se is not a necessary prerequisite because, e.g., RSH (R = Me, Et, Ph; pK_a = 6.5–10.6)[23] removes a μ-oxo group from $\mathrm{Mo_2O_4}^{2+}$, while phenol (pK_a = 10.0)[23] does not. Of comparable importance, then, is the nucleophilicity of sulfur and the subsequent binding of additional ligands. Further, mercaptans easily remove terminal oxo groups, producing non-oxo molybdenum(V) monomers from $\mathrm{Mo_2O_4}^{2+}$, i.e., stripping the molybdenum completely of both bridging and terminal oxo groups. All the successful reactions described above involve -SH groups; if such groups are omitted, the molybdenum complex is recovered unchanged. The aqueous chemistry of molybdenum, particularly in its higher oxidation states, is dominated by oxo-containing species produced from water, but its nonaqueous chemistry may well be equally dominated by the mercaptan, with the formation of sulfur-coordinated species and the occurrence of molybdenum-catalyzed reactions of mercaptans with various substrates.[24] As the Mo-containing sites of enzymes may be hydrophobic in nature, these studies reveal a host of interesting possibilities for their modes of reaction.

Acknowledgment. We thank J. L. Corbin, G. R. Seely, E. I. Stiefel, and G. D. Watt for helpful discussions and Climax Molybdenum Co. for generous gifts of compounds.

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(5) All compounds synthesized in this work have satisfactory elemental analysis and are produced in 70–100% yields (except where otherwise stated). Ir, NMR, and/or EPR also support the formulations shown. All reactions go to completion within 5 h.

(6) $[\mathrm{MoOL'}]_2\mathrm{OS}$ has also been prepared from the reaction of $\mathrm{MoO_2L'_2}$ ($\mathrm{L'} = \mathrm{S_2CN}$-*n*-$\mathrm{Pr_2}$) with $\mathrm{P_4S_{10}}$, but not with $\mathrm{H_2S}$ in the presence of air.[7] In contrast, we isolate only $\mathrm{OMo(S_2)L''_2}$ from $\mathrm{MoO_2L''_2}$($\mathrm{L''} = \mathrm{S_2CNMe_2}$) and $\mathrm{P_4S_{10}}$ anaerobically in benzene while Weiss et al. produce $\mathrm{OMo(S_2)L'_2}$ from $\mathrm{MoO_2L'_2}$ and $\mathrm{H_2S}$ in acetone under air.[7]

(7) J. Dirand, L. Ricard, and R. Weiss, *Inorg. Nucl. Chem. Lett.*, **11,** 661 (1975); *Inorg. Chim. Acta,* **18,** L21 (1976).

(8) Those compounds containing terminal molybdenum–oxygen bonds have the two typical[1] infrared absorptions at ~965 $\mathrm{cm^{-1}}$, which are replaced in $[\mathrm{MoSL}]_2\mathrm{S_2}$ by a similar doublet at ~540 $\mathrm{cm^{-1}}$. ν(MoOMo) occurs at ~730 $\mathrm{cm^{-1}}$ in the μ-$\mathrm{O_2}$ complex[1] and at ~710 $\mathrm{cm^{-1}}$ in the μ-OS complex. No absorption occurs in this region in the μ-$\mathrm{S_2}$ analogue.

(9) T. Sakurai, H. Okabe, and H. Isoyama, *Bull. Jpn. Pet. Inst.,* **13,** 243 (1971); B. Spivak, Z. Dori, and E. I. Stiefel, *Inorg. Nucl. Chem. Lett.*, **11,** 501 (1975).

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(11) If only the oxo group were bridging, then a linear MoOMo system (as in $[\mathrm{MoOL_2}]_2\mathrm{O}$) is most likely, which should absorb at ~510 nm. These compounds are yellow-orange and do not absorb between 450 and 700 nm. Further, their ir Mo═O absorptions are typical of nonlinearly bridged molybdenum(V) dimers,[1,12] e.g., $[\mathrm{MoOL}]_2\mathrm{O_2}$, but are lowered by ~40 $\mathrm{cm^{-1}}$ to ~940 $\mathrm{cm^{-1}}$. The weak ir band at ~750 $\mathrm{cm^{-1}}$ is reminiscent of a single μ-oxo group. These data suggest a bent MoOMo system, probably imposed by other bridging groups. The mercaptides occupy inequivalent positions (two NMR signals are observed at 35 °C in $\mathrm{CDCl_3}$), which also supports a bridging function. The μ^2-OS and μ^2-$\mathrm{SN(CH_3)}$ products exhibit similar ir properties.

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(14) Yields of ~70% are obtained in this reaction for $\mathrm{L} = \mathrm{S_2P}(i\text{-}\mathrm{C_3H_7})_2$.

(15) $\mathrm{MoL}[o\text{-}\mathrm{C_6H_4SN(CH_3)}]_2$ is obtained in 50% yield from the filtrate after removal of precipitated $[\mathrm{MoOL}]_2\mathrm{O}[o\text{-}\mathrm{C_6H_4SN(CH_3)}]$.

(16) I. F. Gainulin, N. S. Garif'yanov, and V. V. Trachevskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2176 (1969).

(17) The complexes $\mathrm{MoL}(o\text{-}\mathrm{C_6H_4XS})_2$ are too insoluble for molecular weight determinations, but their formulation is supported by their EPR spectra.[18] They show no ir absorption assignable to ν(Mo═O) between 900 and 1000 $\mathrm{cm^{-1}}$. With X = NH, ν(NH) is observed at 3290 $\mathrm{cm^{-1}}$, which shifts to 2410 $\mathrm{cm^{-1}}$ on deuteration.

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Monomeric Molybdenum(V) Complexes Showing Hydrogen-1, Hydrogen-2, and Nitrogen-14 Superhyperfine Splitting in Their Electron Paramagnetic Resonance Spectra. Implications for Molybdenum Enzymes

Sir:

An electron paramagnetic resonance (EPR) signal characteristic of molybdenum(V) has been found in all molybdoenzymes which catalyze substrate oxidation.[1,2] Under certain conditions, near isotropic superhyperfine splitting from a single proton is clearly resolved. These results are particularly significant because the hydrogen responsible for this splitting in xanthine oxidase has been shown to originate in the substrate.[3] Evidence indicates that this proton is transferred from substrate to enzyme in conjunction with the flow of two electrons in the same direction.[4,5] Mechanistic schemes based on these results have been suggested for xanthine oxidase[4-6] and other molybdoenzymes.[5-7] Alternate suggestions favor either the location of the exchangeable proton on an N atom ligated to Mo[6,7] or the formation of a molybdenum hydride.[4] Evaluation of the feasibility of these suggestions requires EPR analysis of simple Mo(V) complexes wherein the magnitude of proton and nitrogen superhyperfine couplings can be assessed. Although proton couplings have previously been reported for Mo complexes,[8-10] these have been for species in solution[8,9] or for ill-defined reaction products[10] and no isolated and stoichiometrically distinct compounds which display this property have been studied. This communication describes our results in which both proton and nitrogen superhyperfine splittings have been resolved for isolated Mo(V) compounds. The magnitude of the coupling constants and the observed proton exchangeability are consistent with previous proposals made for Mo enzymes.[5-7] In addition, significant temperature effects on the spectral shape are reported.

The monomeric Mo(V) complexes presented here are prepared by the general procedure of Newton et al.[11] Their EPR spectra (Table I) strongly support the formulas shown. As an example, the spectrum of **1** is discussed. The spectrum, as displayed in Figure 1A, shows hyperfine splitting from the $I = \frac{5}{2}$, ^{95}Mo and ^{97}Mo nuclei (as satellite spectra) although only the central pattern from even Mo isotopes ($I = 0$) is shown. Superhyperfine splitting is clearly resolved for two equivalent N and two equivalent H atoms confirming both the state of ligation of the complex and the state of protonation of the li-

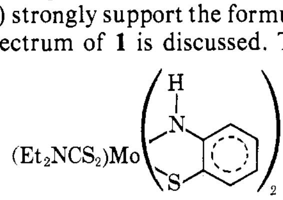

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Table I. EPR Parameters for Some Monomeric Mo(V) Complexes

Complex	Solvent	$\langle g \rangle \pm 0.001$	$\langle A \rangle^{95,97}$Mo, G	$\langle A \rangle_L$, G (L)
$Mo(S_2CNEt_2)(HNSC_6H_4)_2$ (**1**)	$CHCl_3$	1.990	38.0 ± 0.5	2.4 ± 0.1(^{14}N); 7.4 ± 0.1(^{1}H)
$Mo(S_2CNEt_2)(CH_3NSC_6H_4)_2$ (**2**)	$CHCl_3$	1.985	38.0 ± 0.5	2.8 ± 0.1 (^{14}N)
$Mo(S_2CNEt_2)(DNSC_6H_4)_2$ (**3**)	CH_2Cl_2	1.989	38.0 ± 0.5	2.5 ± 0.1 (^{14}N); 2.0 ± 0.1 (^{2}H)
$Mo(S_2CNEt_2)(S_2c_6H_4)_2$	$CHCl_3$	2.000	31.8 ± 0.5	
$MoO[S_2P(i\text{-}Pr)_2](OSC_6H_4)$	CH_2Cl_2	1.971	39.2 ± 1	38 ± 1 (^{31}P)
$MoO[S_2P(i\text{-}Pr)_2](OSC_6H_4)$ + py	CH_2Cl_2	1.976	37.2 ± 1	28.6 ± 1 (^{31}P)
Xanthine oxidase		1.974	*a*	12 (^{1}H)

[a] $\langle A \rangle$ for ^{95}Mo can be estimated as 34 G for the so-called very rapid signal of xanthine oxidase (R. C. Bray and J. C. Swann, *Struct. Bonding* (*Berlin*), **11**, 107 (1972)).

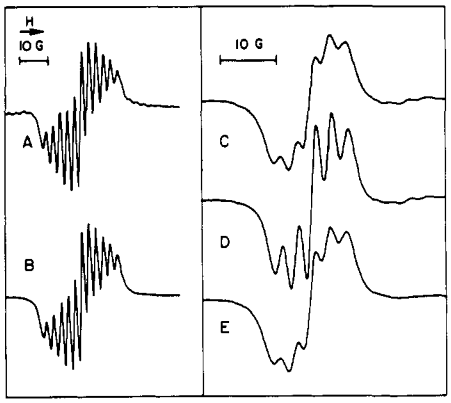

Figure 1. (A) Room temperature EPR spectrum of $Mo(S_2CNEt_2)(HNSC_6H_4)_2$; (B) computer simulation of the above; (C, D, and E) EPR spectra of $Mo(S_2CNEt_2)(CH_3NSC_6H_4)_2$ at room temperature, −40 and −90 °C, respectively.

gand nitrogens. Spectral simulation (Figure 1B) gives a_H = 7.4 and a_N = 2.4 G. These values differ dramatically from those assigned previously[8,9] for similar species prepared only in solution.[12] To confirm these assignments, $Et_2NCS_2Mo[o\text{-}C_6H_4SN(CH_3)]_2$ (**2**) and $Et_2NCS_2Mo[o\text{-}C_6H_4SND]_2$ (**3**) were prepared. The spectrum of the *N*-methyl complex, **2**, shows ^{14}N splitting of 2.8 G in a clear five-line spectrum at −40 °C in CH_2Cl_2 (Figure 1D). The *N*-deuterio complex, **3**, shows a more complex pattern for which simulation reveals a_N = 2.5 ± 0.2 Gauss and a_D = 2.0 ± 0.2 G consistent with the reduced magnetic moment of the deuteron compared to the proton. **3** is prepared from $Mo_2O_4(S_2CNEt_2)_2$ similarly to **1** by using $C_6H_4ND_2SD$ (ν(N-H) 3290 vs. ν(N-D) 2410 cm^{-1}). However, when the *N*-deuterio complex is dissolved in $CHCl_3$ for EPR evaluation, the spectrum of **1** is observed, apparently as a result of H-D exchange with C_2H_5OH present as a preservative in the solvent; a reaction which must occur within the few minutes required to take the spectrum. The N-D complex can be maintained by dissolution in CH_2Cl_2 previously equilibrated with D_2O. These results attest to the exchangeability of the proton in question.

The tabulated *g* and $A(^{95,97}Mo)$ values reveal some interesting trends. All the non-oxo complexes contain at least three coordinated S atoms and display *g* values somewhat higher than those typically found in xanthine oxidase. In general, the larger the number of S ligands, the higher the *g* and lower the $A(^{95,97}Mo)$ values found. The oxo complex $MoO[S_2P(i\text{-}Pr)_2](OSC_6H_4)$, although also possessing three coordinated S atoms, displays a lower *g* value which places both its *g* and *A* value in the range found for the Mo oxidases. The effect of adding pyridine to this nominally pentacoordinate species is to slightly raise *g* and lower *A*. An analogous effect involving substrate binding may produce the similar *g* and *A* shifts observed in xanthine oxidase. Despite these similarities between biological and inorganic systems, we urge strong caution in correlating *g* and *A* values with structure. Both *g* and *A* (but especially *g*) depend not only on the donor atom set but also quite strongly on both coordination number and detailed coordination geometry.[14] For example, the eight coordinate complex $\{Mo[S_2CN(C_2H_5)_2]_4\}^+$ also shows *g* = 1.979 and *A* = 37 G[13] but is clearly very different from the complexes discussed here and from the Mo site in enzymes.

All signals reported herein show temperature dependence with a minimum line width occurring somewhere above the freezing point of the solvent. For the *N*-methyl complex, **2**, the broad room temperature spectrum (Figure 1C) is replaced by a sharper spectrum (Figure 1D) at −40 °C. Further cooling (still above the freezing point) rebroadens the spectrum and, in the frozen glass, the lines are broad (at least down to 100 K) and the hyperfine splittings characteristic of the solution are not resolved.[15] Thus, to attain highest resolution and hence maximum information from solution spectra, variable temperature studies are imperative. It seems highly probable that, as many EPR studies are reported at room temperature and/or liquid N_2 temperature where the solutions are frozen, much inherent information is lost. We strongly recommend that (for Mo(V) and other doublet states) variable temperature studies be routinely performed when increased resolution of hyperfine or superhyperfine structure is desired.[16]

The implications of this work for Mo enzymes are clear. While these compounds in no way represent models for the active site of enzymes, they do illustrate that Mo(V) complexes with coordinated N-H groups display H superhyperfine coupling of the same order of magnitude as that found in the Mo oxidases. Furthermore, N superhyperfine coupling is of sufficiently small magnitude to preclude its resolution in enzymes should Mo-N indeed be present.[18] Our current results thus establish the feasibility (if not the veracity) of recent proposals concerning the mechanism of action of Mo enzymes.

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(12) The spectra obtained by Gainulin et al.[9] for species in solution are very similar to those reported in the present study but the assigned coupling constants differ vastly. For compound **1**, the assignment of Gainulin et al. is $a_N = 5.0 \pm 0.2$ and $a_H = 2.5 \pm 0.2$. Placing these values in our simulation program leads to a spectral pattern similar to that found experimentally. Mathematically either assignment fits the observed spectrum. Upon *N*-methyl substitution, Gainulin et al. note that a_N decreases to 2.8 G. We confirm this experimental result with isolated complexes but, in view of our assignment of a_N, we note that N-CH_3 substitution increases a_N by a small amount. This is certainly a more reasonable result than nearly doubling the constant when H is substituted by CH_3. Proof for our assignment comes from studies on the N-D system discussed in the text.

(13) A. Nieuwpoort, ref 7.

(14) See, for example, W. L. Kwik and E. I. Stiefel, *Inorg. Chem.*, **12**, 2337 (1973).

(15) Frozen glass spectra reveal the complexes to have rhombic or axial *g* tensors with overall *g* spread of less than 0.03. Unfortunately, neither ^1H nor ^{14}N superhyperfine splittings have been clearly resolved in the frozen glass spectra, the analysis of which will be reported in detail in the full paper.

(16) Russian workers[8,9,17] seem to be acutely aware of these temperature effects and often report highly resolved EPR spectra at odd and seemingly arbitrary temperatures. It was from scrutiny of their experimental results that it first occurred to us to vary the temperature of samples.

(17) I. N. Marov, V. K. Belyaeva, A. N. Ermakov, and Y. N. Dubrov, *Russ. J. Inorg. Chem.*, **14**, 1391 (1969).

(18) In support of this argument, we note that ^2H splitting is not resolved in Mo enzymes when ^2H is substituted for ^1H. The estimated ^2H splitting is of the same magnitude as ^{14}N splittings found in Mo(V) complexes[2] and therefore the lack of resolution of ^{14}N splitting in Mo enzymes is not at all unexpected.

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Metal Atom Synthesis of η^6-Toluenebis(*F*-phenyl)cobalt(II) [η^6-$C_6H_5CH_3(C_6F_5)_2Co$], a New Type of π-Arene Complex. X-Ray Structure Determination

Sir:

Simple RMX and R_2M compounds of transition metals such as Fe, Co, Ni, Pd, or Pt have been of interest to quite a number of workers.[1] We have found that the "metal atom technique"[2] (metal vapors condensed with organic compounds) has been quite useful for preparation of some of the simple nonligand stabilized RMX compounds in the absence of complicating donor solvents.[3] Due to the extraordinary robustness of the R_f–M bond,[4] the CF_3I and C_6F_5Br reactants have been quite useful to us in terms of production of stable, characterizable RMX compounds.

Table I. Atomic Coordinates[a]

Atom	Coordinates $10^4 x$	 $10^4 y$	 $10^4 z$
Co	1949 (1)	2500	−74 (1)
C_1	969 (4)	1660 (3)	778 (5)
C_2	1183 (5)	1340 (3)	2090 (6)
C_3	493 (6)	745 (4)	2732 (6)
C_4	−475 (6)	460 (4)	2051 (7)
C_5	−729 (5)	750 (4)	729 (7)
C_6	−5 (4)	1343 (3)	138 (6)
F_2	2133 (3)	1598 (2)	2824 (3)
F_3	752 (4)	450 (3)	4022 (4)
F_4	−1174 (4)	−106 (2)	2668 (5)
F_5	−1663 (3)	462 (2)	39 (5)
F_6	−2829 (3)	1601 (2)	−1181 (4)
C_7	2498 (7)	2500	−2271 (8)
C_8	2821 (5)	1760 (4)	−1605 (7)
C_9	3472 (5)	1764 (5)	−354 (7)
C_{10}	3815 (7)	2500	260 (11)
C_{11}	1784 (10)	2500	−3611 (9)
H_8	2584 (63)	1323 (40)	−1919 (74)
H_9	3641 (59)	1208 (38)	99 (66)
H_{10}	4149 (86)	2500	1093 (100)

[a] Estimated standard deviations are given in parentheses for least significant digit.

$$\text{M atom} + R_fX \rightarrow R_fMX$$

We report here the production of a stable R_2Co compound utilizing the metal atom technique. This compound is formed in the reaction of *F*-bromobenzene with cobalt atoms, and is the first example of an R_2M compound produced by the method.

$$C_6F_5Br + Co \rightarrow \underset{\mathbf{1}}{(C_6F_5)_2Co} + CoBr_2$$

Bis(*F*-phenyl)cobalt(II) (**1**), previously reported by Smith and

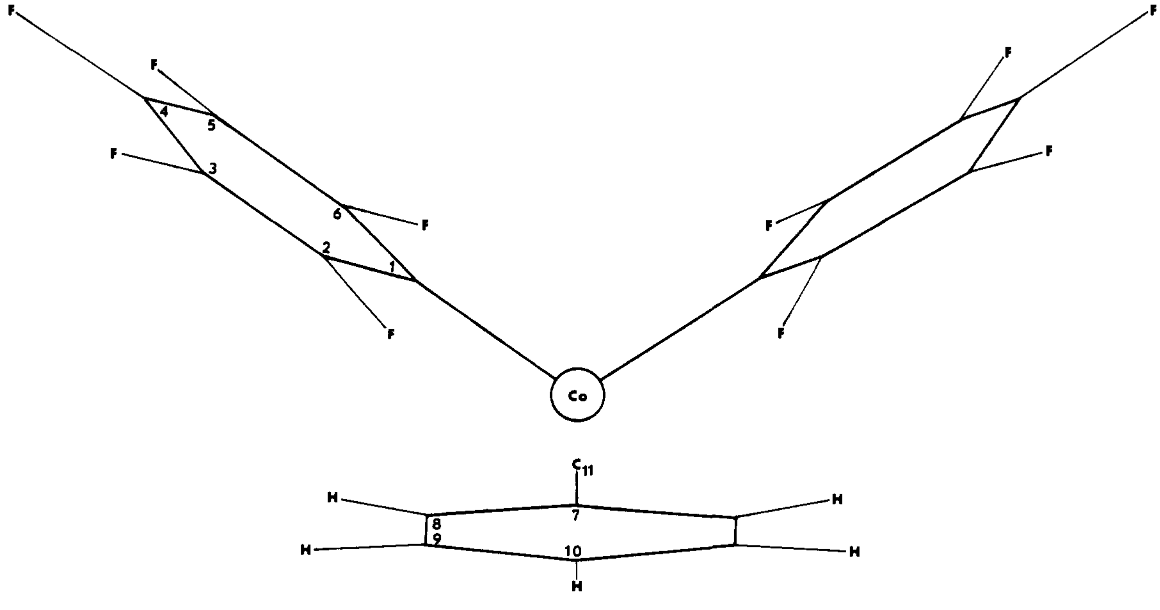

Figure 1. The structure of [η^6-$C_6H_5CH_3(C_6F_5)_2Co$]. The crystallographic mirror plane contains Co, C_7, C_{10}, C_{11}, and H_{10}.