a matrix,[25] and since they absorb at about 800 nm,[25,33] photodecomposition of the Mn(CO)$_5$ radicals by the laser can be excluded. Futhermore, recent studies have shown that CO substitution of the Mn(CO)$_5$ radical may proceed via an associative mechanism.[34,35] Therefore, we propose an associative mechanism for the formation of (CO)$_3$Mn(R-DAB)M'(CO)$_3$ and (THF)(CO$_4$)MnM'(CO)$_3$(R-DAB) (M' = Mn, Re), the nucleophile being the C═N group of the R-DAB ligand (both in the matrix and in PVC) or THF (in PVC).

The complex (CO)$_5$ReRe(CO)$_3$(*i*-Pr-DAB) does not photolyze in the matrix upon irradiation with visible light. It is not yet clear whether this photostability against visible light is due to a stronger metal–metal bond or to a greater stability of the radicals formed.

In PVC several reactions are different because of the higher flexibility of this medium especially at higher temperatures and because of the presence of THF in the film. The higher thermal energy is probably responsible for the formation of (CO)$_5$Mn(R-DAB)Mn(CO)$_3$, which is not formed in the matrix. In the PVC film the Mn(CO)$_3$(R-DAB) radicals have apparently enough activation energy for the changeover from σ,σ- to $\sigma,\sigma,\eta'^2,\eta'^2$-coordination of the R-DAB ligand within their lifetimes. Furthermore, because of the presence of THF in the film, the Mn(CO)$_5$ radicals formed will not only react with the M'(CO)$_3$(R-DAB) radicals but also with THF under formation of (THF)(CO)$_4$MnM'(CO)$_3$(R-DAB). A further difference is that a reaction in PVC can take place from the $^3d_\pi\pi^*$ state, which is prevented in the matrix. Just as for the d^8-M'(CO)$_3$(R-DAB) (M' = Fe, Ru) complexes in solution,[6a] a reaction from this $^3d_\pi\pi^*$ state leads to breaking of a metal–nitrogen bond of (CO)$_5$MnRe(CO)$_3$(R-DAB) dissolved in PVC. Contrary to the situation in the matrix, the R-DAB ligand can now rotate more freely and the open site at Re will be occupied by THF, thus preventing the back-reaction to the parent compound. This reaction appears to be the only reaction for (CO)$_5$MnRe(CO)$_3$(R-DAB) in PVC upon irradiation into the low-energy charge-transfer band. This means that in PVC only the reaction from the $^3d_\pi\pi^*$ state is observed and in the matrix only the reaction from the $^3\sigma_b\pi^*$ tate. Upon photolysis with UV light, reactions may occur from higher excited states belonging to $\sigma_b \rightarrow \sigma^*$ and d_π(M,M') $\rightarrow$ π^*(CO) transitions. This may account for the formation of (CO)$_3$Mn(R-DAB)Re(CO)$_3$ and (CO)$_3$Re(R-DAB)Mn(CO)$_3$ in PVC films, which are not formed in this medium upon photolysis with visible light.

Conclusion

The results reported here clearly show that intramolecular photochemical reactions of metal–metal-bonded carbonyls can be favored by photolysis in inert-gas matrices and PVC films. The PVC film is less rigid than the matrix, and photolysis can take place in this medium at higher temperatures, thus providing the necessary activation energy for secondary thermal reactions of the primary photoproducts.

Acknowledgment. We thank Anja M. F. Brouwers for performing the first experiments leading to this study, Wim de Lange and Henk Gijben for preparing the complexes, and Gerard Schoemaker for assistance during the IR experiments.

Registry No. Corvic D60/11, 9002-86-2; THF, 109-99-9; (CO)$_5$MnMn(CO)$_3$(*i*-Pr-DAB), 71603-98-0; (CO)$_5$MnRe(CO)$_3$(*i*-Pr-DAB), 71604-02-9; (CO)$_5$ReMn(CO)$_3$(*i*-Pr-DAB), 97747-73-4; (CO)$_5$ReRe(CO)$_3$(*i*-Pr-DAB), 97698-45-8; (THF)(CO)$_4$MnMn(CO)$_3$(*i*-Pr-DAB), 98874-72-7; (THF)(CO)$_4$MnRe(CO)$_3$(*i*-Pr-DAB), 98858-64-1; (CO)$_3$Mn(*i*-Pr-DAB)Mn(CO)$_3$, 98858-62-9; (CO)$_3$Mn(*i*-Pr-DAB)Re(CO)$_3$, 98858-60-7; (CO)$_3$Re(*i*-Pr-DAB)Mn(CO)$_3$, 98858-65-2; (CO)$_5$MnMn(CO)$_3$(*p*-Tol-DAB), 71604-00-7; (CO)$_5$MnRe(CO)$_3$(*p*-Tol-DAB), 71604-03-0; (CO)$_5$ReMn(CO)$_3$(*p*-Tol-DAB), 97570-66-6; (CO)$_3$Mn(*p*-Tol-DAB)Mn(CO)$_3$, 98858-61-8; (CO)$_3$Mn(*p*-Tol-DAB)Re(CO)$_3$, 98858-63-0; (CO)$_3$Re(*p*-Tol-DAB)Mn(CO)$_3$, 98858-66-3; (CO)$_3$Mn(*t*-Bu-DAB)Mn(CO)$_3$, 98858-67-4; Re$_2$(CO)$_{10}$, 14285-68-8; CH$_4$, 74-82-8.

---

(33) (a) Waltz, W. L.; Hackelberg, O.; Dorfman, L. M.; Wojcicki, A. *J. Am. Chem. Soc.* **1978**, *100*, 7259. (b) Yasufuku, K.; Yesuka, H.; Kobayashi, T.; Yamazaki, H.; Nagakuru, S. "Proceedings of the Tenth International Conference on Organometallic Chemistry", 1981; p 1002.

(34) Yesaka, H.; Kobayashi, T.; Yasufuko, H.; Nagakuru, S. *J. Am. Chem. Soc.* **1983**, *105*, 6249.

(35) Shi, Q. Z.; Richmond, T.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 71.

Contribution from the Department of Chemistry,
University of Arizona, Tucson, Arizona 85721

^{95}Mo NMR Study of Mononuclear Oxomolybdenum(IV) Complexes

CHARLES G. YOUNG and JOHN H. ENEMARK*

Received April 8, 1985

A total of 38 representative oxo–Mo(IV) compounds have been studied by ^{95}Mo NMR spectroscopy. The compounds include the following: MoO(S-S)$_2$ and MoO(S-S)$_2$(PR'$_3$) (S-S = S$_2$CNR$_2^-$, R = Et, *n*-Pr, *n*-Bu, R' = Me, Et, *n*-Bu; S-S = S$_2$P(OEt)$_2^-$, R' = Me), (PPh$_4$)$_2$[MoO(mnt)$_2$] (mnt = *cis*-1,2-dicyanoethenedithiolate), K$_2$[MoO(SCH$_2$CH$_2$S)$_2$]·2EtOH, K$_4$[MoO$_2$(CN)$_4$]·6H$_2$O, K$_3$[MoO(OH)(CN)$_4$], MoOX$_2$P$_3$ (P = PMe$_3$, X = Cl$^-$, NCO$^-$, NCS$^-$; P = PMe$_2$Ph, X = Cl$^-$, Br$^-$, I$^-$, NCO$^-$, NCS$^-$; P = PPh$_2$Me, X = Cl$^-$; P = PEt$_2$Ph, X = Cl$^-$), MoOCl$_2$(N-N)(PPh$_2$Me) (N-N = 2,2'-bipyridine, 1,10-phenanthroline), MoO(ox)$_2$(PPh$_2$Me) (ox = 8-hydroxyquinolinate), *trans*-[MoOX(CNMe)$_4$]BPh$_4$ (X = Cl$^-$, Br$^-$), *trans*-[MoOCl(dppe)$_2$]BPh$_4$ (dppe = 1,2-bis(diphenylphosphino)ethane), and LMoO(S-S) (L = hydrotris(3,5-dimethylpyrazolyl)borate, S-S = S$_2$CNR$_2^-$, R = Me, Et, *n*-Pr; S-S = S$_2$P(OEt)$_2^-$). The compounds display a large ^{95}Mo chemical shift range (δ 1035–3180) and highly variable line widths ($W_{1/2}$ = 240 to >5000 Hz). The five-coordinate S-donor ligand complexes exhibit resonances over the range δ 1400–2450; the ligand shielding order is S$_2$CNR$_2^-$ < S$_2$P(OEt)$_2^-$ < SCH$_2$CH$_2$S^{2-} < mnt^{2-}. Coordination of phosphines to the MoO(S-S)$_2$ complexes shields the molybdenum nuclei in the order P(*n*-Bu)$_3$ < PEt$_3$ < PMe$_3$. Six-coordinate MoOX$_2$P$_3$ complexes exhibit resonances between δ 1590 and 2200 and display an inverse halogen dependence of the chemical shift. The most deshielded resonances (ca. δ 3180) occur for MoOCl$_2$(N-N)(PPh$_2$Me) complexes whereas the [MoOX(CNMe)$_4$]$^+$ complexes possess the most shielded resonances (δ 1035–1050). The latter also display an inverse halogen dependence of the chemical shift. An experimental methodology for the observation of these broad ^{95}Mo NMR resonances is described.

Introduction

In recent years the characterization of coordination and organometallic complexes of molybdenum by ^{95}Mo NMR spectroscopy has developed rapidly. In general, the measurement of the spectra of Mo(VI), Mo(II), and Mo(0) complexes has become routine and the chemical shift ranges and halogen dependencies of such complexes are well-defined.[1] For these oxidation states,

---

(1) Minelli, M.; Enemark, J. H.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G., *Coord. Chem. Rev.*, in press.

the ability of ^{95}Mo NMR to monitor solution processes,[2,3] distinguish diastereomers,[4-6] and aid solid–solution structure correlations[7] has also been demonstrated. Trinuclear Mo(IV) complexes possessing the $[Mo_3O_4]^{4+}$ core have also been extensively studied by ^{95}Mo NMR.[8,9] The narrow chemical shift range exhibited by these complexes (δ 900–1162) is consistent with the integrity of the $[Mo_3O_4]^{4+}$ core in solution, a fact previously demonstrated by ^{18}O transfer[10] and EXAFS[11] experiments. The trinuclear Mo(IV) complexes are relatively deshielded compared to oxo–Mo(VI) species[12-17] and exhibit line widths ($W_{1/2}$) of 350–1400 Hz. Studies of dinuclear Mo(V),[3,8,9,18] Mo(III),[19] and Mo(I)[19,20] complexes are now establishing a sound ^{95}Mo NMR data base for complexes of these rarer oxidation states.

A strikingly undeveloped area of ^{95}Mo NMR is the characterization of mononuclear Mo(IV) species, particularly those containing the biologically relevant $Mo^{IV}{=}O$ and $Mo^{IV}{=}S$ fragments. To date, only one well-characterized mononuclear Mo(IV) complex, $[Mo(CN)_8]^{4-}$ (δ -1309), has been observed by ^{95}Mo NMR.[21] In previous ^{95}Mo NMR studies[8,9] of trinuclear Mo(IV) complexes it was suggested that the chemical shift range for monomeric Mo(IV) species is δ -300 to -3000; however, the studies cited in support of this range have never been published.

The participation of oxo–Mo(IV) centers in the catalytic cycle of molybdoenzymes such as sulfite oxidase and nitrate reductase[22] provides impetus for the study of oxo–Mo(IV) complexes by ^{95}Mo NMR and for the evaluation of this technique as a direct probe for such enzyme centers. Herein, we describe the first detailed ^{95}Mo NMR study of mononuclear oxo–Mo(IV) complexes and show that their chemical shifts are several thousand ppm more deshielded than previously suggested.[8,9] The halogen dependencies of the chemical shifts and a methodology for observing these broad and hitherto elusive ^{95}Mo NMR resonances are also described.

Table I. ^{95}Mo NMR Data[a]

compd	chem shift,[f] ppm	line width, Hz
$MoO(S_2CNEt_2)_2$	2400	2700
$MoO(S_2CN\text{-}n\text{-}Pr_2)_2$	2400	3900
$MoO(S_2CN\text{-}n\text{-}Bu_2)_2$	2450	>5000
$MoO(S_2P(OEt)_2)_2$	2230	5170
$K_2[MoO(SCH_2CH_2S)_2]\cdot 2EtOH$[b]	1680	1450
$(PPh_4)_2[MoO(mnt)_2]$	1400	1220
$K_4[MoO_2(CN)_4]\cdot 6H_2O$[c]	1220	240
$K_3[MoO(OH)(CN)_4]$[d]	1444	240
$MoO(S_2CNEt_2)_2(PMe_3)$	2300	1360
$MoO(S_2CNEt_2)_2(PEt_3)$	2370	1800
$MoO(S_2CNEt_2)_2(P\text{-}n\text{-}Bu_3)$	2400	2820
$MoO(S_2CN\text{-}n\text{-}Pr_2)_2(PMe_3)$	2290	2120
$MoO(S_2CN\text{-}n\text{-}Pr_2)_2(PEt_3)$	2340	2580
$MoO(S_2CN\text{-}n\text{-}Pr_2)_2(P\text{-}n\text{-}Bu_3)$	2390	>5000
$MoO(S_2CN\text{-}n\text{-}Bu_2)_2(PMe_3)$	2270	3160
$MoO(S_2CN\text{-}n\text{-}Bu_2)_2(PEt_3)$	2330	3800
$MoO(S_2P(OEt)_2)_2(PMe_3)$	1610	1650
$MoOCl_2(PMe_3)_3$	1890	820
$MoO(NCS)_2(PMe_3)_3$	1590	680
$MoO(NCO)_2(PMe_3)_3$	1590	820
$MoOCl_2(PMe_2Ph)_3$ (blue)	2020	1120
$MoOCl_2(PMe_2Ph)_3$ (green)	2020	1000
$MoOBr_2(PMe_2Ph)_3$	2050	1100
$MoOI_2(PMe_2Ph)_3$	2050	1100
$MoO(NCS)_2(PMe_2Ph)_3$	1690	845
$MoO(NCO)_2(PMe_2Ph)_3$	1690	890
$MoOCl_2(PPh_2Me)_3$	2180	1210
$MoOCl_2(PEt_2Ph)_3$	2200	1200
$MoOCl_2(bpy)(PPh_2Me)$	3160	800
$MoOCl_2(phen)(PPh_2Me)$	3180	800
$MoO(ox)_2(PPh_2Me)$	2520	570
$[MoOCl(dppe)_2]BPh_4$	1260	1780
$[MoOCl(CNMe)_4]BPh_4$[e]	1035	330
$[MoOBr(CNMe)_4]BPh_4$[e]	1050	530
$LMoO(S_2CNMe_2)$	3000	2400
$LMoO(S_2CNEt_2)$	3000	2040
$LMoO(S_2CN\text{-}n\text{-}Pr_2)$	3000	1850
$LMoO(S_2P(OEt)_2)$	2950	1750

[a] Measured in CH_2Cl_2 at room temperature unless otherwise stated. [b] In H_2O. [c] In saturated aqueous KOH. [d] Dissolution of $K_4[MoO_2(CN)_4]\cdot 6H_2O$ in H_2O, pH 12.5. [e] In $MeNO_2$ at 70 °C. [f] Deviation ±10 ppm.

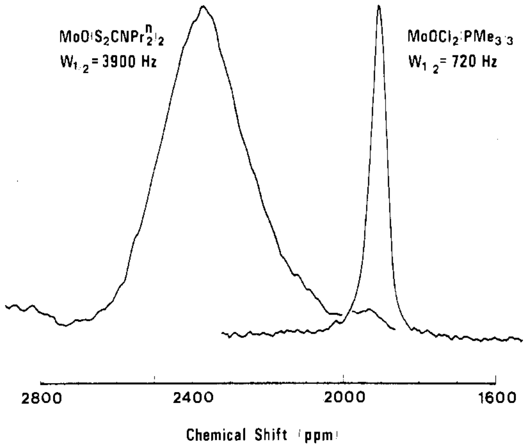

Figure 1. Typical ^{95}Mo NMR spectra for oxo–Mo(IV) complexes. For $MoO(S_2CN\text{-}n\text{-}Pr_2)_2$: number of pulses, 169 800; pulse repetition time, 41 ms; spectral bandwidth, 50 kHz; exponential line broadening, 250 Hz. For $MoOCl_2(PMe_3)_3$: number of pulses, 18 000; pulse repetition time, 41 ms; spectral bandwidth, 50 kHz; exponential line broadening, 80 Hz.

Experimental Section

Sample Preparation. The compounds $MoO(S\text{-}S)_2$[23] (S-S = $S_2CNR_2^-$, R = Et, *n*-Pr, *n*-Bu; S-S = $S_2P(OEt)_2^-$), $(PPh_4)_2[MoO(mnt)_2]$,[24,25] K_2-

---

(2) Minelli, M.; Enemark, J. H.; Wieghardt, K.; Hahn, M. *Inorg. Chem.* **1984**, *22*, 3952–3953.

(3) Wieghardt, K.; Guttman, M.; Chaudhuri, P.; Gebert, W.; Minelli, M.; Young, C. G.; Enemark, J. H. *Inorg. Chem.* **1985**, *24*, 3151–3155. The conversion of *anti*-$[([9]aneN_3)_2Mo_2O_4]I_2$ to the more stable syn isomer was followed by ^{95}Mo NMR.

(4) Minelli, M.; Rockway, T. W.; Enemark, J. H.; Brunner, H.; Muschiol, M. *J. Organomet. Chem.* **1981**, *217*, C34–C36. Brunner, H.; Beier, P.; Frauendorfer, E.; Muschiol, M.; Rastogi, D. K.; Wachter, J.; Minelli, M.; Enemark, J. H. *Inorg. Chim. Acta* **1985**, *96*, L5–L9.

(5) Buchanan, I.; Minelli, M.; Ashby, M. T.; King, T. J.; Enemark, J. H.; Garner, C. D. *Inorg. Chem.* **1984**, *23*, 495–500.

(6) Buchanan, I.; Garner, C. D.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1984**, 1333–1342.

(7) Minelli, M.; Enemark, J. H.; Nicholson, J. R.; Garner, C. D. *Inorg. Chem.* **1984**, *23*, 4384–4386.

(8) Gheller, S. F.; Hambley, T. W.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *J. Am. Chem. Soc.* **1983**, *105*, 1527–1532.

(9) Gheller, S. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. "Proceedings of the Climax Fourth International Conference on the Chemistry and Uses of Molybdenum"; Barry, H. F., Mitchell, P. C. H., Eds.; Climax Chemical Co.: Ann Arbor, MI, 1982; pp 67–70.

(10) Murmann, R. K.; Shelton, M. E. *J. Am. Chem. Soc.* **1980**, *102*, 3984–3985.

(11) Cramer, S. P.; Eidem, P. K.; Paffett, M. T.; Winkler, J. R.; Dori, Z.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 799–802.

(12) Minelli, M.; Young, C. G.; Enemark, J. H. *Inorg. Chem.* **1985**, *24*, 1111–1113.

(13) Gheller, S. F.; Sidney, M.; Masters, A. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Aust. J. Chem.* **1984**, *37*, 1825–1832.

(14) Minelli, M.; Yamanouchi, K.; Enemark, J. H.; Subramanian, P.; Kaul, B. B.; Spence, J. T. *Inorg. Chem.* **1984**, *23*, 2554–2556.

(15) Alyea, E. C.; Topich, J. *Inorg. Chim. Acta* **1982**, *65*, L95–L96.

(16) Gheller, S. F.; Hambley, T. W.; Trail, P. R.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Aust. J. Chem.* **1982**, *35*, 2183–2191.

(17) Christensen, K. A.; Miller, P. E.; Minelli, M.; Rockway, T. W.; Enemark, J. H. *Inorg. Chim. Acta* **1981**, *56*, L27–L28.

(18) Buchanan, I.; Clegg, W.; Garner, C. D.; Sheldrick, G. M. *Inorg. Chem.* **1983**, *22*, 3657–3661.

(19) Young, C. G.; Minelli, M.; Enemark, J. H.; Miessler, G.; Janietz, N.; Kauermann, H.; Wachter, J. *Polyhedron*, in press.

(20) Dysart, S.; Georgii, I.; Mann, B. E. *J. Organomet. Chem.* **1981**, *213*, C10–C12.

(21) Lutz, O.; Nolle, A.; Kroneck, P. *Z. Naturforsch., A: Astrophys., Phys., Phys. Chem.* **1976**, *31A*, 454–456.

(22) Spence, J. T. *Coord. Chem. Rev.* **1983**, *48*, 59–82.

(23) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1976**, *15*, 2612–2615.

$[MoO(SCH_2CH_2S)_2]\cdot 2EtOH$,[26] $K_4[MoO_2(CN)_4]\cdot 6H_2O$,[27] $MoOX_2P_3$ (P = PMe_3, X = Cl^-, NCO^-, NCS^-;[28] P = PMe_2Ph, X = Cl^-, Br^-, I^-, NCO^-, NCS^-; P = PPh_2Me, X = Cl^-; P = PEt_2Ph, X = Cl^-[29]), $MoOCl_2(bpy)(PPh_2Me)$,[30] $MoOCl_2(phen)(PPh_2Me)$,[30] $MoO(ox)_2(PPh_2Me)$,[30] *trans*-$[MoOX(CNMe)_4]BPh_4$ (X = Cl^-, Br^-[31]), and *trans*-$[MoOCl(dppe)_2]BPh_4$[32] were prepared by literature methods or slight modifications thereof. The complexes $MoO(S\text{-}S)_2(PR'_3)$ (S-S = $S_2CNR_2^-$, R′ = Me, Et, *n*-Bu; S-S = $S_2P(OEt)_2^-$, R′ = Me) were prepared in situ by the addition of excess PR'_3 to solutions of $MoO(S\text{-}S)_2$ in CH_2Cl_2.[33] The preparation of the new complexes LMoO(S-S) (L = hydrotris(3,5-dimethylpyrazolyl)borate) will be described in detail elsewhere.[34]

With the exception of the LMoO(S-S) complexes, all NMR samples were prepared under anaerobic conditions by using dried, deoxygenated solvents. Each sample contained 0.5 g of complex/2 mL of solvent (ca. 0.2–0.6 M) or the maximum allowed by solubility properties.

Instrumentation. The NMR spectra were recorded on a Bruker WM 250 spectrometer equipped with a 10-mm molybdenum probe and operating at 16.3 MHz. To reduce the effects of probe ringing[1] a Doty Scientific duplexer and preamplifier with a 16-MHz center was inserted between the probe and the Bruker broad-band preamplifier. The duplexer was gated off during the pulse and for 5 μs after the pulse. With this arrangement the preaquisition delay was reduced to 100 μs. The transmitter output was amplified with a Heathkit SB-201 (1-kW) linear amplifier. The input was attenuated to give a 26-μs 90° pulse. The routine acquisition parameters used in this study were as follows: pulse width, 20 μs; spectral width, 50 kHz; data points, 2K or 4K; number of scans, ca. 15 000–500 000. A 2 M $Na_2[MoO_4]$ solution in D_2O, effective pH 11, was used as external reference, and unless otherwise specified, the spectra were recorded at ambient temperature.

Results and Discussion

The ^{95}Mo NMR data of a wide variety of mononuclear oxo–Mo(IV) complexes are summarized in Table I. The complexes exhibit a montage of ligand types, stereochemistries, and coordination numbers and are representative of the important classes of known oxo–Mo(IV) complex. In contrast to many other Mo(IV) species, such as the binary halides, the pseudohalides, and their derivatives, the oxo–Mo(IV) complexes invariably possess the diamagnetism essential for the observation of ^{95}Mo NMR. Two spectra, typical of those exhibiting the extremes in observed line width, are shown in Figure 1.

The tabulated data are especially noteworthy for three reasons. First, all the oxo–Mo(IV) complexes exhibit resonances in the deshielded portion of the known ^{95}Mo chemical shift range,[1] well outside the range of δ −300 to −3000 previously suggested for mononuclear Mo(IV) species. Secondly, an extensive range (2145 ppm) of ^{95}Mo chemical shifts is observed. The new data, along with previous results,[8,9,21] invest Mo(IV) with the largest chemical shift range presently known for ^{95}Mo in any single oxidation state. The previous champion in this regard, Mo(VI)[1] (δ −610 to 3150), pales in comparison to the 4490 ppm range now established for Mo(IV) species. Thirdly, the observed resonances include the broadest NMR signals yet observed for ^{95}Mo in solution. Equation 1 relates the line width ($W_{1/2}$) to the spin–spin relaxation time (T_{2q}), the electric field gradient (q), the asymmetry of the electric field gradient (η), and the molecular correlation time (τ_c) for isotropic rotation in a homogeneous medium.[35] As the relaxation

$$W_{1/2} = (\pi T_{2q})^{-1} \sim (\pi T_{1q})^{-1} = \frac{3\pi}{10}\left(\frac{2I+3}{I^2(2I-1)}\right)\left(\frac{e^2 q_{zz} Q}{h}\right)^2\left(1+\frac{\eta^2}{3}\right)\tau_c \quad (1)$$

of ^{95}Mo is dominated by a nuclear quadrupole mechanism,[48] the broad resonances may be attributed to the presence of large electric field gradients (q) at the molybdenum nuclei.

The resonances of the oxo–Mo(IV) complexes are significantly more deshielded than those of other known[1] mononuclear oxomolybdenum species, with the exception of members of the thio- and selenomolybdate series.[36,37] The chemical shifts of monooxo–Mo(VI) species[12,38,39] are currently restricted to δ 148 to −610, the most shielded resonance resulting from the atypical $[MoO(O_2)(CN)_4]^{2-}$ anion. The previously mentioned $[Mo_3O_4]^{4+}$ complexes exhibit resonances that are, in general, slightly more shielded than those of the complexes reported herein.[8,9] The wide chemical shift range observed for mononuclear oxo–Mo(IV) complexes contrasts with the narrow range (172 ppm) observed for the trinuclear $[Mo_3O_4]^{4+}$ complexes[8,9] and reflects the considerable influence of differing ligand sets on the electronic nature of the mononuclear oxo–Mo(IV) complexes.

The five-coordinate complexes exhibit resonances over a chemical shift range of δ 1400–2450 and exhibit a ligand-dependent shielding order of $S_2CNR_2^- < S_2P(OEt)_2^- < SCH_2CH_2S^{2-} < mnt^{2-}$. It is interesting to note that the anionic species are relatively shielded compared to the neutral dithio acid complexes. For the $S_2CNR_2^-$ complexes, a steady increase in line width with the increasing steric bulk of R may be ascribed to corresponding increases in τ_c. This effect has been observed for other $S_2CNR_2^-$ complexes.[12] The coordinatively unsaturated $MoO(S_2CNR_2)_2$ complexes readily bind basic phosphine ligands to form the adducts, $MoO(S_2CNR_2)_2(PR'_3)$.[33] In situ formation of these complexes, confirmed here by ^{31}P NMR and electronic spectroscopy, allowed the observation of their relatively shielded ^{95}Mo resonances. The shielding of the ^{95}Mo nucleus increases in the order $P(n\text{-}Bu)_3 < PEt_3 < PMe_3$ in all cases. Line width reductions upon phosphine binding imply a decrease in q, the electric field gradient at Mo. For the $P(n\text{-}Bu)_3$ complexes, the decrease in q is presumably outweighted by line broadening induced as a consequence of an increased τ_c value, due to the large *n*-Bu groups. No ^{95}Mo–^{31}P spin–spin coupling was observed in the above adducts.

The phosphine complexes $MoOCl_2P_3$ (P = tertiary phosphine), originally prepared by Butcher and Chatt,[29] display ^{95}Mo chemical shifts that decrease in the order $PPh_2Me > PMe_2Ph > PMe_3$; the same trend, consistent with the decreasing steric bulk of the ligand, is observed for line widths. Both the green and blue distortional isomers[40–42] of $MoOCl_2(PMe_2Ph)_3$ were prepared and studied; the observed chemical shifts were identical within experimental error. Considering that the chemical shifts of diastereomeric Mo(II)[4] and Mo(VI)[5] complexes differ by less than 30 ppm, it is not unreasonable that the chemical shifts of the green and blue distortional isomers should be indistinguishable. Replacement of two PPh_2Me ligands in $MoOCl_2(PPh_2Me)_3$ by the heterocyclic N-donor ligands bpy or phen produces the most deshielded complexes in the series. The $MoO(ox)_2(PPh_2Me)$ complex exhibits

---

(24) Abbreviations used: mnt, *cis*-1,2-dicyanoethenedithiolate; bpy, 2,2′-bipyridine; phen, 1,10-phenanthroline; ox, 8-hydroxyquinolinate; dppe, 1,2-bis(diphenylphosphino)ethane; L, hydrotris(3,5-dimethylpyrazolyl)borate.

(25) A sample of this compound was kindly provided by Professor C. D. Garner, University of Manchester.

(26) Mitchell, P. C. H.; Pygall, C. F. *Inorg. Chim. Acta* **1979**, *33*, L109–L111.

(27) van de Poel, J.; Neumann, H. M. *Inorg. Chem.* **1968**, *7*, 2086–2091.

(28) Carmona, E.; Galindo, A.; Sanchez, L.; Nielson, A. J.; Wilkinson, G. *Polyhedron* **1984**, *3*, 347–352.

(29) Butcher, A. V.; Chatt, J. *J. Chem. Soc. A* **1970**, 2652–2656.

(30) Rice, C. A.; Spence, J. T. *Inorg. Chem.* **1980**, *19*, 2845–2846.

(31) Novotny, M.; Lippard, S. J. *Inorg. Chem.* **1974**, *13*, 828–831.

(32) Atkinson, L. K.; Mawby, A. H.; Smith, D. C. *J. Chem. Soc., Chem. Commun.* **1970**, 1399–1400.

(33) Newton, W. E.; Watt, G. D.; McDonald, J. W. "Proceedings of the Climax Third International Conference on the Chemistry and Uses of Molybdenum"; Barry, H. F., Mitchell, P. C. H. Eds.; Climax Molybdenum Co.: Ann Arbor, MI, 1979; pp 259–263.

(34) Young, C. G.; Enemark, J. H., manuscript in preparation.

(35) Harris, R. K. In "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; p 17.

(36) Gheller, S. F.; Hambley, T. W.; Rodgers, J. R.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Inorg. Chem.* **1984**, *23*, 2519–2528.

(37) Gheller, S. F.; Gazzana, P. A.; Masters, A. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G.; Rodgers, J. R.; Snow, M. R. *Inorg. Chim. Acta* **1981**, *54*, L131–L132.

(38) Postel, M.; Brevard, C.; Arzoumanian, H.; Riess, J. G. *J. Am. Chem. Soc.* **1983**, *105*, 4922–4926.

(39) Bristow, S.; Enemark, J. H.; Garner, C. D.; Minelli, M.; Morris, G. A.; Ortega, R. B. *Inorg. Chem.*, in press.

(40) Chatt, J.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1971**, 655–656.

(41) Manojlovic-Muir, L. *J. Chem. Soc. A* **1971**, 2796–2800.

(42) Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1972**, 686–690.

a chemical shift similar to those of the $MoO(S\text{-}S)_2$ complexes, probably due to the loss of PPh_2Me to form a five-coordinate complex.[30] Like the phosphine adducts of the $MoO(S\text{-}S)_2$ complexes mentioned above, no ^{95}Mo–^{31}P couplings were observed in the above phosphine complexes.

In order to address the halogen dependency[43] of oxo–Mo(IV) complexes, several series of analogous halide and pseudohalide complexes of the form $MoOX_2P_3$ and $[MoOX(CNMe)_4]^+$ were prepared and studied. For the halide derivatives a small inverse halogen dependence was noted. An inverse halogen dependence is also a characteristic of oxohalomolybdenum(VI) complexes.[12,14] The relatively shielded resonances of the oxo–Mo(IV) complexes containing NCS^- and NCO^- ligands further corroborate the inverse halogen dependence because in other systems displaying this dependence the NCS^- complexes are shielded compared to the analogous halo complexes.[14] The shielding of ^{95}Mo by NCS^- and NCO^- in the present complexes is, however, substantially greater than that previously observed (ca. 300 vs. 90 ppm). The $[MoOX(CNMe)_4]^+$ complexes, which exhibit the most shielded resonances in Table I, also display an inverse halogen dependence of the chemical shift.

A previous ^{95}Mo NMR study of aqueous $K_4[MoO_2(CN)_4]$ solutions assigned the observed resonances to polynuclear complexes.[9] We have reinvestigated the ^{95}Mo NMR spectra of aqueous $K_4[MoO_2(CN)_4]$ solutions and find that the narrow resonance obtained upon initial dissolution of this compound (pH 12.5) is markedly pH dependent. The deep blue color of pH 12.5 solutions is indicative of the $[MoO(OH)(CN)_4]^{3-}$ species, which resonates at ca. δ 1440. Magenta solutions obtained upon near KOH saturation of the initial blue solution exhibit a resonance at δ 1220, which we attribute to $[MoO_2(CN)_4]^{4-}$.

^{95}Mo NMR data for a new[34] series of oxo–Mo(IV) complexes containing hydrotris(3,5-dimethylpyrazolyl)borate and dithio acid ligands are also presented in Table I. Relatively deshielded resonances are observed for these complexes (ca. δ 3000). The usual line width trend found in other $S_2CNR_2^-$ complexes is not observed here due to the steric dominance of the large polypyrazolylborate ligand.

Optimal chemical and instrumental conditions are essential for the observation of broad ^{95}Mo NMR resonances such as those characterizing many oxo–Mo(IV) complexes. The difficulties in observing NMR spectra for quadrupolar nuclei in low-symmetry environments and strategies aimed at overcoming these difficulties have been discussed.[1,44] We employed highly concentrated samples (0.2–0.6 M), low-viscosity solvents, and, in some cases, elevated temperatures to enhance signal observation. Several instrumental modifications, described in the Experimental Section and elsewhere,[1] were also essential to the collection of the data given in Table I. First, narrow-band amplification of the transmitter output produced short, high-power pulses, which increased sensitivity and available spectral width. Secondly, the insertion of a narrow band duplexer and preamplifier between the probe and the broad-band amplifier enabled the preaquisition delay to be reduced from 200 to 100 μs with no loss in spectral quality due to probe ringing.[1,45] Signal decay is extremely rapid for the broad oxo–Mo(IV) resonances (see eq 1) and the shorter preaquisition delay was crucial to their observation.[46] The use of a probe shielded with lead, one of the most effective metals for reducing acoustic ringing, further minimized probe ringing.

Finally, the resonances observed for mono- and trinuclear oxo–Mo(IV) complexes are substantially broader and less shielded than the resonance of $[Mo(CN)_8]^{4-}$ (δ −1309, $W_{1/2}$ = 75 Hz), first reported in 1976.[21] The large differences in chemical shifts and line widths observed for Mo(IV) complexes underscore the need for theoretical studies of the chemical shifts of transition metals,[47] and the need for ^{95}Mo NMR studies of other types of Mo(IV) complexes.

Conclusion

A methodology for the observation of broad ^{95}Mo NMR resonances has been developed and exploited to provide the single most comprehensive collection of ^{95}Mo NMR parameters for mononuclear oxo–Mo(IV) complexes. The chemical shift range for such species is extremely large (2145 ppm), and combined with other data[8,9,21] gives Mo(IV) complexes the greatest chemical shift range for ^{95}Mo in any single oxidation state. The oxo–Mo(IV) complexes display an inverse halogen dependence of the chemical shift. The generally large line widths for oxo–Mo(IV) complexes offer little encouragement for the direct observation of oxo–Mo(IV) centers of enzymes by ^{95}Mo NMR.

Acknowledgment. We thank the U.S. Department of Agriculture for support of this work through Grant No. 84-CRCR-1-1416, Professor C. D. Garner for a sample of $(PPh_4)_2[MoO(mnt)_2]$, and Dr. K. A. Christensen for his technical assistance with the NMR spectrometer.

---

(43) Kidd, R. G. *NATO Adv. Study Inst. Ser., Ser. C* **1983**, *103*, 445–456.

(44) Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93–103. Besecker, C. J.; Klemperer, W. G.; Maltbie, D. J.; Wright, D. A. *Ibid.* **1985**, *24*, 1027–1032.

(45) Pratt, S. L. *J. Mag. Reson.* **1982**, *49*, 161–163.

(46) For a resonance with $W_{1/2}$ = 3000 Hz, the maximum signal remaining to be accumulated increases from 15.2% to 38.9% if the preaquisition delay is decreased from 200 to 100 μs. However, when $W_{1/2}$ = 300 Hz, 82.2% and 94.3% of the maximum signal remain following the same respective preaquisition delays.

(47) Nakatsuji, H.; Kanda, K.; Endo, K.; Yonezawa, T. *J. Am. Chem. Soc.* **1984**, *106*, 4653–4660. Kanda, K.; Nakatsuji, H.; Yonezawa, T. *Ibid.* **1984**, *106*, 5888–5892.

(48) Brownlee, R. T. C.; O'Connor, M. J.; Shehan, B. P.; Wedd, A. G. *J. Mag. Reson.* **1985**, *61*, 516–525.