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Reactions of the Mo═S Bond in the $[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(S)]^-$ Complex with SO_2. An ^1H NMR Study and the Synthesis and Structural Characterization of $[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(L)]^-$ Complexes Containing SO_2-Derived Sulfite, Thiosulfate, and Sulfate Bidentate Chelating Ligands

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Studies of the reactivity of the Mo(O)(S) functional group toward electrophilic reagents such as the $C_2(RCOO)_2$-activated alkynes[1] or CS_2[2] have revealed rich chemistry that derives from the addition of electrophiles to the Mo═S bond. The latter may be activated by the neighboring Mo═O group, as previously suggested by a theoretical study on tetrahedral $(L)_2Mo(O)(O)$ complexes.[3] A significant conclusion from this study, which evaluated the energetics of alkene or alkyne addition to the Mo═O bond, is that the addition to one of the Mo═O groups is thermodynamically driven by the outer ("spectator") Mo═O group. In the latter, the bond order increases to 3 as the coordination geometry around the Mo atom changes from four-coordinate tetrahedral to five-coordinate pyramidal.

The facile electrophilic attack and addition of CS_2 to the Mo═S chromophore[2] prompted us to investigate the reactivity of SO_2 with the same chromophore. Previous studies of the reaction chemistry of SO_2 with sulfur complexes such as $(Cp^*)_2Cr_2S_4$, $(Cp^*)_2Cr_2S_5$,[4] and $(Cp^*)_2Mo_2S_4$[5] have shown that SO_2 initially adds to the bridging sulfido or disulfido ligands to give η^1-S·SO_2 and η^1-SS·SO_2 ligands. Subsequent reactions of the new complexes with SO_2 involve oxygen atom transfer that leads to η^1-S·SO_3 complexes.

The Mo═S bond of the Mo(O)(S) group in the $[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(S)]^-$ complex[6] (I) readily adds SO_2 and depending on reaction conditions affords a multitude of products. These products contain the thiosulfite, thiosulfate, sulfite, and sulfate dianions as bidentate chelating ligands terminally bound to the Mo atom. In this communication we report on the syntheses of the $[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(L)]^-$ ($L = S_2O_3^{2-}, SO_3^{2-}, SO_4^{2-}$) complexes and the structural characterization of the $S_2O_3^{2-}$, SO_3^{2-}, and SO_4^{2-} homologs.

The reactions of Et_4N^+-I with SO_2 in CH_3CN or DMF solution were carried out by adding gaseous SO_2 at various temperatures and for various lengths of time. The products were isolated from the reaction mixtures following unexceptional workup procedures and were recrystallized from CH_3CN or DMF/diethyl ether mixtures. The reaction at 0 °C for ca. 1 h in CH_3CN solution afforded the $[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_3)]^-$ anion (II), which was isolated as a crystalline Et_4N^+ salt in a mixture that was mainly Et_4N^+-I (90%).[7] A similar reaction in CH_3CN solution at ambient temperature for ca. 3 h gave the $[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(S_2O_3)]^-$ anion (III), which was isolated as a crystalline Et_4N^+ salt in 65% yield.[8] The reaction in DMF at temperatures >100 °C, but below the boiling point of the solution, for ca. 3 h gave the $[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]^-$ anion (IV), which was isolated as a pure Et_4N^+ salt in 50% yield.[9]

The reaction of I with SO_2 was monitored by ^1H NMR spectroscopy (Cp^- protons) in a SO_2-saturated CH_3CN solution in a sealed NMR tube over a period of 2 days. The first spectrum obtained 10 min after mixing the reagents shows Cp^- resonances (ppm vs TMS) at 6.36 (vw), 6.33 (vw), 6.31 (s), 6.30 (vw), 6.28 (vw), and 6.13 (vw). After 2 h, the strong resonance at 6.31 ppm is considerably weaker and the resonances at 6.36 and 6.28 ppm dominate the spectra, in addition the resonances at 6.33 and 6.13 ppm appear somewhat stronger. After 2 days, only two resonances are detected at 6.36 (s) and 6.28 (m) ppm. The ^1H NMR spectra of "authentic", structurally characterized, $[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(L)]^-$ complexes ($L = SO_3^{2-}, S_2O_3^{2-}, S_2^{2-}$ [6]) have made it possible to unequivocally assign half of the NMR resonances. Specifically, the resonances at 6.36, 6.33, and 6.13 ppm are due to the complexes with $L = S_2O_3^{2-}$, SO_3^{2-}, and S_2^{2-} respectively. The complex with $L = S_2O^{2-}$ was synthesized by the reaction of the $[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(S_2)]^-$ complex with 3-chloroperbenzoic acid by a procedure similar to that described previously for the synthesis of $[Ir(\eta^2\text{-}S_2O)(dppe)_2]^+$ from $[Ir(\eta^2\text{-}S_2)(dppe)_2]^+$.[10] The Cp^- resonance of this complex[11] is found at 6.28 ppm. A scheme that may account for the formation and possible reactions of the $[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(L)]^-$ complexes is shown in Figure 1.[12] The chemical shifts assigned to the individual entries (Figure 1) hinted of a qualitative dependence on the group electronegativities of the $S_xO_y^{2-}$ ligands. A plot of the chemical shifts (ppm) vs the sum of the Pauling electronegativities for the chalcogen atoms in the $S_xO_y^{2-}$ ligands is remarkably linear, with the larger electronegativity sums associated with the less shielded protons (the Cp^- resonance for SO_4^{2-} is found at 6.38 ppm and for S_2^{2-} at 6.13 ppm). A correlation of chemical shift with electronegativity has been reported previously for the CH_3X[13] and C_2H_5X[14] halides and seems to be valid for structurally and electronically related members within a family of molecules. We have been unable to isolate the short-lived $[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(S_2O_2)]^-$ complex (τ = 6.31 ppm)

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(1) (a) Coucouvanis, D.; Hadjikyriacou, A.; Toupadakis, A.; Koo, S. M.; Ileperuma, O.; Draganjac, M.; Salifoglou, A. *Inorg. Chem.* **1991**, *30*, 754–767. (b) Halbert, T. R.; Pan, W.-H.; Stiefel, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 5476. (c) Coucouvanis, D.; Toupadakis, A.; Koo, Sang-Man; Hadjikyriacou, A. I. *Polyhedron* **1989**, *8*, 1705. (d) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742.

(2) (a) Coucouvanis, D.; Draganjac, M. E.; Koo, S. M.; Toupadakis, A.; Hadjikyriacou, A. I. *Inorg. Chem.* **1992**, *31*, 1186–1196. (b) Coucouvanis, D.; Draganjac, M. *J. Am. Chem. Soc.* **1982**, *104*, 6820.

(3) (a) Rappe, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1980**, *102*, 5115–5117. (b) Rappe, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1982**, *104*, 448–456.

(4) Toupadakis, A.; Kubas, G. J.; Burns, C. J. *Inorg. Chem.* **1992**, *31*, 3810–3817.

(5) Kubas, G. J.; Ryan, R. R.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* **1989**, *111*, 7823.

(6) Coucouvanis, D.; Toupadakis, A.; Lane, J. D.; Koo, S. M.; Kim, C. G.; Hadjikyriacou, A. *J. Am. Chem. Soc.* **1991**, *113*, 5271–5282.

(7) Single crystals of this compound were hand-picked from a mixture that contained Et_4N^+-I in powder form. Analytical and spectroscopic data were obtained from the hand-picked crystals. Anal. Calcd for $(Et_4N)[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_3)]$, $Mo_2S_3O_5NC_{13}H_{25}$ (fw = 563): C, 27.71; H, 4.44; N, 2.49. Found: C, 27.90; H, 4.42; N, 2.55. FT-IR (cm^{-1}, KBr): ν(Mo═O) 962, 906; $\nu(\eta^2\text{-}SO_3)$ 1166, 646, 571, 502. ^1H NMR (ppm, CD_3CN): η^5-Cp^-, 6.33.

(8) Anal. Calcd for $(Et_4N)[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(S_2O_3)]$, $Mo_2S_4O_5NC_{13}H_{25}$ (fw = 595): Mo, 32.22; S, 21.54; C, 26.22; H, 4.23; N, 2.35. Found: Mo, 32.91; S, 21.56; C, 25.75; H, 4.32; N, 2.34. This compound showed in the ^1H NMR spectrum an additional Cp signal that was identified, and subsequently verified crystallographically, as due to IV.[9] The ratio of III to IV was 9:1. FT-IR (cm^{-1}, KBr): ν(Mo═O) 955, 915; $\nu(\eta^2\text{-}S_2O_3^{2-})$ 1277, 1172, 1150, 662, 542; ν(Cp) 3107, 827; $\nu(Mo\text{–}S_b)$ 483, 470. ^1H NMR (ppm, CD_3CN): η^5-Cp^-, 6.359(9), 6.381(1). Mass spectrum, FAB(–): *m/z* 465 (M^-).

(9) Anal. Calcd for $(Et_4N)[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]$, $Mo_2S_3O_6NC_{13}H_{25}$ (fw = 579): Mo, 33.12; S, 16.60; C, 26.95; H, 4.35; N, 2.42. Found: Mo, 33.62; S, 16.96; C, 26.82; H, 4.36; N, 2.38. FT-IR (cm^{-1}, KBr): ν(Mo═O) 969, 909; $\nu(\eta^2\text{-}SO_4^{2-})$ 1307, 1172, 669, 612, 572, 540. ^1H NMR (ppm, CD_3CN): η^5 Cp^-, 6.381(1). Mass spectrum, FAB(–): *m/z* 449 (M^-).

(10) Hoots, J. E.; Lesch, A.; Rauchfuss, T. B. *Inorg. Chem.* **1984**, *23*, 3130–3136.

(11) We have been unable to obtain this complex in analytically pure form. The ^1H NMR spectrum shows that the major impurity is the $[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(S_2)]^-$ complex.[6]

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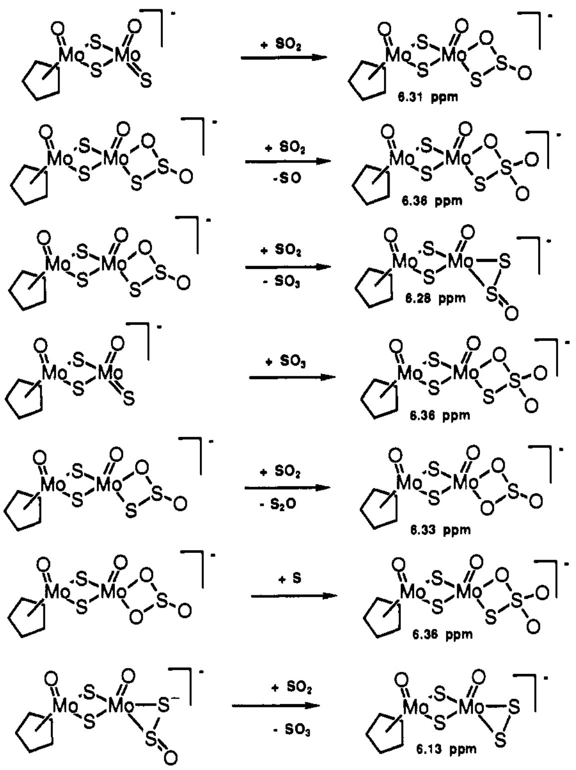

Figure 1. Possible pathways for the reactions of $[(C_5H_5)Mo(O)(\mu\text{-}S)_2Mo(O)(S)]^-$ with SO_2 and actual and proposed derivatives as revealed by ^1H NMR spectroscopy.

that very likely forms initially by addition of SO_2 across the Mo—S bond. This and the subsequent reactions (Figure 1) that give rise to the other $S_xO_y^{2-}$ ligands do not have precedence in previously reported[4,5] SO_2 chemistry in that they involve terminal rather than μ-S bound ligands.

Single crystals of the Et_4N^+ salts of II–IV were obtained by the slow diffusion of diethyl ether into DMF solutions of the complexes.[15] The structural features of the common $[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)]^+$ unit are quite similar in each of the three complexes and also are similar to those of the same unit in the $[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(S_2)]^-$ complex.[6] In II, the S–O_L and S–O_t bond lengths found in the $\eta^2\text{-}SO_3^{2-}$ ligand are 1.586(9) and 1.441(9) Å. In III, the bidentate $S_2O_3^{2-}$ ligand shows the S–S, S–O_L, and S–O_t bonds at 1.991(7), 1.512(11), and 1.429(10) Å, respectively, and in IV, the $\eta^2\text{-}SO_4^{2-}$ S–O_L and S–O_t bonds are found at 1.548(4) and 1.413(4) Å. The values for III are comparable to values previously reported for the $\eta^2\text{-}S_2O_3^{2-}$ ligand in $[(en)_2Co(S_2O_3)]^+$ [16] at 2.007(5), 1.533(8), and 1.45(1) Å. In the S-coordinated $\eta^1\text{-}S_2O_3^{2-}$ ligand in $Na_3Au(S_2O_3)_2{\cdot}2H_2O$,[17] the S–S and S–$O_t$ bond lengths are 2.060(5) and 1.46(1) Å respectively. The S–O distances in IV are comparable to the S–O_L and S–O_t bond lengths reported for the bridging sulfate ligands in the $K_2[Pt_2(SO_4)_4(DMSO)_2]{\cdot}4H_2O$ salt[18] at 1.540(6) and 1.43(1) Å.

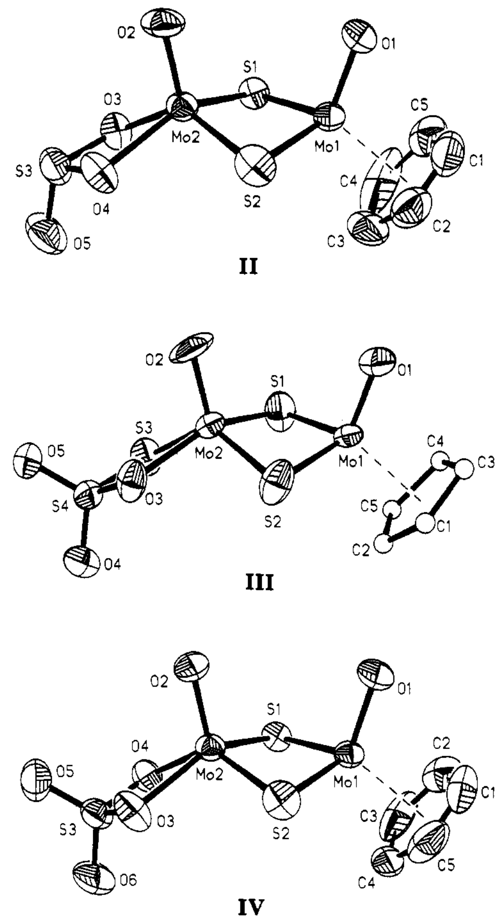

Figure 2. Structure and labeling of the $[(C_5H_5)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_3)]^-$ (II), $[(C_5H_5)Mo(O)(\mu\text{-}S)_2Mo(O)(S_2O_3)]^-$ (II), and $[(C_5H_5)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]^-$ (IV) complexes. Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces. Selected mean bond distances and angles not reported in the text: Mo–Mo, 2.840(5) Å (range 2.831(1)–2.850(2) Å); Mo–S_b, 2.302(6) Å (range 2.279(5)–2.319(6) Å); Mo–S_L, 2.379(5) Å; Mo═O, 1.687(11) Å (range 1.672(3)–1.700(11) Å); Mo–O_L, 2.077(10) Å (range 2.060(7)–2.090(4) Å); Mo–C, 2.38(4) Å (range 2.36(14)–2.45(4) Å); Mo–S_b–Mo, 76.2(2)° (range 75.8(1)–77.3(2)°); S_b–Mo–S_b, 101.6(2)° (range 100.7(2)–102.0(1)°). The numbers in parentheses represent the larger of the individual standard deviations or the standard deviations σ from the mean values for each class of distances or angles in all three structures.

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Supplementary Material Available: Tables S1–3, listing positional parameters, thermal parameters, and selected distances and angles for II–IV (23 pages). Ordering information is given on any current masthead page.

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(12) The first product of SO_2 addition to the Mo═S group is depicted to contain an unprecedented bidentate thiosulfite ligand. There is no real evidence for this *proposed* thiosulfite ligand other than the δ value of the short-lived Cp proton resonance in the NMR spectrum. The latter at 6.31 ppm correlates very well with Cp^- resonances of isostructural complexes with various other bidentate $S_2O_y^{2-}$ ligands in an electronegativity sum/δ plot (see text for details).

(13) Allred, A. L.; Rochow, E. G. *J. Am. Chem. Soc.* **1957**, *79*, 5361.

(14) Dailey, B. P.; Shoolery, J. N. *J. Am. Chem. Soc.* **1955**, *77*, 3977.

(15) Crystal and refinement data: Yellow-orange crystals of $(Et_4N)[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_3)]$ (Et_4N^+-II) are monoclinic, of space group $P2_1/n$, with a = 8.983(4) Å, b = 15.225(5) Å, c = 15.779(10) Å, β = 93.43(5)°, and Z = 4. Orange-yellow crystals of $(Et_4N)[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(S_2O_3)]$ (Et_4N^+-III) are monoclinic, of space group $P2_1/n$, with a = 7.782(2) Å, b = 18.383(6) Å, c = 15.780(5) Å, β = 103.91(1)°, and Z = 4. Orange-yellow crystals of $(Et_4N)[(Cp)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)]$ (Et_4N^+-IV) are monoclinic, of space group $P2_1/n$, with a 9.211(2) Å, b = 14.939(3) Å, c = 15.814(3) Å, β – 94.44(2)°, and Z = 4. Single-crystal X-ray diffraction data for all crystals were collected on a Nicolet P3/F diffractometer using Mo Kα radiation. The solutions of all structures were carried out by a combination of heavy-atom Patterson techniques, direct methods, and Fourier techniques. The refinement of the structures by full-matrix least-squares methods was based on 1960 unique reflections ($2\theta_{max}$ – 45°, $I > 3\sigma(I)$) for Et_4N^+-II, on 1904 unique reflections ($2\theta_{max}$ = 45°, $I > 3\sigma(I)$) for Et_4N^+-III, and on 2318 unique reflections ($2\theta_{max}$ = 45°, $I > 3\sigma(I)$) for Et_4N^+-IV. Anisotropic temperature factors were used for all non-hydrogen atoms in II–IV except for those of the disordered Cp ring in III. At the current stage of refinement on 217 parameters for II, 248 parameters for III, and 226 parameters for IV with all atoms present in the asymmetric units, R_w = 0.046, 0.057, and 0.028, respectively, for II–IV. For all structures, the hydrogen atoms have been included in the structure factor calculations at their calculated positions but have not been refined.

(16) Murdock, A. R.; Tyree, T.; Otterbein, W.; Kinney, L.; Carreras, M.; Cooper, J. N.; Elder, R. C. *Inorg. Chem.* **1985**, *24*, 3674.

(17) Ruben, H.; Zalkin, A.; Faltens, M. O.; Templeton, D. H. *Inorg. Chem.* **1974**, *13*, 1836.

(18) Cotton, F. A.; Falvello, L. R.; Han, S. *Inorg. Chem.* **1982**, *21*, 2889.