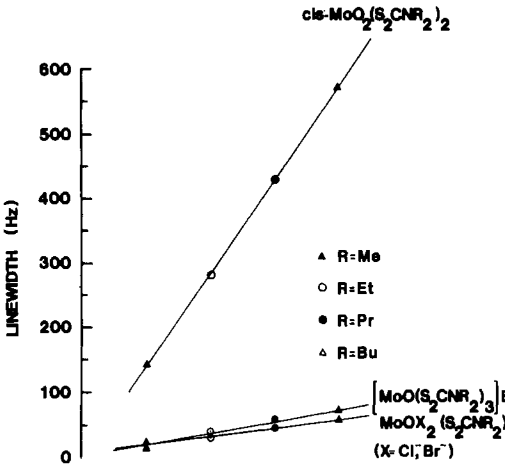

Figure 1. Influence of dithiocarbamato ligand substituent on the ^{95}Mo NMR line width of selected compounds.

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.

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(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.

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Chloroiron(III) Octaethylporphyrin in Pyridine Solution

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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

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minor absorption was simply characteristic of the dipyridyl adduct, though it is completely absent from solutions of the octaethyl complex in *N*-methylimidazole. As part of our studies of the redox chemistry of iron porphyrin complexes, it was found that solutions of chloroiron(III) octaethylporphyrin in pyridine at higher concentration were not reduced by reagents capable of reducing the dipyridyl adduct. This led to an investigation of the nature of species present in pyridine. To our surprise chloroiron(III) octaethylporphyrin exists in pyridine solutions as the high-spin $S = {}^5/_2$ complex in equilibrium with the dipyridyl adduct. The chloride complex can be the dominant species under certain conditions.

Experimental Section

Materials. Chloroiron(III) octaethylporphyrin was obtained and purified in the manner previously described.[6] Zinc octaethylporphyrin was prepared by refluxing the porphyrin with $Zn(OAc)_2 \cdot 2H_2O$ in chloroform–methanol.[7] The recrystallized needles showed a parent at m/e 596 in the mass spectrum. There were no higher mass peaks. Tetraphenylarsonium chloride, sodium tetraphenylborate, and tetra-*n*-butylammonium perchlorate and tetrafluoroborate were analytical grade and were used without purification. Reagent grade pyridine was refluxed with $KMnO_4$, distilled, dried over KOH, and redistilled through a small Vigreux column under argon; bp 115 °C. The solvent was stored over molecular sieves. Phillips research grade cyclohexane, Aldrich Gold Label pyridine-d_5, and Aldrich tetramethylsilane were used without purification.

Physical Measurements. Magnetic Moments. An NMR solvent of 2% cyclohexane or tetramethylsilane in pyridine-d_5 was stored under argon over molecular sieves. Stock solutions of the porphyrin complexes were made to volume and stored over sieves. Commercial two-compartment concentric NMR tubes were used in applying the Evans[8] method for measurement of the magnetic moments. Pyridine-d_5 solutions of iron porphyrins containing Me_4Si or cyclohexane as reference were placed in the outer compartment, and those of Zn(II) octaethylporphyrin at the same concentration of complex and reference were placed in the inner tube. The probe temperature of the Varian EM-390 machine was 34 °C. Under these conditions for pyridine solution

$$\chi_m^{cor} = 5.36 \times 10^{-6} (\Delta f/M) + 406 \times 10^{-6} \qquad (1)$$

where Δf (Hz) is the difference in frequencies observed for the reference in the two solutions and M is the concentration of iron porphyrin. Equation 1 is corrected for density. The last term represents the molar susceptibility of solvent and a diamagnetic correction for Cl^-. From the expressions (1) and (2) a Δf of 28.4 Hz (observed for 0.0112 M iron(III)

$$\mu_{eff} = 2.82(\chi_m^{cor}(307))^{1/2} \qquad (2)$$

porphyrin) corresponded to a μ_{eff} of 5.81 μ. The variation of μ_{eff} with concentration is shown in Figure 3. Repeat measurements of Δf after 4 days agreed within 15%. Duplicate measurements from fresh solutions were also in this range. Magnetic moments measured in the presence of other ions were obtained by adding the same concentrations of salt to the iron porphyrin and zinc porphyrin reference solutions.

Osmometry. A Mechrolab-301 vapor-phase osmometer was calibrated with stock solutions of benzil in pyridine. A plot of ΔR vs. benzil concentration was linear over the range 0.001–0.04 M. Reproducibility was within 11%.

Visible Spectra. A Cary 118C spectrophotometer was employed at 34 °C. A change in temperature from 27 to 34 °C had a negligible effect on the spectrum. A molar extinction coefficient of 4.58×10^3 at 627 nm was obtained for chloroiron(III) octaethylporphyrin in pyridine. The value was calculated from solutions of the complex in pyridine sturated with Cl (Figure 2). An extinction coefficient for the bis(pyridinato) adduct, 1.34×10^3, was determined from solutions of the iron porphyrin in pyridine at very high concentrations of n-Bu4N$^+$ClO$_4^-$ or from very dilute solutions of the complex and long path length cells.

Results

The influence of dilution upon the intensity of the 627-nm charge-transfer band of the chloroiron(III) porphyrin is illustrated in Figure 1. Identical solutions containing 0.15 M Cl^- (Ph_4AsCl) are however isoabsorbing. The influence of Cl^- and other salts is more strikingly shown in Figure 2. The ions were added as the following salts: Ph_4AsCl, $NaBPh_4$, n-Bu_4NClO_4, and n-Bu_4NBF_4. Chloride enhances the absorption to saturation. On the other hand, the salts of BF_4^-, BPh_4^- (not shown), and ClO_4^- all cause a dramatic decrease in absorption and a shift in the spectrum to that associated with the bis(pyridinato) adduct. The same effect is obtained by diluting the complex. These results are consistent with the simple equilibrium (3). Chloride ion

$$PFe{-}Cl \overset{py}{\rightleftharpoons} PFe(py)_2^+ + Cl^- \qquad (3)$$

suppresses the ionization of the Fe–Cl bond, and increased ionic strength favors its dissociation. An equilibrium constant for (3) derived from all of the visible spectra is $(2.5 \pm 0.7) \times 10^{-5}$ mol/L.

The influence of the concentration upon the magnetic moment of the iron complexes is illustrated in Figure 3. Qualitatively, the data show the same trend indicated by the visible spectrum. The more dilute solutions contain an increasing amount of the low-spin bis(pyridinato) adduct. At higher concentrations $>2 \times 10^{-3}$ M the high-spin chloroiron(III) complex predominates. The moments for more dilute solutions could not be measured reliably.

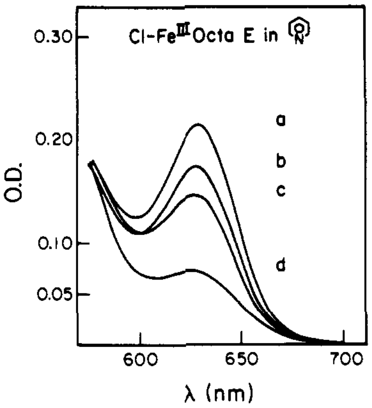

Figure 1. Visible spectrum of chloroiron(III) octaethylporphyrin in pyridine solutions at different concentrations: (a) 5.23×10^{-4} M (0.10-cm cell); (b) 1.05×10^{-4} (0.5 cm); (c) 5.23×10^{-5} M (1.0 cm); (d) 5.23×10^{-6} M (10 cm).

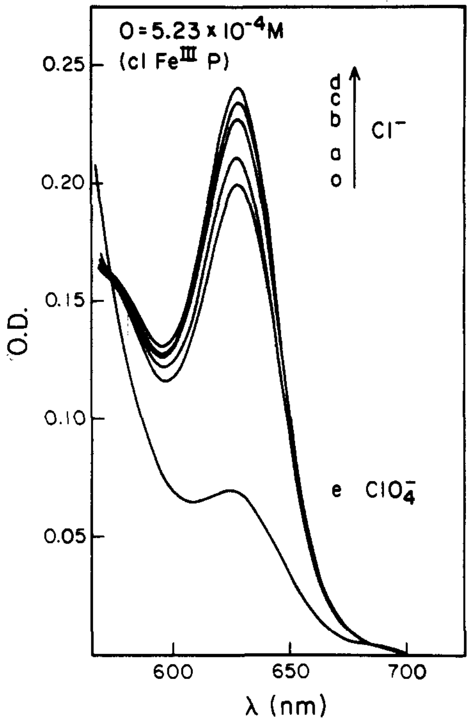

Figure 2. Influence of Cl^- and ClO_4^- salts upon the visible spectrum of chloroiron(III) octaethylporphyrin: (O) no added salt; (a) pyH^+Cl^-, 1.60×10^{-4} M; (b) Ph_4AsCl, 1.78×10^{-4} M; (c) Ph_4AsCl, 8.90×10^{-4} M; (d) Ph_4AsCl, 1.78×10^{-3} and 4.18×10^{-3} M; (e) n-Bu_4NClO_4, 0.18 M.

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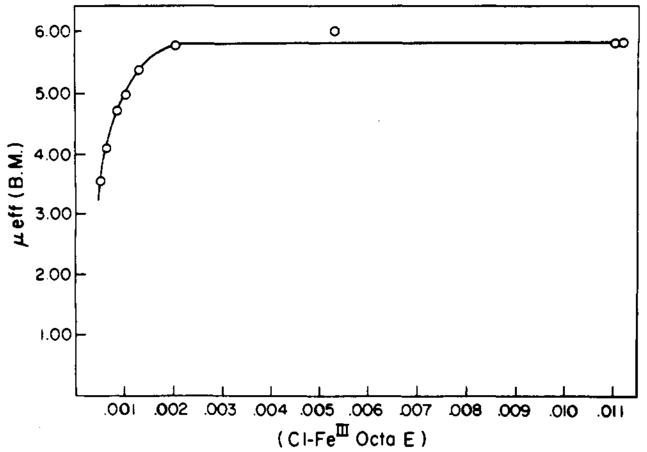

Figure 3. Magnetic moments of iron(III) porphyrin solutions as a function of concentration.

Table I. μ_{eff} of Chloroiron(III) Octaethylporphyrin in Pyridine–Effect of Salts and Water

[Fe^{III}Por], mol/L	anion	[anion], mol/L	μ_{eff}, μ_B	
			exptl	calcd
6.54×10^{-3}			5.87	5.60
	H_2O	0.10	5.17	5.11
2.9×10^{-3}	ClO_4^-	0.102	3.74	3.0
	BF_4^-	0.0822	3.34	3.20
5.23×10^{-3}	BPh_4^-	0.064	2.57	2.24
8.72×10^{-4}	Cl^-	0.13	5.11	5.92

However, a direct comparison of magnetic and spectral data was possible. The influence of water and added salts upon μ_{eff} is portrayed in Table I. The values of μ_{eff} in the final column are those calculated from visible spectra. For this purpose μ_{eff} for the low-spin bis(pyridinato) adduct was taken as 2.24 μ_B. The spin-only value (5.92 μ_B) was used for the chloroiron(III) adduct. The moment was calculated from the distribution of high-spin Fe-Cl and low-spin Fe-$(py)_2^+$ species derived from the optical density at 627 nm or determined from the equilirbium constant. The agreement is within the experimental error of our methodology.

Osmometric measurement of chloroiron(III) octaethylprophyrin in pyridine at 0.01 and 0.001 M indicate only a slightly greater concentration of particles than that observed for the benzil standard. A comparison of octaethylporphyrin at 0.001 M with the chloroiron(III) complex indicated both to be 0.001 M within experimental error.

In sum, chloroiron(III) octaethylporphyrin in pyridine solution exists predominantly as the undissociated adduct at concentrations greater than 10^{-3} M. Indeed, detectable quantities of the nondissociated species exist at 5×10^{-5} M. Water (0.1 M) does not markedly influence the degree of ionization. On the other hand salts not containing chloride increase the ionic strength of the solution and facilitate the dissociation of the complex to the low-spin bis(pyridinato) adduct.

Our results allow no quantitative assessment of the extent of pyridine solvation of the chloroiron(III) adduct. Qualitatively, however, they suggest the monopyridinato adduct is not a major species in these solutions. Thus, it is unlikely that the equilibrium constant for the affiliation of one pyridine with iron(III) would exceed that for two.[9–11] Moreover, the visible spectrum of the chloride salt in pyridine is remarkably similar to that observed in poor conditioning solvents. For example, the extinction coefficient at 627 nm in pyridine and chloroform are the same (±1%), and there is only a slight shift in the center of the broad change-transfer band (chloroform 633 nm; benzene, toluene 630 nm). In contrast, the visible spectrum of the monoimidazole adduct of chloroiron(III) tetraphenylporphyrin[11] differs substantially from that of the parent iron complex.

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Registry No. PFeCl, 28755-93-3; PFe(py)$_2$, 19496-63-0.

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A Reinvestigation of the Bonding in Bis[*N*-(2-mercaptoethyl)salicylidineaminato]oxovanadium(IV)

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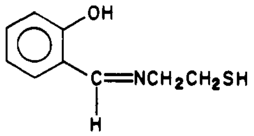
The vanadyl complex of *N*-(2-mercaptoethyl)salicylidineamine (I), a Schiff base ligand derived from the reaction of salicylaldehyde and 2-aminoethanethiol, was first prepared by Syamal.[1] It was reported to be a complex of the VOL_2 type (L = a bidentate, 1– anion) although the ligand has three potential donor atoms: O, N, and S. This is in contrast to the vanadyl complex of *N*-(2-hydroxyethyl)salicylidineamine (II), which is an ONO analogue of I. The latter vanadyl complex was reported to be of the VOL′ type[2] (L′ = a tridentate, 2– anion).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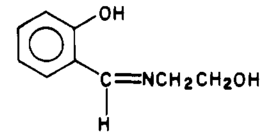
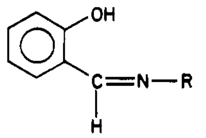

II

Specifically, Syamal[1] states that ligand I behaves as a bidentate monobasic ligand. This, he says, is supported by the IR spectrum, which shows a band at 3100 cm^{-1}. In another paper[3] on a series of vanadium complexes with similar Schiff base ligands, Syamal claims specifically that the 3100-cm^{-1} band is due to the O–H stretch of the ligands. This can only mean that the N and S atoms coordinate to the vanadyl group, leaving the hydroxyl group nonbonded.

We found this conclusion about the bonding in the complex rather unusual because for similar Schiff base ligands derived from salicylaldehyde or substituted salicylaldehyde and amines, the phenolic oxygens are always bonded to metals.[4] Pasquali et al.,[5] for example, showed that the Schiff base ligands III used their phenolic oxygens in bonding to the vanadium atom. The ligand H_2salen [bis(salicylaldehyde) *N,N′*-ethylenediimine] has long been known to use both hydroxyl groups in bonding to metals.[4] It


R=alkyl, Ar, R′-Ar
III

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