

[CONTRIBUTION FROM THE HERCULES RESEARCH CENTER, WILMINGTON, DELAWARE]

Electron Spin Resonance of Some Vanadium and Titanium Compounds

BY JAMES C. W. CHIEN AND CHARLES R. BOSS

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The electron spin resonance, e.s.r., of V(IV) in heptane solutions of VCl_4 (8×10^{-4} to $8 \times 10^{-2}M$ concentrations) and of $VCl_2(O-n-C_4H_9)_{4-x}$, where $x = 0, 1, 2$ and 3 , cannot be observed from 90 to 330°K. $VCl_2(OR)_2(ROH)$, where R is *n*- and *t*-butyl, give well-resolved e.s.r. spectra. The e.s.r. spectra of $(\pi-C_6H_5)_2Ti(C_2H_5)_2$, $(\pi-C_6H_5)_2VCl_2$, $(\pi-C_6H_5)_2V(C_6H_5)_2$ and $(\pi-C_6H_5)_2V(C_6H_4CH_3)_2$ are also presented. The spectra of the last two compounds constitute the first observed room-temperature spin resonance of V(III). These results are interpreted with the paramagnetic relaxation mechanism based on interaction between the ground state and a nearby Stark excited state. The variation of line width and hyperfine constant on the nuclear orientation and on the solvent used are attributed to the "microcrystal" mechanism.

Introduction

Electron spin resonance, e.s.r., has been used widely to elucidate the symmetry of crystals of paramagnetic salts, to study the structures of organic free radicals, to measure the magnetic properties of color centers and to determine the spin densities in aromatic anions and cations. Triplet state molecules, biradicals and carbonaceous materials also have been investigated using this new technique. However, only a few organometallic compounds have been studied. Singer¹ reported the e.s.r. of tris-(acetylacetonato)-Cr(III). Jarrett² extended the measurements to the acetylacetonate complexes of Ti(III), Mn(III), Fe(III), Mo(III) and Rh(III). These authors found a strong axial field in these complexes. Jarrett suggested that the three d_e degenerate orbitals of the metal overlap with the π orbitals of the oxygen. The result of such " π -conjugation" is to lift the degeneracy of the d_e orbitals to give an A, and an E, state and is equivalent to superposing on the cubic field a rhombic crystal field of D_3 symmetry.

Several chelates of Cu(II) have been studied by e.s.r., namely: bis-(dimethylglyoximate)-Cu(II),³ bis-(acetylacetonato)-Cu(II)⁴ and bis-(salicylaldehydeimine)-Cu(II). Spin resonance spectra of vanadyl acetylacetonate⁵ and vanadyl etioporphyrin I⁶ have been reported.

The e.s.r. spectrum of dibenzenechromium cation⁷ shows a *g*-factor of 1.98, a 15-gauss line width and barely resolved proton hyperfine structures. The e.s.r. spectrum of bis-(cyclopentadienyl)-vanadium⁸ shows a *g*-factor of 2.00 and a V^{51} hyperfine splitting of only 26 gauss.

Recently, research activity on the chemistry of organometallic compounds of transition metals has been greatly accelerating. In this note, the first e.s.r. results for several such compounds are presented.

Experimental

VCl_4 was obtained from Stauffer Chemical Co., N. Y. $VCl_2(O-n-C_4H_9)_{4-x}$ was prepared by the slow addition of a heptane solution of VCl_4 to a stirred suspension of $NaO-n-C_4H_9$ in heptane under nitrogen. The heptane solutions

of these vanadium esters were various hues of brown. The vanadium and its oxidation state were determined spectrophotometrically. The Volhard method was used in the chlorine determinations and the Zeisel method was used in the analysis of the butoxy groups. The V:Cl:O-*n*-C₄H₉ mole ratios found were: $VCl_3(O-n-C_4H_9)_2$; 1.0:2.8:0.8; $VCl_2(O-n-C_4H_9)_3$; 1.0:1.8:2.1; $VCl(O-n-C_4H_9)_4$; 1.0:1.3:2.9; and $V(O-n-C_4H_9)_4$; 1.0:0.05:3.9.

The reaction products from VCl_4 and *n*- and *t*-butyl alcohols also were investigated. In these reactions, a heptane solution of the alcohol was added to a heptane solution of VCl_4 under nitrogen. At alcohol to VCl_4 ratios of 2:1 to 6:1, brown to black precipitates were obtained. These precipitates were insoluble in the parent alcohols and contained two chlorines per vanadium. Excess 1-butanol reacted with VCl_4 to give a clear, green solution with an absorption maximum at 14,300 cm^{-1} . Drying this solution gave solid, green $VCl_2(O-n-C_4H_9)_2 \cdot (n-C_4H_9OH)$ (I). Excess *t*-butyl alcohol reacted with VCl_4 to give a clear, blue solution with an absorption maximum at 15,400 cm^{-1} . Drying this solution gave solid, dark green $VCl_2(O-t-C_4H_9)_2 \cdot (t-C_4H_9OH)$ (II).

The brown heptane solution of $VCl_2(O-n-C_4H_9)_2$ turned green upon addition of excess 1-butanol. This solution gave a visible spectrum identical with that of the solution of I.

The compounds $(\pi-C_6H_5)_2Ti(C_2H_5)_2$ and $(\pi-C_6H_5)_2VCl_2$ were prepared by Dr. W. P. Long of this Laboratory. $(\pi-C_6H_5)_2V(C_6H_5)_2$ and $(\pi-C_6H_5)_2V(C_6H_4CH_3)_2$ were gifts from Prof. van der Kerk.⁹

The e.s.r. spectra were obtained with a Varian Associates X-band spectrometer and a 12-in. electromagnet. In these experiments, the concentration of unpaired spins in a specimen was determined by comparing the e.s.r. spectral intensity (first moment) with that of a standard solution of vanadyl acetylacetonate in a medium identical with that of the unknown. Both spectra were obtained with the same modulation amplitude and microwave power. This procedure is necessary because solvents with different values of loss tangent affect the "loaded" Q of the microwave cavity differently. Therefore, the relative e.s.r. spectral intensities of vanadyl acetylacetonate at the same concentrations in benzene, toluene, methylene chloride, chloroform, chlorobenzene, *o*-dichlorobenzene and 1:1 benzene-chlorobenzene were 10.0, 7.0, 6.1, 2.9, 2.7, 1.1 and 4.05, respectively. The cavity resonance disappeared when a dimethylformamide solution of vanadyl acetylacetonate was inserted into the cavity. The relative e.s.r. spectral intensities of α, α' -diphenylpicrylhydrazyl at the same concentrations in benzene, chloroform, chlorobenzene and *o*-dichlorobenzene were 10, 3.1, 2.8 and 1.2, respectively.

Results

The e.s.r. of V(IV) in heptane solutions of VCl_4 (8×10^{-4} to $8 \times 10^{-2}M$ concentrations) cannot be observed from 90 to 300°K. and from 500 to 14,000 gauss. At 90°K., VCl_4 is brilliant green. Heptane solutions of $VCl_2(O-n-C_4H_9)_{4-x}$, where $x = 0, 1, 2$ and 3 , also failed to give observable e.s.r. absorption at both 90 and 300°K. (Table I).

Addition of excess 1-butanol to the brown heptane solution of $VCl_2(O-n-C_4H_9)_2$ changed the color

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TABLE I
 E.S.R. SPECTRAL PARAMETERS OF SOME VANADIUM AND TITANIUM COMPOUNDS

Compound	Solvent	Concn., molar	Temp., °K.	<i>g</i> -value	<i>A</i> , gauss	Line width, gauss	Remark
VCl ₄	Heptane	8 × 10 ⁻⁴ to 8 × 10 ⁻²	90 to 300				Negative ^a
VCl ₃ (<i>O-n</i> -C ₄ H ₉)	Heptane	1 × 10 ⁻²	90 and 300				Negative
VCl ₂ (<i>O-n</i> -C ₄ H ₉) ₂	Heptane	1 × 10 ⁻²	90 and 300				Negative
VCl(<i>O-n</i> -C ₄ H ₉) ₃	Heptane	1 × 10 ⁻²	90 and 300				Negative
V(<i>O-n</i> -C ₄ H ₉) ₄	Heptane	1 × 10 ⁻²	90 and 300				Negative
1VCl ₄ -1 <i>n</i> -C ₄ H ₉ OH	Heptane	7 × 10 ⁻²	300	1.95		360	No hf ^b
1VCl ₄ -3 <i>n</i> -C ₄ H ₉ OH	Heptane	6 × 10 ⁻²	300	^c	98, 131	^d	Two 8-line spectrum
1VCl ₄ -4 <i>n</i> -C ₄ H ₉ OH	Heptane	5 × 10 ⁻²	300	^c	98, 131	^d	Two 8-line spectrum
1VCl ₄ -20 <i>n</i> -C ₄ H ₉ OH	Heptane	7 × 10 ⁻²	300	1.95	112	32	60% of theoretical intensity
1VCl ₄ -30 <i>n</i> -C ₄ H ₉ OH	Heptane	6 × 10 ⁻²	300	1.95	112	25	70% of theoretical intensity
1VCl ₂ (<i>O-n</i> -C ₄ H ₉) ₂ - 30 <i>n</i> -C ₄ H ₉ OH	Heptane	5 × 10 ⁻²	300	1.95	111	25	70% of theoretical intensity
1VCl ₄ -10 <i>t</i> -C ₄ H ₉ OH	Heptane	7 × 10 ⁻²	300	1.95	112.5	24	45% of theoretical intensity
1VCl ₄ -20 <i>t</i> -C ₄ H ₉ OH	Heptane	6 × 10 ⁻²	300	1.95	112.5	21	86% of theoretical intensity
1VCl ₄ -30 <i>t</i> -C ₄ H ₉ OH	Heptane	5 × 10 ⁻²	300	1.95	112.5	21	100% of theoretical intensity
(<i>π</i> -C ₆ H ₆) ₂ VCl ₂	Benzene	0.9 × 10 ⁻³	300	1.99	71.2	7.2	100% of theoretical intensity
(<i>π</i> -C ₆ H ₆) ₂ VCl ₄	Chloroform	4.6 × 10 ⁻³	300	1.99	74.1	10.4	98% of theoretical intensity
(<i>π</i> -C ₆ H ₆) ₂ V(C ₆ H ₆)	Toluene	~1 × 10 ⁻³	300	2.13		1000	No hf
(<i>π</i> -C ₆ H ₆) ₂ V(C ₆ H ₄ CH ₃)	Toluene	~1 × 10 ⁻²	300	2.13		1000	No hf
(<i>π</i> -C ₆ H ₆) ₂ Ti(C ₂ H ₅)	Toluene	~1 × 10 ⁻³	300	1.94		20	No hf

^a No observable e.s.r. absorption. ^b Single line spectrum. ^c Center of spectrum cannot be accurately located. ^d Line width cannot be accurately measured.

to green. This solution gave a well-resolved e.s.r. spectrum with an average V⁵¹ hyperfine splitting, *A*, of 111 gauss, and a *g*-factor of 1.95. The spectral intensity was 70% of the theoretical intensity.

The insoluble reaction product of an equimolar mixture of VCl₄ and 1-butanol gave a very weak and broad spectrum with a line width of about 360 gauss. The 1:3 and 1:4 mixtures had very weak e.s.r. spectra which appeared to consist of 16 lines. Green solutions were obtained when excess 1-butanol was added to VCl₄. The spectral intensities for the 1:20 and 1:30 solutions were 60 and 70% of the theoretical intensity, respectively. The spectral parameters were: *A* = 112 gauss and *g* = 1.95.

Reactions of VCl₄ and *t*-butylalcohol gave products which had e.s.r. spectra similar to the corresponding products from 1-butanol. The blue solutions obtained at VCl₄:*t*-BuOH ratios of 1:10, 1:20 and 1:30 had spectral intensities 45, 86 and 100% of the theoretical intensity, respectively. The spectral parameters were: *A* = 112.5 gauss and *g* = 1.95.

The e.s.r. spectra of (*π*-C₆H₆)₂VCl₂ both in benzene and in chloroform solutions have a near free electron *g*-factor of 1.99. The spectral parameters in the 0.92 × 10⁻³ *M* benzene solution were: *A* = 71.2 gauss and line width = 7.2 gauss. The corresponding parameters in the 4.6 × 10⁻³ chloroform solution were: *A* = 74.1 gauss and line width = 10.4 gauss.

The toluene solutions of (*π*-C₆H₆)₂V(C₆H₆) and (*π*-C₆H₆)₂V(C₆H₄CH₃) gave identical room-temperature e.s.r. spectra. The line width was about 1000 gauss, the complete spectrum had a span of about 5000 gauss. The value for the *g*-factor was 2.13.

A toluene solution of (*π*-C₆H₆)₂Ti(C₂H₅) gave an unsymmetrical room-temperature e.s.r. spectrum. The line width was 20 gauss and the *g*-factor was 1.94.

Discussion of Results

VCl₄ is paramagnetic¹⁰ and has a moment close to that of one unpaired electron spin both in the pure compound and in CCl₄ solution. The magnetic susceptibility of chlorovanadic ester has not been measured. The failure to observe the V(IV) spin resonance in VCl₄ and VCl₂(*O-n*-C₄H₉)_{4-x} is attributed to very short relaxation times in these systems. The line width is related approximately to the relaxation times by

$$\text{Line width} \approx \frac{1}{\pi T_2'} + \frac{1}{\pi T_1}$$

where *T*₁ is the spin-lattice relaxation time and *T*₂' is the transverse relaxation time. Both spin-lattice and spin-spin relaxation processes contribute to *T*₂'.

The failure to observe e.s.r. absorption in these vanadium compounds means that their line widths are in excess of 2000 gauss. Van Vleck¹¹ showed

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that T_1 decreases greatly when there is interaction between the ground state and a nearby excited state. Therefore, transition metal compounds with degenerate ground states or with small separation between the ground state and the next higher state have efficient paramagnetic relaxation. The e.s.r. line widths are broad. For compounds of low symmetry, the ligand field splitting is large, leading to large separation between the ground state and the next excited state. Paramagnetic relaxation is slow and the e.s.r. line width is narrow.

Ti(III) has the $3d^1$ -configuration. In the aquated Ti(III) ions, the octahedral ligand field splits the five-fold orbital level into a Γ_3 and a Γ_5 state, the latter being lower. The ground sextet is further split by spin-orbit coupling into three Kramers' doublets. The separation between them is small. The "turned over" spin is relaxed by the spin-orbit and orbit-lattice perturbation. McGarvey¹² reported that the e.s.r. of aquated Ti(III) ion was not observed. The resonance of the Ti(III) in $\text{CsTi}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was observed¹³ below 8°K. The dominant crystal field was probably cubic.

The intrinsic symmetry of $(\pi\text{-C}_6\text{H}_5)_2\text{Ti}(\text{C}_2\text{H}_5)$ is very low. The strong ligand field of low symmetry increases the separation between the Kramers' doublets. Consequently, the transition probability of paramagnetic relaxation is reduced, leading to narrow line width e.s.r. absorption.

V(IV) also has the $3d^1$ -configuration. VCl_4 was found to be a tetrahedral molecule by electron diffraction measurements.¹⁴ The tetrahedral field splits the five-fold orbital level into a Γ_5 and a Γ_3 state, the latter being lower. The ground quartet is further split to a pair of Kramers' doublets by spin-orbit coupling and by the Jahn-Teller effect. The separation of the two Kramers' doublets must be very small because the e.s.r. absorption of VCl_4 was not observable at 90°K.

The fact that the e.s.r. in $\text{VCl}_2(\text{O}-n\text{-C}_4\text{H}_9)_{4-x}$ was not observed indicates a symmetrical structure for these esters. A probable one is the cyclic trimeric structure of a trigonal prism. This structure also was postulated¹⁵ for the trimeric $\text{Ti}(\text{O}-n\text{-C}_4\text{H}_9)_4$ and $\text{TiCl}(\text{O}-n\text{-C}_4\text{H}_9)_3$. The insoluble products from the reactions of VCl_4 and butyl alcohols probably are polymeric octahedra bridged by alkoxy groups.

Bradley, *et al.*,¹⁶ found that $\text{VCl}_2(\text{OR})_2(\text{ROH})$ is dimeric in boiling benzene and postulated a structure comprising two octahedra bridged by alkoxy groups. Strong axial fields are possible in these dimers. Narrow e.s.r. absorption lines were resolved in I and II. The experimental spectral intensity of II agreed with the theoretical intensity, indicating that $\text{VCl}_2(\text{O}-t\text{-C}_4\text{H}_9)_2 \cdot (t\text{-C}_4\text{H}_9\text{OH})$ is completely dimeric in heptane. On the other hand, the spectral intensity of I was only 60–70% of the calculated intensity. It appears that in I there is an equilibrium between the sol-

vated dimeric species and the non-solvated trimeric species.

The symmetry of $(\pi\text{-C}_6\text{H}_5)_2\text{VCl}_2$ is not known. It is likely that the symmetry is lower than C_{2v} . The e.s.r. spectrum of $(\pi\text{-C}_6\text{H}_5)_2\text{VCl}_2$ consisted of eight well-resolved lines having about the same width, Fig. 1. Rogers and Pake¹⁷ found that for

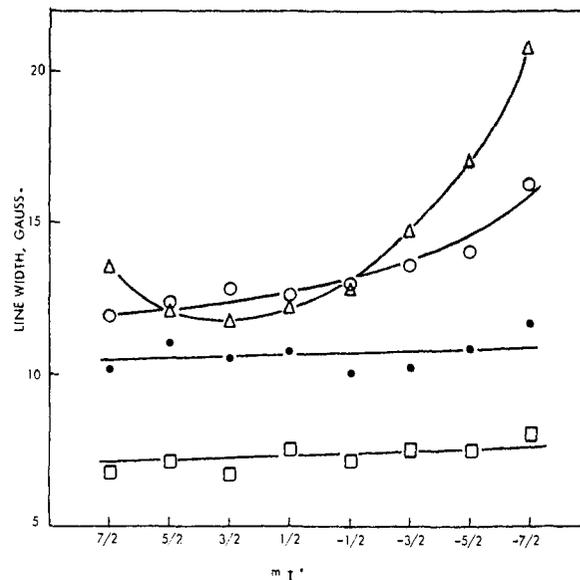


Fig. 1.—Plot of line width versus M_1 at X-band frequency: \square , $0.92 \times 10^{-3} M$ $(\pi\text{-C}_6\text{H}_5)_2\text{VCl}_2$ in benzene; \bullet , $4.6 \times 10^{-3} M$ $(\pi\text{-C}_6\text{H}_5)_2\text{VCl}_2$ in chloroform; \circ , $10^{-2} M$ and $10^{-3} M$ vanadyl acetylacetonate in benzene; Δ , $5 \times 10^{-2} M \text{VO}^{++}$.¹⁸

aqueous solutions of VO^{++} , the electron line width varies with the vanadium nuclear orientation according to the "microcrystalline" mechanism proposed by McConnell.¹⁸ In this mechanism, a relatively stable short-range order between the transition metal ions and the nearest solvent neighbors was postulated to form "microcrystals" giving rise to anisotropies in the g -tensor and in the hyperfine interaction tensor. Therefore, widths of lines in aquated VO^{++} with different values of nuclear spin quantum number, M_1 , differ by as much as 10 gauss¹⁸ (Fig. 1). Similar line width dependence on M_1 was found in benzene solutions of vanadyl acetylacetonate. The lines in the heptane solutions of $\text{VCl}_2(\text{OR})_2(\text{ROH})$ were not sufficiently resolved to be included in these discussions.

The electron line width showed only slight dependence on nuclear orientation in both the benzene solution and the chloroform solution of $(\pi\text{-C}_6\text{H}_5)_2\text{VCl}_2$, (Fig. 1). On the other hand, the e.s.r. spectrum of $(\pi\text{-C}_6\text{H}_5)_2\text{VCl}_2$ in benzene has an average line width of 7.2 gauss and an average hyperfine constant of 71.2 gauss. The spectrum of the chloroform solution of $(\pi\text{-C}_6\text{H}_5)_2\text{VCl}_2$ has an average line width of 10.4 gauss and an average hyperfine constant of 74.1 gauss. The variation of the magnitude of the hyperfine constant and of the line width with the solvent used indicate the presence of "microcrystallites" even though the

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line width variation with M_1 is not significant. Inspection of the equation derived by Kivelson¹⁹ showed that these observations are consistent with small anisotropies in the g -tensor and in the hyperfine interaction tensor. It will be interesting to make line width measurements on $(\pi\text{-C}_6\text{H}_5)_2\text{VCl}_2$ at the K-band frequency to bring out significant line width dependence on nuclear orientation.

The e.s.r. spectra of $(\pi\text{-C}_6\text{H}_5)_2\text{V}(\text{C}_6\text{H}_5)$ and $(\pi\text{-C}_6\text{H}_5)_2\text{V}(\text{C}_6\text{H}_4\text{CH}_3)$ have line-widths of 1000 gauss. The ground state of V(III) is $3F_2$. The seven-fold orbital level is split by a cubic field to Γ_4 , Γ_5 and Γ_2 states, the first being the lowest. No room temperature V(III) spin resonance has been reported before. Jarrett² was not able to observe the spin resonance in tris-(acetylacetonato)-V(III) at liquid nitrogen temperature. The e.s.r. spectrum of tris-(acetylacetonato)-Ti(III) was readily observed under similar experimental conditions. He concluded that in V(III) the orbital degeneracy of the Γ_4 state was not lifted by the axial field. Lambe and Kikuchi²⁰ reported that in $\alpha\text{-Al}_2\text{O}_3$, the spin resonances of V(II) and V(IV) were obtained at room temperature but the spin resonance of V(III) was obtained only at 4°K. Here, the crystalline field was primarily trigonal.

The symmetries in $(\pi\text{-C}_6\text{H}_5)_2\text{V}(\text{C}_6\text{H}_5)$ and in $(\pi\text{-C}_6\text{H}_5)_2\text{V}(\text{C}_6\text{H}_4\text{CH}_3)$ are lower than C_{2v} . These compounds gave the first observed room temperature e.s.r. spectra of V(III). While the line width in the spectrum of $(\pi\text{-C}_6\text{H}_5)_2\text{Ti}(\text{C}_2\text{H}_5)$ is only 20

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gauss, the line widths in the spectra of $(\pi\text{-C}_6\text{H}_5)_2\text{V}(\text{C}_6\text{H}_5)$ and $(\pi\text{-C}_6\text{H}_5)_2\text{V}(\text{C}_6\text{H}_4\text{CH}_3)$ were about 1000 gauss. The difference is partly attributable to the difference in the spin-orbit coupling coefficient for Ti(III) and V(III), the values²¹ are 154 and 217, respectively. Van Vleck¹¹ showed that the paramagnetic relaxation time is inversely proportional to the square of the spin-orbit coupling coefficient. The small coupling coefficient in Ti(III) leads to long relaxation time and narrow e.s.r. line width.

Others have also noticed the dependence of e.s.r. line widths upon field symmetry. Pake and Sands²² obtained a narrow e.s.r. spectrum in aqueous solution of VOSO_4 . The resonance disappeared when the solution was made alkaline. These authors attributed this disappearance to the formation of complex ions in which the field about the V(IV) ion is more symmetrical.

This work points out the importance of symmetry considerations in e.s.r. studies. Lack of success in observing e.s.r. absorption in a transition metal compound may be remedied by lowering the symmetry of the molecule by changing the number or the type of the ligands or both.

Acknowledgments.—The authors appreciate helpful discussions with Dr. H. S. Jarrett of the du Pont Company and Dr. A. D. Liehr of the Bell Telephone Laboratories.

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The Donor Properties of Pyridine N-Oxide

By J. V. QUAGLIANO, J. FUJITA, G. FRANZ, D. J. PHILLIPS, J. A. WALMSLEY AND S. Y. TYREE

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The coördination chemistry of pyridine N-oxide with a variety of acceptors has been investigated. The new substances $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{L}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{L}$, $\text{CoCl}_2 \cdot 3\text{L}$, $\text{CoCl}_2 \cdot \text{L} \cdot \text{H}_2\text{O}$, $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{L}$, $\text{NiCl}_2 \cdot \text{L} \cdot \text{H}_2\text{O}$, $\text{NiBr}_2 \cdot 6\text{L}$, $\text{NiI}_2 \cdot 6\text{L}$, $\text{NiBr}_2 \cdot \text{L} \cdot \text{H}_2\text{O}$, $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{L}$, $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{L}$, $\text{CuCl}_2 \cdot \text{L}$, $\text{CuCl}_2 \cdot 2\text{L}$, $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{L}$, $\text{ZnCl}_2 \cdot 2\text{L}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{L}$, $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{L}$, $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{L}$, and $\text{SnBr}_4 \cdot 2\text{L}$ (where L = pyridine N-oxide) have been isolated and characterized by molecular conductance measurements in non-aqueous solvents, magnetic susceptibility measurements and infrared spectra. All of the perchlorates and some of the nitrates and halides have only the pyridine N-oxide in the first coördination sphere. However, in some cases, both nitrates and halides are coördinated to the central ion.

Introduction

As a logical extension of previous work on the donor properties of substituted phosphine¹ and arsine² oxides, we wish to report now the results of a study of the ability of pyridine N-oxide to behave as a ligand.

We find only three prior pyridine N-oxide adducts, the hydrochloride,³ a 1:1 adduct with SO_3 ,⁴ and the hexakis-(pyridine N-oxide)-cobalt(II) tetracarbonylcobaltate(-1).⁵ However, it

is our understanding that two adducts with zinc chloride have also been prepared.⁶

Experimental

Reagents.—Reagent or analytical grade chemicals were used without further purification except in the cases noted.

Pyridine N-oxide was prepared once by the method of Ochiai.⁷ Other samples were obtained from Reilly Tar and Chemical, and K and K Chemical laboratories. All samples were purified by vacuum distillation, collecting the fraction distilling between 125 and 130° at 8 mm.

N,N-Dimethylformamide (DMF) was purified by a modification of Method I of Rochow.⁸

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