 400 mL of 2-propanol. The yield of the yellow crystalline product was 9.6 g or 45%.

(6) Anal. Calcd for $Mo_2S_4O_5N_3C_9H_{21}$: C, 18.92; N, 7.35; H, 3.70; S, 22.44; Mo, 33.58. Found: C, 19.55; N, 7.43; H, 3.70; S, 21.70; Mo, 32.37. Calcd for $I_2Mo_2S_2O_8N_6C_{18}H_{42}$: C, 22.00; N, 8.57; H, 4.28; S, 6.53; Mo, 19.59; I, 25.92. Found: C, 22.00; N, 8.14; H, 4.53; S, 7.22; Mo, 17.75; I, 24.53. Severe twinning of the well-shaped orange crystals of this compound has prevented us from finding a single crystal suitable for an X-ray determination.

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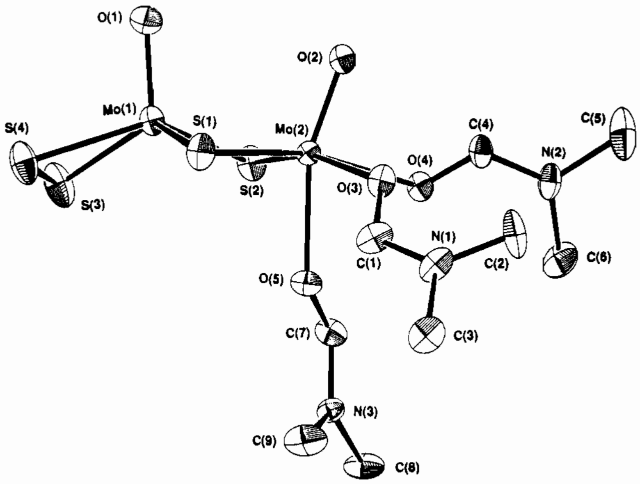

Figure 2. Structure and labeling of the $[Mo_2O_2S_4(DMF)_3]$ complex. Thermal ellipsoids as drawn by ORTEP represent the 50% probability surfaces.

$= 162\ \Omega^{-1}\ cm^{-1}$; [III] $= 10^{-3}$ M) is characteristic for a 2:1 electrolyte[7] and indicates that the I^- anions are not coordinated to the Mo atom(s). The anticipated synthetic utility of II and III is demonstrated in DMF ligand displacement reactions. The reactions of II with either MoS_4^{2-} or the dithiooxalate anion, $[S_2C_2O_2]^{2-}$, afford under mild conditions the $[(\eta^2\text{-}S_2)Mo(O)(\mu\text{-}S)_2Mo(O)(S_2C_2O_2)]^{2-}$ and $[(\eta^2\text{-}S_2)Mo(O)(\mu\text{-}S)_2Mo(O)(MoS_4)]^{2-}$ anions, which have been isolated as crystalline Ph_4P^+ salts.[8,9] In a similar fashion, III reacts with the $[S_2C_2O_2]^{2-}$ ligand to give the $[(S_2C_2O_2)Mo(O)(\mu\text{-}S)_2Mo(O)(S_2C_2O_2)]^{2-}$ anion, which also has been isolated in crystalline form as the Ph_4P^+ salt.[11]

The structure[12] of II is shown in Figure 2. The neutral molecule contains the $[Mo_2(\mu\text{-}S)_2O_2]^{2+}$ core that has been structurally characterized previously in $[Mo_2O_2S_6]^{2-}$ [13] and the $[(L)Mo(O)(\mu\text{-}S)_2Mo(O)(L')]^{n-}$ complexes (L = L′ = $[S_2C_2(CO_2CH_3)_2]^{2-}$, dithiolene,[1] $n = 2$; L = L′ = $[S_2C_2(CO_2CH_3)_2]^{2-}$, vinyl disulfide,[14] $n = 2$; L = S_2^{2-}, L′ = S_4^{2-},[5] $n = 2$; L = L′ = histidine,[15] $n = 0$; L = L′ = ox^{2-}, $n = 2$[16]). The structural features of the $(\eta^2\text{-}S_2)Mo(O)(\mu\text{-}S)_2Mo(O)$ fragment in II are very similar to those in the $[Mo_2O_2S_6]^{2-}$ anion[13] (Table I) and will not be discussed further. The $[Mo_2(\mu\text{-}S)_2O_2]^{2+}$ core shows a dihedral angle of 151.5° between the planes Mo(1)S(1)S(2) and Mo(2)S(1)S(2), within the range of 150–160° usually found for other similar complexes.[13] The molybdenum atoms, Mo(1) and Mo(2), are elevated from the S(1)S(2)S(3)S(4) and S(1)S(2)O(3)O(4) planes toward the oxo ligands by 0.74 and 0.29 Å, respectively. The $(\mu\text{-}S)_2Mo(O)(DMF)_3$ unit in the structure of II contains the Mo(V) ion in a distorted-octahedral coordination with the three DMF ligands arranged facially. As reported previously for the $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$ [17] and $[Mo_2O_2S_2(C_2O_4)_2(H_2O)_2]^{2-}$ [16] complexes, there is only an insignificant trans influence of the oxo group, and the Mo–O distances with the DMF ligands are all within 3σ of each other (Table I).

Table I. Bond Lengths (Å) and Angles (deg) in $[Mo_2O_2S_4(DMF)_3]$ (A) and $[Mo_2O_2S_6]^{2-}$ (B)[13b]

	A	B[a]
Bond Lengths		
Mo(1)–Mo(2)	2.813 (1)	2.828 (1)
Mo(1)–S(1)	2.309 (3)	2.323 (1)
Mo(1)–S(2)	2.320 (3)	2.321 (1)
Mo(2)–S(1)	2.316 (3)	
Mo(2)–S(2)	2.323 (3)	
Mo(1)–S(3)	2.362 (3)	2.385 (4)
Mo(1)–S(4)	2.395 (3)	2.402 (7)
Mo(1)–O(1)	1.689 (6)	1.687 (3)
Mo(2)–O(2)	1.682 (6)	1.679 (3)
Mo(2)–O(3)	2.186 (6)	
Mo(2)–O(4)	2.212 (6)	
Mo(2)–O(5)	2.224 (6)	
S(3)–O(4)	2.053 (4)	2.066 (4)
S(1)–S(2)	3.612 (3)	
Bond Angles		
S(1)–Mo(1)–S(2)	102.6 (1)	102.1 (1)
S(1)–Mo(2)–S(2)	102.3 (1)	
O(2)–Mo(2)–O(4)	88.0 (3)	
O(2)–Mo(2)–O(3)	89.2 (3)	
O(5)–Mo(2)–O(3)	75.9 (2)	
O(5)–Mo(2)–O(4)	77.1 (2)	
O(5)–Mo(2)–O(2)	160.7 (3)	
O(2)–Mo(2)–S(2)	104.2 (2)	
O(2)–Mo(2)–S(1)	104.1 (2)	
Mo(1)–S(1)–Mo(2)	74.9 (1)	75.0 (1)
Mo(1)–S(2)–Mo(2)	74.6 (1)	75.1 (1)

[a] The average values of chemically equivalent bond lengths are given.

The ready availability of II and III in forms that can be stored conveniently and their solubility in both water and organic solvents make them useful as synthetic reagents. The generation, in aqueous solution, of the remarkably acid-stable $[Mo_2O_2S_2(H_2O)_6]^{2+}$ cation has been reported.[18]

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Supplementary Material Available: Positional and thermal parameters for $[Mo_2O_2S_4(DMF)_3]$ (Tables S1 and S2) and bond distances and angles (Table S3) (4 pages); structure factors (Table S4) (7 pages). Ordering information is given on any current masthead page.

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(7) The conductivity of the known 2:1 electrolyte $[Et_4N]_2[Mo_2O_2S_8]$ in the same solvent and molarity was found at 179 $\Omega^{-1}\ cm^{-1}$.

(8) $[Ph_4P]_2[(\eta^2\text{-}S_2)Mo(O)(\mu\text{-}S)_2Mo(O)(MoS_4)]$ Electronic spectrum (nm): 480 (sh), 436, 312 (sh), 282 (sh), 268. Select IR absorptions (cm^{-1}): Mo—S_b, 478 (w); Mo—S_t, 500 (m); S—S, 520 (m); Mo═O, 943 (w), 958 (m). Anal. Calcd for $Mo_3S_8O_2P_2C_{48}H_{40}$: C, 45.93; H, 3.21; S, 20.43; P, 4.94; Mo, 22.93. Found: C, 46.55; H, 3.17; S, 20.49; P, 5.18; Mo, 22.02. $[Ph_4P]_2[(\eta^2\text{-}S_2)Mo(O)(\mu\text{-}S)_2Mo(O)(S_2C_2O_2)]$ Electronic spectrum (nm): 462 (br), 330 (sh), 290 (sh), 265 (sh). Select IR absorptions (cm^{-1}): 451 (w); Mo—S_b, 466 (w); Mo═O, 942 (m), 956 (s); C═O, 1630 (s). Anal. Calcd for $Mo_2S_6O_4P_2C_{50}H_{40}$: C, 52.17; H, 3.50; S, 16.71; P, 5.38; Mo, 16.67. Found: C, 50.79; H, 3.64; S, 17.09; P, 5.71; Mo, 16.68.

(9) The electronic and infrared spectra of $[(\eta^2\text{-}S_2)Mo(O)(\mu\text{-}S)_2Mo(O)(MoS_4)]^{2-}$ can be identified in the spectra reported[10] for a mixture containing this anion and $[(\eta^2\text{-}S_2)Mo(O)(\mu\text{-}S)_2Mo(O)(MoOS_3)]^{2-}$. This mixture was obtained by the reaction of $[Mo_8O_{26}]^{4-}$ with $(Me_3Si)_2S$, and the crystal structure of $(n\text{-}Bu_4N)_2[(\eta^2\text{-}S_2)Mo(O)(\mu\text{-}S)_2Mo(O)(MoXS_3)]$ (X = S, O) has been determined[10] from single crystals that contained equal amounts of the isostructural anions.

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(11) $[Ph_4P]_2[(S_2C_2O_2)Mo(O)(\mu\text{-}S)_2Mo(O)(S_2C_2O_2)]$ Electronic spectrum (nm): 330 (sh), 290 (sh), 266 (sh). Select IR absorptions (cm^{-1}): Mo—S_b, 452 (w); Mo═O, 960 (s); C═O, 1631 (s), 1637 (s). Anal. Calcd for $Mo_2S_6O_6P_2C_{52}H_{40}$: C, 51.74; H, 3.34; S, 15.94; P, 5.13; Mo, 15.9. Found: C, 51.33; H, 3.54; S, 16.37; P, 5.28; Mo, 16.74.

(12) Crystal and refinement data: Orange prisms of $[Mo_2O_2S_4(DMF)_3]$ are orthorhombic, space group *Pcab*, with $a = 13.152$ (3) Å, $b = 17.554$ (5) Å, $c = 17.893$ (5) Å, $Z = 8$, and $\mu = 15.6\ cm^{-1}$. Single-crystal X-ray data were collected (θ–2θ scans) on a crystal 0.20 mm × 0.24 mm × 0.90 mm, at 300 K on a Nicolet P3F four-circle diffractometer using Mo Kα radiation, for an octant of the reciprocal lattice sphere ($+h,+k,+l$). The solution of the structure was carried out by a combination of heavy-atom Patterson, direct-methods, and Fourier techniques. The refinement by full-matrix, least-squares techniques was based on 1089 unique reflections ($2\theta_{max} = 40$, $I > 3\sigma$). Anisotropic temperature factors were used for the non-hydrogen atoms. Refinement converged to a R value of 0.037.

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