less solution was stirred for *ca.* 10 min and 59.5 g (0.48 mol) of sodium carbonate monohydrate was added. The solution, pH 11, was ready for electrolytic oxidation which was carried out at 7–12 V and a current density of between 2 and 6 mA/cm^2 at *ca.* 12° (ice bath cooling). The formation of the nitrosodisulfonate radical was evidenced by the appearance of a deep purple color, absorbing at 540 mμ. After about 4.5 hr (depending on the current density) a quantitative absorption measurement [ϵ 14.5 for the radical anion $\cdot ON(SO_3)_2{}^{2-}$] indicated a 94% yield of the Frémy radical in the reaction mixture. It is recommended that this solution[5] be used as is, although the potassium salt of the radical can be isolated as follows.

To the above cold purple solution was added dropwise, with stirring, a solution of 37.3 g (0.5 mol) of KCl in 100 ml of water. The orange-yellow potassium nitrosodisulfonate crystals precipitated readily. After refrigeration overnight the crystals were filtered by suction and washed with 100 ml of 1 *N* aqueous KOH. The damp crystals weighed 55 g.

A 1-g aliquot of the wet material, dried[6] at room temperature in a desiccator over Drierite, gave 0.76 g of orange crystals. This corresponds to a 72% yield, based on sodium nitrite.

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(5) Such a solution has a half-life of 2 weeks at 0°.

(6) On two occasions small samples of dried material decomposed spontaneously. It is suggested that the electrolyzed solution be used directly or that the isolated Frémy's salt be stored as a slurry in 1 *N* K_2CO_3 at 0°. If stored as a slurry in the indicated manner, 100-g lots have been stable for at least 4 months.

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Electron Paramagnetic Resonance Spectra of Some Low-Coordination Amido Compounds of Titanium and Chromium

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Received May 5, 1970

Electron paramagnetic resonance (epr) of transition metal ions is often difficult to detect at elevated temperatures by reason of low-lying excited states which facilitate rapid spin–lattice relaxations. Often times, liquid helium temperature has to be used to detect these resonances. However, if the compound has a ligand-field component of low symmetry, the energy separation between the ground state and the first excited state can be increased, and epr can be detected even at room temperature. Recently, Bradley, *et al.*,[2] reported the synthesis of tris(diisopropylamino)chromium(III). The compound is remarkable in that even with its unusually low coordination number it is monomeric in solution and in solid state. Paramagnetic compounds of this type should exhibit room-temperature epr spectra and large zero-field splitting when the spin multiplicity exceeds 2. We report here the epr spectra of amido compounds of Ti(III) and Cr(III).

The amido compounds of Ti(III) and Cr(III) were prepared from the respective chlorides and the appropriate secondary amine according to the procedure of Bradley and Thomas.[3] The solvents were purified by vacuum distillation into a tube containing solid potassium and benzophenone to form a solution of K^+(benzophenone)$^-$. The solvent was subsequently distilled out of this solution into an epr sample tube containing the appropriate amido compound. $Cr((i\text{-}C_3H_7)_2N)_3$ was transferred by sublimation into the sample tube. The amido compounds of titanium cannot be sublimed. These were transferred into sample tubes under an inert atmosphere. The epr spectra were obtained with a Varian X-band spectrometer.

A dilute solution ($\sim 10^{-4}$ *M*) of $Ti((i\text{-}C_3H_7)_2N)_3$ in toluene, heptane, or tetrahydrofuran exhibits a single symmetric epr spectrum at temperatures between −85 and +25°. The *g* value is 1.987 and the line width is 20.9 G. Both these spectral parameters are insensitive to temperature variations. The powder spectrum obtained at −145° has an asymmetric line shape and a line width of 20 G indicating $g_{\parallel} \approx g_{\perp}$. No hyperfine interaction with ^{47}Ti, ^{49}Ti, or ^{14}N could be resolved under these conditions. Substantially the same spectra were obtained for solutions of $Ti[(C_6H_5)_2N]_3$.

The epr spectra described above are similar to that given earlier for $(\pi\text{-}C_5H_5)_2Ti(C_2H_5)$.[4] If we assume both $Ti((i\text{-}C_3H_7)_2N)_3$ and $Ti[(C_6H_5)_2N]_3$ to be monomeric like $Cr((i\text{-}C_3H_7)_2N)_3$, then all of the environment of the Ti(III) atom in these compounds must be nearly trigonal. According to the theory of Ti(III) in a trigonal field,[5] the above epr results indicate the ground state to be $^2A_1$ and this $^2A_1$ state is separated from the excited ^2E state by an energy of about 3000 cm^{-1}. A similar separation of 2000–4000 cm^{-1} was found for Ti(acac)$_3$[6] in which complex the cubic field contains a strong trigonal distortion.

At room temperature, solutions of $Cr((i\text{-}C_3H_7)_2N)_3$ exhibit single asymmetric epr spectra (g = 1.975 and line width is 10.8 G). At −195° the signal at normal field shows definite *g* anisotropy. The principal values are $g_{\perp} = 1.982$ and $g_{\parallel} = 1.966$. The g_{av} agrees with the experimentally determined value at 25°. At liquid nitrogen temperature there was found an intense signal at 1650 G having a line width of 63 G. No resonance was detected above the midfield signal up to 10,000 G.

The epr spectra of all Cr(III) compounds obtained so far can be fitted to the spin Hamiltonian[7]

$$\mathcal{H} = \beta \mathbf{S}\cdot\mathbf{g}\cdot\mathbf{H} + D[S_z^2 - {}^5/_4] + E(S_x^2 - S_y^2)$$

When the zero-field splitting is small compared to the microwave frequency, three resonance lines can be observed corresponding to transitions $({}^3/_2 \leftrightarrow {}^1/_2)$, $(-{}^1/_2 \leftrightarrow {}^1/_2)$, and $(-{}^1/_2 \leftrightarrow {}^3/_2)$. The absence of a high-field line indicates that the low-field line does not arise from the $({}^3/_2 \leftrightarrow {}^1/_2)$ transition. Two alternative assignments are possible. In the first one, the zero-field splitting is assumed to be very large and the low-field

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signal is attributed to forbidden transitions, *i.e.*, $(-{}^{3}/_{2} \leftrightarrow {}^{3}/_{2})$, $(-{}^{3}/_{2} \leftrightarrow {}^{1}/_{2})$, or $(-{}^{1}/_{2} \leftrightarrow {}^{3}/_{2})$. However, the integrated intensity of the low-field signal is about the same as the resonance at normal field. This suggests a more probable assignment of the low-field signal to one of the $(-{}^{1}/_{2} \leftrightarrow -{}^{3}/_{2})$ transition. This would result if $D = 2.25$ cm^{-1} (assuming $E = 0$). It appears that zero-field splittings with magnitudes more than 3 times the highest previously reported[8] can be realized for transition metals in strongly trigonal environments. According to this assignment, the normal-field resonance is attributable to the remaining $(-{}^{1}/_{2} \leftrightarrow -{}^{3}/_{2})$ and $({}^{1}/_{2} \leftrightarrow {}^{3}/_{2})$ transitions when H_0 is parallel and perpendicular to the z axis, respectively.

The epr spectrum of tetrakis(diethylamino)vanadium(IV)[9] has been reported. It is interesting to compare that with those spectra described above. No ^{14}N hyperfine splitting was resolved at all temperatures for all three transition metal derivatives. The spin density on the nitrogen atom in an aliphatic nitroxide radical is about 0.9; the hyperfine splitting is about 44 MHz. The observed line width could account for unresolved ^{14}N hyperfine splitting even if the electron density on each nitrogen atom is as high as 0.2. The actual electron density is probably much lower because of resonance structures such as $Ti^{-}{=}^{+}NR_2$. Intramolecular π coordination of this type has been invoked[8] to explain the monomeric structure of the low-coordination amido compounds, steric effect being the other.

Whereas highly anisotropic ^{51}V hyperfine splitting has been observed in $V((C_2H_5)_2N)_4$, the ^{47}Ti and ^{49}Ti splitting was not resolved in $Ti((i\text{-}C_3H_7)_2N)_3$, nor was ^{53}Cr hyperfine splitting discerned in $Cr((i\text{-}C_3H_7)_2N)_3$. The failure to detect these hyperfine features may be due to their low natural abundance (less than one-tenth of ^{51}V) and to their smaller hyperfine coupling constants (also less than one-tenth of ^{51}V values).

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The Hydrogenation of Pentacyanocobaltate(II) at High Pressures

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Received May 11, 1970

The uptake of molecular hydrogen by aqueous solutions of pentacyanocobaltate(II) has been interpreted by several investigators[1-5] in terms of the reversible formation of hydridopentacyanocobaltate(III) according to

$$2Co(CN)_5^{3-} + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2Co(CN)_5H^{3-} \qquad (1)$$

$$-d[Co(CN)_5^{3-}]/dt = 2k_1[Co(CN)_5^{3-}]^2[H_2] - 2k_{-1}[Co(CN)_5H^{3-}]^2 \qquad (2)$$

Although supported by the results of several kinetic and equilibrium investigations, this interpretation has recently been questioned by Banks, *et al.*,[6] who proposed a considerably more complex scheme involving several additional species including cobalt(I) complexes arising from the disproportionation of pentacyanocobaltate(II). The interpretation advanced by these authors was based on several alleged departures from the behavior described by eq 1 and 2, including the observation of an induction period in the hydrogen uptake reaction, and a rather complicated pattern of cyanide dependence and salt effects. In view of the widespread interest in this system and of its importance in relation to various catalytic hydrogenation reactions,[7] an extension of the earlier investigations, with a view to achieving a clarification of these unresolved features, appeared to be warranted.

The study of the hydrogenation of pentacyanocobaltate(II) at atmospheric pressure is severely hampered by the slowness of the reaction, particularly in view of the competing decomposition[2,3,8] according to eq 3.

$$2Co(CN)_5^{3-} + H_2O \longrightarrow Co(CN)_5H^{3-} + Co(CN)_5OH^{3-} \qquad (3)$$

Because the reaction with hydrogen is markedly accelerated by added salts, most of the earlier quantitative studies were conducted at relatively high ionic strengths ($\geqslant 0.5\ M$), *i.e.*, conditions under which the rate of the competing decomposition reaction, unfortunately, is also enhanced. In order to minimize the complications arising both from the competing decomposition reaction and from the uncertain effects of added salts, it seemed desirable to extend the quantitative study of reaction 1 to higher hydrogen pressures and at the same time to the lower ionic strengths that are thereby rendered practical. This paper describes the results of such a study.

Experimental Section

Solutions of the desired composition were prepared by dissolving analytical reagent grade cobalt(II) chloride, potassium cyanide, potassium hydroxide, and potassium chloride (used to adjust the ionic strength) in distilled water with rigorous exclusion of oxygen. The kinetic and equilibrium experiments were conducted in a glass-lined Parr Series 4500 stirred autoclave pressurized to the desired constant partial pressure of hydrogen and thermostated to ±0.2°. Samples of the solution were withdrawn periodically for spectrophotometric analysis in a Cary 14 recording spectrophotometer. The reaction was followed by monitoring the 970-nm (ϵ 290 M^{-1} cm^{-1}) band of $Co(CN)_5^{3-}$. Hydrogen concentrations were computed from the measured partial pressures using literature solubility data.[9]

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