Syntheses and Characterization of Ammonium and Tetraalkylammonium Thiomolybdates and Thiotungstates

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Received November 26, 1982

Improved methods for the preparation of $[NH_4]_2[MO_2S_2]$ *and* $[NH_4]_2[MS_4]$ *are summarized and new syntheses of* $[NH_4]_2[MOS_3]$ *are reported* ($M = Mo, W$)*. The facile conversion of the* $[NH_4]^+$ *salts to* $[Et_4N]^+$ *salts* via *reaction with aqueous* $[Et_4N]OH$ *is also described. Infrared and electronic spectral data for the thiometallates are summarized as an aid to future characterization.*

Introduction

Although the syntheses of group VI thiometallates were first reported in the late 19th century by Krüss [1] and Corleis [2], detailed studies on the chemistry of these species were not begun until the late 1960's by Müller and coworkers, who have pioneered work on the chemistry of these anions, and particularly on their ability to behave as bidentate ligands [3]. More recently, the potential utility of these anions in modeling biological systems has greatly expanded interest in their properties and reactivity. For example, the discovery [4] that an iron–molybdenum–sulfur cluster unit is present in nitrogenase has led to the synthesis of many multinuclear complexes of this nature, all utilizing the tetrathiomolybdate ion as the starting material [5]. In fact, studies on both nitrogenase [6] and its iron–molybdenum cofactor [7] have shown that both $[MoS_4]^{2-}$ and $[MoOS_3]^{2-}$ can be liberated under the proper degradative conditions. Thiomolybdates have also been implicated in the copper–molybdenum antagonism found in ruminants [8] and perhaps will have some utility in modeling other molybdoenzymes since the presence of Mo=S groups in xanthine oxidase has been suggested [9].

Because of our general interest in molybdoenzymes and particularly in the understanding of the mechanism of action of nitrogenase, we have been involved in the synthesis of various thiomolybdates and their tungsten analogs. We now have developed a new procedure for the syntheses of $[NR_4]_2[MOS_3]$ ($R = H, Et$; $M = Mo, W$) and have updated and improved the procedures for $[NR_4]_2[MS_4]$ and $[NR_4]_2[MO_2S_2]$. Herein we describe these methods for synthesis of the group VI thiometallates and provide spectral data which is useful in determining purity. The reactivity of many of the thiometallates will be presented in the future.

Experimental

Methods and Materials

Infrared spectra were recorded on a Beckman IR-20A instrument calibrated with polystyrene and electronic spectra obtained on a Cary 118C spectrophotometer. Elemental analyses for C, H, and N were performed in this laboratory using a Perkin Elmer 240 instrument equipped with Microjector from Control Equipment Corporation. The chemicals H_2WO_4, $Na_2MoO_4 \cdot 2H_2O$, and $[NH_4]_6[Mo_7O_{24}] \cdot 4H_2O$ are commonly available and a variety of sources was used. $[Et_4N]OH$ (10% in H_2O) was purchased from J. T. Baker and C. P. grade H_2S was obtained from Matheson Gas. All reactions were carried out aerobically using standard glassware. Once isolated, however, solids were stored under an inert atmosphere.

Syntheses of $[NH_4]_2[MoS_4]$

$Na_2MoO_4 \cdot 2H_2O$ (5.0 g) was dissolved in a mixture of concentrated NH_4OH (30 ml) and H_2O (10 ml) and the solution filtered. H_2S was bubbled rapidly into the reaction mixture until it was saturated at ambient temperature and then the temperature was raised to 60 °C while maintaining a slow stream of H_2S. After 30 min the mixture was cooled to 0° for 30 min and then the product isolated by filtration, washed with i-PrOH and Et_2O, and dried *in vacuo*. The yield was 5.1 g, 88%. *Anal.* Calcd for $H_8N_2MoS_4$: H, 3.08; N, 10.8. Found: H,

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2.98; N, 10.8. A similar procedure using $[NH_4]_6[Mo_7O_{24}]\cdot4H_2O$ instead of $Na_2MoO_4\cdot2H_2O$ works equally well.

Synthesis of $[NH_4]_2[MoOS_3]$

$Na_2MoO_4\cdot2H_2O$ (8.0 g) was dissolved in a mixture of concentrated NH_4OH (30 ml) and H_2O (18 ml) and the solution cooled in an ice bath after filtration. H_2S was rapidly passed *over the surface* of the solution causing the precipitation of $[NH_4]_2[MoO_2S_2]$. The delivery tube should *not* be immersed in the reaction solution as this will facilitate the formation of $[MoS_4]^{2-}$. The flow was continued until most of the precipitated solid had redissolved and then the reaction mixture was rapidly filtered into ice cold EtOH (700 ml). The precipitated solid was isolated by filtration, washed with EtOH and Et_2O, and dried *in vacuo*. The yield was 6.0 g, 75%. *Anal.* Calcd for $H_8N_2MoOS_3$: H, 3.28; N, 11.5. Found: H, 3.08; N, 11.4.

Synthesis of $[NH_4]_2[MoO_2S_2]$

$[NH_4]_6[Mo_7O_{24}]\cdot6H_2O$ (5.0 g) was dissolved in a mixture of concentrated NH_4OH (25 ml) and H_2O (15 ml) and the solution cooled in an ice bath after filtration. H_2S was passed slowly over the surface of the solution causing the precipitation of the product. The flow of gas *from* the reaction flask was monitored and, when it increased markedly, the delivery of H_2S was halted. After an additional 5 min at 0 °C, the product was isolated by filtration, washed with EtOH and Et_2O, and dried *in vacuo*. The yield was 5.3 g, 81%. *Anal.* Calcd for $H_8N_2MoO_2S_2$: H, 3.51; N, 12.28. Found: H, 3.40, N, 12.14.

Synthesis of $[NH_4]_2[WS_4]$

H_2WO_4 (5.0 g) was treated with concentrated NH_4OH (40 ml), the slurry was saturated with H_2S at room temperature and then heated at 60 °C with stirring for 20 min. After filtration, the solution was again heated at 60 °C and H_2S bubbling continued for 8 hrs. The reaction mixture was cooled to 15 °C while maintaining the H_2S flow and then the solid product was isolated by filtration, washed with i-PrOH and Et_2O, and dried *in vacuo*. The yield was 4.4 g 63%. *Anal.* Calcd for $H_8N_2WS_4$: H, 2.30; N, 8.05. Found: H, 2.35; N, 8.30.

Synthesis of $[NH_4]_2[WOS_3]$

H_2WO_4 (5.09 g) was dissolved in a mixture of concentrated NH_4OH (20 ml) and H_2O (5 ml) and the solution filtered. H_2S was bubbled rapidly into the solution for 15 min at ambient temperature causing the precipitation of a minimal amount of $[NH_4]_2[WO_2S_2]$. The reaction mixture was filtered into ice-cold i-PrOH (500 ml) and the product separated as a yellow solid which was isolated by filtration, washed with i-PrOH and Et_2O and dried *in vacuo*. The yield was 5.1 g, 81%. *Anal.* Calcd for $H_8N_2WOS_3$: H, 2.40; N, 8.43. Found: H, 2.30; N, 8.38.

Synthesis of $[NH_4]_2[WO_2S_2]$

H_2WO_4 (10.0 g) was dissolved in a mixture of concentrated NH_4OH (40 ml) and H_2O (10 ml), the solution filtered and then placed in an ice bath. H_2S was passed rapidly *over the surface* of the solution for 5 min causing the separation of the yellow product which was isolated by filtration, washed with EtOH and Et_2O and dried *in vacuo*. The yield was 10.0 g, 79%. *Anal.* Calcd for $H_8N_2WO_2S_2$: H, 2.53; N, 8.86. Found: H, 2.45; N, 8.78.

Synthesis of $[Et_4N]_2[MoS_4]$

$[NH_4]_2[MoS_4]$ (20.0 g) was dissolved in 10% $[Et_4N]OH$ in H_2O (230 ml), and the solution subjected to pumping for 2 hr to remove NH_3. H_2O was added to replace that lost due to evaporation, and the reaction mixture filtered into i-PrOH (400 ml). The precipitated product was isolated by filtration, washed with i-PrOH and Et_2O and dried *in vacuo*. The yield was 25.0 g, 68%. *Anal.* Calcd for $C_{16}H_{40}N_2MoS_4$: C, 39.7; H, 8.26; N, 5.79. Found: C, 39.6; H, 8.72; N, 5.80.

Synthesis of $[Et_4N]_2[MoOS_3]$

$[NH_4][MoOS_3]$ (3.5 g) was dissolved in 10% $[Et_4N]OH$ in H_2O (44 ml) and the solution subjected to pumping for 30 min to remove NH_3. The reaction mixture was added to i-PrOH (650 ml) and let stand for 15 min. A small amount of $[Et_4N]_2[MoS_4]$ was separated by filtration and a 1:1 mixture of i-PrOH/Et_2O (1000 ml) was added to the filtrate. The yellow product was isolated by filtration, washed with i-PrOH and Et_2O and dried *in vacuo*. The yield was 4.7 g, 70%. *Anal.* Calcd for $C_{16}H_{40}N_2MoOS_3$: C, 41.1; H, 8.54; N, 5.98. Found: C, 40.9; H, 4.91; N, 5.97.

Synthesis of $[Et_4N]_2[MoO_2S_2]$

$[NH_4]_2[MoO_2S_2]$ (5.0 g) was dissolved in 10% $[Et_4N]OH$ in H_2O (66 ml) and the solution subjected to pumping for 30 min to remove NH_3. i-PrOH (200 ml) and Et_2O (400 ml) were added to the reaction mixture causing the product to separate as an oil which was isolated by decantation. The oil was dissolved in i-PrOH (500 ml) and Et_2O (~500 ml) slowly added causing the precipitation of the solid product which was isolated by filtration, washed with Et_2O and dried *in vacuo*. The yield was 7.5 g, 76%. *Anal.* Calcd for $C_{16}H_{40}N_2MoO_2S_2$: C, 42.5; H, 8.85; N, 6.19. Found: C, 41.9; H, 9.3; N, 5.82.

Synthesis of $Cs_2[MoOS_3]$

$[NH_4]_6[Mo_7O_{24}]\cdot6H_2O$ (5.0 g) was dissolved in a solution of CsCl (15 g) in H_2O (20 ml) and concentrated NH_4OH (15 ml). Concentrated acetic acid (~7.5 ml) was added to bring the pH to 10 at which point a white solid separated. Additional concentrated NH_4OH was added dropwise until the solid just dissolved and then H_2S was bubbled into the solution for 10 min at ambient temperature. The crystalline product (10.2 g, 76%) was isolated by filtration, washed with a small amount of H_2O and then with EtOH and Et_2O and dried *in vacuo.*

Synthesis of [Et₄N]₂[WS₄]

$[NH_4]_2[WS_4]$ (3.5 g) was dissolved in 10% $[Et_4N]OH$ in H_2O (28 ml) and 30 ml of additional H_2O. The reaction mixture was subjected to pumping for 2 hr and then H_2O added to replace that lost to evaporation. The solution was added to i-PrOH (350 ml) and the yellow product which separated was isolated by filtration, washed with i-PrOH and Et_2O and dried *in vacuo*. The yield was 4.5 g, 78%. *Anal.* Calcd for $C_{16}H_{40}N_2WS_4$: C, 33.6; H, 6.99; N, 4.90. Found: C, 33.1; H, 7.08; N, 4.80.

Synthesis of [Et₄N]₂[WOS₃]

$[NH_4]_2[WOS_3]$ (3.5 g) was dissolved in 10% $[Et_4N]OH$ in H_2O (33 ml) and the solution subjected to pumping for 2 hr to remove NH_3. The reaction mixture was poured into i-PrOH (600 ml) and the small amount of $[Et_4N]_2[WS_4]$ which precipitated removal by filtration. Et_2O (500 ml) was slowly added to the filtrate and the solid product which formed was isolated by filtration, washed with Et_2O and dried *in vacuo*. The yield was 4.4 g, 76%. *Anal.*: Calcd. for $C_{16}H_{40}N_2WOS_3$: C, 34.5; H, 7.19; N, 5.04. Found: C, 34.4; H, 7.71; N, 5.00.

Synthesis of [Et₄N]₂[WO₂S₂]

$[NH_4]_2[WO_2S_2]$ (6.8 g) was dissolved in 10% $[Et_4N]OH$ in H_2O (65 ml) and the solution subjected to pumping for 1 hr. i-PrOH (400 ml) and then Et_2O (600 ml) were added to the reaction mixture causing the product to separate as an oil. The supernatant liquid was decanted and the oil dissolved in i-PrOH (400 ml) and the solution filtered. Addition of Et_2O (400 ml) to the filtrate caused the precipitation of the product which was isolated by filtration, washed with Et_2O and dried *in vacuo*. *Anal.* Calcd for $C_{16}H_{40}N_2WO_2S_2$: C, 35.6; H, 7.71; N, 5.19. Found: C, 34.6; H, 7.41; N, 4.94.

Results and Discussion

Synthetic Methods

Tetrathiometallates

The methods described herein for the preparation of the $[NH_4]_2[MS_4]$ species are almost identical to those of Krüss (M = Mo) [1] and Corleis (M = W) [2] which were published in the late 19th century. Both syntheses involve the exhaustive treatment by H_2S gas of molybdate or tungstate solutions in concentrated NH_4OH. It should be noted, however, that the synthesis is considerably more facile kinetically for the molybdenum system (requiring only 30 min at 50 °C) than for the tungsten (8 hr at 60 °C). In practice this means that pure $[NH_4]_2[MoS_4]$ is easy to obtain, since longer reaction times do no harm. However, unless prolonged reaction times, high temperatures, and a steady stream of H_2S are employed, the solid obtained from tungsten reaction mixtures may well be contaminated with $[NH_4]_2[WOS_3]$. Fortunately the presence of this impurity is readily detected spectroscopically (*vide infra*).

The syntheses of tetraalkylammonium salts of $[MS_4]^{2-}$ (M = Mo, W) have been carried out by Holm and coworkers [10] using a metathesis reaction between $[NH_4]_2[MS_4]$ and $[R_4N]Cl$ in MeCN. While we have also used this synthetic method with good results, generally we obtain equally pure products in better yields by reaction of the $[NH_4]_2[MS_4]$ species with a stoichiometric amount of aqueous $[Et_4N]OH$ (eqn. 1):

$$[NH_4]_2[MS_4] + 2[Et_4N]OH \xrightarrow{H_2O} [Et_4N]_2[MS_4] + 2H_2O + 2NH_3 \quad (1)$$

By subjecting the reaction solution to a vacuum, the removal of the only by-product of the reaction (NH_3) is effected, leaving pure $[Et_4N]_2[MS_4]$ in solution. The product can then be precipitated by addition of alcohol. The solids obtained in this way are generally powdery in nature but are as pure in terms of elemental analytical and spectroscopic data as the more crystalline products obtained from the metathesis in MeCN [10].

Trithiometallates

The potassium salt of $[WOS_3]^{2-}$ was reported by Corleis, [2] but no similar preparative method for the $[MoOS_3]^{2-}$ ion was described by Krüss [1]. Müller and coworkers [11] have reported that the insolubility of the Cs^+ salts of both $[MoOS_3]^{2-}$ and $[WOS_3]^{2-}$ can be used to facilitate the isolation of these species. We were interested in obtaining the $[NH_4]^+$ salts of the $[MOS_3]^{2-}$ ions so that a reaction analogous to eqn. 1 could be used in the preparation of the $[Et_4N]^+$ salts. The synthesis of $[NH_4]_2[WOS_3]$ is in fact relatively simple since this species is fairly stable toward conversion to $[NH_4]_2[WS_4]$ as evidenced by the stringent conditions required for the preparation of this latter species. H_2S is rapidly bubbled directly into a solution of H_2WO_4 in concentrated NH_4OH for 5 min at ambient

TABLE I. Spectral Data for Thiomolybdates and Thiotungstates.

Compound	Infrared[a]		UV/visible[b]
	$\nu_{M=S}$	$\nu_{M=O}$	
$[Et_4N]_2[MoS_4]$	470	–	467(11,850), 316(16,750), 241(24,700)[c] 472(14,600), 321(22,000)[d]
$[Et_4N]_2[MoOS_3]$	470	865	457(1970), 395(9090), 308(7300)[c] 459(2500), 400(10,750), 310(7620)[d]
$[Et_4N]_2[MoO_2S_2]$	460	860, 840	393(3140), 320(7430)[c] 388(4520), 321(9050)[d]
$[Et_4N]_2[WS_4]$	458	–	393(15,710), 277(24,500)[c] 397(19,600)[d]
$[Et_4N]_2[WOS_3]$	450	885	375(3200), 336(11,400), 268(2860), 240(9900)[c] 375(4500), 340(14,300)[d]
$[Et_4N]_2[WO_2S_2]$	445	885, 845	326(4050), 272(8290), 246(5700)[c] 324(5670)[d]
$[NH_4]_2[MoS_4]$	480	–	e
$[NH_4]_2[MoOS_3]$	485	835	e
$Cs_2[MoOS_3]$	480	855	e
$[NH_4]_2[MoO_2S_2]$	490	830, 792	e
$[NH_4]_2[WS_4]$	460	–	e
$[NH_4]_2[WOS_3]$	470	860	e
$[NH_4]_2[WO_2S_2]$	470	850, 795	e

[a] Spectra taken as KBr pellets; values in wavenumbers, ±5 cm^{-1}. [b] Peak positions in nm with molar absorptivities in parentheses. [c] In H_2O. [d] In MeCN. [e] Peak positions and molar absorptivities (in H_2O) identical within experimental error to the $[NEt_4]^+$ salts.

temperature. Addition of isopropanol to this solution results in the separation of the pure product.

Experimentally, the synthesis of $[NH_4]_2[MoOS_3]$ is somewhat more difficult than that of its tungsten analog. Here, H_2S is not bubbled directly into the solution of $[MoO_4]^{2-}$ in ammonia, since this treatment favors formation of $[MoS_4]^{2-}$, but instead is passed rapidly *over the surface* at 0 °C until the $[NH_4]_2[MoO_2S_2]$ which has formed (see later) has almost dissolved. The reaction mixture is then *immediately and rapidly* filtered into ice-cold isopropanol causing the quick separation of $[NH_4]_2$-$[MoOS_3]$. Speed and low temperatures are critical to this synthetic procedure since $[MoOS_3]^{2-}$ converts to $[MOS_4]^{2-}$ much more rapidly than does its tungsten analog.

Once prepared, the $[NH_4]_2[MOS_3]$ salts are readily converted to $[Et_4N]_2[MOS_3]$ via reaction with $[Et_4N]OH$ as in eqn. 1. The $[Et_4N]_2[MOS_3]$ species are soluble in isopropanol, as opposed to $[Et_4N]_2[MS_4]$, and this property allows for easy removal of any $[MS_4]^{2-}$ which has been inadvertently formed in the synthesis of the $[NH_4]^+$ salts.

Dithiometallates

The $[NH_4]^+$ salts of $[MoO_2S_2]^{2-}$ and $[WO_2S_2]^{2-}$ were reported by Krüss [1] and Corleis [2], respectively, and our method for these species is very similar to theirs. A stream of H_2S is passed over the surface of solutions of the metallates in ammonia and the products precipitate as yellow solids. A marked increase in the flow of the effluent stream provides an indication that the reaction is complete and immediate filtration at this point maximizes the yield of $[NH_4]_2[MO_2S_2]$.

Conversion of $[NH_4]_2[MO_2S_2]$ to $[Et_4N]_2$-$[MO_2S_2]$ via a reaction analogous to eqn. 1 is readily effected. The $[Et_4N]^+$ salts are soluble in isopropanol and, unfortunately, initial addition of ether does not yield the products as well-formed solids, but instead as oils. After decantation of the partially-aqueous supernatant liquid, however, these oils are readily crystallized from isopropanol/ether. The solids $[Et_4N]_2[MO_2S_2]$ (M = Mo, W) are particularly hygroscopic, tending to oil on exposure to moist air. For this reason the filtration of the solid products ideally should be performed under an inert atmosphere.

Spectroscopic Characterization

A combination of infrared and UV/visible spectroscopy can be used effectively to determine the purity of the various thiometallates. Müller [3] has provided a valuable compilation of much of this data along with resonance Raman and structural

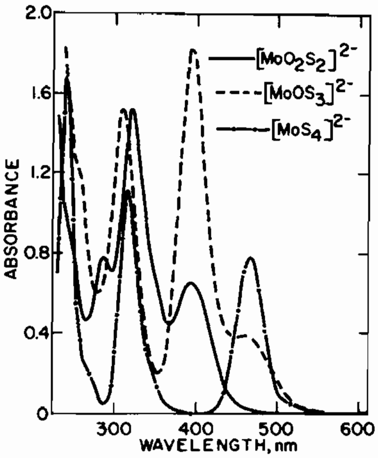

Fig. 1. Electronic spectra of thiomolybdates in H_2O. —— 2.08×10^{-4} *M* $[MoO_2S_2]^{2-}$; ---- 2.01×10^{-4} *M* $[MoOS_3]^{2-}$; –·– 0.68×10^{-4} *M* $[MoS_4]^{2-}$.

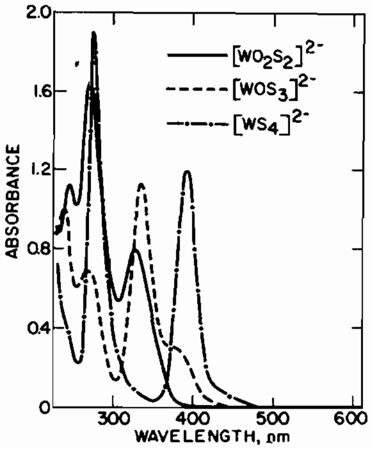

Fig. 2. Electronic spectra of thiotungstates in H_2O. —— 1.92×10^{-4} *M* $[WO_2S_2]^{2-}$; ---- 1.00×10^{-4} *M* $[WOS_3]^{2-}$; –·– 0.77×10^{-4} *M* $[WS_4]$.

data in review articles. He has also discussed in detail the bonding and spectroscopy of these species in terms of molecular orbital theory. For the sake of completeness, we have included spectroscopic data on the thiometallates prepared as described by our methods. The actual UV/visible spectra of the thiomolybdate and thiotungstate species are shown in Figs. 1 and 2 respectively. Band position and molar absorptivities are provided in Table I along with infrared spectral data.

Two features of the overall spectral data are perhaps notable. One is the fact that the positions of the M=S and M=O bands in the solid state infrared spectra of the thiometallates is dependent on the associated cation. The variation is consistent for the $[NH_4]^+$ and $[Et_4N]^+$ salts were $\nu_{M=S}$ is always higher and $\nu_{M=O}$ is always lower in energy for the $[NH_4]^+$ salts. This effect is certainly indicative of solid state cation–anion interactions for these species [12]. The second notable feature is the effect of solvent on the peak positions and particularly on the molar absorptivities in the electronic spectra of the thiometallates. The ϵ values are on the average ~25% higher in MeCN than in H_2O. The reasons for this effect are not known, but it is evident that molar absorptivities obtained in one solvent cannot be used to quantitate the amount of thiometallates in another medium.

The utility of the UV/visible spectra of these thiometallates in determining purity is particularly valuable for the $[MoOS_3]^{2-}$ and $[WS_4]^{2-}$ ions, where contamination by $[MoS_4]^{2-}$ and $[WOS_3]^{2-}$, respectively, is common. The presence of small amounts of $[WOS_3]^{2-}$ impurities in $[WS_4]^{2-}$ preparations can be caused by a variety of conditions, including reaction temperatures which are too low and reaction times which are too short. Because the major peak in the electronic spectrum of $[WOS_3]^{2-}$ (334 nm) occurs at a minimum in the spectrum of $[WS_4]^{2-}$, this impurity is readily detected. For the $[MoOS_3]^{2-}$ ion, the ratio of the intensity of the peaks at 395 and 457 nm should be 4.6 for aqueous samples. Lower values for this ratio almost certainly indicate contamination with MoS_4^{2-} which exhibits a very strong absorption at 467 nm but none at 395 nm. In this light, it should be noted that previous reports [11] of the electronic spectrum of $Cs_2[MoOS_3]$ in H_2O, where molar absorptivities for the peaks at 465 and 392 nm were given as 2300 and 8700 respectively are apparently in error. The low ratio of 3.8 from these numbers can readily be accounted for by the presence of 10% $[MoS_4]^{2-}$ in the sample. Samples of $Cs_2[MoOS_3]$ produced by the method of Müller [11] in our laboratory gave a spectral ratio of 4.65 indicating that the $[MoOS_3]^{2-}$ can indeed be produced free of $[MoS_4]^{2-}$ in this way.

Precise preparative methods and accurate spectral data, including molar absorptivities, for these thiometallates are becoming increasingly important as these ions assume a vital role in bioinorganic chemical research aimed at duplicating the molybdenum-containing prosthetic groups of enzymes [5]. Not only are they important as basic building blocks to produce useful, isolable prototype molecules, but their quantitation as degradative products of these molybdenum-containing sites depends on reliable, accurate data obtainable only from pure samples produced by dependable syntheses.

Acknowledgement

We are grateful for support of this work by a grant from USDA/SEA Competitive Research Grants

Office (59-2394-1-1-675-0). This manuscript constitutes Contribution No. 788 from the Charles F. Kettering Research Laboratory.

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