

the carbon atom in di- $\mu$ -methoxy complexes.<sup>20</sup>

If x-ray and neutron diffraction data were available, most of our qualitative arguments could become semiquantitative within the framework of the angular overlap model. The overwhelming problem will be the process of growing large crystals of the  $\mu$ -oxo complexes.

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**Registry No.** (-)<sub>D</sub>[(phen)<sub>2</sub>Cr(OH)<sub>2</sub>Cr(phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub>, 59204-27-2; [(phen)<sub>2</sub>Cr(OH)<sub>2</sub>Cr(phen)<sub>2</sub>](NO<sub>3</sub>)<sub>4</sub>, 31351-95-8; [(phen)<sub>2</sub>CrO(OH)Cr(phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>, 31351-96-9; [(phen)<sub>2</sub>CrO<sub>2</sub>Cr(phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 31282-17-4; [(bpy)<sub>2</sub>Cr(OH)<sub>2</sub>Cr(bpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub>, 31418-78-7; [(bpy)<sub>2</sub>CrO(OH)Cr(bpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>, 31542-02-6; [(bpy)<sub>2</sub>CrO<sub>2</sub>Cr(bpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 31282-16-3.

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Contribution from the Department of Chemistry,  
Florida Atlantic University, Boca Raton, Florida 33431

## Di- $\mu$ -oxo, $\mu$ -Oxo- $\mu$ -sulfido, and Di- $\mu$ -sulfido Complexes of Molybdenum(V) with EDTA, Cysteine, and Cysteine Ester Ligands. Preparation and Electrochemical and Spectral Properties

VIRGINIA R. OTT, DON S. SWIETER, and FRANKLIN A. SCHULTZ\*

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Preparative methods and electrochemical and spectral properties are reported for binuclear Mo(V) complexes containing di- $\mu$ -oxo (Mo<sub>2</sub>O<sub>4</sub><sup>2+</sup>),  $\mu$ -oxo- $\mu$ -sulfido (Mo<sub>2</sub>O<sub>3</sub>S<sup>2+</sup>), and di- $\mu$ -sulfido (Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub><sup>2+</sup>) centers coordinated to EDTA, cysteine, and ethyl cysteinate ligands. The  $\mu$ -oxo- $\mu$ -sulfido complexes are prepared here for the first time, and improved synthetic procedures are reported for the di- $\mu$ -sulfido complexes. Infrared and electronic absorption spectra of these compounds are sensitive to substitution of sulfur atoms into the bridge system. The systematic changes upon bridge modification are useful in characterizing the compounds and in clarifying assignments of Mo-O and Mo-S bridge stretching frequencies. The EDTA and cysteine complexes undergo electrochemical reduction in a single four-electron step to Mo(III) dimers in aqueous buffers. Although the ease of reduction and electrochemical reversibility of the Mo<sup>V</sup>/Mo<sup>III</sup> couple increase with insertion of S into the bridge system, the Mo(III) dimers become increasingly unstable upon bridge sulfur substitution. The corresponding ethyl cysteinate complexes are reduced by successive one-electron transfers in dimethyl sulfoxide to Mo<sup>V</sup>-Mo<sup>IV</sup> and Mo<sup>IV</sup><sub>2</sub> species. The chemical stability of these reduced products increases in the sequence Mo<sub>2</sub>O<sub>4</sub> < Mo<sub>2</sub>O<sub>3</sub>S < Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub>. The different behavior of sulfido bridging is attributed to greater lability of Mo<sup>III</sup>-S bonds in the former case and to greater electron delocalization by sulfur atoms over the binuclear framework in the latter.

Binuclear molybdenum(V) complexes are currently of interest as models for the redox centers of molybdenum-containing enzymes. A number of complexes containing di- $\mu$ -oxo and di- $\mu$ -sulfido bridging units have been prepared,<sup>1-8</sup> and the structural features and physical and chemical properties of these compounds have been discussed in recent reviews.<sup>9-12</sup> Relatively little has been reported on species containing the intermediate  $\mu$ -oxo- $\mu$ -sulfido bridging moiety. Preparation and study of such compounds would be of interest in understanding the effect of sulfur-bridging atoms on the properties of the binuclear molybdenum unit.

We have previously reported on the electrochemical<sup>13,14</sup> and catalytic<sup>15,16</sup> properties of the di- $\mu$ -oxo species Mo<sub>2</sub>O<sub>4</sub>(EDTA)<sup>2-</sup> and Mo<sub>2</sub>O<sub>4</sub>(Cys)<sub>2</sub><sup>2-</sup>. The latter compound is one of the most widely studied chemical models for the molybdenum-containing site of nitrogenase,<sup>17</sup> and its behavior mimics that of the enzyme in many respects. As a continuation of our studies on the redox properties of binuclear molybdenum centers, we have synthesized a series of complexes containing Mo<sub>2</sub>O<sub>3</sub>S<sup>2+</sup>

cores coordinated to EDTA, cysteine, and ethyl cysteinate ligands. The spectral and electrochemical properties of these compounds are reported in this paper and compared with those of the Mo<sub>2</sub>O<sub>4</sub><sup>2+</sup> and Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub><sup>2+</sup> analogs. The results of this study demonstrate that replacement of oxygen by sulfur bridging atoms exerts a significant and systematic influence on the infrared and electronic spectral properties and electrochemical behavior of the binuclear molybdenum(V) unit.

During the course of this work it was found that some procedures previously published for preparation of di- $\mu$ -sulfido complexes could not be applied successfully to the compounds we wished to prepare. In addition, no synthetic methods were available for preparation of  $\mu$ -oxo- $\mu$ -sulfido complexes. In this work simple synthetic procedures are described which are generally applicable to the direct preparation of complexes containing Mo<sub>2</sub>O<sub>3</sub>S<sup>2+</sup> and Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub><sup>2+</sup> cores and which are particularly effective for preparation of the water-soluble sulfido-bridged Mo(V) derivatives. Since the completion of this work several  $\mu$ -O- $\mu$ -S bridged Mo(V) complexes with

dithiocarbamate<sup>18-21</sup> or dithiophosphinate<sup>20,21</sup> ligands have been prepared using different procedures than described in this paper. In some cases these procedures yield a mixture of products, and chromatographic separation is required to isolate the desired complex.

### Experimental Section

**Preparation of Complexes. Sodium Di- $\mu$ -oxo-bis[(L-cysteinato)oxomolybdate(V)] Pentahydrate,  $\text{Na}_2\text{Mo}_2\text{O}_4(\text{Cys})_2 \cdot 5\text{H}_2\text{O}$  (1).** This compound was synthesized by the dithionite reduction procedure of Kay and Mitchell.<sup>2</sup> Analysis and characterization were consistent with results reported previously.<sup>14</sup>

**Sodium  $\mu$ -Oxo- $\mu$ -sulfido-bis[(L-cysteinato)oxomolybdate(V)] Tetrahydrate,  $\text{Na}_2\text{Mo}_2\text{O}_3\text{S}(\text{Cys})_2 \cdot 4\text{H}_2\text{O}$  (2).** Molybdenum pentachloride (5.5 g, 20 mmol) from Pressure Chemical Co., Pittsburgh, Pa., was dissolved in 100 mL of 3 M HCl and filtered to remove undissolved solids. Hydrogen sulfide (Matheson, 99.6%) was bubbled slowly through the solution for ca. 2 h. The solution was purged with argon to remove excess  $\text{H}_2\text{S}$ , and a small quantity of brown solid was removed by filtration. L-(+)-Cysteine hydrochloride monohydrate (3.5 g, 20 mmol) was dissolved in 15 mL of water and added to the filtrate. The pH of this solution was adjusted to 6.0 with 8 M NaOH while the solution was cooled in an ice bath. Yellow-orange crystals formed immediately. These were recrystallized by dissolving in a minimum quantity of water and allowing slow evaporation of solvent under reduced pressure (partially evacuated desiccator). After several days red-orange crystals formed, and these were washed with a 3:1 ethanol-water mixture and stored in vacuo over  $\text{P}_2\text{O}_5$ .

**Sodium Di- $\mu$ -sulfido-bis[(L-cysteinato)oxomolybdate(V)] Tetrahydrate,  $\text{Na}_2\text{Mo}_2\text{O}_2\text{S}_2(\text{Cys})_2 \cdot 4\text{H}_2\text{O}$  (3).** Hydrogen sulfide was bubbled slowly through a solution of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (4.8 g, 20 mmol) in 100 mL of water for ca. 2 h, or until the solution was saturated with  $\text{H}_2\text{S}$  as indicated by formation of precipitate in a ferric ion trap. The proper duration of hydrogen sulfide treatment resulted in a change of color to a deep, but clear, red-orange hue and a decrease in pH to  $\sim 8.2$ . The solution was purged with argon to remove excess  $\text{H}_2\text{S}$ . A solution of L-(+)-cysteine hydrochloride monohydrate (3.5 g, 20 mmol) in 15 mL of water was adjusted to pH  $\sim 6$  with sodium hydroxide and added to the reduced molybdate solution. After several days orange crystals were collected and recrystallized in the same manner as compound 2.

**Sodium  $\mu$ -(Ethylenediaminetetraacetato)-di- $\mu$ -oxo-bis[oxomolybdate(V)] Monohydrate,  $\text{Na}_2\text{Mo}_2\text{O}_4(\text{EDTA}) \cdot \text{H}_2\text{O}$  (4).** The preparation and analysis of this compound were reported previously.<sup>13</sup>

**Sodium  $\mu$ -(Ethylenediaminetetraacetato)- $\mu$ -oxo- $\mu$ -sulfido-bis[oxomolybdate(V)] Dihydrate,  $\text{Na}_2\text{Mo}_2\text{O}_3\text{S}(\text{EDTA}) \cdot 2\text{H}_2\text{O}$  (5).** The procedure for preparation of compound 2 was followed until addition of ligand. A solution of  $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$  (3.7 g, 10 mmol) in 25 mL of water was added to the molybdate solution, and the pH of the resulting solution was adjusted to 6.0 with 8 M NaOH. The solution was allowed to stand in the open for several days, during which time red-orange crystals formed. These were collected and recrystallized in the same manner as compound 2.

**Sodium  $\mu$ -(Ethylenediaminetetraacetato)-di- $\mu$ -sulfido-bis[oxomolybdate(V)] Dihydrate,  $\text{Na}_2\text{Mo}_2\text{O}_2\text{S}_2(\text{EDTA}) \cdot 2\text{H}_2\text{O}$  (6).** The procedure for preparation of compound 3 was followed until addition of ligand. A solution of  $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$  (3.7 g, 10 mmol) in 25 mL of water was adjusted to pH  $\sim 6$  and added to the reduced molybdate solution. After the mixture stood in the open for several days, red-orange crystals formed. These were collected and recrystallized as described for compound 2.

**Di- $\mu$ -oxo-bis[(L-cysteinato ethyl ester)oxomolybdenum(V)],  $\text{Mo}_2\text{O}_4(\text{Etcys})_2$  (7).** The compound was prepared by Melby's procedure<sup>1</sup> of boiling freshly prepared  $\mu$ -oxo complex,  $\text{Mo}_2\text{O}_3(\text{Etcys})_4$ , in methanol on a steam bath. The product was recrystallized from acetonitrile as bright yellow crystals.

**$\mu$ -Oxo- $\mu$ -sulfido-bis[(L-cysteinato ethyl ester)oxomolybdenum(V)],  $\text{Mo}_2\text{O}_3\text{S}(\text{Etcys})_2$  (8).** The procedure for preparation of compound 2 was followed until addition of ligand. A solution of L-(+)-cysteine ethyl ester hydrochloride (3.7 g, 20 mmol) in 20 mL of water was added to the molybdate solution with vigorous stirring, and 8 M NaOH was added to raise the pH to 6.0. A light brown precipitate formed and was collected and washed with water. The precipitate was dissolved in a minimum quantity of acetone and transferred to a separatory funnel. Distilled water was added until the solution clouded, and the suspension was separated from a dark oily residue which

formed at the surface and placed in a second separatory funnel. Approximately 50 mL of  $\text{CCl}_4$  was added, and the mixture was shaken vigorously. The complex appeared as yellow-orange crystals at the bottom of the  $\text{CCl}_4$  layer. The product was recrystallized from  $\text{CH}_2\text{Cl}_2$  and stored in vacuo over  $\text{P}_2\text{O}_5$ .

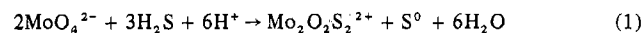
**Di- $\mu$ -sulfido-bis[(L-cysteinato ethyl ester)oxomolybdenum(V)],  $\text{Mo}_2\text{O}_2\text{S}_2(\text{Etcys})_2$  (9).** The procedure for preparation of compound 3 was followed until addition of ligand. A solution of L-(+)-cysteine ethyl ester hydrochloride (3.7 g, 20 mmol) in 20 mL of water was adjusted to pH 8.0-8.4 and slowly added to the reduced molybdate solution with vigorous stirring. The complex precipitated as a light to medium brown solid. This material was treated by the same separation procedure as compound 8, with the complex appearing as orange crystals at the bottom of the  $\text{CCl}_4$  layer. These were dissolved in  $\text{CH}_2\text{Cl}_2$  and evaporated to dryness to remove traces of  $\text{CCl}_4$ . The complex was stored in vacuo over  $\text{P}_2\text{O}_5$ .

**Physical Measurements.** Ultraviolet and visible spectra were recorded for complexes in solutions of distilled water or Spectroquality acetonitrile on a Cary 14 spectrophotometer in 1-cm quartz cells. Infrared spectra were recorded on a Perkin-Elmer 621 grating spectrophotometer for compounds in potassium bromide disks. Voltammetric measurements were made using electrochemical instrumentation described previously.<sup>13</sup> All electrochemical experiments were carried out in a Brinkmann Model E615 cell at ambient temperature under an atmosphere of argon. Nonaqueous electrochemistry was run in Spectroquality dimethyl sulfoxide ( $\text{Me}_2\text{SO}$ , Aldrich Chemical Co.) with 0.1 M tetraethylammonium tetrafluoroborate ( $\text{TEABF}_4$ , Southwestern Analytical Chemicals) as supporting electrolyte. For aqueous electrochemistry the working electrode was a Metrohm Model E410 hanging mercury drop electrode (area 0.022  $\text{cm}^2$ ). For nonaqueous electrochemistry the working electrode was either the mercury drop electrode or a Beckman Model 39273 Pt button electrode (area 0.20  $\text{cm}^2$ ). The reference electrode was an aqueous saturated calomel electrode (SCE) which, for nonaqueous experiments, was separated from the test solution by a salt bridge containing supporting electrolyte solution. All potentials are reported relative to the aqueous SCE.

### Results and Discussion

**Preparation of Complexes.** The analytical data shown in Table I (supplementary material) and the spectroscopic data to be presented later are consistent with the formation of three series of di- $\mu$ -oxo,  $\mu$ -oxo- $\mu$ -sulfido, and di- $\mu$ -sulfido Mo(V) complexes. The preparative procedures described in the Experimental Section are simple and direct routes to the two types of sulfido-bridged compounds. In early synthetic attempts we occasionally obtained mixtures of products with varying degrees of sulfur substitution. However, by trial-and-error adjustment of the rate and duration of  $\text{H}_2\text{S}$  flow, the desired products were readily prepared in pure form.

In unbuffered aqueous solution hydrogen sulfide apparently reduces sodium molybdate to the  $\text{Mo}_2\text{O}_2\text{S}_2^{2+}$  species:



The desired di- $\mu$ -sulfido complex is then formed by adding the appropriate ligand. It is necessary to adjust the pH of the ligand solution to near that of the molybdate solution ( $\sim 8.2$  after reaction with  $\text{H}_2\text{S}$ ) before mixing. This precaution is particularly advisable in the case of the ethyl cysteinate compound. Here, if the ligand solution is too acidic, intractable brown solids or oils form; if the ligand solution is too alkaline and the product is not recovered quickly, hydrolysis to compound 3 occurs almost quantitatively.

A number of other investigators have used addition of  $\text{H}_2\text{S}$  to sodium molybdate or to a previously isolated Mo(VI) complex to prepare  $\text{Mo}_2\text{O}_2\text{S}_2^{2+}$  complexes.<sup>2,5,22</sup> In our opinion this procedure is superior to that of adding  $\text{H}_2\text{S}$  to the corresponding di- $\mu$ -oxo Mo(V) complex for the compounds described in this paper because the reactivity of the oxo-bridged system is too highly dependent upon the ligand. For example, addition of excess hydrogen sulfide to  $\text{Na}_2\text{Mo}_2\text{O}_4(\text{Cys})_2$  leads to extensive decomposition of the complex and formation of

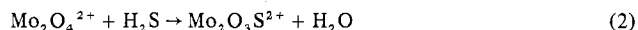
Table II. Infrared and Electronic Spectral Data

|  | Infrared <sup>a</sup>       |                             |                             |                 |              |
|--|-----------------------------|-----------------------------|-----------------------------|-----------------|--------------|
|  | $\nu(\text{Mo}=\text{O})^c$ | $\nu(\text{Mo}-\text{O}_b)$ | $\nu(\text{Mo}-\text{S}_b)$ |                 |              |
| $\text{Na}_2\text{Mo}_2\text{O}_4(\text{Cys})_2$           | 951 s                       | 735 m, 435 m                |                             |                 |              |
| $\text{Na}_2\text{Mo}_2\text{O}_3\text{S}(\text{Cys})_2$   | 950 s                       | 715 m, 498 w                |                             | <i>d</i>        |              |
| $\text{Na}_2\text{Mo}_2\text{O}_2\text{S}_2(\text{Cys})_2$ | 946 s                       |                             |                             | 466 m           |              |
| $\text{Na}_2\text{Mo}_2\text{O}_4(\text{EDTA})$            | 956 sh, 943 s<br>(950)      | 762 s, 480 m                |                             |                 |              |
| $\text{Na}_2\text{Mo}_2\text{O}_3\text{S}(\text{EDTA})$    | 957 s, 941 m<br>(949)       | 756 m, 483 m                |                             | 461 m           |              |
| $\text{Na}_2\text{Mo}_2\text{O}_2\text{S}_2(\text{EDTA})$  | 950 sh, 944 s<br>(947)      |                             |                             | 480 s           |              |
| $\text{Mo}_2\text{O}_4(\text{Etcys})_2$                    | 986 vs, 952 w<br>(969)      | 742 s, 470 m                |                             |                 |              |
| $\text{Mo}_2\text{O}_3\text{S}(\text{Etcys})_2$            | 956 s, 930 m<br>(943)       | 734 s, 518 w                |                             | 450 w           |              |
| $\text{Mo}_2\text{O}_2\text{S}_2(\text{Etcys})_2$          | 964 s, 942 m<br>(953)       |                             |                             | 455 m           |              |
| Electronic <sup>b</sup>                                    |                             |                             |                             |                 |              |
|  | 1                           | 2                           | 3                           | 4               | 5            |
| $\text{Na}_2\text{Mo}_2\text{O}_4(\text{Cys})_2$           | 485 sh (170)                |                             |                             | 306 (12 400)    |              |
| $\text{Na}_2\text{Mo}_2\text{O}_3\text{S}(\text{Cys})_2$   | 455 sh (220)                |                             | 326 sh (7450)               | 286 (12 400)    | 214 (25 700) |
| $\text{Na}_2\text{Mo}_2\text{O}_2\text{S}_2(\text{Cys})_2$ |                             | 374 sh (3170)               | 312 sh (7200)               | 273 sh (10 000) | 227 (24 500) |
| $\text{Na}_2\text{Mo}_2\text{O}_4(\text{EDTA})$            |                             | 392 (350)                   |                             | 298 (10 400)    |              |
| $\text{Na}_2\text{Mo}_2\text{O}_3\text{S}(\text{EDTA})$    | 465 sh (110)                |                             | 313 (5980)                  | 282 (8120)      |              |
| $\text{Na}_2\text{Mo}_2\text{O}_2\text{S}_2(\text{EDTA})$  | 468 sh (120)                | 347 sh (2490)               | 308 sh (5700)               | 278 (10 800)    |              |
| $\text{Mo}_2\text{O}_4(\text{Etcys})_2$                    |                             | 340 sh (3500)               | 288 (9550)                  | 277 (9610)      | 222 (17 000) |
| $\text{Mo}_2\text{O}_3\text{S}(\text{Etcys})_2$            | 440 sh (340)                | 336 sh (4200)               |                             | 276 (13 600)    |              |
| $\text{Mo}_2\text{O}_2\text{S}_2(\text{Etcys})_2$          | 430 sh (640)                | 332 sh (5680)               | 292 (10 400)                | 254 (13 000)    | 223 (26 800) |
| Calculated Spectra <sup>e</sup>                            |                             |                             |                             |                 |              |
| $\text{Mo}_2\text{O}_4^{2+}$                               | 493                         | 365                         | 324                         | 280             |              |
| $\text{Mo}_2\text{O}_2\text{S}_2^{2+}$                     | 463                         | 340                         | 311                         | 277             | 226          |

<sup>a</sup> Frequency in  $\text{cm}^{-1}$ . <sup>b</sup>  $\lambda_{\text{max}}$  in nm ( $\epsilon$  in  $\text{M}^{-1} \text{cm}^{-1}$ ). Data for compounds 1-6 in water; for compounds 7-9 in acetonitrile. <sup>c</sup> Average frequency in parentheses. <sup>d</sup> Band obscured by ligand vibration. <sup>e</sup> References 33 and 34.

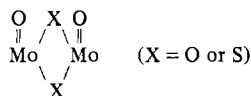
unidentified brown material.<sup>23</sup> At the other extreme,  $\text{Na}_2\text{Mo}_2\text{O}_4(\text{EDTA})$  reacts very slowly or not at all with  $\text{H}_2\text{S}$ , presumably because the bridging EDTA ligand shields the binuclear center from nucleophilic attack.

Preparation of  $\mu\text{-O}-\mu\text{-S}$  species is accomplished by adding  $\text{H}_2\text{S}$  to  $\text{Mo}(\text{V})$  in 3 M HCl, where the predominant species is the  $\text{Mo}_2\text{O}_4^{2+}$  dimer.<sup>25</sup> High acidity apparently limits substitution in the bridge to one sulfur atom.



Addition of ligand and neutralization to pH 6 yields the appropriate complex. The EDTA and cysteine complexes are the first examples of water-soluble  $\text{Mo}(\text{V})$  complexes containing the  $\mu\text{-oxo}-\mu\text{-sulfido}$  moiety. Spivack and Dori<sup>3</sup> reported a compound which they formulated as a sulfido-bridged  $\text{Mo}(\text{VI})$  dimer,  $\text{K}_2\text{Mo}_2\text{O}_4\text{S}(\text{EDTA}) \cdot \text{H}_2\text{O}$ , from reaction of  $\text{K}_2\text{Mo}_2\text{O}_4$  with  $\text{K}_2\text{H}_2\text{EDTA}$  at pH 6. The infrared and electronic absorption spectra of their product match those of compound **5** very closely (vide infra), and thus it should probably be represented as a  $\mu\text{-oxo}-\mu\text{-sulfido}$   $\text{Mo}(\text{V})$  species,  $\text{K}_2\text{Mo}_2\text{O}_3\text{S}(\text{EDTA}) \cdot 2\text{H}_2\text{O}$ .

**Infrared Spectra.** Replacement of oxygen by sulfur bridging atoms produces predictable and systematic changes in the vibrational spectra of the  $\text{Mo}_2\text{O}_2\text{X}_2$  core:



The characteristic spectra which result are useful not only in identifying the oxo- and sulfido-bridged species but also in establishing correct assignments for  $\text{Mo}-\text{O}$  and  $\text{Mo}-\text{S}$  bridge stretching vibrations, a subject of considerable controversy in the recent past.<sup>20,26-28</sup> The results of the present work are in

good agreement with a recent study<sup>20</sup> in which comparative spectra of  $^{16}\text{O}$  and  $^{18}\text{O}$  species were used to provide vibrational assignments for oxo-bridged  $\text{Mo}(\text{V})$  dimers.

Infrared spectral data for bridge and terminal stretching vibrations are collected in Table II. For  $\text{Mo}_2\text{O}_2\text{X}_2$  complexes as many as four bridge vibrational modes may be observed. Only two of these modes are commonly observed in the infrared spectra of di- $\mu\text{-oxo}$  compounds, and prominent bands at 735-765 and 430-480  $\text{cm}^{-1}$  are assigned to  $\text{Mo}-\text{O}$  bridge vibrations in accord with most recent studies.<sup>1,6,7,27</sup> Newton and McDonald<sup>20</sup> observed a third, weak, infrared-active vibration at 710-715  $\text{cm}^{-1}$  in the complexes  $\text{Mo}_2\text{O}_4[\text{S}_2\text{C}-\text{N}(\text{C}_2\text{H}_5)_2]_2$  and  $\text{Mo}_2\text{O}_4[\text{S}_2\text{P}(i\text{-C}_3\text{H}_7)_2]_2$ , but this band could not be located with certainty for any of the compounds in Table II. These results indicate that assignment<sup>26</sup> of three infrared-active frequencies between 600 and 750  $\text{cm}^{-1}$  is incorrect for  $\text{Mo}_2\text{O}_4$  structures.

Substitution of sulfur for one of the bridging oxygen atoms causes two of the four  $\text{Mo}-\text{O}_b$  bands to be replaced by  $\text{Mo}-\text{S}_b$  bands. The molybdenum-oxygen absorptions also undergo a decrease in intensity and a shift in frequency such that the splitting between the two bands decreases upon sulfur substitution. The decrease in splitting is small ( $\sim 10 \text{ cm}^{-1}$ ) for the EDTA complex, but substantially larger ( $\sim 60-80 \text{ cm}^{-1}$ ) for the cys and Etcys complexes which are not bridged by the ligand as well. A single  $\text{Mo}-\text{S}_b$  frequency is observed at 450-460  $\text{cm}^{-1}$ . Newton and McDonald<sup>20</sup> reported four infrared-active modes at  $\sim 710$  and 515  $\text{cm}^{-1}$  ( $\text{Mo}-\text{O}_b$ ) and  $\sim 460$  and 365  $\text{cm}^{-1}$  ( $\text{Mo}-\text{S}_b$ ) for  $\text{Mo}_2\text{O}_3\text{S}$  systems.<sup>29</sup> The results in Table II are in good agreement with these assignments, with the exception that the lower frequency  $\text{Mo}-\text{S}_b$  band is obscured by ligand vibrations in the compounds we have studied. Upon substitution of the second S atom, the oxygen bridge bands disappear, and the higher frequency sulfur

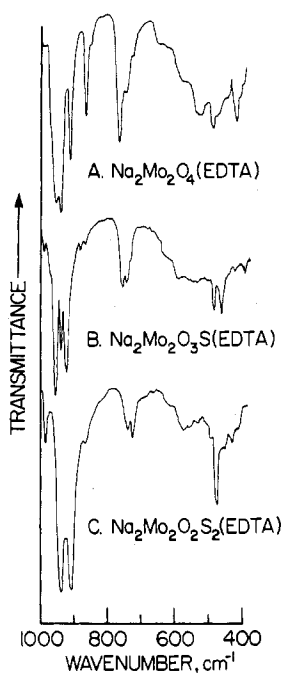


Figure 1. Infrared spectra of  $\text{Na}_2\text{Mo}_2\text{O}_4\text{X}_2(\text{EDTA})$  complexes.

bridge band shifts to higher energy at 455–480  $\text{cm}^{-1}$  and increases in intensity. A second Mo–S<sub>b</sub> frequency predicted<sup>24</sup> at  $\sim 340 \text{ cm}^{-1}$  for  $\text{Mo}_2\text{O}_2\text{S}_2$  centers is again obscured by ligand bands. Infrared spectra of the EDTA complexes (Figure 1) are representative of the behavior observed upon sequential sulfur substitution in the binuclear Mo(V) centers. In the absence of S substitution experiments the two ligand bands at  $\sim 725$  and  $740 \text{ cm}^{-1}$  could be mistaken for Mo–O<sub>b</sub> bands in the EDTA complexes.

Assignment of terminal molybdenum–oxygen stretching frequencies is still a source of confusion for some binuclear complexes. Although no more than two Mo=O bands may be expected for complexes with  $\text{Mo}_2\text{O}_4$  centers, as many as three or four<sup>1,4</sup> bands have been assigned to Mo–O vibrations in the 900–1000- $\text{cm}^{-1}$  region. Oxygen-18 substitution studies<sup>20</sup> have assigned two bands centered around  $970 \text{ cm}^{-1}$  to the Mo=O absorption in a number of  $\text{Mo}_2\text{O}_4$  complexes. The absorptions are usually split by 15–20  $\text{cm}^{-1}$ , and the higher frequency band is the more intense of the two. For some of the compounds reported in Table II, it appears that no observable splitting of  $\nu(\text{Mo}=\text{O})$  occurs. Thus, in the cysteine complexes a single, strong absorption is observed at  $\sim 950 \text{ cm}^{-1}$ . This band shifts slightly to lower frequency on sulfur substitution. Two additional bands at 970 and 929  $\text{cm}^{-1}$ , which are observed in all three cysteine complexes, are unaffected by S substitution and are much weaker than the central band. We feel these absorptions probably should be assigned to ligand rather than Mo–O<sub>t</sub> modes.

The situation is somewhat more complex in the case of the EDTA complexes. A band centered at  $\sim 950 \text{ cm}^{-1}$  is clearly split in the  $\text{Mo}_2\text{O}_3\text{S}$  compound, but incompletely so or not at all in the case of the  $\text{Mo}_2\text{O}_4$  and  $\text{Mo}_2\text{O}_2\text{S}_2$  species. An unknown band is located at 911, 925, and 917  $\text{cm}^{-1}$  in compounds 4, 5, and 6, respectively, and with the terminal oxo band(s) gives the appearance of a doublet or triplet structure in the 900–1000- $\text{cm}^{-1}$  region (Figure 1). Among these bands only the one or two vibrations at  $\sim 950 \text{ cm}^{-1}$  are attributed to Mo–O<sub>t</sub>. This assignment gives good agreement between the average band energies of the EDTA complexes and the single  $\nu(\text{Mo}=\text{O})$  of the cysteine complexes and a slight shift to lower frequency with S substitution. Furthermore, the two Mo–O<sub>b</sub> bands are the only ones shifted to lower frequency (by 10–15

$\text{cm}^{-1}$ ) upon isolation of the acid complex,  $\text{H}_2\text{Mo}_2\text{O}_4 \cdot (\text{EDTA}) \cdot 2\text{H}_2\text{O}$ .<sup>4</sup> Hydrogen bonding of protons to terminal Mo=O would be expected to decrease the vibrational frequency of these groups. A complete and fully accurate assignment of terminal oxo vibrations for the EDTA and cysteine complexes can probably be achieved only through isotope substitution studies.

In the Etcys complexes the principal Mo–O<sub>t</sub> vibration is readily identified as a strong, sharp band. The pronounced effect of sulfur substitution on  $\nu(\text{Mo}=\text{O})$ , however, is somewhat unusual. The observed behavior can probably be attributed to the fact that in the Etcys complexes no atom is coordinated directly trans to the terminal oxo group and that the trigonal-bipyramidal coordination geometry around Mo<sup>30</sup> differs from the more usual square-pyramidal arrangement of other five-coordinate  $\text{Mo}_2\text{O}_2\text{X}_2\text{L}_2$  complexes.<sup>12,18,31,32</sup>

**Electronic Spectra.** Electronic spectral data for the nine complexes are listed in Table II along with theoretical spectra calculated by SCF–MO methods for  $\text{Mo}_2\text{O}_4^{2+}$  and  $\text{Mo}_2\text{O}_2\text{S}_2^{2+}$  centers.<sup>33,34</sup> Agreement between the experimental and calculated spectra is very good. Placement of sulfur atoms in the bridge system can be seen to exert a systematic effect on the electronic spectra, and this is useful in the qualitative identification of the compounds. The most significant effect is the shift of the characteristic band for  $\text{Mo}_2\text{O}_4$  complexes at 280–310 nm to higher energy with increasing bridge sulfur substitution. The same behavior is generally true of the absorption maxima and shoulders represented among bands 1–3. On the other hand, a high-intensity band at  $\sim 220 \text{ nm}$ , which is observed in the cys and Etcys compounds, shifts to lower energy with increased sulfur bridging. A shoulder of moderate intensity at  $\sim 450 \text{ nm}$  is observed for most of the sulfido-bridged species. This band is close to the wavelength predicted for the lowest energy transition of  $\text{Mo}_2\text{O}_2\text{S}_2^{2+}$  complexes.<sup>34</sup>

The theoretical study of Brown et al.<sup>33,34</sup> identifies the highest energy filled orbital in  $\text{Mo}_2\text{O}_4^{2+}$  and  $\text{Mo}_2\text{O}_2\text{S}_2^{2+}$  systems as a d<sub>σ</sub> Mo–Mo bonding orbital with some contribution from the bridging atoms. The five unfilled molecular orbitals of lowest energy are Mo–Mo bonding or antibonding orbitals which also have some bridging or terminal atom character. Since the spectra in Table II are largely unaffected by ligand, it is plausible that the electronic transitions represented by bands 1–5 are located primarily within the binuclear molybdenum core. The ground and excited states of these systems contain partial contributions from the bridging atom groups, and this factor is responsible for the observed spectral shifts upon sulfur substitution.

**Aqueous Electrochemistry.** Our earlier electrochemical studies<sup>13,14</sup> demonstrated that  $\text{Mo}_2\text{O}_4(\text{EDTA})_2^{2-}$  and  $\text{Mo}_2\text{O}_4(\text{Cys})_2^{2-}$  are reduced in a single four-electron step to binuclear Mo(III) products in aqueous buffers. Depending on the choice of ligand and solution conditions the dimeric Mo(III) products have appreciable stability and can be re-oxidized to the initial Mo<sup>V</sup><sub>2</sub> species. The process is electrochemically quasi-reversible, and the separation between cathodic and anodic peak potentials can be as large as 300–600 mV. The voltammetric peak current parameters for the  $\mu$ -oxo- $\mu$ -sulfido and di- $\mu$ -sulfido EDTA and cysteine complexes are of comparable magnitude to values for the analogous di- $\mu$ -oxo compounds (Table III). These results indicate that the sulfido-bridged complexes also are reduced in a single four-electron step at mercury electrodes. By further analogy to the di- $\mu$ -oxo compounds it is assumed that four protons are transferred in the reduction step, and the overall electrode process can be written as

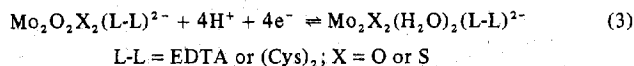


Table III. Cyclic Voltammetric Data for Reduction of  $\text{Mo}_2\text{O}_2\text{X}_2(\text{Cys})_2^{2-}$  and  $\text{Mo}_2\text{O}_2\text{X}_2(\text{EDTA})^{2-}$  Complexes in Aqueous Buffers<sup>a</sup>

|  | $E_{pc}$ , V                     | $E_p - E_{p/2}$ , mV | $E_{pa}$ , V | $\Delta E_p$ , mV | $E_c^{\circ}$ , <sup>b</sup> V | $i_{pc}/\nu^{1/2}C$ ,<br>$\mu\text{A s}^{1/2}$<br>$\text{V}^{-1/2} \text{mM}^{-1}$ | $i_r/i_f$ |
|--|----------------------------------|----------------------|--------------|-------------------|--------------------------------|--|-----------|
| Acetate Buffer <sup>c,d</sup>                          |                                  |                      |              |                   |                                |  |           |
| $\text{Mo}_2\text{O}_4(\text{EDTA})^{2-}$ <sup>e</sup> | -1.130                           | 72                   | -0.620       | 510               | -0.875                         | 53.6   | 0.44      |
| $\text{Mo}_2\text{O}_3\text{S}(\text{EDTA})^{2-}$      | -0.717                           | 31                   | -0.673       | 44                | -0.695                         | 74.0   | 1.03      |
| $\text{Mo}_2\text{O}_2\text{S}_2(\text{EDTA})^{2-}$    | -0.720                           | 25                   | -0.688       | 32                | -0.704                         | 78.6   | 1.03      |
| Borate Buffer <sup>f</sup>                             |                                  |                      |              |                   |                                |  |           |
| $\text{Mo}_2\text{O}_4(\text{EDTA})^{2-}$              | -1.248                           | 53                   | -0.866       | 382               | -1.057                         | 59.1   | 0.73      |
| $\text{Mo}_2\text{O}_3\text{S}(\text{EDTA})^{2-}$      | -1.079                           | 52                   | -0.907       | 172               | -0.993                         | 60.1   | 0.91      |
| $\text{Mo}_2\text{O}_2\text{S}_2(\text{EDTA})^{2-}$    | -1.068                           | 55                   | -0.898       | 170               | -0.983                         | 57.9   | 0.87      |
| $\text{Mo}_2\text{O}_4(\text{Cys})_2^{2-}$             | -1.310                           | 56                   | -0.788       | 522               | -1.049                         | 57.0   | 0.62      |
| $\text{Mo}_2\text{O}_3\text{S}(\text{Cys})_2^{2-}$     | -1.213                           | 79                   | -0.917       | 296               | -1.065                         | 49.2   | 0.51      |
| $\text{Mo}_2\text{O}_2\text{S}_2(\text{Cys})_2^{2-}$   | -1.29 sh<br>(-1.39) <sup>g</sup> | 90<br>(96)           | (-0.88)      | (510)             | (-1.14)                        | (46.6)   | (0.59)    |

<sup>a</sup> Data recorded for  $\sim 1$  mM complexes at  $\nu = 0.1$  V s<sup>-1</sup> at a hanging mercury drop electrode. <sup>b</sup>  $E_c^{\circ} = (E_{pc} + E_{pa})/2$ . <sup>c</sup> 0.2 M HOAc/0.2 M NaOAc, pH 4.70. <sup>d</sup> No reduction wave observed for  $\text{Mo}_2\text{O}_2\text{X}_2(\text{Cys})_2^{2-}$  complexes in acetate buffer. <sup>e</sup> 0.025 M HOAc/0.075 M NaOAc/0.142 M Na<sub>2</sub>SO<sub>4</sub>, pH 4.93. <sup>f</sup> 0.1 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, pH 9.18. <sup>g</sup> Data in parentheses recorded at  $\nu = 20$  V s<sup>-1</sup>.

Presence of sulfur bridging atom(s) in the  $\text{Mo}_2\text{O}_2\text{X}_2^{2+}$  complexes markedly influences fundamental properties such as the formal reduction potential, electrochemical reversibility, and stability of the  $\text{Mo}^{\text{III}}_2$  electrode products. A striking example is the increase in reversibility of the  $\text{Mo}^{\text{V}}_2/\text{Mo}^{\text{III}}_2$  couple in acetate buffer upon substitution of one or two S atoms into the bridge of  $\text{Mo}_2\text{O}_4(\text{EDTA})^{2-}$  (Figure 2). Similar but less dramatic effects are observed for the cysteine and EDTA complexes in borate buffer. In acetate medium reduction of  $\text{Mo}_2\text{O}_2\text{X}_2(\text{EDTA})^{2-}$  changes from a highly irreversible process for the di- $\mu$ -oxo species ( $\Delta E_p \approx 500$  mV) to an almost perfectly reversible four-electron transfer for the sulfido-bridged compounds. At slow scan rates the values of  $E_p - E_{p/2}$  and  $\Delta E_p$  for  $\text{Mo}_2\text{O}_3\text{S}(\text{EDTA})^{2-}$  and  $\text{Mo}_2\text{O}_2\text{S}_2(\text{EDTA})^{2-}$  approach the limits of  $56/n = 14$  mV and  $60/n = 15$  mV for a reversible four-electron couple.<sup>35</sup> The increase in reversibility also is responsible for larger values of  $i_{pc}/\nu^{1/2}C$  for the latter compounds in acetate buffer relative to the other values in Table III. Interestingly enough, there seems to be little difference in behavior between the mono- and disulfido products.

Voltammetric peak potentials and formal reduction potentials shift in the positive direction with sulfur substitution. The effects are more pronounced for the EDTA than the cysteine complexes, and there is little difference in behavior between insertion of the first and second sulfur atom. Nevertheless, the shifts of 100–400 mV in  $E_{pc}$  and 60–180 mV in  $E_c^{\circ}$  are significant and are in the direction of increasing ease of reduction with bridge sulfur substitution. The differences in peak potentials enable a convenient assay to be made of product purity using voltammetric techniques. For example, it is possible to use linear sweep or other voltammetric methods to detect small amounts of the  $\text{Mo}_2\text{O}_4^{2+}$  complexes in the presence of their sulfido-bridged counterparts.

Sulfur-bridge substitution has a significant influence on the stability of the binuclear  $\text{Mo}(\text{III})$  electrode products. The effect is more pronounced for the cysteine complexes since the presence of EDTA as a bridging ligand greatly enhances the stability of the binuclear molybdenum unit. Thus, all  $\text{Mo}^{\text{III}}_2$ -EDTA electrode products appear to be stable on the time scale of cyclic voltammetry.<sup>36,37</sup> The cyclic voltammetric curves in Figure 3 depict a far different situation for the cysteine complexes. The anodic peak current for reoxidation of the binuclear  $\text{Mo}(\text{III})$  product at  $-0.7$  to  $-0.9$  V vs. SCE decreases noticeably at constant scan rate on going from the di- $\mu$ -oxo to  $\mu$ -oxo- $\mu$ -sulfido to di- $\mu$ -sulfido derivative. The behavior of  $\text{Mo}_2\text{O}_2\text{S}_2(\text{Cys})_2^{2-}$  is difficult to observe because rapid decomposition of the initial product leads to a species

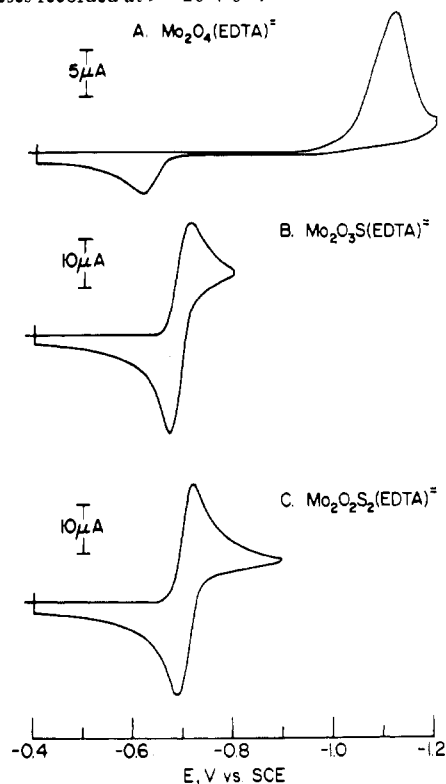


Figure 2. Cyclic voltammetric reduction of 1 mM  $\text{Mo}_2\text{O}_2\text{X}_2(\text{EDTA})^{2-}$  complexes at a hanging mercury drop electrode in acetate buffer. Solution conditions as in Table III;  $\nu = 0.1$  V s<sup>-1</sup>.

which catalyzes  $\text{H}^+$  reduction at the mercury electrode, thereby obscuring the  $\text{Mo}^{\text{V}}_2$  reduction peak. At faster scan rates the decomposition reaction is less extensive, and the characteristic peaks of the  $\text{Mo}^{\text{V}}_2/\text{Mo}^{\text{III}}_2$  redox process can be identified (see inset, Figure 3c). We have not completed a thorough study of the chemical reactions of the sulfido-bridged molybdenum(III)-cysteine products. However, by using the previously determined rate constant for  $\text{Mo}_2\text{O}_2(\text{H}_2\text{O})_2(\text{Cys})_2^{2-}$  decomposition in borate buffer<sup>14</sup> and the  $i_r/i_f$  values in Table III, an estimate can be made of the effect of sulfido bridging on the rate of decomposition of the initial electrode product. This approximation assumes that the chemical reaction is first order and follows a simple EC mechanism.<sup>35</sup> The estimated rate constants in 0.1 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> are  $\sim 0.004$ , 1, and  $100$  s<sup>-1</sup> for  $\text{Mo}_2\text{O}_4(\text{Cys})_2^{2-}$ ,  $\text{Mo}_2\text{O}_3\text{S}(\text{Cys})_2^{2-}$ , and  $\text{Mo}_2\text{O}_2\text{S}_2(\text{Cys})_2^{2-}$ , respectively. The surprising feature of this result is that substitution of sulfur bridging atoms systematically destabilizes

Table IV. Cyclic Voltammetric Data for Reduction of  $\text{Mo}_2\text{O}_2\text{X}_2(\text{Etcys})_2$  Complexes in Dimethyl Sulfoxide<sup>a</sup>

|   | Electrode       | $\nu$ , $\text{V s}^{-1}$ | $E_{p_1}$ , V | $E_p - E_{p/2}$ , mV | $E_1^\circ$ , <sup>b</sup> V | $i_{p_1}/\nu^{1/2}C$ ,<br>$\mu\text{A s}^{1/2}$<br>$\text{V}^{-1/2}$<br>$\text{mM}^{-1}$ | $E_{p_2}$ , V       | $i_{p_2}/\nu^{1/2}C$ ,<br>$\mu\text{A s}^{1/2}$<br>$\text{V}^{-1/2}$<br>$\text{mM}^{-1}$ | $k_f$ , $\text{s}^{-1}$ |
|---|-----------------|---------------------------|---------------|----------------------|------------------------------|--|---------------------|--|-------------------------|
| $\text{Mo}_2\text{O}_4(\text{Etcys})_2$           | Hg <sup>c</sup> | 0.02–200                  | -1.619        | 78                   | -1.671                       | 6.35   | -2.00               | 5.93   | $320 \pm 60$            |
|   | Pt <sup>c</sup> | 0.03–100                  | -1.633        | 79                   | <i>d</i>                     | 45.9   | -1.96               | 47.7   | <i>d</i>                |
| $\text{Mo}_2\text{O}_3\text{S}(\text{Etcys})_2$   | Hg              | 0.02–100                  | -1.496        | 76                   | -1.516                       | 6.96   | -1.856              | 7.51   | $110 \pm 20$            |
|   | Pt              | 0.02–100                  | -1.493        | 71                   | -1.560                       | 45.3   | -1.835              | 45.6   | $90 \pm 10$             |
| $\text{Mo}_2\text{O}_2\text{S}_2(\text{Etcys})_2$ | Hg              | 0.02–100                  | -1.441        | 67                   | -1.431                       | 6.02   | -1.628 <sup>e</sup> | 5.52   | $11.6 \pm 1.6$          |
|   | Pt              | 0.02–10                   | -1.442        | 63                   | -1.439                       | 47.0   | -1.658              | 36.3   | $9 \pm 2$               |

<sup>a</sup> Data recorded for  $\sim 1$  mM complexes in 0.1 M TEABF<sub>4</sub>. Values of  $E_{p_1}$ ,  $E_{p_2}$ , and  $E_p - E_{p/2}$  are recorded at  $\nu = 0.1$  V s<sup>-1</sup>; other quantities are average values over the range of scan rates indicated. <sup>b</sup>  $E_1^\circ$  is calculated from the average of cathodic and anodic peak potentials at scan rates where a reverse peak is observed. <sup>c</sup> 0.1 M TEAClO<sub>4</sub>. <sup>d</sup> No anodic peak observed on scan reversal at Pt. <sup>e</sup> Second reduction step for  $\text{Mo}_2\text{O}_2\text{S}_2(\text{Etcys})_2$  on Hg is reversible at  $\nu \geq 4$  V s<sup>-1</sup> and has  $E_2^\circ = -1.594$  V.

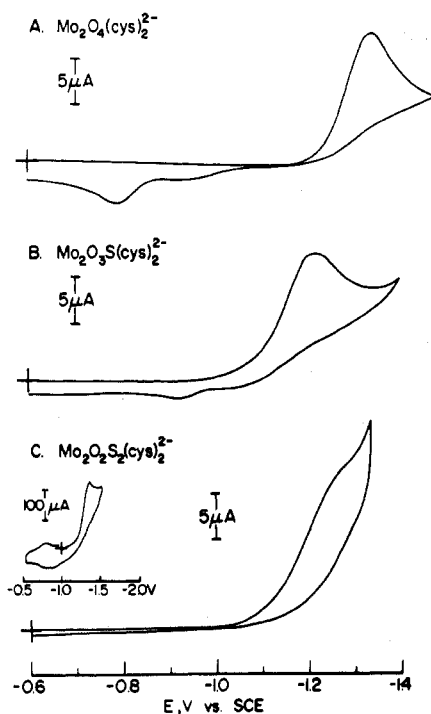


Figure 3. Cyclic voltammetric reduction of 1 mM  $\text{Mo}_2\text{O}_2\text{X}_2(\text{Cys})_2^{2-}$  complexes at a hanging mercury drop electrode in 0.1 M  $\text{Na}_2\text{B}_4\text{O}_7$ .  $\nu = 0.1$  V s<sup>-1</sup>; for inset C,  $\nu = 20$  V s<sup>-1</sup>.

the binuclear Mo(III) electrode product. This behavior may be contrasted to that of di- $\mu$ -sulfido Mo(V) species, which have been reported to be less reactive than their oxo-bridged analogues.<sup>6</sup> It has recently been noted that thiol ligands increase the ease of substitution in Cr(III) complexes (trans-labilizing effect) and that the Cr-S bonds themselves are much more labile than Cr-O bonds.<sup>38,39</sup> Similar effects could be responsible for the increased reactivity of the sulfido-bridged Mo(III) centers.

**Nonaqueous Electrochemistry.** The electrochemistry of the  $\text{Mo}_2\text{O}_2\text{X}_2$  center changes drastically on going from an aqueous to a nonaqueous environment. In an aprotic medium the tendency for coupled proton-electron transfer is limited by the low proton availability in the solvent; therefore single-electron rather than multielectron steps are more commonly observed. Cyclic voltammetric data for reduction of the  $\text{Mo}_2\text{O}_2\text{X}_2(\text{Etcys})_2$  complexes in  $\text{Me}_2\text{SO}$  at Hg and Pt electrodes are shown in Figure 4 and Table IV. Each complex is reduced by successive one-electron steps to  $\text{Mo}^{\text{V}}\text{-Mo}^{\text{IV}}$  and  $\text{Mo}^{\text{IV}}_2$  species:

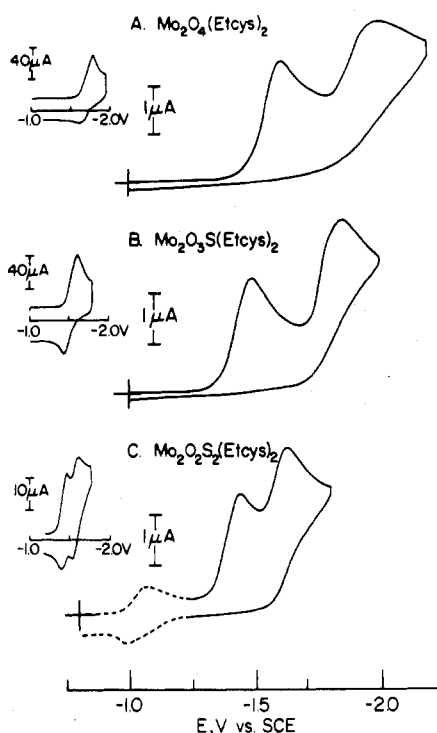
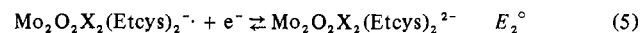


Figure 4. Cyclic voltammetric reduction of 1 mM  $\text{Mo}_2\text{O}_2\text{X}_2(\text{Etcys})_2$  complexes at a hanging mercury drop electrode in dimethyl sulfoxide.  $\nu = 0.1$  V s<sup>-1</sup>;  $\nu = 80, 100,$  and  $10$  V s<sup>-1</sup> for insets A, B, and C, respectively. The dotted segment of C is the result of an impurity.

Evidence for the transfer of one electron in the first step of the electrode reaction consists of the reversible behavior of reaction 4 observed for each compound at fast scan rates (see insets, Figure 4) and the similarity of  $i_{p_1}/\nu^{1/2}C$  values to those for compounds known to undergo one-electron reduction in  $\text{Me}_2\text{SO}$ . (The model compounds used for this comparison are di- $\mu$ -sulfido Mo(V) complexes with dialkyldithiocarbamate and 1,1-dicyanoethylene-2,2-dithiolate ligands.<sup>21</sup>) If current-time curves are recorded following a step to a potential (-1.7 V) beyond the first wave and to a potential (-2.0 V) beyond the second wave for  $\text{Mo}_2\text{O}_4(\text{Etcys})_2$  reduction, constant chronoamperometric parameters of  $it^{1/2}/AC = 65 \pm 2$  and  $134 \pm 8$  A cm s<sup>1/2</sup> mol<sup>-1</sup> are obtained. Substitution of these quantities into the Cottrell equation<sup>40</sup>

$$i = nFAC(D/\pi t)^{1/2} \quad (6)$$

with  $n = 1$  in the first case and  $n = 2$  in the second yields a diffusion coefficient of  $(1.4\text{--}1.5) \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> for  $\text{Mo}_2\text{O}_4(\text{Etcys})_2$  in  $\text{Me}_2\text{SO}$ . This result is in reasonable agreement with the value  $D = 2.2 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> calculated for the dimeric  $\mu$ -oxo-bridged 8-quinolinol complex  $\text{Mo}_2\text{O}_3\text{Q}_4$ , from

chronopotentiometric measurements in dimethyl sulfoxide.<sup>41</sup> The chronoamperometric results confirm the assignment of successive one-electron transfers (eq 4 and 5) to the reduction of the  $\text{Mo}_2\text{O}_2\text{X}_2(\text{Etcys})_2$  complexes. In addition to a reversible first electron transfer, the second electron transfer of  $\text{Mo}_2\text{O}_2\text{S}_2(\text{Etcys})_2$  also becomes reversible at  $\nu \geq 4 \text{ V s}^{-1}$ . At slow scan rates the products of the first electron-transfer steps for all three  $\text{Mo}_2\text{O}_2\text{X}_2(\text{Etcys})_2$  complexes are not stable, but their decomposition does not lead to more easily reducible species. Consequently, the values of  $i_{p1}/\nu^{1/2}C$  for each compound are constant over the entire range of scan rates. It is interesting to note that  $\text{Mo}_2\text{O}_4(\text{Etcys})_2$  undergoes an initial one-electron reduction, whereas analogous di- $\mu$ -oxo complexes with dithiocarbamate and 8-quinolinolate ligands undergo direct two-electron reduction in  $\text{Me}_2\text{SO}$ .<sup>21,42,43</sup>

A significant influence of sulfido bridging on the electrochemistry of these compounds is apparent from the data in Table IV and Figure 4. Both the voltammetric peak potentials and formal reduction potentials shift in the direction of more facile reduction by roughly 100 mV per sulfur atom. Small decreases in voltammetric peak width ( $E_p - E_{p/2}$ ) and peak potential separation ( $\Delta E_p$ ) indicate an increase in electrochemical reversibility with sulfur substitution. These trends parallel the behavior found in the four-electron-transfer step of the water-soluble derivatives. In contrast to the aqueous systems, however, sulfido bridging stabilizes the initial electrode reaction product of the ethyl cysteinyl complexes. The rate constants ( $k_f$ ) for decomposition of the mixed-valence species generated in reaction 4 were estimated by measuring the voltammetric peak current ratios for the first reduction step and comparing these values to the working curve for an EC mechanism.<sup>35</sup> Although the mechanism has not been fully confirmed, the data give a good fit to a first-order chemical process. The values of  $k_f$  listed in the last column of Table IV indicate that sulfido bridging enhances the stability of the products by approximately one order of magnitude per sulfur atom. Stabilization of  $\text{Mo}^V\text{-Mo}^{\text{IV}}$  mixed-valence species by the di- $\mu$ -sulfido bridging unit has been noted in the nonaqueous electrochemistry of other molybdenum compounds.<sup>21,42,43</sup>

An understanding of the effect of sulfido bridging on the electrochemistry of the  $\text{Mo}_2\text{O}_2\text{X}_2(\text{Etcys})_2$  complexes can be gained from recent electronic state calculations of the  $\text{Mo}_2\text{O}_4^{2+}$  and  $\text{Mo}_2\text{O}_2\text{S}_2^{2+}$  centers.<sup>33,34</sup> In these systems the five unfilled molecular orbitals of lowest energy are located primarily within the bimetallic center and are either Mo-Mo bonding or antibonding in nature with partial contribution from bridging and terminal groups. To a first approximation electron transfer into these orbitals should be only slightly affected by ligand. This conclusion is confirmed by the relative similarity of formal redox potentials for the  $\text{Mo}_2\text{O}_2\text{X}_2(\text{EDTA})^{2-}$  and  $\text{Mo}_2\text{O}_2\text{X}_2(\text{Cys})_2^{2-}$  complexes in aqueous media and for comparable ethyl cysteinyl, dithiocarbamate, and 1,1-dicyanoethylene-2,2-dithiolate complexes in  $\text{Me}_2\text{SO}$ .<sup>21,42,43</sup> Calculated atomic charges in the  $\text{Mo}_2\text{O}_4^{2+}$  unit<sup>33</sup> show relatively high negative charge density on the terminal and bridging O atoms and relatively high positive charge density on the Mo atoms. The extent of charge separation is substantially diminished in the  $\text{Mo}_2\text{O}_2\text{S}_2^{2+}$  center.<sup>34</sup> The di- $\mu$ -sulfido system also contains significant bonding interactions between the two bridging S atoms, between bridging S and terminal O, and between bridging S and the S atom of coordinated cysteine. These interactions and the more even charge distribution can be attributed to the presence of sulfur d orbitals. Placement of sulfur in the bridging positions therefore provides the capability for greater electron delocalization within the binuclear unit. This delocalization may be expected to provide (i) orbitals of lower energy for occupancy by an additional electron and (ii) stabilization of the reduced species by more effective charge

distribution thereby making them less susceptible to attack by protic species, which is the probable mode of their decomposition. These effects of bridge sulfur substitution are substantiated by the measurements we have made on the  $\text{Mo}_2\text{O}_2\text{X}_2(\text{Etcys})_2$  complexes, which indicate that the ease of production and chemical stability of the one-electron reduction products increase in the sequence  $\text{Mo}_2\text{O}_4^{2+} < \text{Mo}_2\text{O}_3\text{S}^{2+} < \text{Mo}_2\text{O}_2\text{S}_2^{2+}$ . The formally  $\text{Mo}^V\text{-Mo}^{\text{IV}}$  mixed-valence species are probably best represented as anion radicals in which the additional electron is delocalized over the entire bridged bimetallic unit.

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**Supplementary Material Available:** Table I, analytical data for the compounds (1 page). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,  
 The University of Akron, Akron, Ohio 44325

## Olefin Metathesis by Pyridinepentacarbonylmolybdenum and Related Catalysts: Reactions and Mechanism

VICTOR W. MOTZ and MICHAEL F. FARONA\*

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The catalytic system  $\text{Mo}(\text{CO})_5\text{py}/\text{RAlCl}_2/(\text{C}_4\text{H}_9)_4\text{NCl}$  ( $\text{R} = \text{C}_2\text{H}_5, \text{CH}_3$ ) was found to promote the metathesis of terminal olefins. Gas evolution studies indicated that the formation of the initial coordinated carbene which promotes metathesis is dependent on the solvent. In chlorobenzene, the initial carbenes are ethylidene and methylene with cocatalysts  $\text{C}_2\text{H}_5\text{AlCl}_2$  and  $\text{CH}_3\text{AlCl}_2$ , respectively, but in heptane solvent, coordinated propylidene and ethylidene arise from the respective cocatalysts. Studies on the first-formed olefin in solution (other than the normal metathesis products) in the metathesis of 1,7-octadiene revealed that the amount of first-formed olefin varied directly with the amount of catalyst added to the solution, but was independent of the initial amount of olefin. Interpretation of these data is in accord with current theories on the mechanism of the olefin metathesis reaction, wherein the reaction is both initiated and propagated by coordinated carbenes. In addition, processes for the formation of the initial coordinated carbene in chlorobenzene and heptane are proposed.

### Introduction

Recent research has shown that the olefin metathesis reaction in homogeneous catalyst systems is both initiated and propagated by coordinated carbenes.<sup>1-3</sup> In some reactions promoted by the catalyst  $\text{W}(\text{CO})_5\text{C}(\text{C}_6\text{H}_5)_2$ , the coordinated carbene is reactive toward metathesis and no cocatalyst is required.<sup>4</sup> However, homogeneous catalysts which do not initially contain a carbene group require the synergistic use of an organometallic cocatalyst to show activity. One of the purposes of the cocatalyst is to furnish an alkyl group to the transition metal from which the coordinated carbene is formed. At least two methods of formation of the initial carbene have been reported: for tungsten chloride systems, coordination of an alkyl group to tungsten followed by  $\alpha$ -hydrogen abstraction,<sup>5</sup> and in the case of  $\text{Re}(\text{CO})_5\text{Cl}$ , attack of alkyl on carbonyl carbon followed by hydrogen-for-oxygen exchange. These methods of carbene formation can be distinguished by gas evolution studies in the formation of the active catalyst.

A report in the patent literature claimed that the system  $\text{Mo}(\text{CO})_5\text{py}/(\text{CH}_3)_3\text{Al}_2\text{Cl}_3/\text{R}_4\text{NCl}$  constituted an effective catalyst for the metathesis of olefins.<sup>6</sup> This research is concerned with studies on modified forms of the catalyst system, particularly in the alkylaluminum cocatalyst, in reactions and mechanism of the metathesis reaction.<sup>7</sup>

### Experimental Section

**Starting Materials.** Acyclic olefins were obtained from Aldrich, Chemical Samples, or J. T. Baker and were purged with nitrogen gas while cyclic olefins were distilled immediately before use. Chlorobenzene solvent was purified by distillation; the first 10% of the distillate was discarded and the remainder collected and stored over molecular sieves.

Ethylaluminum dichloride was purchased as the neat substance from Ethyl Corp. and made up in 2.0 M solutions in chlorobenzene and heptane under nitrogen. The solutions were contained in 4-oz. bottles with perforated screw-cap lids containing a self-sealing rubber liner. Methylaluminum dichloride (2.0 M in chlorobenzene) was kindly

donated by Goodyear Research. Methylaluminum dichloride (2.0 M solution in hexane) was purchased from Ethyl Corp.

Tetrabutylammonium chloride was purchased from Eastman, dried in vacuo, and stored in a nitrogen-atmosphere glovebox.

$\text{Mo}(\text{CO})_5\text{py}$ ,<sup>8</sup>  $\text{Mo}(\text{CO})_4\text{py}_2$ ,<sup>8</sup>  $\text{Mo}(\text{CO})_4\text{bpy}$ ,<sup>9,10</sup> and  $\text{Mo}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$ <sup>11</sup> ( $\text{py} = \text{pyridine}$ ;  $\text{bpy} = 2,2'$ -bipyridyl) were prepared and purified by literature methods. Characterization of the carbonyl derivatives was accomplished by comparison of the CO stretching bands and melting points with those reported in the literature.

**Physical Methods.** For the analyses of products in metathesis reactions, a Hewlett-Packard 5750-B gas chromatography unit was employed. A stainless steel column of dimensions 10 ft  $\times$  1/8 in. containing 5% silicone rubber UCW-982 on 80-100 Mesh silica was incorporated in the unit; helium was the carrier gas and a thermal conductivity detector was employed. The products were identified by a comparison of retention times with those of authentic samples. The areas of the peaks were determined by triangulation and these were converted to molar amounts by the use of a known amount of bromobenzene as the internal standard, correcting for detector response ratios.

For gas analysis, the same gas chromatography system was used, except that the columns (6 ft  $\times$  1/4 in.) were packed with 4A molecular sieves. The gases investigated were carbon monoxide, ethylene, ethane, methane, and nitrogen. In order to separate methane, nitrogen, and carbon monoxide from each other, it was necessary to cool the columns with dry ice. Any ethane or ethylene injected with the other gases was retained by the column at this temperature. After elution of the former gases, the temperature of the column was raised to 250 °C whereupon the ethylene and ethane were eluted and separated.

**Metathesis Reactions.** The experimental procedures for all metathesis reactions are analogous; therefore, only the metathesis of 1-hexene is given in detail. Differences in procedures are pointed out where appropriate.

Into a 100-mL, three-neck flask fitted with a nitrogen inlet, a condenser connected to an oil bubbler, and a septum, were placed 0.16 g (0.50 mmol) of  $\text{Mo}(\text{CO})_5\text{py}$ , 0.07 g (0.25 mmol) of  $(\text{C}_4\text{H}_9)_4\text{NCl}$ , and 10 mL of chlorobenzene. The system was flushed with nitrogen and heated to 70 °C. Through the septum was injected 2.0 mL (4.0 mmol) of ethylaluminum dichloride-chlorobenzene solution. Finally, 10 mL of 1-hexene was injected slowly so that it was added