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^{95}Mo NMR Studies of *cis*-Dinitrosylmolybdenum Complexes Containing the $[Mo(NO)_2]^{2+}$ Unit[1]

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Received June 14, 1983

The ^{95}Mo NMR spectra of a wide variety of six-coordinate complexes containing the *cis*-$[Mo(NO)_2]^{2+}$ unit have been studied at 16.3 MHz. The chemical shifts range from +200 to −1000 ppm and do not correlate with the NO stretching frequency or the energy of the first electronic transition (12 500–16 260 cm^{-1}). The chemical shifts generally decrease with the increasing ability of the ancillary ligands to delocalize electrons from the metal atom. The line widths range from 20 to 440 Hz and depend on the viscosity of the solvent. The pattern of chemical shifts for $[Mo(NO)_2]^{2+}$ complexes is different from that observed for $[MoO_2]^{2+}$ complexes for the same ligands. The electronic spectra for the $[Mo(NO)_2]^{2+}$ complexes are consistent with an $\{Mo(NO)_2\}^6$ electron configuration that is only slightly perturbed by the other ligands coordinated to the metal. The two major absorptions in the visible spectrum (12 500–16 260 cm^{-1} and 20 800–28 250 cm^{-1}) are assigned to transitions within the $\{Mo(NO)_2\}^6$ group.

Introduction

The availability of sensitive multinuclear NMR spectrometers and the growing interest in molybdenum chemistry have resulted in several reports on the application of ^{95}Mo NMR to a wide variety of chemical systems in the past few years.[2] This study of *cis*-$[Mo(NO)_2]^{2+}$ complexes is part of our investigation of the ^{95}Mo NMR spectra of six-coordinate low-symmetry molybdenum complexes containing a *cis*-$[Mo(X)_2]^{2+}$ unit where X = O, CO, or NO. We and others have previously reported[2g,t,w,aa] that six-coordinate complexes containing the *cis*-$[MoO_2]^{2+}$ core show a chemical shift range of about 800 ppm. The chemical shifts are sensitive to the donor atoms in the coordination sphere of the molybdenum, and the chemical shifts are large relative to the line widths. Although a wide variety of six-coordinate $[Mo(NO)_2]^{2+}$ complexes are accessible,[3] this is the first study of such systems by ^{95}Mo NMR. The ^{95}Mo NMR spectra of these complexes are also of bioinorganic interest because the NO$^+$ ligand is formally

Table I. ^{95}Mo NMR Data

compd	solvent	chem shift,[a] ppm	line width, Hz
$Mo(NO)_2(\eta^5\text{-}C_5H_5)I$	CH_2Cl_2	−985	70
$Mo(NO)_2(\eta^5\text{-}C_5H_5)Br$	CH_2Cl_2	−883	70
$Mo(NO)_2(\eta^5\text{-}C_5H_5)Cl$	CH_2Cl_2	−852	70
$Mo(NO)_2(\eta^5\text{-}Me_5C_5)Cl$	CH_3CN	−800	70
$Mo(NO)_2Cl_2(P(C_6H_5)_3)_2$	DMF	−500	430
$Mo(NO)_2(Me_2dtc)_2$	DMF	−438	90
	CH_3CN	−437	70
	acetone	−438	60
	Me_2SO	−435	150
$Mo(NO)_2(Et_2dtc)_2$	DMF	−430	120
	CH_3CN	−430	80
	acetone	−431	80
	Me_2SO	−425	170
$Mo(NO)_2(HB(3,5\text{-}Me_2Pz)_3)Cl$	CH_2Cl_2	−384	180
$Mo(NO)_2(acac)_2$	DMF	−298	190
	CH_3CN	−298	90
	acetone	−296	90
	Me_2SO	−282	315
	methanol	−286	105
	CH_2Cl_2	−283	110
	CH_2ClCH_2Cl	−285	190
	benzene	−281	135
	toluene	−281	125
	isopentyl alcohol	−271	435
$Mo(NO)_2Cl_2$(*o*-phen)	DMF	−265	160
	CH_3CN	−265	170
	acetone	−265, −280	90
$Mo(NO)_2Cl_2(bpy)$	DMF	−263	170
	CH_3CN	−255	120
	acetone	−264, −280	100
$[Et_4N]_2[Mo(NO)_2(CN)_4]$	DMF	−104	20
	CH_3CN	−98	20
	H_2O	−105	20
$Cs_2[Mo(NO)_2Cl_4]$	HCl	+152	170
$[Et_4N]_2[Mo(NO)_2(ox)_2]$	DMF	+201	110

[a] Relative to external 2 M Na_2MoO_4 in H_2O at pH 11 and room temperature.

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(1) Presented in part at the 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 28–April 3, 1982; see Abstracts, No. INOR 90.

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Table II. IR and UV-Vis Data for $[Mo(NO)_2]^{2+}$ Complexes

		UV-Vis^b	
compd	IR^a ν_{NO}, cm^{-1}	λ_{max}, cm^{-1}	ϵ, M^{-1} cm^{-1}
$Mo(NO)_2(\eta^5\text{-}C_5H_5)I$	1760	12 500	60
	1655	22 570	810
$Mo(NO)_2(\eta^5\text{-}C_5H_5)Br$	1755	12 740	80
	1650	22 270	1220
$Mo(NO)_2(\eta^5\text{-}C_5H_5)Cl$	1755	12 890	60
	1655	22 680	1030
$Mo(NO)_2(\eta^5\text{-}Me_5C_5)Cl$	1725	*f*	
	1640		
$Mo(NO)_2Cl_2(P(C_6H_5)_3)_2$	1790	16 260	50
	1670	22 320	840
		28 250	1800
$Mo(NO)_2(Me_2dtc)_2$	1760	14 310	110^c
	1655	20 830	2240
$Mo(NO)_2(Et_2dtc)_2$	1755	14 030	130^c
	1645	20 830	2260
$Mo(NO)_2(HB(3,5\text{-}Me_2Pz)_3)Cl$	1790	*f*	
	1680		
$Mo(NO)_2(acac)_2$	1765	13 610	70
	1650	22 470	2100
$Mo(NO)_2Cl_2$(*o*-phen)	1780	14 090	40
	1670	22 730	1800
$Mo(NO)_2Cl_2$(bpy)	1785	13 250	40
	1675	22 730	1100
$[Et_4N]_2[Mo(NO)_2(CN)]_4$	1785	14 540	40
	1675	22 470	2110
$Cs_2[Mo(NO)_2Cl_4]$	1765	14 290	50^e
	1620	23 810	1430
$[Et_4N]_2[Mo(NO)_2(ox)_2]$	1785	12 990	50
	1630	23 260	1100

^{a} KBr pellet. ^{b} In DMF. ^{c} In $CHCl_3$; ref 15. ^{d} In DMSO; ref 17. ^{e} In aqueous 1 M HCl; ref 17. ^{f} Data not available.

isoelectronic with N_2, the substrate of nitrogenase.

Experimental Section

Materials. (a) Ligands. 2,2′-Bipyridyl (bpy) (Aldrich), 1,10-phenanthroline hydrate (*o*-phen) (Aldrich), 2,4-pentanedione (acac) (Eastman), sodium dimethyldithiocarbamate hydrate (Me_2dtc) (Aldrich), sodium diethyldithiocarbamate trihydrate (Et_2dtc) (Baker), sodium cyanide (Fisher), oxalic acid dihydrate (ox) (Matheson Coleman and Bell), and triphenylphosphine ($P(C_6H_5)_3$) (Strem) were used as received. Hydrotris(3,5-dimethylpyrazolyl)borate, potassium salt ($HB(3,5\text{-}Me_2Pz)_3$), was synthesized according to Trofimenko.[4]

(b) Solvents were generally AR grade. Dimethylformamide (DMF) (Fisher) was distilled twice under vacuum over P_2O_5 and then stored over molecular sieves. Acetone (Matheson Coleman and Bell), acetonitrile (Fisher), and dichloromethane (Matheson Coleman and Bell) were dried over P_2O_5 and distilled under nitrogen immediately before use. Methanol and ethanol were dried with magnesium turnings and iodine and then distilled. Benzene, toluene, dichloroethane, and isopentyl alcohol were from Matheson Coleman and Bell and used without further purification.

(c) Other Reagents. Ammonium molybdate tetrahydrate (Baker), tetraethylammonium chloride tetrahydrate (Baker), and hydroxylamine hydrochloride (ACS grade, Allied) were used as received.

Syntheses. The $[Mo(NO)_2]^{2+}$ complexes were synthesized according to the methods of Johnson et al.,[3a] Feltham et al.,[3b] Subramanian,[3c] Hoyano et al.,[3d] Kolthammer et al.,[3e] and Trofimenko.[3f]

Physical Measurements. The infrared spectra were recorded on a Perkin-Elmer 398 spectrometer and on a Perkin-Elmer 983 spectrometer as KBr pellets. The UV-vis spectra were recorded on Perkin-Elmer 552, Cary 14, and Cary 19 spectrophotometers at room temperature.

The ^{95}Mo NMR spectra were obtained on a Bruker WM250 spectrometer. A broad-band probe (10–35 MHz) and a molybdenum probe (16.3 MHz) were used for the measurements. The 90° pulse was found to be 83 μs for the broad-band probe and 35 μs for the molybdenum probe. An acquisition delay of 200 μs was applied to reduce the effects of probe ringing. All spectra were recorded without field-frequency lock. The external standard was 2 M Na_2MoO_4 at pH 11. No appreciable drift of the field was observed. Solution concentrations were usually 0.1 M; less soluble complexes were measured as saturated solutions. All measurements were conducted at room temperature.

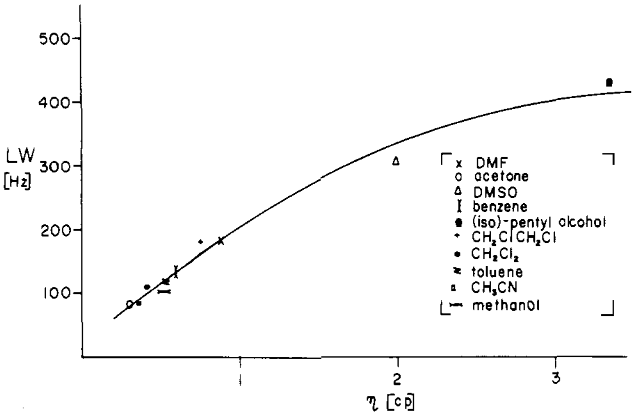

Figure 1. Dependence of the line width (LW) on the viscosity of the solvent (η) for $Mo(NO)_2(acac)_2$.

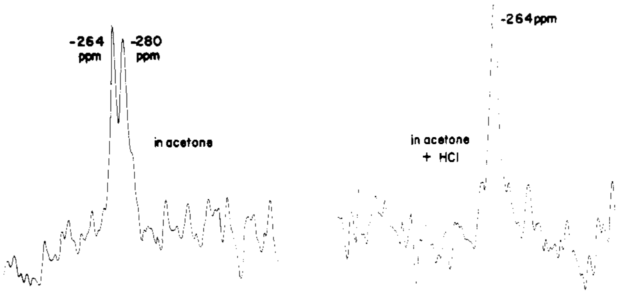

Figure 2. Chloride dissociation of the $Mo(NO)_2Cl_2(bpy)$ complex in acetone at room temperature.

Results and Discussion

^{95}Mo NMR Spectra. Table I lists the ^{95}Mo NMR chemical shifts for 14 *cis*-dinitrosyl complexes of molybdenum. Table II gives the two NO stretching frequencies observed for each complex and the absorption maxima in the electronic spectra.

The ^{95}Mo NMR chemical shifts range from −985 ppm for $Mo(NO)_2(\eta^5\text{-}C_5H_5)I$ to +201 ppm for $[Et_4N]_2[Mo(NO)_2(ox)_2]$. Minor solvent dependence of the chemical shift was observed for most complexes. For example, the variation of the chemical shifts of $Mo(NO)_2(acac)_2$ for ten different solvents is 25 ppm. This solvent dependence of the chemical shift is less than the 100 ppm variation that has been found[2f] for MoS_4^{2-}.

The line widths for the complexes were solvent dependent and varied from 20 to 435 Hz. For $Mo(NO)_2(acac)_2$ the line widths increased smoothly with increasing viscosity of the solvent (Figure 1).

The ^{95}Mo NMR spectrum of $Mo(NO)_2Cl_2$(*o*-phen) appeared as a single peak at −265 ppm in DMF and acetonitrile, whereas in acetone two peaks were observed (Table I). Addition of HCl to an acetone solution produced a single peak with the same chemical shift as found in DMF and acetonitrile. Similar behavior was found for $Mo(NO)_2Cl_2(bpy)$ in these solvents (Figure 2). These results suggest that both of these complexes undergo partial dissociation in acetone (reaction 1) and that the addition of excess chloride shifts the equilibrium to the left.

$$Mo(NO)_2Cl_2(bpy) \rightleftharpoons Mo(NO)_2Cl(bpy)^+ + Cl^- \quad (1)$$

Several reports of ^{95}Mo NMR spectra have appeared recently.[2] The chemical shift range for the $[Mo(NO)_2]^{2+}$ complexes in Table I (1200 ppm) is to be compared to the presently

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[4] Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288.

known chemical shift range of 7000 ppm for ^{95}Mo NMR.[2p,x] The chemical shift range of the $[Mo(NO)_2]^{2+}$ complexes is somewhat larger than the 800 ppm chemical shift range of the six-coordinate $[MoO_2]^{2+}$ complexes.[2g,t,w,aa] The observed chemical shifts for $[Mo(NO)_2]^{2+}$ complexes (−985 to +201 ppm) overlap the range for $[MoO_2]^{2+}$ complexes (−220 to +650 ppm),[2g,t,w,aa] which formally contain Mo(VI), and the range for Mo(0) complexes (−445 to −2200 ppm).[2v,y]

In general, the chemical shifts for heavy nuclei have been explained by the Ramsey formulation[5,6] of diamagnetic and paramagnetic contributions to the nuclear shielding. These two terms are usually of opposite sign. For transition-metal ions the variation in the paramagnetic term is the major contributor to the changes in chemical shifts.[6] Low-lying excited states with substantial d-orbital character lead to deshielding of the nucleus and hence to increases in the observed chemical shift.[6,7]

The substantial increases in chemical shift (decreased shielding) for the series MoO_4^{2-} (0 ppm) < MoS_4^{2-} (~2250 ppm) < $MoSe_4^{2-}$ (~3500 ppm) demonstrate the increase of $\delta(^{95}Mo)$ with a decrease of the lowest energy electronic transition (ΔE) for these molybdenum complexes.[2c,f] A similar correlation of $\delta(^{95}Mo)$ with ΔE is found for $MoXY(ONR_2)_2$ compounds (X = O, S, Se).[2w,aa] For the $[Mo(NO)_2]^{2+}$ complexes of the present study, however, relatively small changes are observed in ΔE of the first electronic transition for a wide variety of ligands (Table II). The first absorption band occurs between 12 500 and 16 260 cm^{-1}, but there is no correlation between ΔE and $\delta(^{95}Mo)$. The second absorption band (20 800–28 250 cm^{-1}) also shows little dependence on the ancillary ligands and shows no correlation with $\delta(^{95}Mo)$. Additional discussion of these electronic spectra appears in a succeeding section.

The paramagnetic contribution to the nuclear shielding also depends upon the delocalization of electrons from the metal atom.[5,6] Delocalization of electrons over the ligands will decrease the paramagnetic contribution to the shielding of the central metal atom and lead to decreased chemical shifts. For six-coordinate cobalt(III) complexes it has long been known that ligands with small nephelauxetic ratios (soft ligands) give smaller chemical shifts (more shielding).[6,7]

The nephelauxetic ratios for many ligands have been investigated by optical spectroscopy.[8] The observed ordering ox > Cl > CN > dtc parallels the decrease in chemical shift for those $Mo(NO)_2L_4$ complexes in which all four L are identical (Table I). Likewise, substitution of oxalate by the delocalizing ligand acac results in a decrease of the chemical shift from +201 to −298 ppm. Increased electron delocalization in phen and bpy compared to that in Cl is consistent with the smaller chemical shifts in $Mo(NO)_2Cl_2$(bpy) and $Mo(NO)_2Cl_2$(*o*-phen) compared to those in $[Mo(NO)_2Cl_4]^{2-}$. Another example for this behavior is the order of the chemical shift in the $Mo(NO)(\eta^5\text{-}C_5H_5)X$ complexes, X = Cl > Br > I. For this type of complex it is also interesting to note, however, that the molybdenum chemical shift increases for $Mo(NO)_2LCl$ complexes in the order L = $\eta^5\text{-}C_5H_5$ < $\eta^5\text{-}Me_5C_5$ < $HB(3,5\text{-}Me_2Pz)_3$. The same pattern of deshielding of the molybdenum atom has been found for the $MoL(CO)_2(NO)$ complexes[2z] of these three polydentate ligands.

Electronic Structure. The bonding in complexes of the $[Mo(NO)_2]^{2+}$ unit has been qualitatively discussed elsewhere[9] as dominated by the $\{Mo(NO)_2\}^6$ group, in which six electrons are associated with the molybdenum 4d and π^*(NO) orbitals. Recent photoelectron spectra[10,11] of $M(NO)_2(\eta^5\text{-}C_5H_5)X$ complexes (M = Cr, W; X = Cl, Br, I) clearly demonstrate that the bonding is dominated by the $[Mo(NO)_2]^{2+}$ unit and that there is a large splitting of the filled pseudo-t_{2g} set of oribitals of the $\{Mo(NO)_2\}^6$ group due to the strong π-acceptor ability of the NO group. The principal interactions between the metal d and π^*(NO) orbitals are sketched in Figure 3. In C_{2v} symmetry the highest occupied molecular orbitals (HOMO) are $a_2(d_{xy}, \pi^*(NO))$ and $b_2(d_{yz}, \pi^*(NO))$, which are nearly degenerate for $M(NO)_2(\eta^5\text{-}C_5H_5)X$ complexes.[10,11] These orbitals are also π-antibonding with respect to the other ligands coordinated to the metal so that the composition of the HOMO is strongly dependent on the nature of the other ligands. For $M(NO)_2(\eta^5\text{-}C_5H_5)X$ complexes the percentage of X character in the HOMO increases as X becomes more polarizable (Cl < Br < I).[10]

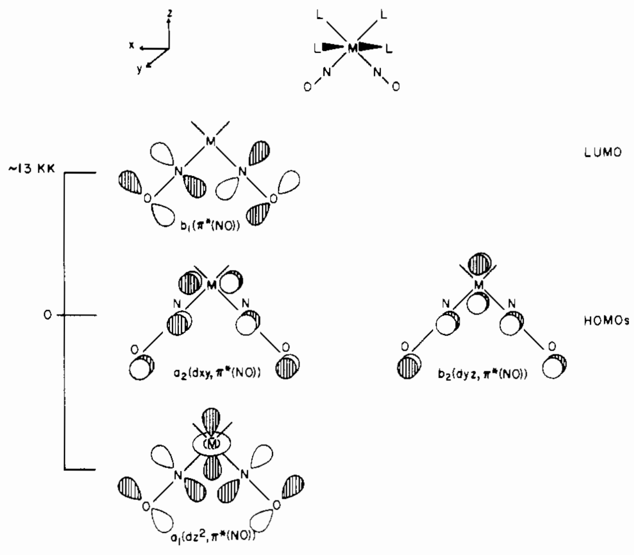

Figure 3. Qualitative sketch of the molecular orbitals used to explain the electronic spectra of $[Mo(NO)_2]^{2+}$ complexes. The $b_1(\pi^*(NO))$ orbital is proposed to be the LUMO. The first low-intensity band in the visible spectrum is assigned to transitions from $a_2(d_{xy}, \pi^*(NO))$ or $b_2(d_{yz}, \pi^*(NO))$ to $b_1(\pi^*(NO))$. The second more intense band is from $a_1(d_{z^2}, \pi^*(NO))$ to $b_1(\pi^*(NO))$.

A unique feature of the electronic structure of *cis*-dinitrosyl complexes is the importance of the low-lying $b_1(\pi^*(NO))$ orbital (Figure 3). As has been emphasized previously,[9,10] this orbital will have no bonding interaction with the d_{xz} orbital (which also has b_1 symmetry) if the ON–Mo–NO angle is ~90°. Few X-ray structures are available for $\{Mo(NO)_2\}^6$ complexes,[12] but for $Mo(NO)_2(Et_2dtc)_2$ the ON–Mo–NO angle is 88.0 (4)°.[13] The $b_1(\pi^*(NO))$ orbital is predicted to be the lowest unoccupied molecular orbital (LUMO) in the $[Mo(NO)_2]^{2+}$ complexes studied here.[9] We assign the electronic absorption at 12 000–16 260 cm^{-1} to a transition within the $\{Mo(NO)_2\}^6$ group from $a_2(d_{xy}, \pi^*(NO))$ or $b_2(d_{yz}, \pi^*(NO))$ to the $b_1(\pi^*(NO))$ orbital. The transition from the b_2 orbital is electric dipole forbidden in rigorous C_{2v} symmetry, consistent with the relatively weak intensity for the band (Table II) even though it would have much d → π^*(NO) character. Finally, we point out that $a_2 \rightarrow b_1$ and $b_2 \rightarrow b_1$ both involve transitions between orthogonal π^*(NO) orbitals. Such

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[13] Broomhead, J. A., private communication.

Table III. Comparison of the Chemical Shifts of $[MoO_2]^{2+}$ and $[Mo(NO)_2]^{2+}$ Complexes

	X = O		X = NO[a]	
complex	chem shift, ppm	line width, Hz	chem shift, ppm	line width, Hz
$Mo(X)_2(Et_2dtc)_2$	176[b]	275 (CH_2Cl_2)	−430	120 (DMF)
$Mo(X)_2(HB(3,5\text{-}Me_2Pz)_3)Cl$	84[c]	420 (DMF)	−384	180 (CH_2Cl_2)
$Mo(X)_2(acac)_2$	41[d]	115 (DMF)	−298	190 (DMF)

[a] This work. [b] Reference 2g. [c] Prepared by K. Yamanouchi, unpublished results. [d] The chemical shift for $MoO_2(acac)_2$ was erroneously reported as −45 ppm in ref 2g.

$\pi^*_x(NO) \rightarrow \pi^*_y(NO)$ character for these transitions of the $\{Mo(NO)_2\}^6$ group is also consistent with the small extinction coefficient for the first absorption band in these complexes. The absorption seems too low in energy for a ligand field absorption in a 4d transition metal.[9,14]

Broomhead and co-workers[15] assigned the band at about 14000 cm^{-1} in $Mo(NO)_2(dtc)_2$ complexes to a dithiocarbamate transition. However, the occurrence of a band of similar intensity and energy in the wide variety of $[Mo(NO)_2]^{2+}$ complexes of Table II seems more consistent with the assignment proposed here. Our assignment also agrees with the elegant EPR results of Broomhead and co-workers[15] for the $[Mo(NO)_2(R_2dtc)_2]^-$ anion, which they generated electrochemically. They found that the unpaired electron resided in an orbital that showed hyperfine splitting from two equivalent nitrogen atoms and no hyperfine interaction with the molybdenum, consistent with b_1 being the LUMO of the $[Mo(NO)_2]^{2+}$ complexes. The assignment of b_1 as the LUMO is also consistent with the synthesis and properties of the 19-electron $W(NO)_2(\eta^5\text{-}C_5H_5)(PR_3)$ complexes reported by Angelici and co-workers.[16]

We assign the more intense absorption band at ca. 22000 cm^{-1} to a transition from $a_1(d_{z^2}, \pi^*(NO))$ to $b_1(\pi^*(NO))$ of the $\{Mo(NO)_2\}^6$ group. The $\pi^*(NO)$ components of both a_1 and b_1 are in the same plane, consistent with the larger extinction coefficients.

The designation of $b_1(\pi^*(NO))$ as the LUMO in these complexes also explains the absence of any correlation between the ^{95}Mo chemical shifts and the electronic absorptions. To a first approximation the LUMO has no contribution from orbitals on the molybdenum atom and therefore will not contribute significantly to the paramagnetic term of the nuclear shielding.

Conclusions

For $[Mo(NO)_2]^{2+}$ complexes the ^{95}Mo chemical shifts correlate qualitatively with the electron-delocalizing ability of the coordinating ligands. Soft, polarizable ligands and ligands with delocalized electronic structures produce more negative chemical shifts (increased shielding) compared to those of hard, anionic ligands. These trends for ^{95}Mo chemical shifts of complexes of the $\{Mo(NO)_2\}^6$ group are qualitatively similar to the trends found previously for a series of Mo(0) complexes, which formally have a 4d^6 electron configuration.[2y]

The ^{95}Mo NMR results obtained for six-coordinate $[Mo(NO)_2]^{2+}$ complexes contrast strikingly with the chemical shifts observed previously[2g,t] for six-coordinate $[MoO_2]^{2+}$ complexes. For the $[MoO_2]^{2+}$ complexes, soft polarizable ligands (sulfur donor atoms) produce more positive chemical shifts (decreased shielding) whereas oxygen and nitrogen donors result in more negative chemical shifts.[2g,t,w,aa] Table III illustrates this differing response of the $[MoO_2]^{2+}$ and $[Mo(NO)_2]^{2+}$ groups to the same ligands. Clearly, additional work is needed before ^{95}Mo NMR can be confidently applied to chemical and biochemical systems of unknown composition.

Finally, we emphasize that the six-coordinate $[Mo(NO)_2]^{2+}$ complexes are *not* isoelectronic with the $[MoO_2]^{2+}$ complexes. The $[Mo(NO)_2]^{2+}$ complexes contain the $\{Mo(NO)_2\}^6$ group whereas the $[MoO_2]^{2+}$ complexes contain the $\{MoO_2\}^8$ group.[9] We suggest that there are inherent differences in the responses of these two groups to ligand substitution. Additional NMR studies are in progress to assess the role of coordination geometry, coordination number, electronic structure, and other factors in determining the chemical shifts of ^{95}Mo and other heavy nuclei.

Acknowledgment. We thank the U.S. Department of Agriculture for supporting this work under Grant No. 81-CRCR-1-0626. We also thank Dr. Subramanian for providing a copy of his dissertation, Dr. J. A. Broomhead for unpublished results, Dr. K. A. Christensen for his assistance with the NMR spectrometer, Dr. K. Yamanouchi for synthesis of one of the complexes, and Prof. R. D. Feltham and Dr. J. Mason for helpful discussions. We gratefully acknowledge a grant from the National Science Foundation for purchase of the NMR spectrometer.

Registry No. $Mo(NO)_2(\eta^5\text{-}C_5H_5)I$, 56403-79-3; $Mo(NO)_2(\eta^5\text{-}C_5H_5)Br$, 56403-78-2; $Mo(NO)_2(\eta^5\text{-}C_5H_5)Cl$, 12305-00-9; $Mo(NO)_2(\eta^5\text{-}Me_5C_5)Cl$, 88563-26-2; $Mo(NO)_2Cl_2(P(C_6H_6)_3)_2$, 14730-11-1; $Mo(NO)_2(Me_2dtc)_2$, 26087-84-3; $Mo(NO)_2(Et_2dtc)_2$, 39797-80-3; $Mo(NO)_2(HB(3,5\text{-}Me_2Pz)_3)Cl$, 24899-10-3; $Mo(NO)_2(acac)_2$, 39797-78-9; $Mo(NO)_2Cl_2$(*o*-phen), 14049-93-5; $Mo(NO)_2Cl_2(bpy)$, 14324-79-9; $[Et_4N]_2[Mo(NO)_2(CN)_4]$, 88563-27-3; $Cs_2[Mo(NO)_2Cl_4]$, 69878-80-4; $[Et_4N]_2[Mo(NO)_2(ox)_2]$, 88563-29-5; ^{95}Mo, 14392-17-7.

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