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The Investigation of Protonation of $[\text{Mo}_2(\text{NTo})_2(\text{S}_2\text{P}(\text{OEt})_2)_2(\text{SO})(\text{SBn})(\text{O}_2\text{CMe})]$

By

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Introduction

Metal-sulfur complexes have been of interest for many years due to their roles in a wide variety of biological and industrial practices. Molybdenum, a not so commonly known element, has a very high affinity for sulfur. Mo-S linkages are known in many biological enzymes, from bacteria through humans, and are known in industrial and even geochemical processes. The importance of these systems has provided a major impetus in fundamental studies of molybdenum-sulfur chemistry. Molybdenum-sulfur chemistry and SO_x -type ligands have also been of fundamental interest for many years for metals in general.

The most important molybdoenzyme is nitrogenase which catalyzes the reduction of N_2 to NH_3 .¹ This is a very important catalytic reaction for the nitrogen cycle on Earth. In hydrosulfurization (HDS) and hydronitrogenation (HDN), Mo-S compounds play a role as industrial catalysts. Both of these reactions are vital to the removal of sulfur and nitrogen, respectively, from petroleum feedstock. With the removal of such contaminants, the combustion of the petroleum can be done with decreased production of sulfur oxides and nitrogen oxides which cause acid rain. Therefore, it is important to understand reactions of molybdosulfur complexes.

The present work involves $[\text{Mo}_2(\text{NTo})_2(\text{S}_2\text{P}(\text{OEt})_2)_2(\text{SO})(\text{SBn})(\text{O}_2\text{CMe})]$ which contains the $\text{Mo}_2(\mu\text{-SO})$ functional group. (Bn= benzyl and To= p-tolyl, and other abbreviations are standard.) The structure is diagrammed below with a partial ligand set at left. (The dithiophosphate ligands and the tolyl groups are not shown for clarity.) For even more simplicity, this is truncated to give the diagram at right. Corresponding to that diagram, the formula $[\text{Mo}_2(\text{NTo})_2(\text{S}_2\text{P}(\text{OEt})_2)_2(\text{SO})(\text{SBn})(\text{O}_2\text{CMe})]$ is abbreviated as BnSMo_2SO .

The synthesis of BnSMo₂SO was published in 1996 by Wang et al.¹ The preparation of BnSMo₂SO was done using a methylene chloride slush bath (-95 °C) under red light. All handling of this compound was conducted under red light because it was believed at the time to be sensitive to white light. The work-up was done with column chromatography, also under red light. However, a new and far easier preparation was developed later and published in 2009.² Using this procedure, the compound can be synthesized under normal lighting since it was discovered that the prior light sensitivity was due to an impurity. The new preparation was done in a simple ice bath (0 °C) and does not require -95 °C. The pure compound, however, is temperature sensitive, decomposing slowly at room temperature as crystals and much more rapidly as an evaporated residue. With this new procedure a fuller characterization of the compound has been enabled in recent years. In fact, it was discovered that the oxygen of the S-O bridge is considerably nucleophilic, and alkylation occurs at the oxygen. That work was reported in 2009.² BnSMo₂SO was known also to be weakly basic but, for a number of years, protonation studies were inconclusive and seemingly contradictory until it was realized that the outcome depended on the acid being used. Weak acids gave an equilibrium and strong acids were needed for stoichiometric reaction. The anion of the strong acid could not be a coordinating ligand of itself, since these were known to displace the acetate bridge which is also present in the complex.

Figure 1. Crystal structure of the cation $\text{BnSMo}_2\text{SOH}^+$ illustrating O-H protonation site

As such, this eliminated many of the common strong acids. For example, Wang had done preliminary work with trifluoroacetic acid, $\text{CF}_3\text{CO}_2\text{H}$, which resulted in an S-H stretch in the IR spectrum in solution. However, this acid slowly displaced the acetate bridge and another acid was desired. The acid of choice became aqueous HBF_4 which did not displace the acetate bridge. Protonation with this acid was studied extensively for a number of years. An x-ray crystal structure of the protonation product with aqueous HBF_4 , however, showed an O-H bond and not an S-H bond (Figure 1).³ The synthesis itself using HBF_4 was also plagued by an impurity which added further complications.

Ultimately, these studies progressed to reveal an acid dependence for the site of protonation. More recently investigated acids include perhenic acid, triflic acid, and p-toluene sulfonic acid. These acids give protonation at S, while HBF_4 , so far, is the only acid to give

Figure 2. Crystal structure of the cation $\text{MeSMo}_2\text{SHO}^+$ illustrating S-H protonation site

protonation at O in the isolated solid. Furthermore, the impurity problem with HBF_4 was eventually solved when it was learned that “aqueous HBF_4 ” is actually an equilibrium mixture including some H_2OBF_3 ; this was the source of the impurity in the isolated solid.

Definitive confirmation of protonation at S was just recently obtained by x-ray crystallography (Figure 2). This particular compound derives from MeSMo_2SO , which contains a methylthiolate bridge instead of a benzylthiolate. This was in progress by a colleague, Mary Sherry; protonation using $\text{CF}_3\text{SO}_3\text{H}$ produced $\text{MeSMo}_2\text{SHO}^+ \text{CF}_3\text{SO}_3^-$.

Of particular interest now is the possibility of tautomeric equilibria which may be operating in solution. It is hypothesized that, in the HBF_4 studies, the protonation observed at O in the solid phase is due to lattice effects which arise from hydrogen bonding with the BF_4^- anion. In contrast, other acid studies, such as triflic and perrhenic acids, have yielded protonation at S in the solid phase. Although only one protonation site, S or O, was obtained in an isolated

solid for a particular derivative, it was anticipated that solution studies will allow for protonation at both S and O to be observed, since the solution phase will involve weaker ion pairing than in the solid phase. Various parameters have been studied such as choice of acid and also of solvent.

Having shown that protonation at S and at O in the isolated solids varies with the acid used, the question becomes why does protonation occur at the two sites and what factors are responsible? This question is best addressed by solution studies.

Several solvents were considered for the solution work. Both polar and nonpolar solvents are desired although hydrogen bonding solvents are avoided. A preliminary list of solvents includes p-xylene, methylene chloride, chloroform-D, and chlorobenzene as possible choices because these lack hydrogen bonding capabilities which could interfere with determining the protonation site. However, it was determined that p-xylene would not be used, as preliminary runs showed limited solubility of the compounds in this solvent. CDCl_3 was selected for preliminary solution studies. The location of the C-Cl and C-D stretches in the IR spectrum would not interfere with the resolution of either an O-H or S-H stretch in the spectrum (the peaks of interest).

Experimental section

m-Chloroperoxybenzoic acid (MCPBA) was prepared for use by drying in a desiccator for several days to remove the water in the commercial impure reagent (which also contained m-chlorobenzoic acid). All other solvents or reagents were used as received. All procedures were done open to air.

The tool of primary importance was IR spectroscopy since this has the ability to clearly distinguish S-H vs. O-H stretches. The solution studies were started on the ATR-IR Perkin Elmer Spectrum 100. However, the solvent evaporated too quickly causing questions of concentration

fluctuation. Therefore, KBr solution cells were used in the Mattson FT-IR in an attempt to control the concentration of the solution. Under the guidance of Dr. Richmond, the IR studies were carried out using the solvent system as the background rather than using the subtraction function, which is unreliable. NMR spectroscopy (^1H and $^{31}\text{P}\{^1\text{H}\}$) was used for assessing the purity of compounds. All NMR spectra were taken on the Varian Inova400 NMR spectrometer.

BnSMo₂S. This compound was synthesized by the modification reported in 2009.³ [Mo(NT_o)(S₂P(OC₂H₅)₂)S]₄ (1.2552g; 0.750 mmol) was dissolved in benzene (15 mL). Acetic acid (0.11 mL; 1.9 mmol) was added, followed by BnCl (0.22 mL; 1.9 mmol), and then followed by Et₃N (0.26 mL; 1.9 mmol). After stirring for 60 min, the slurry was rotavapped and then chased twice with two aliquots of THF (3.0 mL each). After the final rotavapping, the residue was dissolved in minimal THF. 2:1 EtOH:H₂O solution (15 mL) was added to precipitate the product; addition was slow to prevent oiling. The dried crystals appeared red. The crude product was characterized by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Recrystallization of the crude product was done with acetone (10 mL) and 2:1 MeOH:H₂O (20 mL) as the solvent system. The red solid was washed with a 3:1 MeOH:H₂O solution (24 mL) and suctioned dried. A final purified product was stored at room temperature for further use as the starting material used to produce BnSMo₂SO. The BnSMo₂S compound was synthesized with a 78% yield.

BnSMo₂SO. The synthesis followed the procedure reported in 2009.¹ BnSMo₂S (0.4935 g; 0.500 mmol) was dissolved in acetone (1 mL) and chilled in an ice bath. Acetic acid (0.11 mL, 1.9 mmol) was added, followed in close succession by HBF₄ (0.13 mL; 1.00 mmol) and then a chilled solution of MCPBA (0.0992 g; 0.575 mmol dissolved in 2.4 mL acetone). Two final aliquots of 0.5 mL acetone allowed for a quantitative transfer of the MCPBA. After stirring for approximately 3 min, a solution of NaHCO₃ (0.3360 g; 4.00 mmol) in 5.0 mL H₂O was slowly

added dropwise. The reaction flask was removed from the ice bath. Over a long period of time to prevent oiling (approximately 20 min), 13 mL of water was added. An olive green solid precipitated and was washed with 1:2 acetone:H₂O (15 mL). The solid was filtered and suction dried. After drying, the crude product was stored in the freezer until recrystallization was carried out. A ³¹P{¹H} NMR spectrum was obtained for the crude product to assess purity. The recrystallization was done using a methylene chloride-silica gel slurry (4.7004 g in 18 mL); the desired product adhered to the silica gel, while impurities were washed out by filtration. Acetone (38 mL) was then used to free the desired product from the silica gel, which was filtered off. The solution was rotavapped. Minimal EtOH (2.3 mL) was used to dissolve the solid, followed by the addition of H₂O to precipitate the solid. Final wash was done with 1:2 EtOH:H₂O (30 mL). Drying was promptly completed because of temperature sensitivity. The reaction had a 63% yield. The reaction can be seen below (eq 1).

1

BnSMo₂SHO⁺/MeC₆H₄SO₃⁻. Various acids including triflic, perrhenic, tetrafluoroboric, and p-toluenesulfonic acids, have been used. The preparation of the protonated product from p-toluenesulfonic acid is as follows. BnSMo₂SO (0.100 g, 0.0997 mmol) was slurried in diethyl ether (1.6 mL). EtOH (0.1 mL) was added. While stirring, p-toluenesulfonic acid (0.0189 g, 0.100 mmol) was added, followed by additional EtOH (0.8 mL). The product precipitated during 25 minutes of vigorous stirring. A yellow solid and yellow supernatant were present. The precipitate was collected by suction filtration, washed with diethyl ether (8 mL), and suction

dried. This synthesis produced a bright yellow powder in 62% yield. The IR spectrum of the solid (supplementary materials Figure S1) shows an S-H stretch at 2411 cm^{-1} .

$\text{BnSMo}_2\text{SHO}^+/\text{MeC}_6\text{H}_4\text{SO}_3^-$ was characterized also by using NMR (^1H and $^{31}\text{P}\{^1\text{H}\}$) in CDCl_3 to ensure purity. The compound gives isomers in solution, which can be seen in the $^{31}\text{P}\{^1\text{H}\}$ NMR and ^1H NMR spectra, supplementary materials Figures S2-S6. Four isomer structures are possible, as shown below. The other acid preparations were conducted

analogously. The products from the various acid preps were dissolved into CDCl_3 , and analyzed via IR spectroscopy. Here it would be clearly observed if the protonation in solution is in equilibrium between S-H and O-H.

Crystallographic studies. The group (also including Dylan Shields) had collectively explored crystal growing using $\text{MeSMo}_2\text{SHO}^+$ or $\text{BnSMo}_2\text{SHO}^+$, using different anions and using different solvents as illustrated in Table I. Ultimately, crystal selection was done by the crystallographer, Dr. Mark Mashuta, who selected batch C. The choice was made based on the size, color, and morphology. The crystals were grown utilizing liquid-liquid diffusion. The different compounds were placed into a test tube and then a chosen

Table I. Variations used for growing crystals

Crystal Identification	Cation/Anion	Solvent System Used for Crystal Growth
A	$\text{BnSMo}_2\text{SHO}^+ / \text{CF}_3\text{SO}_3^-$	Acetone / petroleum ether
B	$\text{BnSMo}_2\text{SHO}^+ / \text{ReO}_4^-$	CH_2Cl_2 / n- C_7H_{16}
*C	$\text{MeSMo}_2\text{SHO}^+ / \text{CF}_3\text{SO}_3^-$	CH_2Cl_2 / petroleum ether
D	$\text{MeSMo}_2\text{SHO}^+ / \text{CF}_3\text{SO}_3^-$	THF / c- C_6H_{12}
E	$\text{MeSMo}_2\text{SHO}^+ / \text{CF}_3\text{SO}_3^-$	CH_2Cl_2 / c- C_6H_{12}
F	$\text{BnSMo}_2\text{SHO}^+ / \text{ReO}_4^-$	THF / n- C_7H_{16}
G	$\text{BnSMo}_2\text{SHO}^+ / \text{ReO}_4^-$	CH_2Cl_2 / n- C_7H_{16}
H	$\text{BnSMo}_2\text{SHO}^+ / \text{CF}_3\text{SO}_3^-$	THF / n- C_7H_{16}
I	$\text{BnSMo}_2\text{SHO}^+ / \text{CF}_3\text{SO}_3^-$	CH_2Cl_2 / petroleum ether
J	$\text{MeSMo}_2\text{SHO}^+ / \text{ReO}_4^-$	CH_2Cl_2 / petroleum ether
K	$\text{MeSMo}_2\text{SHO}^+ / \text{ReO}_4^-$	Acetone/ c- C_6H_{12}

solvent was added to dissolve. A less dense crystallizing solvent was selected and slowly pipetted onto the first layer. Caution was taken to prevent vigorous mixing of the layers. The top was capped and the sample was allowed to sit for several days, undisturbed. Crystal growth was observed and documented. The liquid-liquid diffusion produced crystals in most cases and a crystal structure was obtained (Figure 2).

Solution studies. The three acids (triflic acid, perrhenic acid, and p-toluene sulfonic acid) were used to produce the protonated product, $\text{BnSMo}_2\text{SHO}^+$. Each anion was studied and spectra from the solution studies can be seen in the supplementary materials Figures S8-S10. The samples were prepared by weighing the chosen product (0.0488 g of $\text{BnSMo}_2\text{SHO}^+\text{MeC}_6\text{H}_4\text{SO}_3^-$) and dissolving in CDCl_3 (1 mL). This preparation was done in the IR room to limit the evaporation time prior to loading the KBr plate. A background was taken of the KBr cell with CDCl_3 , which can be seen in supplementary materials Figure S7. The cells were then flushed with dry air several times and loaded with the dissolved product. After completing the plotting, the plates were cleaned with methylene chloride and placed in a desiccator for storage.

Results

BnSMo₂SHO⁺MeC₆H₄SO₃⁻. The average yield for this synthesis is 55%. All products were characterized by IR spectroscopy and NMR spectroscopy (¹H and ³¹P{¹H}). The IR spectrum showed a CH stretch at 2985 cm⁻¹, SH stretch at 2410 cm⁻¹, and a weak C=C stretch at 1591 cm⁻¹. Also observed were the acetate C-O stretch at 1456 cm⁻¹, the C-N stretch at 1151 cm⁻¹ and the P-O-C stretch at 996 cm⁻¹. This spectrum was analogous to spectra from the other acid preps. ¹H and ³¹P NMR spectra illustrate the invertomers present in the compound. The ³¹P NMR spectrum (Figure S2) shows only two of the four possible isomers with a ratio of 2:1, at 110.3 and 110.9 ppm. The ¹H NMR spectra (Figure S3-S6) has been labeled with the structure provided on the full spectrum. Only the major invertomer peaks will be mentioned here. ¹H NMR (ppm): tos-H 8.04 d, 7.18 d; Bn-H 7.64 d, 7.51 t, 7.44 d; To-H 6.60 d, 6.46 d; POCH₂ 4.21 m, 4.02 m; BnCH₂ 3.83 s; To-CH₃ 2.34 s; OCCH₃ 1.43 s; POCCH₃ 1.19 m, 1.39 m.

Solution studies. The solvent used for the solution studies was CDCl₃. Because of the solvent volatility, the ATR-IR produced unreliable solution spectra. The FT-IR was used with KBr solution cells. The background IR spectrum (supplementary materials Figure S7) was provided to illustrate the presence of carbon dioxide and CDCl₃ in the samples. The background IR showed a CO₂ stretch at 2437 cm⁻¹ and a CD stretch located at 2293 cm⁻¹. These peaks were visible in the solution study IR spectra of the various anions. The IR spectrum of BnSMo₂SHO⁺MeC₆H₄SO₃⁻ showed a C-H stretch at 2986 cm⁻¹, and an SH stretch at 2466 cm⁻¹. A C=C stretch was observed at 1593 cm⁻¹, an acetate C-O stretch at 1455 cm⁻¹, and a P-O-C stretch at 1008 cm⁻¹. The spectra of the cations were very similar for both BnSMo₂SHO⁺CF₃SO₃⁻ and BnSMo₂SHO⁺ReO₄⁻. The IR spectrum of BnSMo₂SHO⁺CF₃SO₃⁻ showed a C-H stretch a 2988 cm⁻¹, an SH stretch at 2577 cm⁻¹. A C=C stretch was seen at 1593 cm⁻¹, an acetate

C-O stretch at 1455 cm^{-1} , and a P-O-C stretch at 1010 cm^{-1} . The IR spectrum of $\text{BnSMo}_2\text{SHO}^+\text{ReO}_4^-$ shows a C-H stretch at 2984 cm^{-1} , an SH stretch at 2546 cm^{-1} . A C=C stretch was observed at 1593 cm^{-1} , an acetate C-O stretch at 1455 cm^{-1} , and a P-O-C stretch at 1010 cm^{-1} .

Discussion

$\text{BnSMo}_2\text{SHO}^+\text{MeC}_6\text{H}_4\text{SO}_3^-$. The S-H stretch observable in the IR spectrum of $\text{BnSMo}_2\text{SHO}^+\text{MeC}_6\text{H}_4\text{SO}_3^-$ is often very weak. This anion was originally chosen because it was a weaker acid than others; however concerns arose over its hydrogen bonding capabilities. It appears in the solid IR spectrum of this compound, that the CH stretch is also wider than normal. This could indicate the presence of both an O-H and an S-H, as the O-H stretch could be buried in the CH stretch. This is a real possibility, as the ^1H NMR spectrum does not appear to have an S-H proton peak present in the spectrum for $\text{BnSMo}_2\text{SHO}^+\text{MeC}_6\text{H}_4\text{SO}_3^-$, indicating a possible equilibrium or hydrogen bonding. The other anions that produced a very strong SH stretch in the solid IR spectrum also showed the SH peaks as two broad singlets below 9 ppm in the ^1H NMR spectrum. The concerns of hydrogen bonding with O of the anion in the $\text{BnSMo}_2\text{SHO}^+\text{MeC}_6\text{H}_4\text{SO}_3^-$ compound are increased when solution studies were undertaken.

Solution studies. The various anion spectra from the solution studies showed an SH stretch around 2500 cm^{-1} . However, the solution IR spectrum of $\text{BnSMo}_2\text{SHO}^+\text{MeC}_6\text{H}_4\text{SO}_3^-$ compound showed a weak SH stretch and a broad CH stretch. This could, again, indicate the presence of a buried OH stretch. This was not the case for $\text{BnSMo}_2\text{SHO}^+\text{CF}_3\text{SO}_3^-$ and $\text{BnSMo}_2\text{SHO}^+\text{ReO}_4^-$, which had very strong and narrower SH stretch in the solution IR spectra. The crystal structure (Figure 2), derived from the triflic anion showed a definitive SH bond. Therefore, the $\text{BnSMo}_2\text{SHO}^+\text{CF}_3\text{SO}_3^-$ and $\text{BnSMo}_2\text{SHO}^+\text{ReO}_4^-$ compounds supported the presence of the sulfur site of protonation through the solid IR spectra, the crystal structure, and

the solution studies. The $\text{BnSMo}_2\text{SHO}^+\text{MeC}_6\text{H}_4\text{SO}_3^-$ compound had unclear results that may be from hydrogen bonding capabilities, as the IR spectrum of the solid and of the solution showed a weak SH stretch.

These results were not totally expected. It was thought that an equilibrium between the OH and SH site of protonation would be apparent in the solution studies because of the contradictory findings seen in crystal structures (Figure 1 and Figure 2), the previous work done on BF_4^- , and the current work with three different acids. However, the solution IR spectra failed to clearly show the OH stretch.

Future Directions

Future studies will be undertaken to further investigate the possibility of protonation at oxygen in solution. By using a deuterated solvent in the recrystallization of $\text{BnSMo}_2\text{SHO}^+\text{MeC}_6\text{H}_4\text{SO}_3^-$, such as EtOD, the SH stretch in the IR spectrum will be replaced with an SD stretch at a lower frequency. This process will also replace any OH stretch buried in the CH stretches with an OD stretch at lower frequency.

Studies will also be continued using HBF_4 . Work was done previously using this acid, which showed an O site of protonation (Figure 1). However, further studies will be conducted to prove the site of protonation is, in fact, at the O in solution.

References

- (1) Wang, Runtong. "Synthesis, Reactivity and Structural Studies of Dimolybdenum(V) Complexes With Sulfur Oxides, Disulfide and Oxide Bridges." Diss. University of Louisville, 1997. Print.
- (2) Tuong, Chi Minh, Whitney K. Hammons, Ashley L. Howarth, Kelly E. Lutz, Ackim D. Maduvu, Laura B. Haysley, Brian R. T. Allred, Lenore K. Hoyt, Mark S. Mashuta, and Mark E. Noble. "Alkylation of a Dimolybdenum SO Bridge, Subsequent Reactions, and Characterization of the Thioperoxide Bridge." *Inorganic Chemistry* 48.11 (2009): 5027-038. Print.

- (3) West, Michael; Mashuta, Mark S.; Noble, Mark E., unpublished results.
- (4) Wang, Runtong, Mark S. Mashuta, John F. Richardson, and Mark E. Noble. "Oxidation at a Dimolybdenum(V) Sulfur Bridge. Formation of SO and SO₂ Bridges. Facile Extrusion of SO from the SO₂ Bridge." *Inorganic Chemistry* 35.10 (1996): 3022-030. Print.

Figure S1. $\text{BnSMo}_2\text{SHO}^+\text{MeC}_6\text{H}_4\text{SO}_3^-$ IR spectrum

Figure S2. ^{31}P NMR of $\text{BnSMo}_2\text{SHO}^+\text{MeC}_6\text{H}_4\text{SO}_3^-$

Figure S3. ^1H NMR of $\text{BnSMo}_2\text{SHO}^+\text{MeC}_6\text{H}_4\text{SO}_3^-$ full spectrum

Figure S4. ^1H NMR of $\text{BnSMO}_2\text{SHO}^+\text{MeC}_6\text{H}_4\text{SO}_3^-$ expanded spectrum

Figure S5. ^1H NMR of $\text{BnSMO}_2\text{SHO}^+\text{MeC}_6\text{H}_4\text{SO}_3^-$ expanded spectrum

Figure S6. ^1H NMR of $\text{BnSMO}_2\text{SHO}^+\text{MeC}_6\text{H}_4\text{SO}_3^-$ expanded spectrum

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Figure S7. KBr solution cell background IR spectrum

Figure S8. Solution studies $\text{BnSMo}_2\text{SHO}^+\text{MeC}_6\text{H}_4\text{SO}_3^-$ IR spectrum

Figure S9. Solution studies $\text{BnSMo}_2\text{SHO}^+ \text{CF}_3\text{SO}_3^-$ IR spectrum

Figure S10. Solution studies $\text{BnSMo}_2\text{SHO}^+ \text{ReO}_4^-$ IR spectrum

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