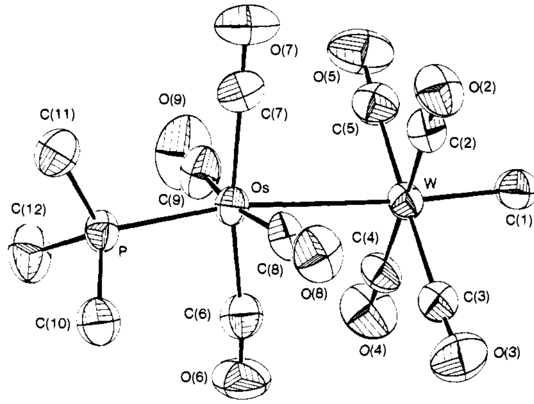
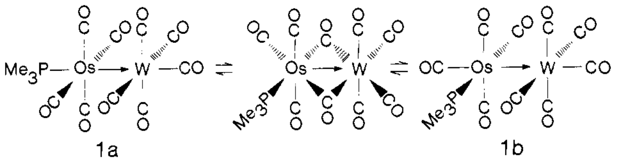


**Figure 1.** ORTEP diagram for $(Me_3P)(OC)_4OsW(CO)_5$. Selected distances (Å), Os–W = 3.0756 (5), Os–P = 2.359 (2), Os–C range 1.941 (7)–1.954 (8), W–C(1) = 1.964 (8), W–C(equatorial) range 2.021 (7)–2.045 (8), and angles (deg) W–Os–P = 171.31 (4); W–Os–C range 80.2 (2)–89.1 (2); Os–W–C(equatorial) 84.7 (2)–93.9 (2).

Scheme I



(C(6)–Os–C(7) = 169.0 (3)°, C(8)–Os–C(9) = 167.9 (3)°) has its counterpart in decacarbonyldirhenium.[6]

The strongest signals in the $^{13}C$ NMR spectrum of **1** ($CH_2Cl_2/CD_2Cl_2$ solution) were consistent with the solid-state structure (**1a**). However, minor peaks were observed, the intensity of which did not change even after further chromatography and recrystallization of the sample. The $^1H$ NMR spectrum of **1** in $CD_2Cl_2$ similarly showed two methyl doublets centered at $\delta$ 2.01 ($J_{P-C}$ = 10.5 Hz) and 1.92 ($J_{P-C}$ = 10.3 Hz) in the ratio 7.1:1. The minor signals in each case were assigned to the isomer of **1** that had the trimethylphosphine ligand in a radial position on osmium, i.e., **1b** (Scheme I, eclipsed forms drawn for convenience). This conclusion was confirmed by the solution $^{13}C$ NMR spectrum of **1** prepared from $Os(CO)_4(PMe_3)$ that had been enriched in $^{13}CO$.[7] Previously unobserved signals were entirely consistent with the presence of ~14% of the **b** form of **1**. Of special interest was that the $^{13}C$ labeled carbonyls had become scrambled between the osmium *and the tungsten atoms*.[8]

Evidence that the two isomers were in dynamic equilibium was provided by a spin saturation transfer NMR experiment. Saturation of the signal at 2.03 ppm (assigned to **1a**) in the $^1H$ NMR of **1** in $CD_2Cl_2$ caused transfer to the signal at 1.93 ppm (assigned to **1b**). A similar experiment was carried out with $Os(CO)_4(PMe_3)$ added to the solution. There was no transfer to the doublet due to the added component, nor was the transfer to the signal due to **1b** affected (Figure 2). This result indicated that dissociation of **1** to give $Os(CO)_4(PMe_3)$ and $W(CO)_5$ was not involved in the isomerization. Furthermore, **1** did not exchange with $^{13}CO$ when it was stirred in $CH_2Cl_2$ under 1 atm of this reagent nor did it react, in solution at room temperature, with $PMe_2Ph$.[9]

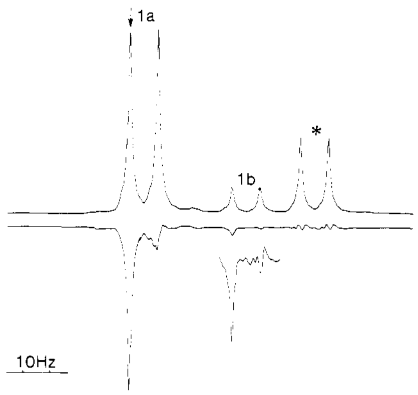


**Figure 2.** Spin saturation transfer experiment on $(Me_3P)(OC)_4OsW(CO)_5$. Irradiation of the lowest field $^1H$ NMR resonance due to one isomer (**1a**) resulted in transfer to the corresponding signal of the second isomer (**1b**). No transfer occurred to the signals due to added $Os(CO)_4(PMe_3)$ (*).

A mechanism that accounts for the isomerization and the nondissociative carbonyl migration from osmium to tungsten is shown in Scheme I (it is assumed that there is rotation about the Os–W bond in the unbridged forms). The suggested mechanism implies that the isomerization occurs at the same rate as carbonyl exchange, which has not, as yet, been established.

**Acknowledgment.** We are grateful to the Natural Sciences and Engineering Council of Canada and the President's Research Fund (Simon Fraser University) for financial support.

**Supplementary Material Available:** Tables of atomic coordinates, temperature factors, and bond lengths and angles (6 pages). Ordering information is given on any current masthead page.

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[7] The $^{13}CO$ enrichment was achieved by the mild ultraviolet irradiation of $Os(CO)_4(PMe_3)$ in hexane under ca. 1.5 atm of $^{13}CO$.

[8] The complete $^{13}C\{^1H\}$ NMR spectrum of **1** in $CD_2Cl_2/CH_2Cl_2$ (1:5): **1a**, $\delta$ 204.6 (1, d, $J_{P-C}$ = 2.2, $J_{^{183}W-C}$ = 179.1 Hz), 202.8 (4, s, $J_{^{183}W-C}$ = 124.9 Hz), 186.7 (4, d, $J_{P-C}$ = 3.0, $J_{^{187}Os-C}$ = ~92 Hz), 23.2 ($J_{P-C}$ = 37.1 Hz); **1b**, 202.9 (1, s), 202.5 (4, s, $J_{^{183}W-C}$ = 125.2), 188.3 (2, d, $J_{P-C}$ = 13.2 Hz), 176.0 (1, d, $J_{P-C}$ = 71.1 Hz), 170.3 (1, d, $J_{P-C}$ = 8.9 Hz), 20.8 ppm (d, $J_{P-C}$ = 37.7 Hz). The first number in parenthesis for the carbonyl resonances represents the approximate, overall intensity of the signal relative to the other carbonyl signals of the isomer.

[9] Solutions of **1** did show some decomposition after 24 h; $W(CO)_6$ was identified as one of the decomposition products. The amount of $W(CO)_6$ did not appear to increase when solutions of **1** were stirred under CO (65 atm) for 24 h. Rapid decomposition in solution above 60 °C precluded NMR line-broadening studies on **1**.

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## Novel and Stereospecific Imide Synthesis

Howard Alper* and Chulangani P. Mahatantila

*Department of Chemistry, University of Ottawa*
*Ottawa, Ontario, Canada K1N 9B4*

Frederick W. B. Einstein and Anthony C. Willis

*Department of Chemistry, Simon Fraser University*
*Burnaby, British Columbia V5A 1S6*

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The past 10 years have witnessed an increased awareness of the importance of transition-metal complexes as reagents, and as catalysts, in heterocyclic synthesis.[1] One facet of this subject involves the utilization of strained-ring heterocycles as precursors to other heterocyclic systems via appropriate ring opening and closing reactions.[2] For example, azirines are convertible to pyrazines, isoxazoles, pyrazoles, or pyrroles on exposure to molybdenum and other group 6 metal carbonyls,[3] indoles using cobalt carbonyl,[4] and bicyclic $\beta$-lactams with tetrakis(triphenylphosphine)palladium(0) and carbon monoxide.[5] Recently, $\beta$-lactams were synthesized by the rhodium(I)-catalyzed carbonylation of aziridines.[6]

The reaction of azirines with nucleophilic reagents has been investigated in some detail.[7,8] A question that arises is whether

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[1] Davidson, J. L.; Preston, P. N. *Adv. Heterocycl. Chem.* **1982**, *30*, 319.

[2] Alper, H. *Isr. J. Chem.* **1981**, *21*, 203.

[3] Alper, H.; Prickett, J. E.; Wollowitz, S. *J. Am. Chem. Soc.* **1977**, *99*, 4330.

[4] Alper, H.; Prickett, J. E. *Tetrahedron Lett.* **1976**, 2589.

[5] Alper, H.; Perera, C. P.; Ahmed, F. R. *J. Am. Chem. Soc.* **1981**, *103*, 1289.

[6] Alper, H.; Urso, F.; Smith, D. J. H. *J. Am. Chem. Soc.* **1983**, *105*, 6737.

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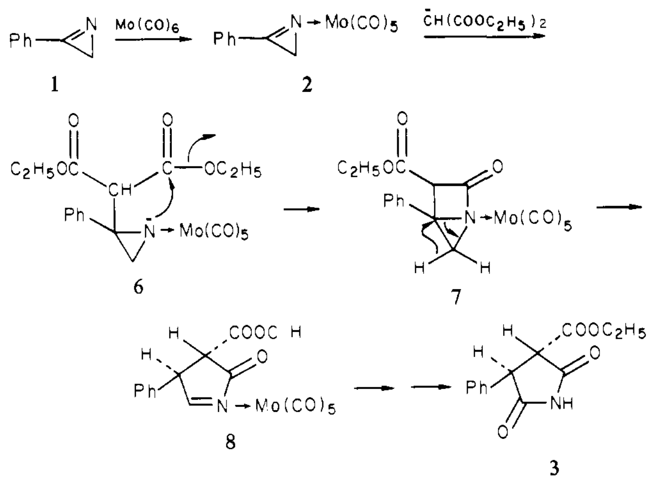
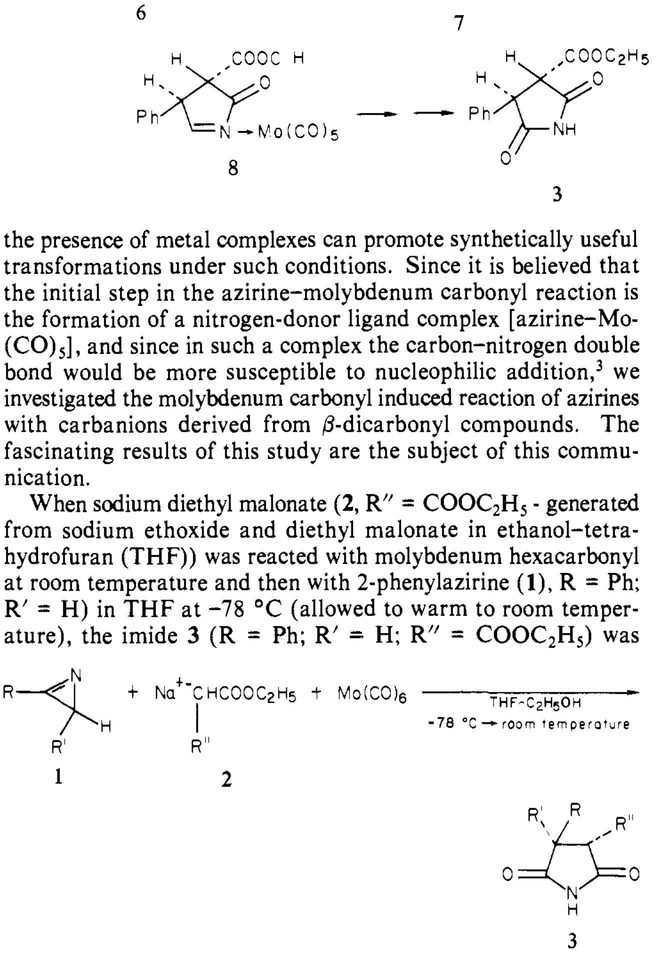
Scheme I



the presence of metal complexes can promote synthetically useful transformations under such conditions. Since it is believed that the initial step in the azirine–molybdenum carbonyl reaction is the formation of a nitrogen-donor ligand complex [azirine–Mo$(CO)_5$], and since in such a complex the carbon–nitrogen double bond would be more susceptible to nucleophilic addition,[3] we investigated the molybdenum carbonyl induced reaction of azirines with carbanions derived from β-dicarbonyl compounds. The fascinating results of this study are the subject of this communication.

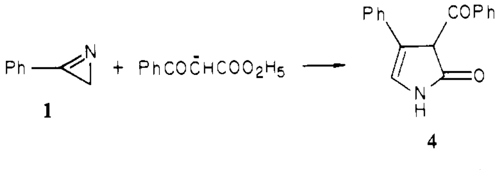


When sodium diethyl malonate (**2**, R″ = $COOC_2H_5$ - generated from sodium ethoxide and diethyl malonate in ethanol–tetrahydrofuran (THF)) was reacted with molybdenum hexacarbonyl at room temperature and then with 2-phenylazirine (**1**), R = Ph; R′ = H) in THF at −78 °C (allowed to warm to room temperature), the imide **3** (R = Ph; R′ = H; R″ = $COOC_2H_5$) was obtained in 46% yield. Equimolar amounts of **1** and $Mo(CO)_6$ were used, with 1.5 equiv of **2**. The reaction is a stereospecific one with the two substituent groups of **3** in a trans relationship, as shown from spectral data and by an X-ray crystal determination.[9] The infrared spectrum ($CHCl_3$) displayed an NH stretching absorption at 3410 $cm^{-1}$. The methine protons of **3** (R = Ph, R′ = H; R″ = $COOC_2H_5$) gave doublet signals in the proton magnetic resonance spectrum at δ 3.80 and 4.42, while those for the carbon atoms bearing these hydrogens occurred at δ 51.02 and 56.21 in the carbon magnetic resonance spectrum, respectively.

This novel reaction is applicable to a variety of azirines (**1**, R = $p$-$BrC_6H_4$, $p$-$CH_3OC_6H_4$, $p$-$CH_3C_6H_4$, $o$-$CH_3C_6H_4$, $p$-$ClC_6H_4$; R′ = H) affording disubstituted imides in 27–68% yield (see Table I, supplementary material, for yields and pertinent spectral data). In the case of 2-phenyl-3-methylazirine (**1**, R = Ph; R′ = $CH_3$) only **3** (R = Ph; R′ = $CH_3$; R″ = $COOC_2H_5$) was formed in 74% yield. The reaction also proceeds for carbanions derived from ethyl benzoylacetate **2** (R″ = PhCO) and ethyl cyanoacetate **2** (R″ = CN].

It should be noted that reverse addition (i.e., dropwise addition of **2** (R″ = $COOC_2H_5$) to a mixture of **1** (R = Ph; R′ = H) and $Mo(CO)_6$ in THF) also results in the isolation of imide, albeit in somewhat lower yield (32–33%). Significant inhibition of the above reaction was observed by using a carbon monoxide rather than a nitrogen atmosphere.

In 1967, Sato and co-workers[10] reported that reaction of 2-phenylazirine with **2** (R″ = PhCO), generated from ethyl benzoylacetate and methylsulfinyl carbanion in dimethyl sulfoxide, gave a compound for which structure **4** was suggested. The latter compound was not formed when the reaction was effected in THF–ethanol, with or without $Mo(CO)_6$ (i.e., the blank reaction). In addition, compound **4** is not convertible to imide on overnight exposure to $Mo(CO)_6$ in THF at room temperature.



A possible mechanism for the conversion of azirines to imides is outlined in Scheme I (illustrated for 2-phenylazirine and diethyl malonate anion). Initial coordination of the nitrogen lone pair to molybdenum would give **5**, which can react with the carbanion to give **6**. Intramolecular cyclization of **6** by ethoxide ion displacement would afford the bicyclic β-lactam **7** which on hydrogen migration and ring scission would give the 5-membered ring heterocyclic complex **8**. Conversion of **8** to **3** may take place via hydration (note that excess 99% ethanol is used in the generation of the carbanion **2**) of **8** followed by dehydration or alternatively by oxidation during workup.[11]

The following general procedure was used: to sodium ethoxide (prepared from the reaction of sodium (4–7 mmol) in 99% ethanol (5 mL)), **2** (4–7 mmol) in THF (10 mL) was added, and the mixture was heated at 50 °C ($N_2$ atmosphere for 4 h). After cooling to room temperature THF (25 mL) was added followed by $Mo(CO)_6$ (2.7–4.7 mmol) in THF (5 mL). After 30 min, the solution was cooled to −78 °C and azirine (2.7–4.7 mmol) in THF (5 mL) was added dropwise over a 1-h period to the stirred solution. The mixture was then allowed to warm up to room temperature, and stirring was continued until reaction was complete (followed by thin-layer chromatography). The reaction mixture was added to distilled water, extracted with ether, dried ($MgSO_4$), and concentrated to give the crude imide, which was purified by silica gel column chromatography [3:2 ether–hexane].

In conclusion, molybdenum carbonyl can effect the remarkable conversion of azirines and carbanions to imides. The reaction is completely stereospecific. Since it is well-known that imides can be ring opened under a variety of conditions, the described process constitutes a simple and convenient entry into acyclic compounds of defined stereochemistry (e.g., succinic acids). Hydride reduction would afford trans-3,4-disubstituted pyrrolidines.[12]

**Acknowledgment.** We are grateful to the Natural Sciences and Engineering Research Council for support of this research.

**Registry No. 1** (R = Ph; R′ = H), 7654-06-0; **1** (R = $p$-$BrC_6H_4$; R′ = H), 17631-26-4; **1** (R = $p$-$CH_3OC_6H_4$; R′ = H), 32687-32-4; **1** (R = $p$-$CH_3C_6H_4$; R′ = H), 32687-33-5; **1** (R = $o$-$CH_3C_6H_4$; R′ = H), 88089-30-9; **1** (R = $p$-$ClC_6H_4$; R′ = H), 32687-35-7; **1** (R = Ph; R′ = $CH_3$), 16205-14-4; **3** (R = Ph; R′ = H; R″ = $CO_2Et$), 89414-82-4; **3** (R = $p$-$BrC_6H_4$; Rr′ = H; R″ = $CO_2Et$), 89414-83-5; **3** (R = $p$-$CH_3OC_6H_4$; R′ = H; R″ = $CO_2Et$), 89414-84-6; **3** (R = $p$-$CH_3C_6H_4$; R′ = H; R″ = $CO_2Et$), 89414-85-7; **3** (R = $o$-$CH_3C_6H_4$; R′ = H; R″ = $CO_2Et$),

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(9) Single crystals of $C_{13}H_{13}NO_4$ were monoclinic, space group $P2_1n$, with $a$ = 15.286 (3) Å, $b$ = 5.377 (2) Å, $c$ = 16.218 (4) Å, β = 109.72 (2)°. Full-matrix least-squared refinement converged at $R_1$ = 0.046, $R_2$ = 0.055.

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(11) Another conceivable mechanism would involve initial attack of the carbanion at a carbonyl carbon of the metal atom of $Mo(CO)_6$ followed by reaction with the azirine.

(12) Wheeler, O. H.; Rosado, O. "The Chemistry of Amides"; Zabicky, J., Ed.; Interscience: New York, 1970; pp 355–381.

89414-86-8; **3** (R = $p$-ClC$_6$H$_4$; R′ = H; R″ = CO$_2$Et), 89414-87-9; **3** (R = Ph; R′ = CH$_3$; R″ = CO$_2$Et), 89414-88-0; diethyl malonate, 105-53-3; Mo(CO)$_6$, 13939-06-5.

**Supplementary Material Available:** ORTEP diagram of **3** and Tables I–VI of spectral data, crystal data, data collection and refinement, fractional atomic coordinates, interatomic distances and angles, and final thermal parameters (9 pages). Ordering information is given on any current masthead page.

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# Sulfur-Capped Trinuclear Molybdenum(IV) Ion, $\mathrm{Mo_3O_3S^{4+}}$

Takashi Shibahara,* Hiroshi Hattori, and Hisao Kuroya

*Department of Chemistry*
*Okayama University of Science*
*1-1 Ridai-cho, Okayama 700, Japan*

*Received December 12, 1983*

The presence of a $\mathrm{Mo_3O_4^{4+}}$ core structure in the Mo(IV) aqua ion has been confirmed by single-crystal X-ray structure analyses,[1] $^{95}$Mo NMR,[1c] EXAFS structure analysis,[2] and $^{18}$O-labeling experiment,[3] after many contradictory reports had appeared.[4] The information on the reduction products of the Mo(IV) aqua ion also is available.[5]

We will describe here the preparation and characterization of a sulfur-capped trinuclear Mo(IV) ion, $\mathrm{Mo_3O_3S^{4+}}$ and the X-ray structure analysis of $\mathrm{Ba[Mo_3O_3S(Hnta)_3]\cdot 10H_2O}$ (H$_3$nta; nitrilotriacetic acid) having the $\mathrm{Mo_3O_3S^{4+}}$ core structure. The investigation of sulfur-bridged Mo(IV) complexes will give valuable information on the role of sulfur in the trinuclear Mo(IV) cluster system.

The mixture of the ($\mu$-oxo)($\mu$-sulfido)molybdenum(V) dimer $\mathrm{Mg[Mo_2O_3S(edta)]\cdot 6H_2O}$[6] (1.0 g) and K$_2$CO$_3$ (3.5 g) in water (50 mL) was heated (ca. 1 h) with stirring and then cooled by ice water. Neutralization of K$_2$CO$_3$ and acidification of the mixture to **4** M were made with concentrated HCl, and it was allowed to stand overnight and filtered. After the filtrate was diluted 10 times, the brown solution was absorbed on a Dowex 50W-X2 cation exchanger, which was washed with 0.5 M HCl. The red eluent obtained by the use of 2 M HCl was diluted twice with water, and Sephadex G-10 column chromatography was applied for purification (1 M HCl). The resultant solution (**1**) was analyzed to give Mo/S = 3.0 ± 0.2 (four determinations). Yield was ca. 20% based on starting binuclear complex. The absorption of the ion on the cation exchanger from HCl solution followed by the elution of it with 2 M HPTS gave the HPTS solution of the ion. The charge of the ion was estimated to be 4+ on the basis of its behavior similar to that of the $\mathrm{Mo_3O_4^{4+}}$ aqua ion on the ion exchanger.[7]

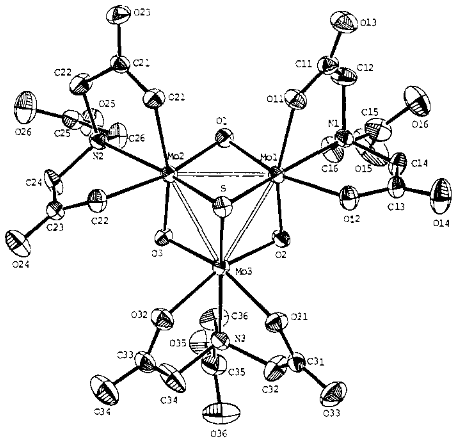

**Figure 1.** Perspective view of $[\mathrm{Mo_3O_3S(Hnta)_3}]^{2-}$. The average Mo--Mo, Mo--S, Mo--O(bridge), Mo--O(ligand), and Mo--N distances are 2.589, 2.360, 1.917, 2.097, and 2.264 Å, respectively.

The Mo/S ratio and the electronic spectrum of the red solution ($\lambda_{\max}$ ($\epsilon$) 333 (932) and 512 nm (153 M$^{-1}$ cm$^{-1}$) in 2 M HPTS) indicate the probable existence of a $\mathrm{Mo_3O_3S^{4+}}$ ion,[8] which prompted us to prepare crystals of a complex with the $\mathrm{Mo_3O_3S^{4+}}$ core structure.

H$_3$nta (H$_3$nta/Mo = 2.5) was dissolved in the solution **1**, and the pH was adjusted to 1.2 by addition of concentrated NaOH. Dark red distorted cubic crystals were obtained by addition of BaCl$_2$ after several days storage. The crystals were analyzed to be $\mathrm{Ba[Mo_3O_3S(Hnta)_3]\cdot 10H_2O}$,[9] of which peak positions, nm, ($\epsilon$) of the electronic spectrum in water were 330 (1830) and 530 (352).

X-ray crystal structure analysis[10] revealed the existence of a sulfur-capped trinuclear molybdenum core structure, $\mathrm{Mo_3O_3S^{4+}}$ in the $[\mathrm{Mo_3O_3S(Hnta)_3}]^{2-}$ anion (Figure 1). The core can be regarded as an incomplete cube,[11] as in the case of the $\mathrm{Mo_3O_4^{4+}}$ core.[1] Every Mo has a distorted octahedral coordination by S and two O atoms from the core and two O and N from the Hnta$^{2-}$ ligand. The Mo--Mo distance is slightly longer than and the Mo--O (bridge) distance is similar to the corresponding value in $[\mathrm{Mo_3O_4(ox)_3(H_2O)_3}]^{2-}$,[1a] $[(\mathrm{Mo_3O_4})_2(\mathrm{edta})_3]^{4-}$,[1b] and $[\mathrm{Mo_3O_4(mida)_3}]^{2-}$.[1c] The Mo--S distance is similar to that in $[\mathrm{Mo_3S(S_2)_6}]^{2-}$.[12] One uncoordinated CO$_2$ group in each Hnta$^{2-}$ ligand has a long (av 1.325 Å) and a short (1.205 Å) distance indicating the existence of three –COOH groups in the whole complex anion, in accord with the presence of an absorption band at 1725 cm$^{-1}$ in the infrared spectrum.

This X-ray structure analysis supports the existence of a $\mathrm{Mo_3O_3S^{4+}}$ ion (probably $[\mathrm{Mo_3O_3S(H_2O)_9}]^{4+}$) in solution. Electrochemical and other studies of the present and related compounds are in progress.

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(1) (a) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1978**, *100*, 5252–5253; (b) *Ibid.* **1979**, *101*, 3842–3847. (c) Gheller, S. F.; Hambley, T. W.; Brownlee, R. T. C.; O'Conner, M. J.; Show, M. R.; Wedd, A. J. *Ibid.* **1983**, *105*, 1527–1532.

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(5) (a) Richens, D. T.; Sykes, A. G. *Inorg. Chim. Acta* **1981**, *54*, L3–4; (b) *Inorg. Chem.* **1982**, *21*, 418–422. (c) Paffet, M. T.; Anson, F. C. *Ibid.* **1983**, *22*, 1347–1355.

(6) Otto, V. R.; Swieter, D. S.; Schultz, F. A. *Inorg. Chem.* **1977**, *16*, 2538–2545. edta, ethylenediaminetetraacetate (4–) anion.

(7) The oxygen-bridged complex $\mathrm{Mo_3O_4^{4+}}$ could be prepared by the same method by using $\mathrm{Na_2[Mo_2O_4(edta)]\cdot 4H_2O}$ as a starting material and a dinitrogen atmosphere. The mechanism and reducing agent of the formation reaction of $\mathrm{Mo_3O_3S^{4+}}$ ion are not clear at present.

(8) The $\mathrm{Mo_3O_3S^{4+}}$ ion is very stable and the electronic spectrum remains unchanged after more than 10 days in the air.

(9) Anal. Found (calcd): N, 3.52 (3.35); C, 17.40 (17.26); H, 2.95 (3.30).

(10) Crystal data: triclinic system, space group $P\bar{1}$, $a$ = 15.602 (3) Å, $b$ = 11.614 (2) Å, $c$ = 11.150 (2) Å, $\alpha$ = 100.89 (1)°, $\beta$ = 95.42 (1)°, $\gamma$ = 99.70 (1)°, $V$ = 1939.1 (7) Å$^3$, $Z$ = 2. Intensity data were collected on an automated four-circle diffractometer by use of graphite-monochromated Mo K$\alpha$ radiation on the $2\theta \leq 46°$ range. The coordinates of four Mo's, S, and three $\mu$-O's were determined by means of MULTAN, and the remaining nonhydrogen atoms were located from difference maps. The current $R$ value is 0.0335 for 4245 reflections ($F_o^2 \geq 3\sigma(F_o^2)$).

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