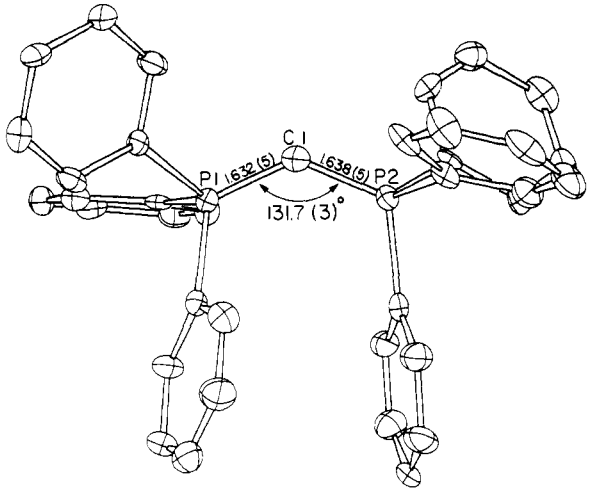

Figure 1. Molecular structure of the nontriboluminescent form of $(Ph_3P)_2C$.

Systems containing adjacent double bonds on a central carbon (e.g., C=C=C, C=C=N, or N=C=N) are expected to be linear by conventional bonding schemes. Studies on crystals of molecules containing these units have shown that the bond angle about the central carbon can deviate from linearity by at most only 10° owing to lattice forces.[8-11] When a phosphorus atom is included in the chian, adjacent double bond angles as small as 130° have been observed.[4] In salts of the isoelectronic $(Ph_3P)_2N^+$ cation, P-N-P bond angles range from 134.6 to 180° as the anion is changed.[12-18] Both linear and bent forms of this cation can exist in the same unit cell.[19]

Microcrystals of triboluminescent hexaphenylcarbodiphosphorane obtained by more rapid cooling of a diglyme solution in an insulated flask exhibit different spectroscopic properties from crystal A. The photoluminescence of microcrystals of B consists of a broad band centered at 530 nm, while that of crystal form A is centered at 575 nm. When the microcrystals of B are left standing for a long period of time at room temperature, the luminescence shifts to 575 nm with no chemical decomposition of the crystals and the triboluminescence disappears as they convert slowly to crystal form A. In addition to the luminescence differences, Raman spectra of powdered samples of the triboluminescent phase include two peaks of roughly equal intensity at 661 and 652 cm^{-1}, while the nontriboluminescent sample shows only one vibration at 661 cm^{-1}. These bands are tentatively assigned to the P-C-P symmetric stretches of the molecules with bond angles of 130 and 144°, respectively, in the TL-active phase and the molecule with the 132° angle in the TL-inactive phase.

The different molecular geometries and crystal structures of the TL-active and -inactive phases illustrate the sensitivity of the P-C-P bond angle to packing forces. The difference in the packing forces, calculated using the model of Williams,[20] is only on the order of 1 kcal/mol. More importantly, the polymorphs illustrate the sensitivity of TL to structure. The piezoelectric properties of the crystal are a significant difference between the two polymorphs and perhaps are pertinent to the TL mechanism.[3] The TL-active phase belongs to a polar space group, while the TL-inactive phase is nonpolar and can exhibit piezoelectric charging only under torsion.

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Monomeric Molybdenum(V) Oxo Complexes with Tetradentate Aminoethanethiols

Sir:

Much of the current understanding of molybdenum enzymes is based on electron spin resonance (ESR) investigations of Mo(V) signals arising during turnover of the enzymes.[1] These studies strongly suggest one (or more) of the ligands of the Mo(V) binding site in xanthine oxidase, aldehyde oxidase, sulfite oxidase, and nitrate reductase is the sulfur of a cysteine side chain.[1-3] As pointed out by Bray,[2] there is, however, a lack of ESR data from well-characterized monomeric Mo(V) complexes which could be used, by comparison, to obtain structural information concerning the enzymatic Mo(V) centers. Moreover, there are no ESR data for complexes of known structures bonded to thiol ligands within a saturated framework.[4] A number of solution ESR spectra of such complexes have been reported, but these are generally for a small amount of monomer of unknown structure in equilibrium with an ESR inactive dimer.[4-6]

We report the preparation, ESR, visible and IR spectra, and electrochemical parameters of two monomeric Mo(V) ovo complexes with tetradentate aminoethanethiols. These appear to be the first such Mo(V) complexes to be described and their properties are of considerable interest with respect to the possible structure of enzymatic Mo(V) centers (in addition to cysteine sulfur, an NH ligand has been proposed as a likely group present at the Mo binding site of xanthine oxidase[1,2,4]).

The complexes have the formula MoOClL, where L = *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)ethylenediamine (L_1)[7] and *N,N'*-bis(2-methyl-2-mercaptopropyl)ethylenediamine (L_2).[8] The complexes were obtained by refluxing, under nitrogen, a dilute (0.010 M) equal molar mixture of the ligand

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Table I. ESR Parameters

complex	g values (±0.001)					A values (^{95}Mo, ^{97}Mo, cm^{-1} × 10^4; ±1.0 × 10^4 cm^{-1})			
	$\langle g\rangle$[a]	$\langle g\rangle'$[b]	g_x	g_y	g_z	$\langle A\rangle'$[c]	A_x	A_y	A_z
$MoOClL_1$[d]	1.966	1.965	1.940	1.949	2.006	37.8	38.0	15.0	60.5
$MoOClL_2$[d]	1.970	1.971	1.944	1.958	2.011	38.7	36.0	22.5	57.5
$MoOCl(8\text{-mercaptoquinoline})_2$[d]	1.969	1.967	1.948	1.950	2.003	38.8	38.5	20.0	58.4
xanthine oxidase[e] (very rapid signal)		1.977	1.951	1.956	2.025	31.7	35	22	38

[a] X band, room temperature. [b] $\langle g\rangle' = (g_x + g_y + g_z)/3$. [c] $\langle A\rangle' = (A_x + A_y + A_z)/3$. [d] DMF.[17] [e] Reference 1.

Table II. Properties of Complexes

complex	visible electronic spectra[a] λ_{max} (nm)	visible electronic spectra[a] ϵ (cm^{-1} M^{-1})	IR (Mo-O),[b] ν (cm^{-1})	electrochemistry E_p[c]	electrochemistry n[d]
$MoOClL_1$	526	2.65×10^3	958	−0.910[e]	0.99 ± .01
$MoOClL_2$	510	2.10×10^3	968	−0.495[f]	0.84 ± .04

[a] DMF. [b] Solid. [c] E_p = first reduction peak, volts vs. SCE, scan rate 0.100 V/s, 0.10 M Et_4NCl, DMF.[14] [d] Electrons/molecule. [e] Irreversible. [f] Quasi-reversible.

dihydrochloride and $(NH_4)_2MoOCl_5$ in carefully dried 1:1 C_2H_5OH–CH_3CN in the presence of a fourfold excess of $NaOCH_3$. After removal of most of the solvent, the complexes were isolated as solids, which, after drying in vacuo over P_2O_5, gave satisfactory analyses ($MoOClC_8H_{18}N_2S_2$, $MoOClC_{10}H_{22}N_2S_2$). Their monomeric nature was established by quantitative ESR measurements. IR shows the presence of very strong Mo–O stretching frequencies in the range expected for monooxo Mo(V) complexes,[4,10] and a lack of Mo–O–Mo bridge absorption.[4,10] Conductivity measurements in DMF indicate that the complexes are uncharged; upon standing, however, the conductivity slowly increases, probably owing to some Cl^- dissociation as observed with electrochemical studies.[14]

Several features of the ESR spectra are of interest with respect to the problem of enzymatic Mo(V) (Table I, Figure 1). Both complexes exhibit rhombic distortion in their ESR spectra, as does the very rapid signal from xanthine oxidase.[1] While some of the anisotropic g and A values are close to those of the enzyme, the $\langle g\rangle$ values are somewhat lower, and the $\langle A\rangle$ values are significantly higher than the values for the xanthine oxidase very rapid signal.

Recently, the ESR parameters of $MoO[S_2P(i\text{Pr})_2](OSC_6H_4)$ have been reported,[11] and they are somewhat closer to those of xanthine oxidase. This complex has three sulfur ligands, however, and the higher $\langle g\rangle$ and lower $\langle A\rangle$ may be due to this. Increasing the number of sulfur ligands in complexes with similar geometry appears to increase $\langle g\rangle$ and decrease $\langle A\rangle$, as observed with the recently reported complex, $Et_4NMoO(SC_6H_5)_4$.[15]

Four stereoisomers for the MoOClL complexes are possible: one cis and three trans (cis or trans refer to the position of the ligand with respect to the oxo group).

An analysis of both X- and Q-band ESR spectra for the MoOClL complexes reveals that the principal magnetic axes are noncoincident in the XY plane. The presence of noncoincident g_{xx} and A_{xx}, and g_{yy} and A_{yy} tensor components requires that there be no mirror plane perpendicular to the XY plane or proper rotation axis contained within it. Thus, if we take the Z direction of the magnetic tensors as the Mo–O bond as is usually the case for molybdenyl complexes,[4] then the cis isomer is highly unlikely since it contains a mirror plane. Furthermore, the ESR parameters for $MoOCl(8\text{-mercaptoquinoline})_2$ (Table I), which has recently been determined by X-ray crystallography to have the trans structure (N trans to oxo, two S atoms trans to each other),[16,17] are remarkably similar to those of the MoOClL complexes. Thus, a trans structure for both complexes seems probable.

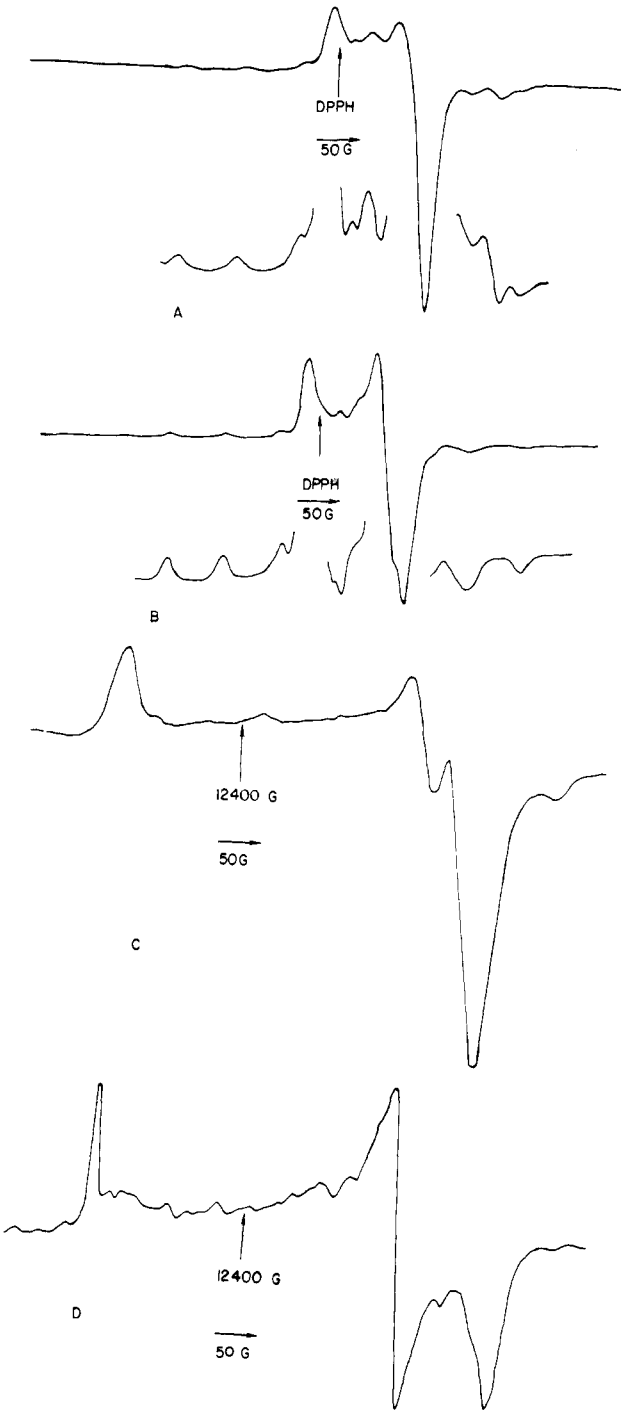
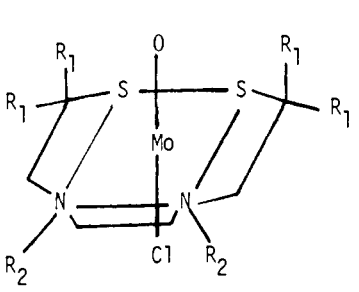
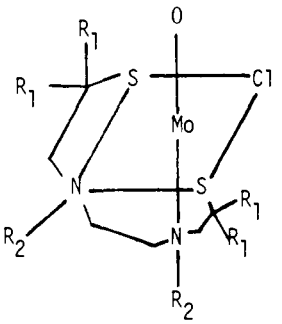


Figure 1. ESR spectra: A, C, $MoOClL_1$; B, D, $MoOClL_2$; A, B, 9.068 GHz, 77 K, DMF; C, D, 34.618 GHz, 77 K, DMF.



cis-MoOClL



trans-MoOClL
(one of 3 isomers)

L_1: R_1 = H, R_2 = CH_3

L_2: R_1 = CH_3, R_2 = H

The xanthine oxidase signal exhibits proton superhyperfine splitting,[1] and ESR signals of nonoxo sulfur complexes, such as $Mo(S_2CNEt_2)(HNSC_6H_4)_2$, exhibit both proton and nitrogen superhyperfine splitting.[11] These nonoxo complexes have distorted trigonal prismatic geometry[12] and a short intramolecular Mo–N distance, indicating considerably multiple-bond character. It has been suggested the consequently short Mo··H distance may be an important factor in the large ^1H splittings observed.[12] The $MoOClL_2$ complex, however, gave no evidence for such splitting over a wide temperature range, from ambient to frozen in both DMF and $CHCl_3$. This lack of superhyperfine splitting may have its origin in differences in geometry, or in the absence in $MoOClL_2$ of extensive delocalization of the Mo(V) electron into an aromatic system in comparison with $Mo(S_2CNEt_2)(HNSC_6H_4)_2$.

Cyclic voltammetry and controlled potential coulometry at a platinum cathode indicate that both complexes are facilely reduced in a one electron step to Mo(IV) species (Table II). In the voltage range used (+0.50 to −2.50 V vs. SCE), however, the complexes could not be oxidized to the Mo(VI) state, indicating the Mo(VI)–Mo(V)–Mo(IV) complexes may not represent a simple redox series.[14] This is most likely due to the necessity of adding a second oxo group to the Mo(VI) dioxo complexes, requiring an oxo donor not present in the electrochemical system.[14] A detailed electrochemical study of these and other Mo(V) complexes will be published elsewhere.[14]

While the complexes reported here model reasonably well some of the ESR parameters of xanthine oxidase, the differences in $\langle g \rangle$ and, particularly, $\langle A \rangle$, as well as a lack of proton superhyperfine splitting, suggest the Mo(V) site of the enzyme is, for whatever reasons, somewhat different. Work with a variety of other complexes, which may provide additional evidence concerning this important question, is underway and will be reported later.

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Descysteaminylthienamycin

Sir:

Thienamycin (**1**), isolated from *Streptomyces cattleya*,[1] is a rather unusual bicyclic β-lactam antibiotic. In contrast to the well-known penam and cephem antibiotics, it contains no sulfur atom in the ring system and the two β-lactam ring protons are trans to one another.[2] More interestingly, thienamycin displays potent, broad spectrum antibacterial activities against both Gram-positive and Gram-negative microorganisms (including *Pseudomonas spp.*) and is resistant to bacterial β-lactamases.[3]

One of our objectives in chemically modifying thienamycin was to substitute the aminoethylthio (cysteamine) side chain with a hydrogen atom and determine the antibacterial activities of the resultant product, i.e., of descysteaminylthienamycin (**4**). However, despite intensive efforts to carry out a reductive cleavage reaction directly on thienamycin under a variety of conditions known to cleave carbon–sulfur bonds, all reactions destroyed the β-lactam.[4] We now report the successful preparation of this simple but novel bicyclic β-lactam ring system and its potent antibacterial activity against most microorganisms.

The previously unsuccessful attempts to cleave directly the thienamycin side chain led us to believe that nucleophilicity of the cleavage products, ethylamine or cysteamine, was responsible for the destruction of the β-lactam ring. Therefore, instead of operating directly upon thienamycin, the amino group of thienamycin was first protected with a phenoxyacetyl group before hydrogenolysis. This protecting group serves two purposes: (1) the phenoxyacetyl group diminishes the nucleophilicity of the nitrogen, and (2) the aromatic ring of this group facilitates the final purification step in which an XAD-2 resin is used.[5]

N-Acylation of thienamycin was accomplished under Schotten–Baumann conditions in the presence of 2.5 equiv of phenoxyacetyl chloride (0 °C for 20 min in a 1:1 0.1 M aqueous sodium phosphate buffer–dioxane solvent system maintained at pH 8.5–9.0 with 2.5 N sodium hydroxide), followed by chromatography on an XAD-2 column eluted first with water and then with 10% tetrahydrofuran (THF) in water, to

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