cases, a solvent such as benzene, hexane, or toluene may be added to the reaction mixture to keep the alkoxide in solution and facilitate separation from sodium or ammonium nitrate. When anhydrous ammonia is used as a base, 4 mol is sufficient as required by anhydrous reaction stoichiometry.

$$(NO_3)_4Ce{\cdot}2NH_4NO_3 + 4ROH + 4NH_3 \rightarrow Ce(OR)_4 + 6NH_4NO_3$$

When an alkali alkoxide is used instead of ammonia, it is preferable to provide some excess (up to 2 equiv) over the required 4 equivalents.

$$(NO_3)_4Ce{\cdot}2NH_4NO_3 + 4ROH + 6NaOCH_3 \rightarrow Ce(OR)_4 + 6NaNO_3 + 2NH_3 + 6CH_3OH$$

The excess of alkali alkoxide converts the $NH_4NO_3$ into alkali nitrate and ammonia, which makes the choice of workup less ambiguous and the material balance easier to establish.

## Experimental Section

**General Procedures.** Ceric ammonium nitrate was dried at 115 °C overnight and stored under argon. Methanol was dried with sodium and distilled prior to use. Octyl alcohol was stored over Linde 3-Å molecular sieves. Ammonia gas was passed through a calcium oxide column before entering the reaction vessel. Fresh reagent grade 25% sodium methoxide in methanol was used. Weighing, filtering, and the preparation of cerium(IV) methoxide were done in an argon-filled glovebag. Distillations and the preparations of $Ce(OC_8H_{17})_4$ were done on the bench.

**Cerium(IV) Methoxide.** At room temperature under argon, 0.03 mol of ceric ammonium nitrate (16.45 g) (Rhone-Poulec Inc.) was dissolved in 304 g of methanol, resulting in a deep red solution. The argon flow was stopped, and ammonia gas was passed over the reaction solution. The absorption of the ammonia was so rapid that it was necessary to restore positive pressure by resuming the flow of argon. The ammonia uptake (24.7 g) was completed in 0.5 h, giving a bright yellow slurry. This reaction mixture was allowed to stir overnight.

In a glovebag, the product was filtered into a tared fritted glass funnel. The bright yellow product (10.1 g) was washed with methanol three times and dried in a desiccator over magnesium perchlorate under vacuum. Anal. Calcd for $Ce(OCH_3)_4{\cdot}CH_3OH$: C, 20.27; H, 5.44; Ce, 47.29; N, 0.00. Found: C, 18.70; H, 5.37; Ce, 46.58; N, <0.3%. To establish stoichiometry the colorless filtrate was distilled to dryness, giving 14.28 g of ammonium nitrate (calculated 14.41 g).

Ceric tetramethoxide can also be prepared from sodium methoxide instead of ammonia. The resulting sodium nitrate is separated from the product by extraction with methanol in a Soxhlet extractor.

**Ceric Tetrakis(octyloxide).** To a deep red solution of 0.01 mol of ceric ammonium nitrate (5.48 g) in 20.0 g of methanol was added 0.04 mol (5.2 g) of normal octyl alcohol followed by 13.1 g (0.06 mol) of 25% sodium methoxide solution (Aldrich Chemical Co., Milwaukee, WI). A bright yellow precipitate, probably the methoxide, formed immediately. The mixture was diluted with 25.3 g of toluene and stirred overnight. The methanol was completely removed by distillation, more toluene was added, and the sodium nitrate was removed by filtration and washed with five portions, 8 g each, of toluene. The mass of sodium nitrate recovered after drying was 5.0 g (calculated 5.1 g).

The toluene in the filtrate was removed under vacuum at room temperature (0.1 mm pressure), yielding 6.76 g of orange-red oil. Anal. Calcd for $Ce(OC_8H_{17})_4$: C, 58.50; H, 10.43; Ce, 21.3. Found: C, 58.44; H, 10.47; Ce, 21.8. $^1H$ NMR ($CDCl_3$): $\delta$ 0.90 (t, 3 H), 1.27 (s, 12 H), 3.56 (t, 2 H).

## Discussion

In some cases the alkoxides can be used as intermediates for subsequent reactions directly in the reaction mixture in the presence of the nitrates. For instance, addition of acetylacetone instantly converts the alkoxide into ceric acetylacetonate. Thus, unnecessary workup can be avoided.

The methoxides, especially, are susceptible to rapid hydrolytic decomposition by the action of humidity. Only carefully handled samples show correct elemental analyses. The byproduct nitrates, however, can be separated from the product with relative ease; the amount recovered indicated quantitative reaction in most cases.

The octyloxides seem to be less susceptible to hydrolysis than the methoxides. Samples of $Ce(OC_8H_{17})_4$ were successfully prepared outside the glovebag in Boulder, CO, under the local, usually relatively low, humidity. However, $Ce(OC_8H_{17})_4$ is not as thermally stable as $Ce(OCH_3)_4$. It decomposes at 240–260 °C, while the methoxide is stable to at least 280 °C. A brownish yellow solid remained in the capillary tube used to obtain mass spectra of $Ce(OC_8H_{17})_4$. The largest peaks observed in the mass spectrum were at $m/e$ 398 and 400, corresponding to $^{140}Ce(OC_8H_{17})_2^+$ and $^{142}Ce(OC_8H_{17})_2^+$ (70-eV electron impact ionization). The $Ce(OCH_3)_4$ showed no tendency to be volatilized in the mass spectrometer, possibly indicating that it forms a nonvolatile oligomer.

During all of these syntheses, we did not observe violent reactions between the ceric ammonium nitrate and the organic alcohols and solvents. One generally tries to avoid mixing organic materials with strong oxidizing agents such as Ce(IV). These reactions, however, are highly dependent on the acidity of the solution.[7] In strongly alkaline solutions the explosion hazards appear to be minimal.

**Registry No.** $(NO)_3)_4Ce{\cdot}2NH_4NO_3$, 22549-43-5; $Ce(OCH_3)_4$, 94957-38-7; $Ce(OC_8H_{17})_4$, 94957-39-8; $CH_3OH$, 67-56-1; sodium methoxide, 124-41-4; octyl alcohol, 111-87-5.

(7) Richardson, W. H. In "Oxidation in Organic Chemistry"; Wiberg, K. B., Ed.; Academic Press: New York, London, 1965; Part A, Chapter IV.

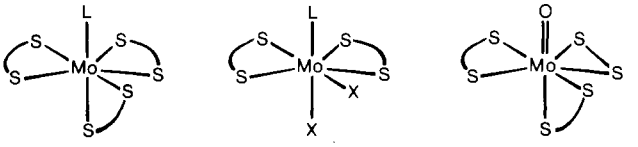
Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona 85721

# $^{95}$Mo NMR Studies of Seven-Coordinate Molybdenum(VI) Monooxo, Nitrido, and Phenylimido Complexes and Their Derivatives

Martin Minelli, Charles G. Young, and John H. Enemark*

*Received July 10, 1984*

Molybdenum(VI) dioxo complexes have been extensively studied[1-7] by $^{95}$Mo NMR, partly because the catalytic molybdenum center in enzymes such as sulfite oxidase and nitrate reductase is believed to have a $[MoO_2]^{2+}$ core in the oxidized state.[8,9] In contrast, no $^{95}$Mo NMR data have been reported for Mo(VI) monooxo, nitrido, and phenylimido complexes. Here, we report the first $^{95}$Mo NMR study of such complexes. The majority of the complexes studied possess one of the seven-coordinate structures shown (bidentate ligand = $S_2CNR_2^-$).




L = O, NPh (1+) N, NO, NS. L = O, NPh. X = Cl, Br.

(1) Christensen, K. A.; Miller, P. E.; Minelli, M.; Rockway, T. W.; Enemark, J. H. *Inorg. Chim. Acta* **1981**, *56*, L27.
(2) Minelli, M.; Enemark, J. H.; Wieghardt, K.; Hahn, M. *Inorg. Chem.* **1983**, *22*, 3952.
(3) Gheller, S. F.; Hambley, T. W.; Traill, P. R.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Aust. J. Chem.* **1982**, *35*, 2183.
(4) 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.
(5) Alyea, E. C.; Topich, J. *Inorg. Chim. Acta* **1982**, *65*, L95.
(6) Buchanan, I.; Minelli, M.; Ashby, M. T.; King, T. J.; Enemark, J. H. *Inorg. Chem.* **1984**, *23*, 495.
(7) Minelli, M.; Yamanouchi, K.; Enemark, J. H.; Subramanian, P.; Kaul, B. B.; Spence, J. T. *Inorg. Chem.* **1984**, *23*, 2554.
(8) (a) Coughlan, M. P., Ed. "Molybdenum and Molybdenum Containing Enzymes"; Pergamon Press: Oxford, 1980. (b) Spence, J. T. *Coord. Chem. Rev.* **1983**, *48*, 59.
(9) Cramer, S. P.; Wahl, R.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1981**, *103*, 7721.

0020-1669/85/1324-1111$01.50/0 

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

| compd | chem shift, ppm | line width, Hz |
|---|---|---|
| $MoO_2(S_2CNMe_2)_2$ | 151 | 140 |
| $MoO_2(S_2CNEt_2)_2$[c] | 176 | 280 |
| $MoO_2(S_2CN\text{-}n\text{-}Pr_2)_2$ | 173 | 430 |
| $MoO_2(S_2CN\text{-}n\text{-}Bu_2)_2$ | 175 | 570 |
| $[MoO(S_2CNMe_2)_3]BF_4$ | 55 | 20 |
| $[MoO(S_2CNEt_2)_3]BF_4$ | 80 | 40 |
| $[MoO(S_2CN\text{-}n\text{-}Pr_2)_3]BF_4$ | 78 | 55 |
| $[MoO(S_2CN\text{-}n\text{-}Bu_2)_3]BF_4$ | 79 | 70 |
| $MoOCl_2(S_2CNMe_2)_2$ | 117 | 30 |
| $MoOBr_2(S_2CNMe_2)_2$ | 163 | 20 |
| $MoOCl_2(S_2CNEt_2)_2$ | 137 | 30 |
| $MoOBr_2(S_2CNEt_2)_2$ | 182 | 30 |
| $MoOCl_2(S_2CN\text{-}n\text{-}Pr_2)_2$ | 137 | 40 |
| $MoOBr_2(S_2CN\text{-}n\text{-}Pr_2)_2$ | 182 | 50 |
| $MoOCl_2(S_2CN\text{-}n\text{-}Bu_2)_2$ | 138 | 55 |
| $MoOBr_2(S_2CN\text{-}n\text{-}Bu_2)_2$ | 183 | 60 |
| $MoO(S_2)(S_2CNMe_2)_2$ | 139 | 50 |
| $MoO(S_2)(S_2CNEt_2)_2$ | 148 | 70 |
| $MoN(S_2CNMe_2)_3$ | −121 | 40 |
| $MoN(S_2CNEt_2)_3$ | −103 | 40 |
| $MoN(O\text{-}t\text{-}Bu)_3$ | 55 | 40 |
| $MoNCl_3$[b] | 952 | 80 |
| $PPh_4[MoNCl_4]$ | 1106 | <20 |
| $(PPh_4)_2[MoNCl_5]$ | 395 | 50 |
| $[Mo(NPh)(S_2CNEt_2)_3]BF_4$ | −294 | 450 |
| $Mo(NPh)Cl_2(S_2CNEt_2)_2$ | −254 | 480 |
| $Mo(NPh)Br_2(S_2CNEt_2)_2$ | −218 | 400 |
| $Mo(NO)_2(S_2CNMe_2)_2$[b,d] | −437 | 70 |
| $Mo(NO)_2(S_2CNEt_2)_2$[b,d] | −430 | 80 |
| $Mo(NO)(S_2CNMe_2)_3$ | −212 | 900 |
| $Mo(NO)(S_2CNEt_2)_3$ | −206 | 900 |
| $Mo(NS)(S_2CNMe_2)_3$ | 140 | 650 |
| $Mo(NS)(S_2CNEt_2)_3$ | 142 | 850 |

[a] Measured in $CH_2Cl_2$ at room temperature. [b] Measured in $CH_3CN$ at room temperature. [c] Reference 1. [d] Reference 22.

## Experimental Section

The complexes $MoO_2(S_2CNR_2)_2$,[10] $[MoO(S_2CNR_2)_3]BF_4$,[11] $MoOX_2(S_2CNR_2)_2$,[11,12] $MoN(S_2CNR_2)_3$,[13] $MoNCl_3$,[14] $PPh_4[MoNCl_4]$,[15] $(PPh_4)_2[MoNCl_5]$,[15] $[Mo(NPh)(S_2CNR_2)_3]BF_4$,[11,16] $Mo(NPh)X_2(S_2CNR_2)_2$,[16,17] $Mo(NO)(S_2CNR_2)_3$,[18] and $Mo(NS)(S_2CNR_2)_3$[19] (R = Me, Et, *n*-Pr, *n*-Bu; X = $Cl^-$, $Br^-$; $X_2 = S_2^{2-}$; Ph = $C_6H_5$) have been synthesized according to literature methods or modifications thereof.

The NMR spectra were obtained on a Bruker WM250 NMR spectrometer using dichloromethane, distilled from $P_2O_5$, as solvent in most cases.

The $^{95}$Mo NMR spectra were measured with a 10-mm molybdenum probe (16.3 MHz). To reduce the effects of probe ringing, 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 preacquistion delay was reduced to 100 μs. The transmitter output was amplified with a Heathkit 5B-201 (1 kW) linear amplifier. The input was attenuated to give a 26-μs 90° pulse. A 2 M $Na_2[MoO_4]$ solution in $D_2O$, effective pH 11, was used as external standard. Positive chemical shifts are deshielded relative to the standard.

The $^{14}$N spectra were measured at 18.1 MHz with a digitally selected 10-mm broad-band probe (12.3–101 MHz) on the same experimental arrangement described above for molybdenum. The $^{14}$N chemical shifts are reported relative to neat nitromethane.

Table II. $^{14}$N NMR Data for the $MoL(S_2CNR_2)_3$ (L = NO, NS) Compounds[a]

| compd | chem shift, ppm | line width, Hz |
|---|---|---|
| $Mo(NO)(S_2CNMe_2)_3$ | −14 | 40 |
| $Mo(NO)(S_2CNEt_2)_3$ | −14 | 40 |
| $Mo(NS)(S_2CNMe_2)_3$ | 42 | 150 |
| $Mo(NS)(S_2CNEt_2)_3$ | 39 | 140 |

[a] L ligand resonance only, in $CH_2Cl_2$ relative to external neat nitromethane at room temperature.

## Results and Discussion

The $^{95}$Mo NMR chemical shifts of the $[MoO(S_2CNR_2)_3]^+$ and $MoOX_2(S_2CNR_2)_2$ (R = Me, Et, *n*-Pr, *n*-Bu) complexes range from 55 to 183 ppm (Table I). The dimethyldithiocarbamato complexes are more shielded than their analogues; the ethyl, *n*-propyl and *n*-butyl complexes of a given series all exhibit very similar chemical shifts. The shielding effect of the dimethyldithiocarbamato ligand is a feature of all the series of dithiocarbamato complexes measured here; the shielding varies from 2 to 25 ppm. The monooxo complexes are shielded by about 100 ppm compared to the parent dioxo complexes, $MoO_2(S_2CNR_2)_2$ (ref 1 and this study). Replacement of one dithiocarbamato ligand of the $[MoO(S_2CNR_2)_3]^+$ complexes by two halo ligands deshields the $^{95}$Mo nucleus. The $MoOX_2(S_2CNR_2)_2$ complexes show an inverse halogen dependence;[20] i.e., the $^{95}$Mo nuclei of the chloro complexes are more shielded, by about 45 ppm, than those of the bromo complexes. The corresponding disulfido complexes absorb around 150 ppm, suggesting a shielding effect intermediate to $Cl^-$ and $Br^-$ for the $S_2^{2-}$ ligand. It should be noted, however, that the disulfido and halo complexes have cis *fac* and cis *mer* pentagonal-bipyramidal structures, respectively.[12,21]

In the nitrido complexes, $MoN(S_2CNR_2)_3$ (R = Me, Et), the $^{95}$Mo nuclei are shielded by about 180 ppm compared to the analogous monooxo complexes. These complexes absorb at the shielded end of the chemical shift range for nitrido complexes (Table I). The other extreme of the chemical shift range is defined by $[MoNCl_4]^-$. Addition of a chloro ligand to the latter complex leads to $[MoNCl_5]^{2-}$,[15] which is relatively more shielded and has an increased line width. In the complexes $MoNX_3$ (X = $Cl^-$, *t*-$BuO^-$), the chloro complex is relatively deshielded.

Of the seven-coordinate complexes studied, the $[Mo(NPh)]^{4+}$ complexes exhibit the lowest chemical shifts, i.e., have the most shielded $^{95}$Mo nuclei (Table I). Replacement of one dithiocarbamato ligand of $[Mo(NPh)(S_2CNEt_2)_3]^+$ by two $Cl^-$ or $Br^-$ ligands deshields the $^{95}$Mo nucleus, as found for the monooxo complexes. The $Mo(NPh)X_2(S_2CNEt_2)_2$ complexes also show an inverse halogen dependence. Indeed, an inverse halogen dependence appears to be a general feature of Mo(VI) complexes.[7,22]

Compared to the $[Mo(NPh)(S_2CNEt_2)_3]^+$ complex, the $[Mo(NO)]^{3+}$-containing complex $Mo(NO)(S_2CNEt_2)_3$ is deshielded by 88 ppm. The $Mo(NO)(S_2CNR_2)_3$ complexes are deshielded by 225 ppm relative to the corresponding dinitrosyl complexes, $Mo(NO)_2(S_2CNR_2)_2$ (Table I; ref 22).

Replacement of the nitrosyl group of $Mo(NO)(S_2CNR_2)_3$ by a thionitrosyl group deshields the molybdenum by about 350 ppm. This deshielding is small compared to the 551 ppm chemical shift difference that has been found for the complexes $MoL'(CO)_2(NO)$ and $MoL'(CO)_2(NS)$ [L′ = hydrotris(3,5-dimethylpyrazolyl)-

(10) Moore, F. N.; Larson, M. L. *Inorg. Chem.* **1967**, *6*, 998.
(11) Young, C. G.; Broomhead, J. A.; Boreham, C. J. *J. Chem. Soc., Dalton Trans.* **1983**, 2135.
(12) Dirand, J.; Ricard, L.; Weiss, R. *J. Chem. Soc., Dalton Trans.* **1976**, 278.
(13) Chatt, J.; Dilworth, J. R. *J. Indian Chem. Soc.* **1977**, *54*, 13.
(14) Dehnicke, K.; Weiher, U.; Straehle, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 1485.
(15) Dehnicke, K.; Kynast, U. *Z. Anorg. Allg. Chem.*, in press.
(16) Maatta, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 2409.
(17) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chim. Acta* **1980**, *41*, 49.
(18) Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Hursthouse, M. B.; Motevalli M. *J. Less-Common Met.* **1977**, *54*, 487.
(19) Bishop, M. W.; Chatt, J.; Dilworth, J. R. *J. Chem. Soc., Dalton Trans.* **1979**, 1.
(20) Kidd, R. G. NATO *Adv. Study Inst. Ser., Ser. C* **1983**, 445.
(21) (a) Dirand-Colin, J.; Ricard, L.; Weiss, R.; Schappacher, J. *J. Less-Common Met.* **1977**, *54*, 91. (b) Dirand, J.; Ricard, L.; Weiss, R. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 661.
(22) Minelli, M.; Hubbard, J. L.; Enemark, J. H. *Inorg. Chem.* **1984**, *23*, 970.

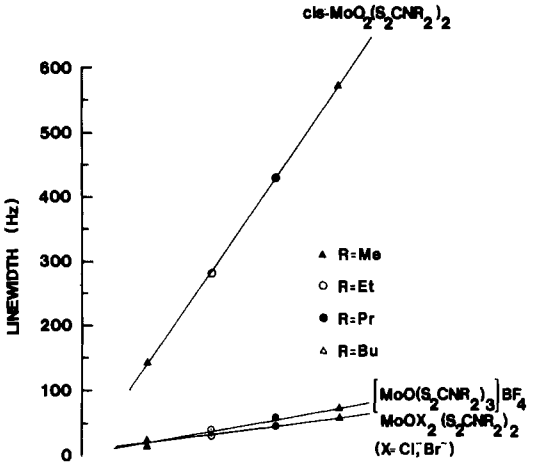



**Figure 1.** Influence of dithiocarbamato ligand substituent on the $^{95}$Mo NMR line width of selected compounds.

borate].[22] The $^{14}$N NMR data for the nitrosyl and thionitrosyl groups are listed in Table II; the $^{14}$N nuclei of the nitrosyl ligands are more shielded than those of the thionitrosyl ligands, as previously observed.[23] The analogous neutral $MoN(S_2CNR_2)_3$ complexes did not exhibit $^{14}$N resonances under similar experimental conditions.[24]

Neglecting the differences in formal oxidation state, the shielding of the $^{95}$Mo nucleus in the $[MoL(S_2CNR_2)_3]^{0/+}$ complexes increases in the order L = NS < O < N < NO < NPh. Attempts to synthesize the sulfur analogues, $[MoS(S_2CNR_2)_3]^+$, have not been successful to date. From the data reported for $[MoY_4]^{2-}$ complexes (Y = $O^{2-}$, $S^{2-}$, $Se^{2-}$)[4,25] one would expect such complexes to be deshielded relative to the oxo analogues.

The line width of a $^{95}$Mo NMR signal is determined by the relaxation time of the observed nucleus. In practice, this relaxation time is influenced by two important factors:[26] First, the local electric field gradient experienced by the nucleus may provide an efficient mechanism for relaxation via coupling to the nuclear quadrupole moment ($I = {}^5/_2$), resulting in extremely broad lines. Second, the molecular correlation time has a direct effect on the relaxation time of the nucleus. In a series of compounds having a similar electric field at the $^{95}$Mo nuclei, the predominant effect on line width should be the correlation time, a property of the molecular size, steric bulk, and solvent interaction. Such an effect is clearly illustrated by the steady increase in line width with increasing alkyl chain length observed for each class of compound studied herein (Table I). Figure 1 shows plots of the line widths of the $MoO_2(S_2CNR_2)_2$, $MoOX_2(S_2CNR_2)_2$ (X = $Cl^-$, $Br^-$), and $[MoO(S_2CNR_2)_3]^+$ complexes as a function of the length of the *n*-alkyl chain of the dithiocarbamato ligand. For a given alkyl group the $^{95}$Mo line width of the $MoO_2(S_2CNR_2)_2$ complex is ca. 7 times greater than the related monooxomolybdenum(VI) complex. From Figure 1, an *intrinsic line width* can be defined as the line width associated with a particular molybdenum coordination environment surrounded by minimum substituent steric bulk (i.e., the methyl complexes in the dithiocarbamato series). Clearly, the intrinsic line width associated with $MoO_2(S_2CNR_2)_2$ complexes is substantially greater than that of the $[MoO(S_2CNR_2)_3]^+$ complexes. It is important to note that the intrinsic line width would appear to be a property of the complete ligand set because other *cis*-dioxo complexes[7] exhibit smaller line widths than the *cis*-dioxodithiocarbamato complexes above. Given the similar molecular volumes and masses of the dimethyldithiocarbamato derivatives described herein, the intrinsic line width of each class of complex should be a semiquantitative measure of the electric field gradient of a $^{95}$Mo nucleus in a given coordination environment. From the data of Table I, the intrinsic line widths, and therefore the magnitudes of the electric field gradients, of the $[MoL(S_2CNR_2)_3]^{0/+}$ complexes follow the order L = O < N ≪ NPh < NS < NO.

This work has defined the $^{95}$Mo NMR characteristics of sulfur donor ligand complexes containing $[MoO]^{4+}$, $[MoN]^{3+}$, and $[Mo(NPh)]^{4+}$ moieties. The relative intrinsic line widths of the various coordination environments and the effect of steric bulk on the molecular correlation time have been determined by successively increasing the alkyl chain length of the dithiocarbamato ligands of the complexes. These results suggest that the observation of $^{95}$Mo NMR signals from molybdoenzymes will be difficult and that the intrinsic line width of the molybdenum center will play a large part in determining whether such signals can be detected.

**Acknowledgment.** We thank the U.S. Department of Agriculture for support of this work through Grant No. 81-CRCR-1-0626. We thank Dr. E. M. Kober for providing a sample of $MoN(O\text{-}t\text{-}Bu)_3$, Prof. K. Dehnicke for samples of $MoNCl_3$ and $PPh_4[MoNCl_4]$ and for providing us with information on new synthetic routes for the nitrido halide complexes, and Dr. K. A. Christensen for his technical assistance with the NMR spectrometer.

**Registry No.** $MoO_2(S_2CNMe_2)_2$, 39248-36-7; $MoO_2(S_2CNEt_2)_2$, 18078-69-8; $MoO_2(S_2CN\text{-}n\text{-}Pr_2)_2$, 18078-70-1; $MoO_2(S_2CN\text{-}n\text{-}Bu_2)_2$, 18078-71-2; $[MoO(S_2CNMe_2)_3]BF_4$, 88545-66-8; $[MoO(S_2CNEt_2)_3]BF_4$, 70788-19-1; $[MoO(S_2CN\text{-}n\text{-}Pr_2)_3]BF_4$, 94930-20-8; $[MoO(S_2CN\text{-}n\text{-}Bu_2)_3]BF_4$, 94930-22-0; $MoOCl_2(S_2CNMe_2)_2$, 59491-19-9; $MoOBr_2(S_2CNMe_2)_2$, 57146-53-9; $MoOCl_2(S_2CNEt_2)_2$, 57146-54-0; $MoOBr_2(S_2CNEt_2)_2$, 95042-41-4; $MoOCl_2(S_2CN\text{-}n\text{-}Pr)_2$, 59491-20-2; $MoOBr_2(S_2CN\text{-}n\text{-}Pr)_2$, 59491-21-3; $MoOCl_2(S_2CN\text{-}n\text{-}Bu)_2$, 94930-23-1; $MoOBr_2(S_2CN\text{-}n\text{-}Bu)_2$, 94930-24-2; $MoO(S_2)(S_2CNMe_2)_2$, 71393-29-8; $MoO(S_2)(S_2CNEt_2)_2$, 64525-55-9; $MoN(S_2CNMe_2)_3$, 54171-59-4; $MoN(S_2CNEt_2)_3$, 54171-60-7; $MoN(O\text{-}t\text{-}Bu)_3$, 82209-31-2; $MoNCl_3$, 14259-70-2; $PPh_4[MoNCl_4]$, 94930-25-3; $(PPh_4)_2[MoNCl_5]$, 94943-97-2; $[Mo(NPh)(S_2CNEt_2)_3]BF_4$, 88588-12-9; $Mo(NPh)Cl_2(S_2CNEt_2)_2$, 70749-53-0; $Mo(NPh)Br_2(S_2CNEt_2)_2$, 70749-54-1; $Mo(NO)_2(S_2CNMe_2)_2$, 26087-84-3; $Mo(NO)_2(S_2CNEt_2)_2$, 18810-45-2; $Mo(NO)(S_2CNMe_2)_3$, 20960-02-5; $Mo(NO)(S_2CNEt_2)_3$, 20960-03-6; $Mo(NS)(S_2CNMe_2)_3$, 54171-62-9; $Mo(NS)(S_2CNEt_2)_3$, 54171-63-0; $^{95}$Mo, 14392-17-7.

(23) Minelli, M.; Hubbard, J. L.; Lichtenberger, D. L.; Enemark, J. H. *Inorg. Chem.* **1984**, *23*, 2721.
(24) $^{14}$N signals were also undetectable for the other nitrido complexes in Table I. Presumably, this is due to a large electric field gradient at the $^{14}$N nuclei.
(25) Lutz, O.; Nolle, A.; Kroneck, P. *Z. Naturforsch., A* **1977**, *32a*, 505.
(26) Minelli, M.; Enemark, J. H.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G., submitted for publication in *Coord. Chem. Rev.*

Contribution from the Department of Nematology, University of California, Riverside, California 92521

## Chloroiron(III) Octaethylporphyrin in Pyridine Solution

C. E. Castro* and S. E. Anderson

*Received August 8, 1984*

The structure of iron(III) porphyrins in pyridine–water solutions has received considerable attention.[1-3] Depending upon pH μ-oxo dimers and pyridyl adducts can be obtained. In neat dry pyridine, or in organic solvents containing adequate concentrations of pyridine, however, it is generally held that the iron complexes exist as low-spin dipyridyl adducts. The visible[4] and NMR spectra[5] of these solutions accord with this view. Even at concentrations as low as $10^{-5}$ M in pyridine, however, there is a slight band in the visible centered around 627 nm.[4] We had assumed this very

(1) Gallagher, W. A.; Elliot, W. B. *Biochem. J.* **1968**, *108*, 131.
(2) Caughey, W. S.; Barlow, C. H.; O'Keefe, D. H.; O'Toole, M. C. *ann. N.Y. Acad. Sci.* **1973**, *206*, 296.
(3) White, W. L. In "The Porphyrins"; Dolphin D., Ed.; Academic Press: New York, 1978; Vol. V., Chapter 7, p 324.
(4) Chu, M. M. L.; Castro, C. E.; Hathaway, G. M. *Biochemistry* **1978**, *17*, 481.
(5) MaMar, G. N.; Bold, T. J.; Satterlee, J. D. *Biochim. Biophys. Acta* **1977**, *498*, 189.

0020-1669/85/1324-1113$01.50/0 