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.

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

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The presence of a $Mo_3O_4^{4+}$ 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, $Mo_3O_3S^{4+}$ and the X-ray structure analysis of Ba[$Mo_3O_3S(Hnta)_3$]·10H$_2$O (H$_3$nta; nitrilotriacetic acid) having the $Mo_3O_3S^{4+}$ 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 (μ-oxo)(μ-sulfido)molybdenum(V) dimer Mg[$Mo_2O_3S(edta)$]·6H$_2$O[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 $Mo_3O_4^{4+}$ aqua ion on the ion exchanger.[7]

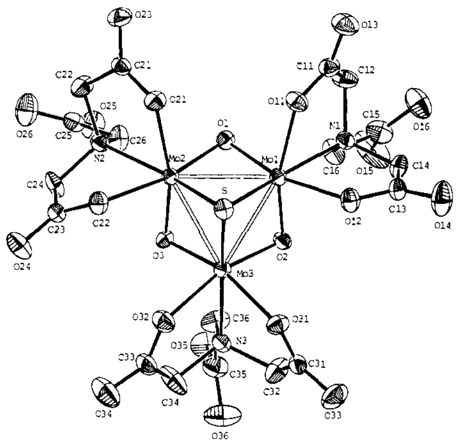

Figure 1. Perspective view of [$Mo_3O_3S(Hnta)_3$]$^{2-}$. The average Mo--Mo, Mo--S, Mo--O(bridge), Mo--O(ligand), and Mo--N distances are 2.589, 2.360, 1.917, 2.097, and 2.264 Å, respectively.

The Mo/S ratio and the electronic spectrum of the red solution (λ_{max} (ϵ) 333 (932) and 512 nm (153 M^{-1} cm^{-1}) in 2 M HPTS) indicate the probable existence of a $Mo_3O_3S^{4+}$ ion,[8] which prompted us to prepare crystals of a complex with the $Mo_3O_3S^{4+}$ 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 Ba[$Mo_3O_3S(Hnta)_3$]·10H$_2$O,[9] of which peak positions, nm, (ϵ) 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, $Mo_3O_3S^{4+}$ in the [$Mo_3O_3S(Hnta)_3$]$^{2-}$ anion (Figure 1). The core can be regarded as an incomplete cube,[11] as in the case of the $Mo_3O_4^{4+}$ 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 [$Mo_3O_4(ox)_3(H_2O)_3$]$^{2-}$,[1a] [(Mo_3O_4)$_2$(edta)$_3$]$^{4-}$,[1b] and [Mo_3O_4(mida)$_3$]$^{2-}$.[1c] The Mo--S distance is similar to that in [$Mo_3S(S_2)_6$]$^{2-}$.[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 $Mo_3O_3S^{4+}$ ion (probably [$Mo_3O_3S(H_2O)_9$]$^{4+}$) in solution. Electrochemical and other studies of the present and related compounds are in progress.

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(7) The oxygen-bridged complex $Mo_3O_4^{4+}$ could be prepared by the same method by using Na$_2$[Mo_2O_4(edta)]·4H$_2$O as a starting material and a dinitrogen atmosphere. The mechanism and reducing agent of the formation reaction of $Mo_3O_3S^{4+}$ ion are not clear at present.

(8) The $Mo_3O_3S^{4+}$ 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, α = 100.89 (1)°, β = 95.42 (1)°, γ = 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 Kα radiation on the $2\theta \leq 46°$ range. The coordinates of four Mo's, S, and three μ-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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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond distances, and bond angles and electronic spectra (4 pages). Ordering information is given on any current masthead page.

Photoinitiated Electron-Transfer Reactions. The Radical Cations of Bicyclo[1.1.0]butane Derivatives

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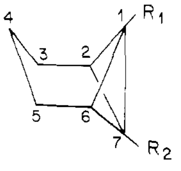
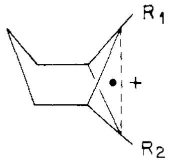
The interaction between photoexcited electron acceptors and several derivatives (**1**) of the bicyclo[1.1.0]butane system have been found to generate strong nuclear spin polarization effects. These results give an insight into the structure of the radical cations of **1** and reveal an unusually rapid isomerization of one of these cations.

The reactions of bicyclo[1.1.0]butane derivatives with excited-singlet electron acceptors have been studied under varied reaction conditions.[1] The structures of the reaction products are compatible with the intermediacy of radical cations, **2**, in which the C1–C7 bond is broken or weakened. Such a structure is readily rationalized on the basis of the bicyclo[1.1.0]butane HOMO, which is bonding principally between the two bridgehead carbons.[2]



1



2

a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$
c, $R_1 = R_2 = CH_3$

In an attempt to obtain further insight into the structures of these radical cations and to assess the involvement of other high-lying bicyclo[1.1.0]butane orbitals, we have applied the CIDNP technique to photoreactions of excited-singlet acceptors such as 1-cyanonaphthalene (1-CN) or triplet acceptors such as chloranil (CA) with bicyclo[1.1.0]butane derivatives. The CIDNP method has proved to be a powerful tool in the elucidation of radical cation structures, especially those derived from strained-ring hydrocarbons.[3]

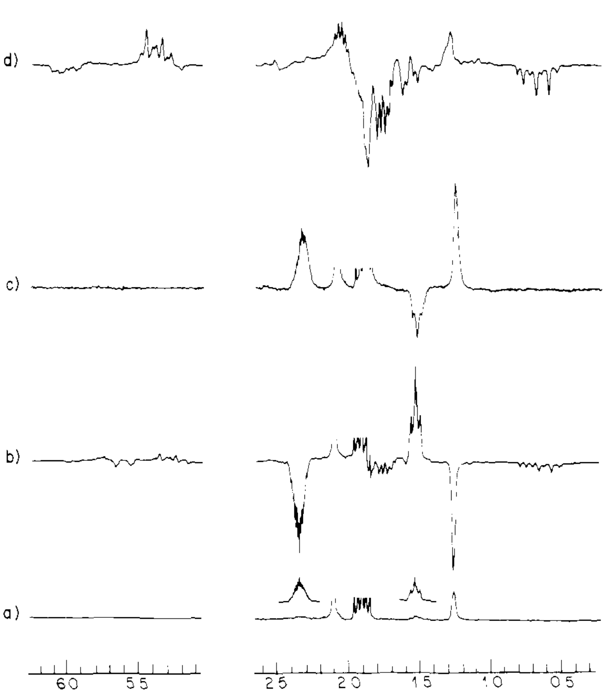


Figure 1. PMR spectra (90 MHz) of (a) an acetonitrile-d_3 solution of 0.02 M tricyclo[4.1.0.0^{2,7}]heptane (**1a**) and 0.02 M chloranil in the dark (insets show detailed spectra for protons at C2 and C6 at ~2.3 ppm and for protons at C1 and C7 at ~1.5 ppm), (b) the same solution during UV irradiation, (c) an acetonitrile-d_3 solution of 0.02 M **1a** and 0.02 M 1-cyanonaphthalene during UV irradiation, and (d) and acetone-d_6 solution of 0.02 M **1a** and 0.02 M chloranil during UV irradiation. A CIDNP spectrum essentially identical with trace d is observed during the irradiation of 0.02 M chloranil in the presence of 0.02 M norcar-2-ene (**6**).

The irradiation of 1-CN or CA in acetonitrile solutions containing tricyclo[4.1.0.0^{2,7}]heptane (Moore's hydrocarbon, **1a**)[4] resulted in strong nuclear spin polarization for all signals of the strained-ring hydrocarbon (Figure 1). Significantly, the polarization observed for the triplet near 1.5 ppm (H_1, H_7) was opposite to the effects observed for the broad signal at 2.3 ppm (H_2, H_6) and for the multiplet at 1.3 ppm, which represents the protons at C3, C4, and C5. This polarization can be rationalized as being induced by a reaction sequence initiated via electron transfer (eq 1) from **1a** to the photoexcited electron acceptor of spin multiplicity

$$^{m}A^{*} + D \rightarrow {}^{m}\overline{A^{-}\cdot D^{+}\cdot} \qquad (1)$$

$$^{m}\overline{A^{-}\cdot D^{+}\cdot} \rightleftharpoons {}^{n}\overline{A^{-}\cdot D^{+}\cdot} \qquad (2)$$

$$^{1}\overline{A^{-}\cdot D^{+}\cdot} \rightarrow A + D^{\dagger} \qquad (3)$$

$$^{3}\overline{A^{-}\cdot D^{+}\cdot} \rightarrow {}^{2}A^{-}\cdot + {}^{2}D^{+}\cdot \qquad (4)$$

* signifies an excited state and † signifies nuclear spin polarization

m (m = 1 for 1-CN, m = 3 for CA). The resulting cation radical–anion radical pairs begin random diffusion as well as intersystem crossing. The latter process (eq 2) may be either slightly accelerated or somewhat retarded due to the involvement of different nuclear spin states in the radical cations. Depending on the prevailing electron spin multiplicity at the time of a secondary encounter, the pairs may recombine, usually from the singlet state (eq 3), or diffuse apart (eq 4).

On the basis of this mechanism and on the assumption that the bicyclo[1.1.0]butane radical cation has a lower g factor than either of the acceptor anions ($CA^{-}\cdot$ g = 2.0051; 1-$CN^{-}\cdot$ g = 2.0031), the polarization of the regenerated starting material can be used to assign the hyperfine coupling (hfc) pattern of the cation radical. The results observed during the photoreaction with 1-CN (Figure 1c) indicate negative hfc's for H_1 and H_7 and positive hfc's for H_2, H_6, and also $H_{3,3'}$ and $H_{5,5'}$ of the intermediate. This pattern supports a radical cation with a broken (or weakened) C1–C7 bond, in full agreement with the structure assigned on the basis of the reaction products.[1]

Surprisingly, an entirely different result is obtained during the photoreaction of CA with **1a** under only slightly different reaction

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