

Chart I

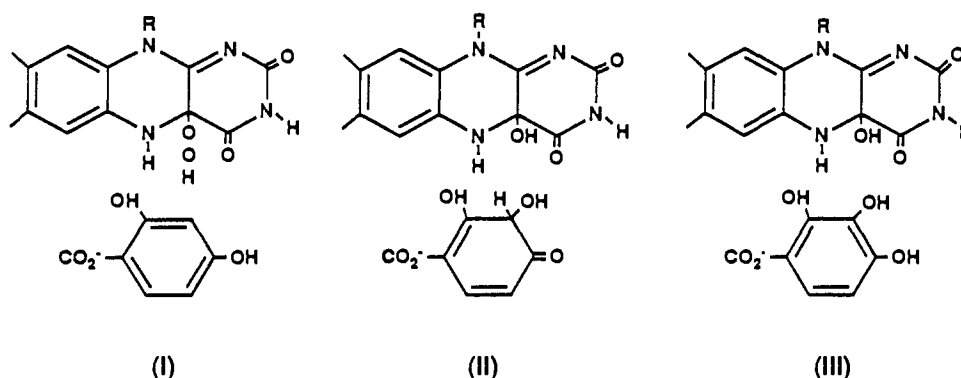
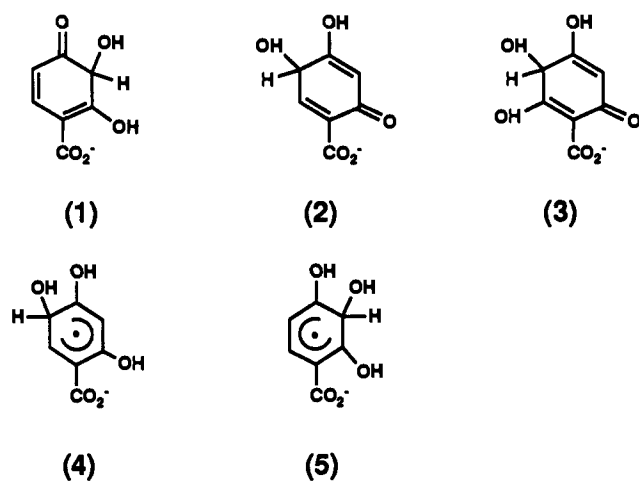


Chart II



respectively, the extinction coefficients of the phenoxyl radical, ferricyanide and ferrocyanide (all determined in separate experiments), and by OD, the measured optical densities, we obtain the relationship between Figure 1 and the experimental quantities:

$$\sum x_i \epsilon_i = (OD - \alpha c_0 \epsilon_{Ph} + (1 - \alpha) c_0 (\epsilon_{Fe(III)} - \epsilon_{Fe(II)})) / (1 - \alpha) c_0$$

The difference between the raw spectra and those in Figure 1 decreases with decreasing wavelength, being <30% below 400 nm. Spectra a and b are almost identical and do not change when oxygen instead of ferrocyanide is the oxidant. This confirms that the species are cyclohexadienones and that they are in the same protonation state between pH 6 and 8.3.

The sole detected⁴ trihydroxy benzoate was 3-OH DHBA, making up but 50% of initial OH[•] adducts. We believe that, about 50% 5-OH DHBA may have formed but has been further oxidized. Absence of 6-OH DHBA (which should be stable), rules out 6 addition. Ascribing spectrum d to species 3, we assign the short and long wavelength components in spectra a and b to species 2 and 1, respectively. Since protons apparently suppress the absorbance around 360 nm, spectrum c should belong to species 1, present with a fraction of 0.5. Thus we estimate the extinction coefficient of 1 at its peak maximum to be 6500 M⁻¹ cm⁻¹. We note that both spectral size and shape of 1 are in good agreement with that of the difference spectrum between intermediate II and III.^{2,14} Unlike species 1 intermediate II displays a spectral shift¹⁴ with a pK_a around 8, similar to the pK_a = 7.8¹⁵ of the Tyr201¹⁶ in the enzyme. It could be that loss of a hydrogen bond between Tyr201 and 1 causes the spectrum of the latter to red-shift.

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Further speculation must await knowledge of the protonation characteristics of 1.

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Model Complexes for Molybdopterin-Containing Enzymes: Preparation and Crystallographic Characterization of a Molybdenum-Ene-1-perthiolate-2-thiolate (Trithiolate) Complex

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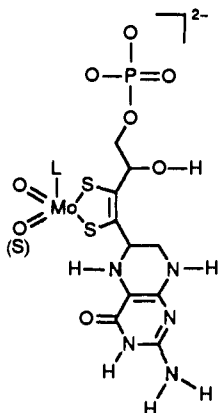
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With the exception of nitrogenase, all molybdenum enzymes are believed to contain the pterin cofactor designated Moco.¹ The lack of this cofactor or its improper function is linked to human disorders including gout, sulfite allergy, and the often fatal oxidase deficiency.² It is generally accepted that Moco is a C(6)-substituted pterin with a four-carbon side chain to which molybdenum is bound via a 1,2-ene dithiolate linkage.³ We seek to prepare

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metal complexes that accurately mimic the metal-pterin linkage in these enzymes and to develop a strategy for the total synthesis of biochemically active Moco.

Transition-metal di- and polysulfide complexes have been found to react with substituted alkynes to yield metallo-1,2-enedithiolate complexes.⁴ Here we report that this reaction extends to alkyne C(6)-substituted pterins and to alkyne C(2)-substituted quinoxalines allowing us to approach synthetically a number of the key features of the active sites of molybdopterin-containing enzymes. Moreover, two unprecedented "trithiolate" complexes have been prepared for the first time.

In previous work,⁵ alkyne-substituted pterins were prepared by the palladium-catalyzed coupling of C(6) chloro-substituted pterins with terminal alkynes and this has now been extended to C(2) chloro-substituted quinoxalines. Quinoxalines were chosen to facilitate product crystallization while retaining the pyrazine redox site of the pterin.

The reaction of either alkyne C(6)-substituted pterin **1** or the alkyne C(2)-substituted quinoxaline **2**⁶ with Cp₂MoS₄⁷ results in the formation of complexes **3** (62%) and **4** (36%), respectively. These compounds have a new sulfur-containing ligand, formulated as an ene-1-perthiolate-2-thiolate (henceforth trithiolate) as shown in Scheme I. Addition of 1 equiv of PPh₃ to either complex **3** or **4** results in sulfur abstraction, elimination of SPPH₃, and formation of the desired molybdenum-1,2-enedithiolate complexes **5** and **6**, both in >95% yield.

Crystallographic⁸ and spectroscopic data for complex **4** both implicate a single trithiolate isomer with the S₂ linkage bound

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(8) Crystal data **4**: C₂₂H₁₈N₂MoOS₃·acetone, monoclinic, P2₁/c, a = 11.776 (3) Å, b = 20.313 (5) Å, c = 10.518 (3) Å, β = 97.38 (2)°, V = 2495 (1) Å³, D_{calc} = 1.535 g/cm³, μ(Mo Kα) = 7.68 cm⁻¹, R_F = 4.95%, R_w = 6.11% for 3112 absorption corrected reflections 293 K, 4 ≤ 2θ ≤ 52°, F_o ≥ 5σ(F_o). Nicolet diffractometer, Mo Kα.

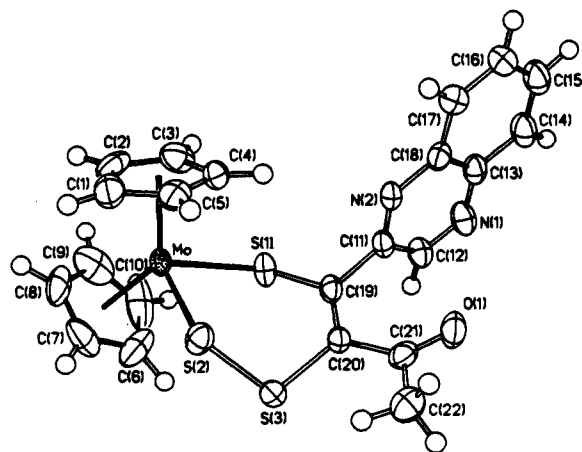


Figure 1. An ORTEP drawing of Cp₂MoS₂C₂(2-quinoxaline)(C(O)Me), **4**, with the thermal ellipsoids drawn at 35% probability and a listing of selected bond lengths (Å) and angles (deg): Mo-S(1), 2.510 (2); Mo-S(2), 2.451 (2); Mo-S(3), 3.704 (2); S(1)-C(19), 1.746 (5); S(3)-C(20), 1.757 (6); C(19)-C(20), 1.364 (8); Mo-CNT(1), 1.994 (3); Mo-CNT(2), 1.993 (3); Mo-S(1)-C(19), 116.4 (2); Mo-S(2)-S(3), 109.6 (1); S(2)-S(3)-C(20), 103.5 (2); S(1)-C(19)-C(20), 126.8 (4); S(3)-C(20)-C(19), 119.8 (4); S(1)-C(19)-C(11), 111.6 (4); S(3)-C(20)-C(21), 118.4 (4); C(19)-C(11)-N(2), 118.6 (5); CNT(1)-Mo-CNT(2), 135.1 (2).

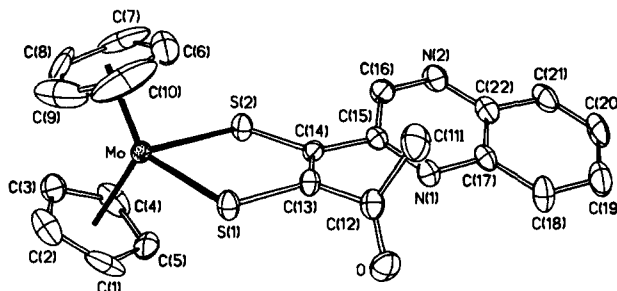


Figure 2. An ORTEP drawing of Cp₂MoS₂C₂(2-quinoxaline)(C(O)Me), **6**, with the thermal ellipsoids drawn at 35% probability and a listing of selected bond lengths (Å) and angles (deg): Mo-S(1), 2.436 (2); Mo-S(2), 2.438 (2); S(1)-C(13), 1.7566 (8); S(2)-C(14), 1.768 (6); C(13)-C(14), 1.338 (12); Mo-CNT(1), 2.002 (4); Mo-CNT(2), 1.990 (4); Mo-S(1)-C(13), 106.8 (3); Mo-S(2)-C(14), 107.2 (3); S(1)-C(13)-C(14), 122.6 (5); S(2)-C(14)-C(13), 120.9 (6); CNT(1)-Mo-CNT(2), 132.5 (3).

to the alkyne carbon flanked by the carbonyl group, Figure 1. An interesting feature is the single four-atom plane formed by S(1), S(3), C(19) and C(20), which is flat within the estimated standard deviations for the atomic positions. The Mo-S(1) bond length at 2.510 (2) Å is rather long but the Mo-S(2) bond length at 2.451 (2) Å is not unlike the Mo-S distances found in molybdenum-1,2-enedithiolate and di- or polysulfide complexes.^{4c,d,9,10} The S(2)-S(3) bond length at 2.074 (2) Å is best described as a S-S single bond, and S(3) is not within bonding distance of the metal center (Mo-S(3) 3.704(2) Å).

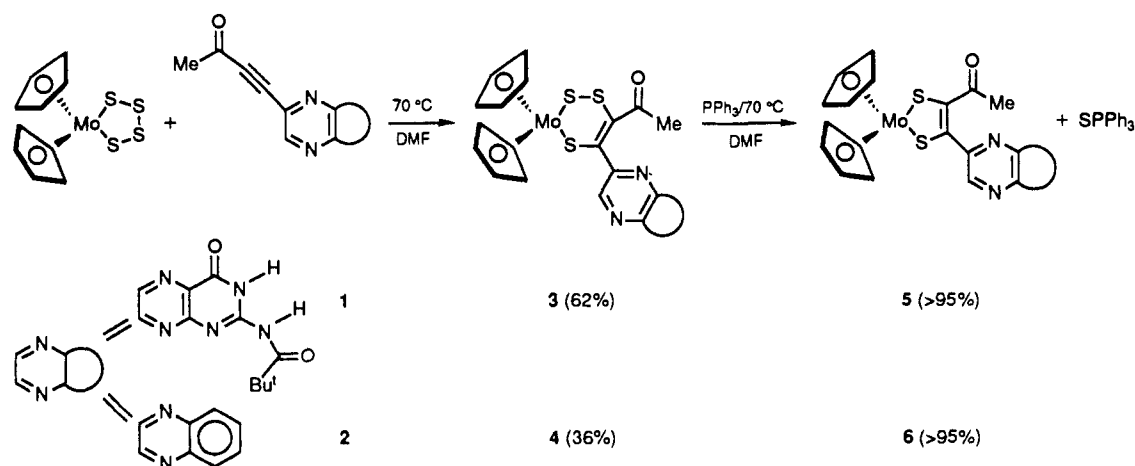
The dithiolate complex, **6**, was also crystallographically characterized,¹¹ Figure 2. The five-membered metalocycle formed by Mo, S(1), S(2), C(13), and C(14) is essentially planar

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(11) Crystal data **6**: C₂₂H₁₈N₂MoOS₂, monoclinic, P2₁/c, a = 12.424 (2) Å, b = 14.335 (3) Å, c = 12.533 (3) Å, β = 115.72 (1)°, V = 2010.9 (1) Å³, D_{calc} = 1.607 g/cm³, μ(Mo Kα) = 8.50 cm⁻¹, R_F = 5.02%, R_w = 6.15% for 2200 absorption corrected reflections 293 K, 4 ≤ 2θ ≤ 48°, F_o ≥ 5σ(F_o). Nicolet diffractometer, Mo Kα.

Scheme I



with a deviation from planarity of only 0.01 Å. This plane bisects the dihedral angles defined by the cyclopentadienyl rings. The bond lengths and angles in complex **6** are similar to other crystallographically characterized 1,2-enedithiolate complexes of molybdenum.^{4c,49} The plane of the quinoxaline ring forms a 94.0° angle with the S(1), C(19), C(20), S(3) plane in complex **8** and a 19.5° angle with the S(1), C(13), C(14), S(2) plane of complex **6**.

The preparation of complexes **3** and **4** and the conversion of these complexes to **5** and **6**, respectively, are important to the mechanistic understanding of 1,2-enedithiolate synthesis from the reaction of metal polysulfides and alkynes. In many instances vinyl disulfides are the initial products from the reaction of a metal polysulfide complex and an alkyne. The vinyl disulfides are isomerized to the 1,2-enedithiolate complexes by exogenous sulfur,^{4c-8} and the trithiolate complex is a likely intermediate.^{4d} Here we provide the first definitive examples of such complexes and demonstrate that they are indeed readily converted to 1,2-enedithiolates.

Complex **5** was ≥90% enriched in ³⁴S and the natural abundance and ³⁴S-enriched samples have been studied by resonance Raman spectroscopy. The Mo-S stretch in complex **5** is identified as a band at 349 cm⁻¹ which upon ³⁴S enrichment shifts to 341 cm⁻¹.¹² The Moco enzyme DMSO reductase (oxidized) from *Rhodobacter sphaeroides* has a band at 350 cm⁻¹, which upon ³⁴S enrichment shifts to 341 cm⁻¹.¹³

An interesting feature of complexes **3** and **5** is the weak fluorescence of the oxidized pterin. This stands in contrast to the very strong fluorescence of **1**, which emits at 496 nm with excitation maxima at 362 nm or 420 nm. At the same concentration as compound **1**, complexes **3** and **5** show greater than 95% quenching of the fluorescence. Since the observed fluorescence has the identical excitation profile as compound **1**, it is likely that complexes **3** and **5** are not fluorescent and that a small impurity of compound **1** causes the observed fluorescence. In any case, it is clear that metalodithiolates on the C(6) side chain of an oxidized pterin quench the fluorescence of the pterin.

The results presented here show that the reaction of a molybdenum polysulfide and an alkyne could be an important component of the total synthesis of active molybdenum cofactor. Moreover, the pterin-dithiolene complexes that have now been produced are the closest structural analogues of the molybdenum-dithiolene-pterin portion of the Moco active site and as such are useful spectroscopic and reactivity models for the native center. Work

(12) The spectra of **5** (natural abundance and ³⁴S labeled) were obtained with a backscattering geometry from a KCl pellet mounted on a cold finger cooled to 77 K. The spectra were collected with 568.1-nm laser excitation from a coherent Kr⁺ ion laser. Conditions: 80 mw laser output and 4-cm⁻¹ resolution. The light was dispersed through a Spex 1401 double monochromator equipped with photon-counting electronics.

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on synthetic, spectroscopic, and reactivity aspects of these complexes is continuing.

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Supplementary Material Available: Tables of crystallographic data, atomic coordinates, bond distances and angles, and anisotropic thermal parameters, spectroscopic data for complexes **3-6** and the preparation of Cp₂Mo³⁴S₄ (11 pages); structure factor tables for **4** and **6** (17 pages). Ordering information is given on any current masthead page.

Isolation and Characterization of Stereoisomers of Pentacoordinated Phosphorus. Hydrolysis of Unsymmetrically Substituted Chiral Monocyclic Oxyphosphoranes

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Pentacoordinated phosphorus compounds (phosphoranes) have attracted attention as models for the intermediate or transition state in nonenzymatic and enzymatic phosphoryl transfer reactions.¹ The stereochemical course and product distribution of

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