Figure 2. $[Mo_3S_4(C_2O_4)_3(H_2O)_3]^{2-}$ ion as found in the cesium salt described in the text.

several days. They have been fully characterized by crystallography[10] and their solution spectrum is that of the oxalate trimer obtained from the reaction of $[Mo_3S_{13}]^{2-}$ and oxalic acid.[4] The structure of the anion is shown in Figure 2.

An analogous reaction carried out with $W(CO)_6$ gives a more complicated array of products (at least four, somewhat depending on the quantity of Na_2S used). One of these has been shown to be the $W_3S_4{}^{4+}$(aq) ion and the others are still under investigation.

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Supplementary Material Available: A table of crystallographic parameters and a table of fractional coordinates (3 pages). Ordering information is given on any current masthead page.

(10) Green prismatic crystals with a pronounced tendency for twin growth; $Cs_2Mo_3S_4O_{18}C_6H_6$; $P\bar{1}$, $a = 9.677$ (3) Å, $b = 20.753$ (6) Å, $c = 6.654$ (2) Å, $\alpha = 97.03$ (3)°, $\beta = 106.17$ (2)°, $\gamma = 79.79$ (3)°, $Z = 2$, $V = 1259$ (1) Å^3, $R = 0.054$, $R_w = 0.065$.

The Cuboidal $Mo_4S_4{}^{6+}$ Aquo Ion and Its Derivatives

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Interest in tri- and tetranuclear molybdenum–sulfur cluster species has been growing rapidly in recent years. In addition to the perthio species[2–15] $Mo_3S_4{}^{n+}$ and $Mo_4S_4{}^{n+}$, there have been

† Texas A&M University.
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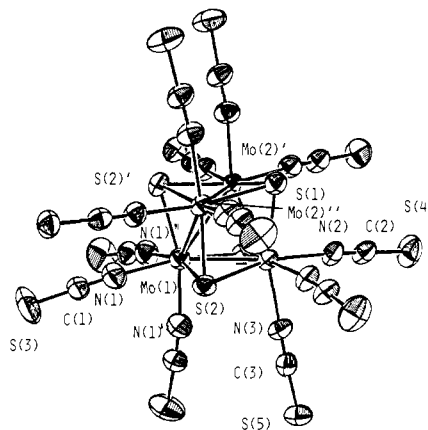

Figure 1. Structure of the $[Mo_4S_4(NCS)_{12}]^{6-}$ ion. The Mo–Mo distances have the following values: Mo(1)–Mo(2), 2.791 (1) Å; Mo(2)–Mo(2)′, 2.869 (1) Å.
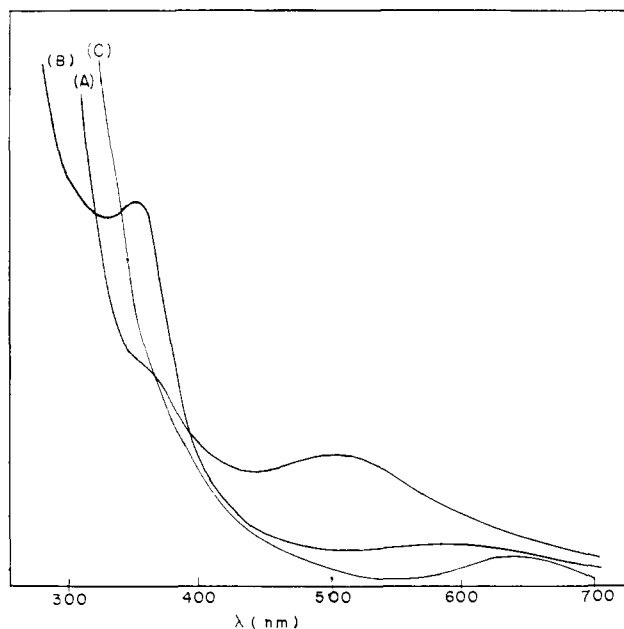

Figure 2. Electronic absorption spectra of the $Mo_3S_4{}^{4+}$(aq) ion (B), $Mo_4S_4{}^{6+}$(aq) ion (C), and $[Mo_4S_4(NCS)_{12}]^{6-}$ ion. (A).

recent reports of the mixed oxo–thio species[14–17] $Mo_3O_3S^{4+}$, $Mo_3O_2S_2{}^{4+}$ and $Mo_3OS_3{}^{4+}$ (each of which occurs in two isomeric forms). The trinuclear species so far described are all of the electron-precise type, that is, they contain the exact number of cluster electrons (six) necessary to form a full set (three) of Mo–Mo bonds. The tetranuclear species with a central Mo_4S_4 core vary in their electron count.[18] The $[Mo_4S_4(CN)_{12}]^{8-}$ species[8]

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is electron-precise (12 electrons) while $[Mo_4S_4(edta)_2]^{3-}$ and $[Mo_4S_4(NCS)_{12}]^{7-}$ are species[7,10] with 11-electron counts and $[Mo_4S_4(Et_2NCS_2)_6]$ has 10 electrons.[12] The 12-electron species has essentially T_d symmetry, while $[Mo_4S_4(edta)_2]^{3-}$ has Mo–Mo distances ranging from 2.755 to 2.880Å,[10] and the 10-electron species has distances to 2.732 (5) (2×) and 2.861 (16) Å (4×).

We wish to report the preparation of the $Mo_4S_4^{6+}$(aq) ion and a compound derived therefrom, $(NH_4)_6[Mo_4S_4(NCS)_{12}]\cdot10H_2O$, which are important in the context of the facts just summarized for two reasons. They are 10-electron species not constrained by any bridging ligands and the method of preparation differs from all those used previously to make Mo_4S_4 containing compounds. In our recent report[6] of the preparation of the $Mo_3S_4^{4+}$(aq) ion by refluxing a mixture of $Mo(CO)_6$ and Na_2S in acetic anhydride, followed by aqueous workup employing a cation exchange resin, we noted that in addition to the dark green $Mo_3S_4^{4+}$(aq) ion there was a second, paler green ion (denoted II) that adhered more firmly to the resin. From the eluate containing this second green ion we have been able to crystallize the compound $(NH_4)_6$-$[Mo_4S_4(NCS)_{12}]\cdot10H_2O$ and determine its structure.[19]   The structure of the tetranuclear anion is shown in Figure 1.

The $[Mo_4S_4(NCS)_{12}]^{6-}$ ion resides on a crystallographic site of $3m$ (C_{3v}) symmetry. Instead of the T_d symmetry potentially possible for this cuboidal species, it has only C_{3v} symmetry, as can be seen clearly in the Mo–Mo distances. The Mo_4 unit is a triangular pyramid, with slant edges of length 2.791 (1) Å and basal edges of length 2.869 (1) Å. Each face of the pyramid is capped by a sulfur atom and each molybdenum atom has three N-bonded thiocyanate ions attached to it.

The green solution eluted from the cation exchange column with 2 M HCl is believed to contain the $Mo_4S_4^{6+}$(aq) ion, whose absorption spectrum is shown in Figure 2, along with the spectra of the $Mo_3S_4^{4+}$(aq) and $[Mo_4S_4(NCS)_{12}]^{6-}$ ions.

The pronounced distortion of the Mo_4 cluster in the $[Mo_4S_4$-$(NCS)_{12}]^{6-}$ ion from T_d to C_{3v} symmetry requires an explanation. It seems unlikely to us that this is due to intermolecular (packing) forces. A molecular orbital calculation (Fenske–Hall method[20]) shows that the HOMO of a $[Mo_4S_4(NCS)_{12}]^{8-}$ ion (12e$^-$) would be a fully occupied t_2 orbital. For a C_{3v} distortion of the type observed in the $[Mo_4S_4(NCS)_{12}]^{6-}$ ion (10e$^-$), the t_2 orbital is split into a lower, filled e orbital and an upper, empty a_2 orbital. These results support (but do not prove) our view that the 10e$^-$ system undergoes a Jahn–Teller distortion along one coordinate of a T_2 vibration, thus splitting the degeneracy of the t_2 orbitals.[21]

During our preparation we observed a most interesting chemical interconversion of the Mo_3S_4 and the Mo_4S_4 cores. While the Mo_3S_4 species have previously been described as incomplete cubes, the topological similarity of the two species does not a priori necessitate a chemically tractable reaction pathway between the two. We now find that the cubane aquo ion is converted to the Mo_3S_4 trimer aquo ion by simple air oxidation. If solutions of the purified second ion (eluted with 4 M HCl and diluted to 0.4 M) are rechromatographed after exposure to air the Mo_3S_4 aquo species is isolated together with unreacted Mo_4S_4. In the presence of ligands that stabilize the trimer, such as oxalate, complete conversion is achieved within 2 days.

(18) The $(\eta^5\text{-}C_5H_5)_4Mo_4S_4^{0,+1,+2}$ species form the only set in which exact stoichiometric analogues with differing electron counts are known so far. Cf.: Bandy, J. A.; Davies, C. E.; Green, J. C.; Green, M. L. H.; Prout, K.; Rodgers, D. P. S. *J. Chem. Soc., Chem. Commun.* **1983**, 1395.

(19) Crystallographic data: Hexagonal, $P6_3mc$, $a = 17.500$ (3) Å, $c = 10.275$ (2) Å, $Z = 2$, $R = 0.030$, $R_w = 0.041$. One hundred and eleven parameters were refined using 1049 independent reflections with $F_o^2 > 3\sigma$-(F_o^2).

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(21) The significance of the previous observation of a D_{2d} distortion in a 10e$^-$ system[12] is uncertain because the two short Mo–Mo distances are bridged by dithiocarbamate ligands.

Synthetic Receptors: Size and Shape Recognition within a Molecular Cleft

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Because the idea is prevalent that host–guest chemistry can be a useful model for substrate–receptor biochemistry, bioorganic chemists have developed a number of systems capable of reversible binding interactions for such studies. Macrocyclic compounds such as polyethers,[1] cyclodextrins,[2] and cyclophanes[3] have dominated this area, presumably because their interactions with smaller molecules are easily conceptualized. We recently introduced[4] synthetic structures featuring a *molecular cleft* and here give evidence of their unusual binding properties. In these compounds carboxyl derivatives converge to provide *receptors* for molecules of complementary size, shape, and hydrogen-bonding capacity.

The new molecules are prepared by the condensation of the triacid[5] **1** with appropriate aromatic diamines such as the dye acridine yellow (**2**) (eq 1). The resulting diacid functions of **3** are constrained to the relative orientation shown; the aliphatic methyl groups prevent epimerization of the carboxyls while the aromatic methyls prevent rotation about the C_{aryl}–N_{imide} bonds. Molecular mechanics calculations and CPK models indicate a distance of about 8 Å between the opposing carboxyl oxygens of **3**, and the estimates are supported by its binding behavior toward appropriate diamines.

For example, in $CDCl_3$ the NMR signal of H_4 and H_5 moves *upfield* (>0.5 ppm) in the presence of pyrazine **4**, whereas with bases of inappropriate size (4,4'-bipyridyl, pyridine, or triethylamine) only conventional acid/base chemistry occurs, and this signal moves downfield 0.2 ppm. A stoichiometric complex of **3** with diazabicyclooctane (DABCO) was also observed.[6]   In general, complexation rates were rapid at room temperature; an activation barrier ($\Delta G^{\ddagger}_c$) of 10.5 kcal/mol was determined for the exchange of DABCO between molecules of **3** at $T_c = 208$ K.

Binding of **3** of diketopiperazines of simple amino acids was also observed, but with molecules of inappropriate shape (uracil) or hydrogen-bonding capabilities (sarcosine anhydride) no complexes were formed. The diamide **6**, mp >340 °C, prepared from **3** with $SOCl_2$ followed by NH_3,[8] also showed binding to diketo-

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