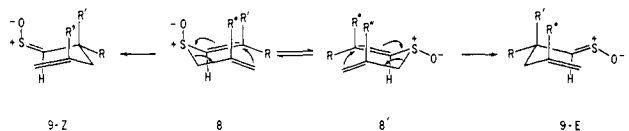


Attempts to achieve this same transformation by way of sulfide **6** were unsuccessful due to the instability of this compound and its transformation products under the conditions required for the normal thio-Claisen reaction. An important consequence of the mild conditions used for the sulfoxide thio-Claisen and sulfine hydrolysis is that overall yields are in general superior to those obtained by the thio-Claisen route.^{2a}

Examination of the sulfines formed from variously substituted 1-alkenyl 2-alkenyl sulfides **7** (Table I)¹⁰ reveals an interesting stereochemical effect. Thus for **7a-e** *Z* stereochemistry is favored, as it is for alkanethial *S*-oxides prepared by other routes;^{4,11} while for **7f-h** (e.g., where $R' \neq H$) *E* stereochemistry is favored. We find that the (*E*)-sulfines, which in some cases can be obtained in stereochemically pure form by chromatography,¹² rearrange thermally and photochemically to the thermodynamically more stable (*Z*)-sulfines.^{11,12} If it is assumed that rearrangement of sulfoxides **8** to sulfines **9** involves a chairlike transition state then pseudoaxial or pseudoequatorial orientations are possible for the sulfoxide oxygen. For thiane *S*-oxides an axial oxygen orientation is favored *except* when there are substituents at the 3- or 5-positions cis to sulfoxide oxygen, such as 3,3-dimethylthiane *S*-oxide where the equatorial/axial oxygen ratio is >95:5.¹³ We suggest that similar effects prevail in the sulfoxide thio-Claisen favoring **8'** over **8** when $R, R' \neq H$ (eq 3). The decreased ability



(3)

of the C-R'' bond compared to the C-R' bond to shift the sulfoxide oxygen from its normally favored pseudoaxial orientation may

(8) 2-Propenyl 3-chloro-1-propenyl sulfide, prepared in 100% yield by treatment of diallyl sulfide with NCS/CCl₄ at 0 °C,⁹ was oxidized with CH₃CO₃H (0 °C), warmed to 25 °C (1 h), washed (NaHCO₃), dried, and concentrated in vacuo giving (*Z*)-2-(chloromethyl)-4-pentenethial *S*-oxide (90%): ¹H NMR (CDCl₃) δ 8.11 (d, 1 H, *J* = 7 Hz), 5.74 (m, 1 H), 5.12 (m, 2 H), 3.85 (m, 3 H), 2.42 (m, 2 H); ¹³C NMR δ 176.4, 133.3, 118.7, 45.6, 38.1, 35.5; ca. 5% of the (*E*)-sulfine was also present. The sulfine in THF was added to HgO and BF₃-Et₂O (1:1) in THF-H₂O (85:15) at 25-45 °C for 2.5 h. Workup (ether-brine washing, drying, concentration in vacuo) gave 2-(chloromethyl)-4-pentalen (94% yield). This unstable compound was treated with an equimolar amount of DBU at 25 °C (15 min), diluted with pentane, water washed, dried, concentrated (Vigreux column), and distilled giving 2-methylene-4-pentalen (63%): IR 1690, 1640 cm⁻¹; ¹H NMR δ 9.67 (s, 1 H), 6.24 (br s, 1 H), 6.03 (br s, 1 H), 5.79 (m, 1 H), 5.09 (m, 2 H), 2.96 (m, 2 H).

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(12) 2-Allyl 2-adamantanethiocarbonyl *S*-oxide (**9h**) was separated by preparative TLC into *E* and *Z* isomers whose configurational assignments follow past work.⁴ The *E* isomer had mp 35-36 °C. Anal. C, H, IR 1093 (s) cm⁻¹; ¹H NMR δ 8.82 (s, 1 H, CH=SO) in CDCl₃ and 8.50 in C₆D₆; ¹³C NMR δ 192.5 (C=SO, *J*_{C-H} = 163.2 Hz), 131.7, 119.7 (C=C). The *Z* isomer had mp 50-51 °C. Anal. C, H, IR 1115 (s) cm⁻¹; ¹H NMR δ 7.42 (s, 1 H, CH=SO) in CDCl₃ and 6.83 in C₆D₆; ¹³C NMR δ 182.3 (C=SO, *J*_{C-H} = 157.1 Hz), 133.4, 118.1 (C=C). After 36 h at 90 °C, conversion of (*E*)-**9h** to (*Z*)-**9h** was complete.

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be due to the greater distance of the C-R'' bond from the S-O bond compared to the C-R' bond in the rearrangement transition state.¹⁴

In addition to the stereoselectivity seen at sulfur in the sulfoxide thio-Claisen rearrangement, possibilities exist for intramolecular chirality transfer from sulfur to carbon in the case of *chiral* 1-alkenyl 2-alkenyl sulfoxides. Efforts to prepare these compounds are in progress.

Acknowledgment. We thank Professors Shelton Bank and Barry Carpenter for helpful discussions and gratefully acknowledge support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, the Société Nationale Elf Aquitaine, and the Northeastern New York Chapter of the American Heart Association. Support from the National Science Foundation for the purchase of a Varian XL-300 NMR spectrometer is acknowledged.

(14) The S-O bond is separated from the C-R' bond by an sp² C-sulfoxide bond and a C-C double bond (which in the transition state becomes a sulfine thiocarbonyl bond and an sp³-sp² C-C bond, respectively) and from the C-R'' bond by an sp²-sp³ C-C bond and an sp³ C-sulfoxide bond (the latter is broken in the transition state).

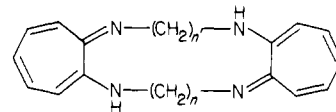
Dicopper(I) Tropocoronands: Synthesis, X-ray Crystal Structure, and Spectral Properties of Neutral Binuclear Copper(I) Complexes Bridged by Symmetrically Substituted Alkynes

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We have been exploring the coordination chemistry of the tropocoronands, H₂(TC-*n,n'*), a new class of macrocycles¹ which



(TC-*n,n'*)H₂

n,n' = 3,3; 4,4; 4,5; 5,5; 6,6

bind divalent metal ions with loss of two enamino protons to form stable neutral mononuclear complexes.^{2,3} Binuclear species form in the reaction of cupric acetate monohydrate with H₂(TC-6,6) in methanol, which yields the doubly bridged μ -acetato- μ -methoxo derivative [Cu₂(OAc)(OMe)(TC-6,6)] (**1**).⁴ Because of the great current interest in the chemistry of binuclear cuprous sites,⁵ we have recently turned our attention to the synthesis and characterization of discrete binuclear copper(I) species using tropoco-

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ronand ligands with $n, n' \geq 5$, in the hope of providing the proper environment for binding and activating small organic molecules. Here we report the synthesis, X-ray crystal structure determination, and spectral properties of $[\text{Cu}_2(\mu\text{-RC}\equiv\text{CR})(\text{TC-6,6})] \mathbf{2a}$ ($\text{R} = \text{CO}_2\text{CH}_2\text{CH}_3$), $\mathbf{2b}$ ($\text{R} = \text{CO}_2\text{CH}_3$), and $\mathbf{2c}$ ($\text{R} = \text{CH}_3$), which, to our knowledge, are the first examples of neutral alkyne-bridged binuclear copper(I) complexes.

Compound $\mathbf{2a}$ was synthesized by the gradual addition of a 15.2 μM THF solution of $\text{Li}_2(\text{TC-6,6})$ (10 mL) to a THF/ CH_3CN (1:1, v/v, 20 mL) solution of tetrakis(acetonitrile)copper(I) tetrafluoroborate (95.2 mg, 0.303 mmol) at -78°C under N_2 . To the resulting yellow mixture was immediately added a solution of diethyl acetylenedicarboxylate (DEAD, 25 μL , 1.0 equiv) in THF (2 mL). After it was stirred for 0.5 h at -78°C , the mixture was allowed to warm to room temperature and then filtered under N_2 . The volatile components of the filtrate were removed in vacuo, and the residual red solid was recrystallized from toluene/pentane at -30°C . Dark red air-stable crystals (47.6 mg, 45%)⁶ suitable for X-ray analysis⁷ were obtained. Compound $\mathbf{2b}$ was prepared in the same fashion by using 1.0 equiv of dimethyl acetylenedicarboxylate (DMAD, 48% yield).⁸ Alternatively, $\mathbf{2b}$ may be prepared in 57% yield by displacement with DMAD of bound CO from an intermediate carbonyl complex ($\nu_{\text{CO}} 2070 \text{ cm}^{-1}$) of $[\text{Cu}_2(\text{TC-6,6})]$.⁹

A slightly different procedure was employed for the synthesis of $\mathbf{2c}$. A THF solution of $\text{Li}_2(\text{TC-6,6})$ (11.8 μM , 10.0 mL) was added dropwise to a stirred suspension of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ (74.4 mg, 0.237 mmol) and 2-butyne (1 mL) in 10 mL of THF at -78°C under N_2 . The resulting yellow-green mixture was then treated as described above for the preparation of $\mathbf{2a}$ and $\mathbf{2b}$. Golden plates (26 mg, 38%) were obtained, the elemental analyses and spectroscopic data¹⁰ for which are consistent with the formula $[\text{Cu}_2(2\text{-butyne})(\text{TC-6,6})]$. Bright red crystals of the diphenylacetylene analogue ($\mathbf{2d}$, $\text{R} = \text{Ph}$) were also prepared by this procedure.⁹

The structure of $\mathbf{2a}$, shown in Figure 1, consists of two copper atoms bound on the "saddle" of the tropocoronand ligand by the nitrogen donor atoms of the two aminotroponimine fragments and bridged by a molecule of DEAD oriented perpendicular to the copper-copper vector. Each copper atom lies slightly (0.04

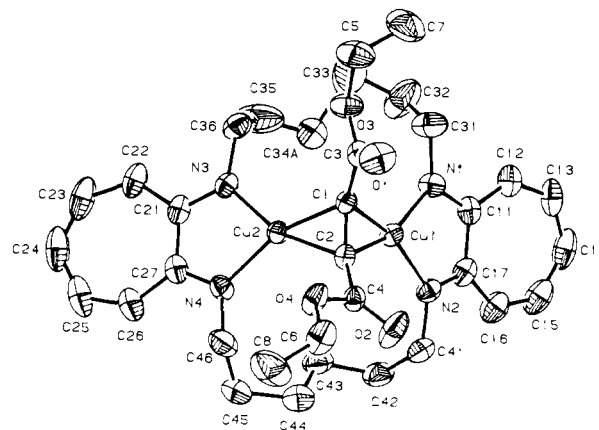


Figure 1. Structure of $[\text{Cu}_2(\mu\text{-DEAD})(\text{TC-6,6})] (\mathbf{2a})$ showing the 50% probability thermal ellipsoids and atom labeling scheme. Atom C34A is disordered over two sites, only one of which is depicted. Selected interatomic distances (Å) and angles (deg) are as follows: C1-C2 1.320 (6), Cu1-C1 1.937 (4), Cu1-C2 1.955 (4), Cu2-C1 1.961 (4), Cu2-C2 1.939 (4), Cu1-N1 1.912 (3), Cu1-N2 1.907 (3), Cu2-N3 1.907 (3), Cu2-N4 1.910 (3), Cu1...Cu2 2.806 (1), C1-Cu1-C2 39.6 (2), C1-Cu2-C2 39.6 (2), N1-Cu1-N2 83.7 (2), N3-Cu2-N4 84.0 (2), C1-C2-C4 138.7 (4), C2-C1-C3 136.9 (4). The torsion angle for C3-C1-C2-C4 is 0.0° .

Å) above the plane defined by the center of the C-C multiple bond and its two bonded nitrogen atoms. The geometry about each copper atom resembles that found for cationic mononuclear complexes of copper(I) with bidentate amine and unsaturated hydrocarbon ligands.¹¹ As anticipated, the alkyne moiety is able to bridge the short Cu-Cu distance of 2.806 (1) Å, occupying the third coordination site for both copper atoms. Unlike previous binuclear copper-alkyne complexes,^{5f,12} a single DEAD molecule serves as a 4e donor. The bond order of the coordinated alkyne functionality is substantially diminished, as revealed by the C-C distance of 1.320 (6) Å. This value is slightly shorter than the 1.38 (5) Å distance found in a tetranuclear copper(I)-acetylide cluster, where the acetylide ligand bridges the four metal atoms in both a σ and π fashion.¹³

The relative π -donor abilities of the alkynes are reflected in the visible and infrared spectra of the complexes.^{6,8,10} The electron-withdrawing ester substituents in the DEAD and DMAD derivatives lower the C-C infrared stretching frequency and, by removing electron density from copper, raise the energy of the metal-to-aminotroponimine charge-transfer band. This effect is also manifest in the ^1H NMR spectra of $\mathbf{2a}^6$ and $\mathbf{2c}$.¹⁰ The eight methylene protons α to the nitrogen atoms, which in $\text{H}_2(\text{TC-6,6})$ appear as a triplet ($J = 7 \text{ Hz}$) at $\delta 3.24$, are split into two equal multiplets at $\delta 3.96$ and 3.85 in $\mathbf{2a}$. The corresponding resonances in $\mathbf{2c}$ are less deshielded, occurring at $\delta 3.87$ and 3.50 . The chemical shift difference between $\mathbf{2c}$ and $\mathbf{2a}$ or $\mathbf{2b}$ reflects the greater electron density near the tropocoronand α carbon atoms in the more electron releasing 2-butyne complex. The NMR data also indicate that the structure shown in Figure 1 is maintained in solution, since the α protons within the cavity (closer to the metal atoms) vs. those outside the cavity (away from the metals) of the macrocycle are magnetically nonequivalent.

In summary, novel dicopper(I) complexes of the tropocoronand ligand, in which simple alkynes are coordinated as 4e-donor, neutral bridging ligands, have been synthesized and extensively characterized. The reaction is a general one since both electron-withdrawing and electron-donating alkynes can be incorporated into the bridging position. We are currently exploring the

(6) Anal. Calcd for $\text{C}_{34}\text{H}_{44}\text{Cu}_2\text{N}_4\text{O}_4$ ($\mathbf{2a}$): C, 58.36; H, 6.34; N, 8.01. Found: C, 58.60; H, 6.18; N, 8.05. IR spectrum (KBr, cm^{-1}) 1717 and 1710 sh (s, C=O), 1635 and 1647 sh (m, C \equiv C), 1599 (s, C=C), 1207 (s, C-O), 749 (s, C-H); ^1H NMR (295 K, C_6D_6) (250 MHz) δ 6.89 (4 H, t, $J = 11 \text{ Hz}$), 6.59 (4 H, d, $J = 12 \text{ Hz}$), 6.34 (2 H, t, $J = 10 \text{ Hz}$), 4.06 (4 H, q, $J = 7 \text{ Hz}$), 3.96 (4 H, m), 3.85 (4 H, m), br signal centered at 1.66 (16 H) and 0.98 (6 H, t, $J = 7 \text{ Hz}$); ^{13}C NMR (22.4 MHz) δ 159.37, 62.12, 14.24, 164.73, 112.23, 133.74, 117.38, 51.18, 28.05, and 28.70 for carbons C3, C5, C7, C11, C12, C13, C14, C31, C32, and C33, respectively (see Figure 1); a resonance for C1 (or C2) was not observed.

(7) Crystal data for $\mathbf{2a}$: $\text{C}_{34}\text{H}_{44}\text{Cu}_2\text{N}_4\text{O}_4$, M_r 699.8, monoclinic, $P2_1/c$, $a = 11.979$ (2) Å, $b = 16.691$ (1) Å, $c = 16.233$ (4) Å, $\beta = 94.57$ (2) $^\circ$, $V = 3235$ Å 3 , $Z = 4$, $\rho_{\text{calcd}} = 1.432 \text{ g cm}^{-3}$, $\rho_{\text{obsd}} = 1.426$ (7) g cm^{-3} . For 3507 unique observed $|F_o| \geq 4\sigma(F_o)$ reflections measured at 18°C by diffractometer, the structure was solved and refined to a current value for the discrepancy index $R_1 = 0.036$.

(8) Crystal data for $\mathbf{2b}$: $\text{C}_{32}\text{H}_{40}\text{Cu}_2\text{N}_4\text{O}_4$, M_r 671.8, orthorhombic, space group $Pna2_1$, $a = 10.950$ (1) Å, $b = 16.093$ (2) Å, $c = 17.505$ (5) Å, $V = 3084$ Å 3 , $Z = 4$, $\rho_{\text{calcd}} = 1.447 \text{ g cm}^{-3}$, $\rho_{\text{obsd}} = 1.449$ (2) g cm^{-3} . Details as for $\mathbf{2a}$ with $R_1 = 0.033$ for 2286 data. Anal. Calcd for $\text{C}_{32}\text{H}_{40}\text{Cu}_2\text{N}_4\text{O}_4$: C, 57.22; H, 6.00; N, 8.34. Found: C, 56.61; H, 5.92; N, 8.05. UV-vis spectrum (benzene) λ 271 nm (ϵ 57 200 $\text{cm}^{-1} \text{ M}^{-1}$), 283 (60 380), 394 (45 760), 415 (21 210), 420 sh (20 450), 452 (23 100), 480-560 (br sh 1440); IR (KBr, cm^{-1}) 1732 and 1712 (s, C=O), 1648 and 1638 (w, C \equiv C), 1598 (s, C=C), 1217 (s, C-O), 745 (s, C-H).

(9) Villacorta, G. M.; Lippard, S. J., unpublished results. **Note Added in Proof:** The X-ray structure of the homologous $[\text{Cu}_2(\text{CO})_2(\text{TC-5,5})]$ complex has been determined and found to contain trigonally coordinated copper atoms, each with a terminally bound CO.

(10) Anal. Calcd for $\text{C}_{30}\text{H}_{40}\text{Cu}_2\text{N}_4$ ($\mathbf{2c}$): C, 61.73; H, 6.91; N, 9.60. Found: C, 61.81; H, 6.36; N, 9.34. Spectroscopic data: IR (KBr, cm^{-1}) 1750 (w, C \equiv C), 1597 (s, C=C), 736 (s, C-H); ^1H NMR spectrum (270 MHz, 295 K, C_6D_6) δ 7.00 (4 H, t, $J = 9 \text{ Hz}$), 6.65 (4 H, d, $J = 10 \text{ Hz}$), 6.40 (2 H, t, $J = 8 \text{ Hz}$), 3.87 (4 H, m), 3.50 (4 H, m), 1.98 (6 H, s), and a broad signal centered at 1.66 (16 H); ^{13}C NMR spectrum (22.4 MHz, 295 K, toluene- d_6) δ 9.76, 164.26, 111.06, 133.49, 115.83, 51.69, 28.07, and 28.94 for the butyne- CH_3 carbon and carbons C11, C12, C13, C14, C31, C32, and C33 (see ref 6 and Figure 1), respectively.

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chemistry of these and other complexes in which small molecules are bound and activated between two metals attached to binucleating tropocoronands.

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Supplementary Material Available: Tables of atomic positional and thermal parameters for compounds **2a** and **2b** (6 pages). Ordering information is given on any current masthead page.

The Mo₃S₄⁴⁺ Aquo Ion

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There is an extensive chemistry of the Mo₃O₄⁴⁺ aquo ion,¹⁻³ whose complete formula is almost certainly [Mo₃O₄(H₂O)₉]⁴⁺, although no compound containing the ion itself has yet been reported. It is well-known that molybdenum has an extraordinary proclivity to form binuclear and cluster compounds containing terminal μ₂ or μ₃ sulfur atoms, some of which are of biological importance. We have, therefore, been working on the chemistry of compounds containing equilateral triangular arrays of molybdenum atoms in which there are μ₂-S and/or μ₃-S groups. We⁴ and others⁵⁻⁷ have previously reported reactions giving complexes of the Mo₃S₄⁴⁺ ion by employing the compound (NH₄)₂[Mo₃S(S₂)₆] as a starting material.⁸ For a number of reasons, we have been seeking ways to obtain the Mo₃S₄⁴⁺(aq) ion cleanly in aqueous solution and then use it to produce complexes and other derivatives conveniently. We report here our success in doing this.

One method of obtaining the [Mo₃S₄(H₂O)_n]⁴⁺ ion (where n is probably 9) begins with the previously reported [Mo₃S₄(HNTA)₃]²⁻ complex⁴ (where HNTA²⁻ = [N(CH₂CO₂)₂(CH₂CO₂H)]²⁻). Hydrolysis of this anion in 2 M HCl for 8 h was essentially quantitative and gave a clear green solution, which was diluted with a 3-fold volume of water and passed through a Dowex 50W × 2 cationic exchange column. The green species was adsorbed on the column as a sharp green band at the top, which could be eluted only with relatively strong simple acids, such as 2 M HClO₄ or 4 M HCl. This is consistent with the presence of a highly charged ion such as Mo₃S₄⁴⁺(aq). The 4 M HCl eluate has a visible spectrum, Figure 1, very similar to that of the [Mo₃S₄(HNTA)₃]²⁻ ion and also quantitatively comparable to that of the Mo₃O₄⁴⁺(aq) ion. When this HCl solution was freeze-dried only an oily green deposit was obtained. However,

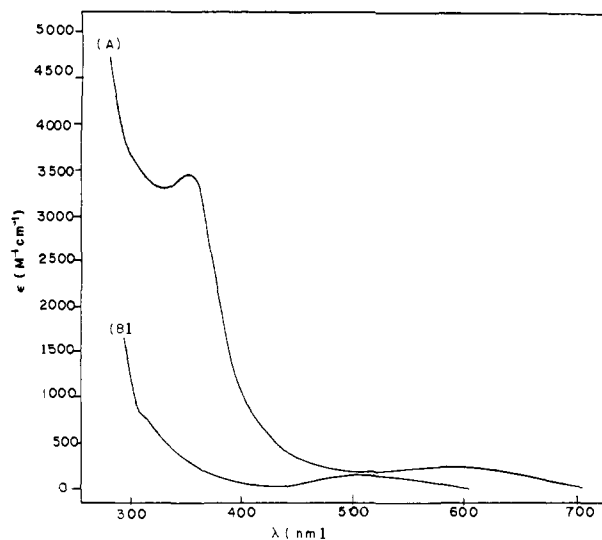


Figure 1. Electronic absorption spectra of (A) the Mo₃S₄⁴⁺(aq) ion and (B) the Mo₃O₄⁴⁺(aq) ion in 2 M HClO₄.

this easily redissolved in 0.01 M HCl to give a clear green solution that is stable in air for days, at least. To place the absorbance scale for the spectrum of the Mo₃S₄⁴⁺(aq) ion on an absolute scale, an accurately weighed amount of the [Mo₃S₄(HNTA)₃]²⁻ compound was completely hydrolyzed, the ion was collected on the cation exchange resin, and then quantitatively eluted to form a known volume of solution, whose spectrum was recorded.

Addition of nitrilotriacetic acid, oxalic acid, or KCN to this solution allows the isolation of salts of the [Mo₃S₄(HNTA)₃]²⁻, [Mo₃S₄(C₂O₄)₃(H₂O)₃]²⁻, and [Mo₃S₄(CN)₉]⁵⁻ ions. It is also possible to elute the green band from the column directly with 0.1 M solutions of H₃NTA/(NH₄)₃NTA, H₂C₂O₄/Na₂C₂O₄, or NaCN and isolate these same complexes from the eluates.

Although the results just summarized showed that the Mo₃S₄⁴⁺(aq) ion can be prepared, that it is stable in aqueous solution in air, and that anionic complexes of it can then be simply obtained, a convenient method for preparing the solution of Mo₃S₄⁴⁺ was not yet available. Such a method has been found which employs an entirely new reaction.

Molybdenum carbonyl (1.0 g), dry sodium sulfide (0.6 g), and 100 mL of acetic anhydride were refluxed for about 10 h under nitrogen. After it was cooled to room temperature, the solution was placed in the refrigerator for several hours and then filtered. The filtrate was hydrolyzed with 500 mL of water overnight, filtered, and passed through a Dowex 50W × 2 cation exchange column. The column was washed with 0.2 M HCl and then eluted with 1.0 M HClO₄ to give a green solution (species I). A second green ion (species II) which is left on the column was then eluted with 4 M HCl. The perchloric acid solution of the green ion I was diluted with water and passed again through the column depositing a green band, which was then eluted with 2 M HCl. The green ion in this solution, I, was identified as the Mo₃S₄⁴⁺ aquo ions by its spectrum and formation of anionic salts as above. The relative amounts of I and II vary somewhat with reaction conditions. Typical yields are 15% of the Mo₃S₄⁴⁺ ion in 20% of species II (assuming an E comparable to that of I).

The solution of the green ion II, as obtained by elution with 4 M HCl, has an electronic spectrum very similar to, but not identical with, that of the aquo ion, I. There is only a shoulder at 640 nm (band at 620 nm in I) and, diagnostically more important, no band between 300 and 400 nm. Species II can also be removed from the column by treating it with 0.5 M H₂C₂O₄ under argon for ca. 8 h to give a solution of an oxalate derivative.⁹ Again, the spectrum is not identical with that of the authentic [Mo₃S₄(C₂O₄)₃(H₂O)₃]²⁻. However, upon addition of CsCl, crystals of Cs₂[Mo₃S₄(C₂O₄)₃(H₂O)₃]·3H₂O are deposited after

(9) We have now been able to show that species II is the Mo₃S₄⁴⁺(aq) ion. See the following paper in this issue.

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† The Technion.

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