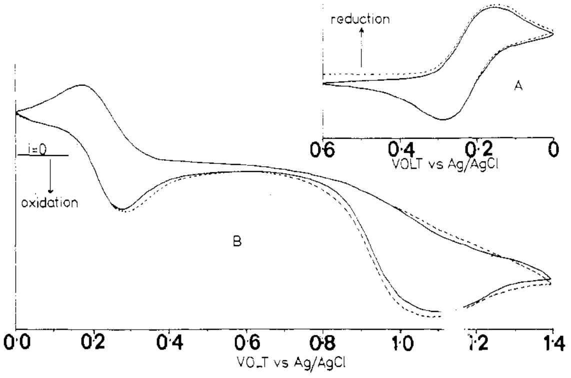

Figure 7. Cyclic voltammogram of $V(CO)_6$ in dichloromethane (0.2 M Bu_4NClO_4); scan rate 200 mV/s: A, scan of the electrode process $V(CO)_6 + e^- \rightleftharpoons V(CO)_6^-$; B, scan of all processes.

oxidation wave can be seen. Progressive addition of diglyme caused the oxidation wave to adopt the form obtained from $[Na(diglyme)_2][V(CO)_6]$ (see Figure 6B). This demonstrates that the $Na(diglyme)_2^+$ cation dissociates in CH_2Cl_2 and the apparent discrepancies in the electrochemistry of $V(CO)_6$ and $V(CO)_6^-$ are partly due to the presence of diglyme. Note also that in the cyclic voltammograms of $V(CO)_6$ the $V(CO)_6^-/V(CO)_6$ couple is not perturbed by altering the switching potential. This suggests that a redox reaction between an unidentified vanadium species generated at the electrode surface and $V(CO)_6^-$ in solution plays an integral role in the electrochemical behavior in both acetone and dichloromethane.

Conclusions

The vanadium–carbonyl system exhibits very solvent-dependent behavior, which is clearly reflected in both the chemistry and the electrochemistry of the system. In noncoordinating solvents $V(CO)_6$ is completely stable, but since $V(CO)_6^+$ is extremely reactive toward substitution, a catalytic disproportionation can occur in coordinating solvents to give $V(CO)_6^-$ and $V(solvent)_x^{2+}$ so that in acetone and similar solvents $V(CO)_6$ has no stability at all. The vanadium cation V^{2+} is only stable when coordinated by solvent or ligand and on removal of the coordinating ligand the equilibrium

$$V(CO)_6 + \text{“}V^{+}\text{”} \rightleftharpoons V(CO)_6^- + \text{“}V^{2+}\text{”}$$

is shifted to the left.

It is interesting to compare the behavior of the 17-electron $V(CO)_6$ with the isoelectronic $Cr(CO)_5I$ (which also disproportionates at ambient temperature in acetone[6]) and also with $Cr(CO)_6^+$ which exhibits similar behavior in a range of coordinating solvents.[4] In each case it would appear that the 17-electron species undergoes a disproportionation to generate a stable 18-electron carbonyl compound and a very reactive 16-electron carbonyl species which rapidly reacts further to give as the final product a non-carbonyl-containing compound. The substitution of the 16-electron intermediate would now appear to be the driving force in the disproportionation.

The electrochemical data on $V(CO)_6$ briefly reported by Pickett and Pletcher[4] would now appear to be incorrectly interpreted in view of our findings. In our hands, infrared studies in tetrahydrofuran and acetonitrile (the two solvents used by these workers) demonstrated that, as in acetone and diglyme, $V(CO)_6$ disproportionates to give $V(CO)_6^-$. In addition, others[2,7] have reported the disproportionation of $V(CO)_6$ in THF. These workers would therefore appear to have been describing the electrochemistry of $V(CO)_6^-$ rather than $V(CO)_6$. Furthermore, the degree of reversibility for the $V(CO)_6^-/V(CO)_6$ couple was found to be far higher in the present work and the additional waves corresponding to oxidation of $V(CO)_6$ were not reported by them. The reason for this last discrepancy is not clear to us, but it does seem very probable that the data of Pickett and Pletcher cannot be those for $V(CO)_6$.[8]

Registry No. $[Na(diglyme)_2][V(CO)_6]$, 12110-22-4; $V(CO)_6$, 14024-00-1.

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Electrochemical Evidence for Reversible Five-Membered Electron Transfer Chains in Octahedral Chromium Complexes

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A voltammetric (dc and ac polarography, cyclic voltammetry, and controlled potential electrolysis) study of complexes of chromium(II) and chromium(III) with the ligands bipyridine, terpyridine, and phenanthroline in acetonitrile has shown that in complexes with all three ligands chromium forms reversible, five-membered redox chains with the metal in formal oxidation states of 3+, 2+, 1+, 0, and 1–. Further examination of the redox behavior indicates that in the first three redox couples for each complex (3+ → 2+, 2+ → 1+, 1+ → 0), the ligands help to stabilize the addition of electrons to molecular orbitals which are primarily metal centered, while for the last couple (0 → 1–) the metal helps to stabilize the addition of an electron to a ligand-centered molecular orbital.

Considerable interest has been shown in recent years in the study of complexes which exhibit what have been termed “electron-transfer chains”, that is, a series of one-electron, reversible charge transfers between a number of formal oxidation states of the complex. Most of this work has been done on square-planar complexes of two general classes of ligand, the dithiolenes[1,2] and macrocycles.[3-7]

A few such electron-transfer chains have been reported for octahedral complexes of first row transition metals.[8-12] The work was invariably done in a nonaqueous solvent, such as acetonitrile, which reduces and oxidizes with much more difficulty than water, and thus yields a much larger potential

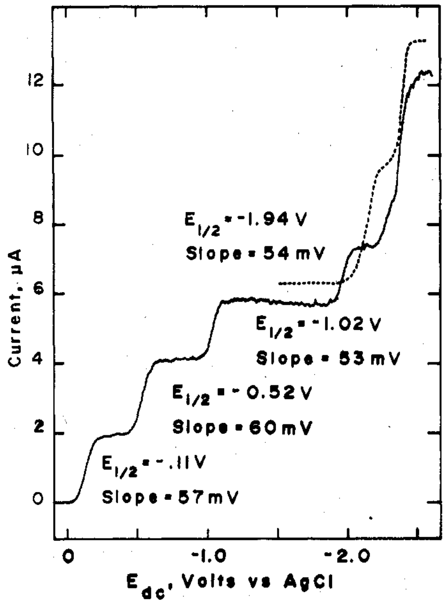

Figure 1. Dc polarogram of $Cr(terpy)_2^{3+}$ in 0.1 M $TEABF_4$, spectro acetonitrile. The dotted line is a dc polarogram of free terpyridine.

range in which complexes of unusually high or low oxidation states may be stable. With a few exceptions[13-16] the members of such charge-transfer series have not been isolated, and the only evidence for inferring the existence of most members of such series has been dc polarography, a technique where applicability is limited, as it is impossible to determine both the reversibility and electron number of a charge-transfer process from a dc polarogram alone.

A very significant problem in the study of such electron transfer chains is the localization of charge in the complexes which are members of such series. Spectrophotometric measurements have been made on $V(bipy)_3^{n+}$ and $Cr(bipy)_3^{n+}$, where bipy = 2,2′-bipyridine and $n = 3$, 2, 1, and 0, which allowed for tentative placement of the complex electron primarily on either the ligand or the metal, depending on the formal oxidation state of the metal in the complex.[14-16] A recent study of the electron spin resonance of a large number of nickel macrocycles has shown the effect of ligand structure on the localization of the redox orbital in nickel(I) and nickel(III) macrocycles.[7]

Complexes of chromium with imine ligands have been shown to give redox chains in both aqueous and nonaqueous media.[10,17]

Experimental Section

Bis(terpyridine)chromium(III) perchlorate and tris(phenanthroline)chromium(III) perchlorate were the same compounds whose syntheses and analyses were reported previously.[17] The compounds were dried by heating at 80 °C in vacuo over P_2O_5 for 8 h.

Tris(bipyridine)chromium(III) perchlorate was prepared and dried by the same procedure used for the other compounds.

Bis(terpyridine)chromium(II) perchlorate was prepared by the same procedure previously reported for bis(terpyridine)chromium(III) perchlorate,[17] except that the precipitated chromium(II) complex perchlorate was filtered and dried under nitrogen and then in vacuo.

Bipyridine, terpyridine, and phenanthroline were used as received from the G. Frederick Smith Chemical Co. Tetraethylammonium tetrafluoroborate ($TEABF_4$) was electrometric grade from Southwestern Analytical Chemicals and was dried at 50 °C in vacuo over P_2O_5 for 8 h. It gave a potential window in spectro grade acetonitrile of +0.65 to −2.80 V vs. Ag|AgCl (saturated NaCl) at the dropping mercury electrode.

Eastman spectro grade and reagent grade (less than 0.01% water) acetonitrile were used as received. Eastman reagent grade acetonitrile was also purified by the method of Coetzee.[18]

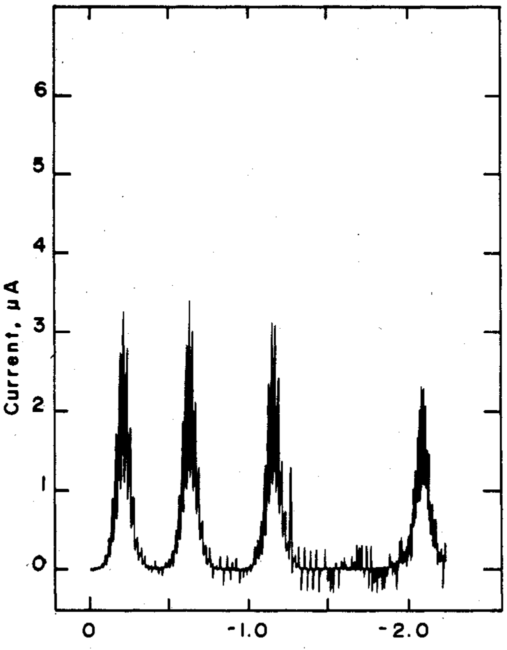

Figure 2. In-phase ac polarogram of $Cr(terpy)_2^{3+}$ in 0.1 M $TEABF_4$, spectro acetonitrile. Applied frequency = 22 Hz, applied potential = 5 mV.

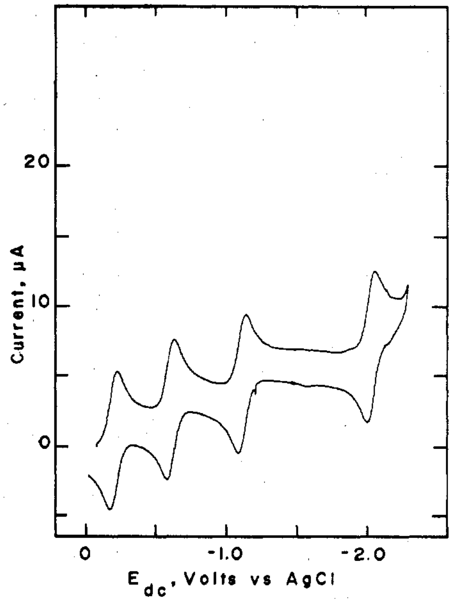

Figure 3. Cyclic voltammogram of the first four reduction waves of $Cr(terpy)_2^{3+}$ in 0.1 M $TEABF_4$, spectro acetonitrile. Scan rate = 100 mV/s on hanging mercury drop electrode.

Identical results were obtained in all three solvents. Ac and dc polarograms and cyclic voltammograms were run on an instrument assembled from operational amplifiers and other standard components as has been reported previously.[17] A conventional polarographic H-cell was used in which the reference electrode was separated from the working compartment by a fine porosity frit. The reference electrode was an aqueous silver–silver chloride (saturated NaCl) electrode. Constant potential electrolyses were done at a platinum gauze electrode. Current–time curves were recorded and electron numbers were determined by numerical integration.

Results and Discussion

The electrochemical parameters for the chromium complexes of the three ligands are given in Table I. Figures 1, 2, and 3 show dc and ac polarograms and a cyclic voltammogram, respectively, of the $Cr(terpy)_2^{3+}$ complex in 0.1 M

Table I. Voltammetric Data for the Chromium Complexes

Complex couple	Dc Polarography			Ac Polarography[a]			Cyclic voltammetry[b]
	$E_{1/2}$,[c] V	Slope, mV	i_d/C, μA/mM	E_p,[c] V	I_p/C, μA/mM	$\Delta E_p/2$, mV	ΔE_p, mV
$Cr(terpy)_2$							
III → II	−0.110	51	3.15	−0.120	3.30	95	60
II → I	−0.516	65	3.40	−0.525	3.40	95	60
I → 0	−1.030	50	3.35	−1.035	3.30	92	60
0 → (−I)	−1.95	58	3.10	−1.95	2.20	92	70
$Cr(bipy)_3$							
III → II	−0.209	58	3.35	−0.200	3.45	92	60
II → I	−0.715	60	3.60	−0.710	3.40	90	60
I → 0	−1.28	56	3.20	−1.28	3.50	85	60
0 → (−I)	−1.91	60	2.70	−1.89	2.50	96	60
$Cr(phen)_3$							
III → II	−0.237	61	3.35	−0.228	3.50	95	60
II → I	−0.732	65	3.35	−0.838	3.30	96	60
I → 0	−1.29	63	3.35	−1.28	3.30	96	70[d]
0 → (−I)	−1.79	65	2.70	−1.79	1.70	105	

[a] Applied frequency, 22 Hz; applied potential, 5 mV p-p; ir compensation, 225 Ω. [b] Scan rate is 100 mV/s at the hanging mercury drop electrode. [c] All voltages are referenced against the Ag/AgCl, saturated NaCl electrode. [d] 70-mV peak splitting for the I → 0 couple is in the presence of excess ligand. No value could be obtained for the 0 → (−I) couple due to poor definition of the oxidation wave.

$TEABF_4$ in acetonitrile. A total of six reduction waves are observed for each complex. The voltammetric behavior of the first four reductions shows clearly that they are due to reversible, one-electron charge transfers. Figures 1–3 and the discussion below refer to the first four reductions. The last two will be dealt with separately.

In the dc polarograms of the three chromium(III) complexes the first four reduction waves are of equal height. In addition, all four waves for each complex are diffusion controlled ($i_d/h_{1/2}$ is constant) and all four waves show log $[i/(i_d - i)]$ vs. E slopes which are consistent with reversible one-electron charge transfers.

Cyclic voltammetry of the complexes shows that the first four waves for $Cr(terpy)_2{}^{3+}$ and $Cr(bipy)_3{}^{3+}$ are one-electron reversible charge transfers. Cyclic voltammograms of the $Cr(phen)_3{}^{3+}$ complex give evidence of an absorption process affecting the third and fourth waves. The addition of excess ligand improves the definition of these waves, but accurate measurement of the peak splitting of the fourth wave is still impossible.

The ac polarograms are also consistent with reversible, one-electron transfers for each of the first four waves exhibited by the complexes with the half-peak widths being within the limits of 92 ± 5 mV prescribed for reversible, one-electron transfer.[19]

Constant potential electrolysis was done on $Cr(terpy)_2{}^{2+}$. Reduction of this compound to the univalent state, i.e., $Cr(terpy)_2{}^{+}$, required 0.94 electron per molecule. Further reduction of $Cr(terpy)_2{}^{+}$ to the zero-valent state, $Cr(terpy)_2{}^{0}$, required 0.83 electron per molecule. The dc polarographic half-wave potentials for the Cr(II)–Cr(III), Cr(I)–Cr(II), and Cr(0)–Cr(I) bis(terpyridine) oxidations agreed to within 5 mV with the $E_{1/2}$ values for the corresponding reductions which are shown in Table I. Electrolysis at a potential on the plateau of the fourth reduction wave indicates that a large, indeterminate number of electrons per molecule is involved in the electrode reaction. In addition a precipitate was produced.

The voltammetric evidence indicates that each of the three complexes undergoes four one-electron transfers which are reversible on the voltammetric time scale. Thus, each complex gives a redox chain which contains four reversible redox couples with the central metal atom in the formal oxidation states 3+, 2+, 1+, 0, and 1−, respectively. The fact that the dc polarographic half-wave potentials are reversible means that these observed values can be equated to the formal redox potentials for each couple.

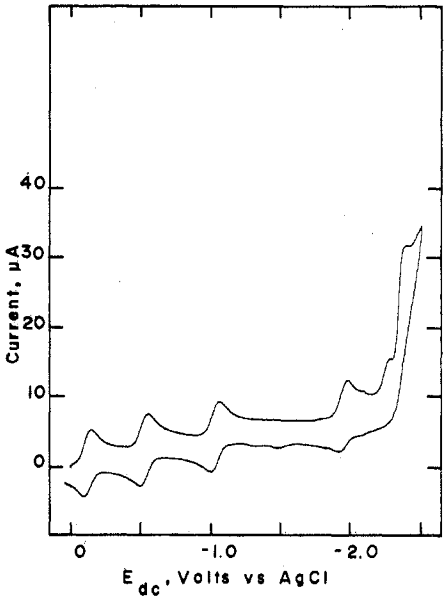

Figure 4. Complete cyclic voltammogram of $Cr(terpy)_2{}^{3+}$. Same conditions as Figure 3.

For the first three couples of each complex the redox potentials follow predictable behavior, with the ligands phenanthroline and bipyridine being nearly identical in their ability to stabilize the lower oxidation states of chromium, and terpyridine showing an increasingly greater stabilization of the metal in successively lower oxidation states relative to the other two ligands. The fourth redox couple shows clearly contrasting behavior with the apparent order of ability to stabilize the formal Cr(−I) oxidation state being the reverse of that observed for the higher oxidation states, that is, phen > bipy ~ terpy.

The fourth wave observed for the complexes is not a reduction of the free ligand. The polarography of bipyridine and phenanthroline in acetonitrile has been reported.[20,21] Both note a first reduction wave at about −2.1 V vs. Ag|AgCl, saturated NaCl. Terpyridine shows a first reduction wave at about −2.05 V. The reductions for all three free ligands are irreversible. Figure 4 is a complete cyclic voltammogram of $Cr(terpy)_2{}^{3+}$, showing all six observed reductions. The last two reductions show behavior with respect to their current and reversibility which is distinctly different from the first four reductions, but very closely resembles the irreversible waves

Table II. Dc Half-Wave Potentials for the Chromium Complexes in the Presence of Excess Ligand

Complex couple	$E_{1/2}$, vs. Ag/AgCl (sat NaCl)	Complex couple	$E_{1/2}$, vs. Ag/AgCl (sat NaCl)	Complex couple	$E_{1/2}$, vs. Ag/AgCl (sat NaCl)
$Cr(terpy)_2$		$Cr(bipy)_3$		$Cr(phen)_3$	
III → II	−0.110	III → II	−0.210	III → II	−0.237
II → I	−0.510	II → I	−0.725	II → I	−0.738
I → 0	−1.030	I → 0	−1.28	I → 0	−1.29
0 → (−I)	*a*	0 → (−I)	−1.91	0 → (−I)	−1.80

[a] A large free ligand wave makes the slope of the diffusion plateau too steep to measure $E_{1/2}$ accurately.

of the free ligand. The last two reduction waves occur at potentials which are slightly more negative than those of the corresponding free ligands. If these two waves are due to the reduction of free ligand produced by a prior dissociation of the complex, then the effect of any preceding reaction on the observed reduction potential would be expected to be a negative shift.

Table II shows the effect of added excess free ligand on the dc polarographic half-wave potentials for the first four reduction waves of each complex (the complex concentration is about 1 mM and the free ligand concentration is about 20 mM in each case). The added free ligand completely obscures the last two reduction waves, but has no significant effect on the potential of the first four waves, indicating that none of the first four reduction waves is due to a charge transfer which involves the free ligand, or which is coupled to the free ligand by any chemical reaction whose rate is significant on the dc polarographic time scale.

All of the electrochemical behavior observed for the first four reduction waves of the complexes is consistent with the interpretation that they are due to reversible, one-electron charge-transfer processes involving the complex, and not the free ligand. It appears that the only satisfactory explanation for the inconsistent potential behavior of the fourth reduction wave is that this wave is due to a reduction on a molecular orbital whose localization is considerably different from those involved in the first three reductions.

Further insight into this assumption may be gained by considering the first reduction wave of heteroaromatic compounds in aprotic solvents. Such reductions have been shown to be markedly affected by the addition of a proton donor, such as water, in which case the currents of each reduction are considerably enhanced. The mechanism which has been proposed and discussed in some detail[21-23] is shown below:

$$L + e^- \rightarrow L^- \qquad E_{1/2}{}^1$$

$$L + H^+ \rightarrow LH\cdot$$

$$LH + e^- \rightarrow LH^- \qquad E_{1/2}{}^2$$

where

$$E_{1/2}{}^2 > E_{1/2}{}^1.$$

The addition of the first electron to the ligand, L, produces the anion, L^-, which reacts with a proton to form the radical, $LH\cdot$. This radical has been shown to reduce at more positive potentials than either the ligand anion, L^-, or the original ligand, L.[22,23] Reduction of L in the presence of a proton donor will show a much larger wave than expected for a one-electron reduction, due to the concurrent reduction of both L and $LH\cdot$ at the reduction potential of the reaction $L + e^- \rightarrow L^-$.

If water is added to a solution of $Cr(phen)_3{}^{3+}$ in dry acetonitrile (dried by the method of Coetzee[18]), only the current of the fourth reduction wave is affected, except for a slight decrease due to dilution. The fourth reduction wave becomes split, and the current increases drastically. The bipyridine and terpyridine complexes show similar behavior. This is further evidence that the fourth reduction takes place on a molecular orbital which is primarily ligand in character. Electronic[14] and vibrational spectroscopy[16] have shown that the ligands in $Cr(bipy)_3{}^0$ have a great deal of anion character. Recently, theoretical calculations have shown that even in $Cr(bipy)_3{}^+$ the assumption of considerable anion character on the ligands is consistent with observed electronic and electron spin resonance spectra.[24]

It seems reasonable to assume that further reduction to a formal oxidation state of (1−) will place the added electron primarily on the ligands, rather than on the metal. The redox orbital is still a molecular orbital of the complex and must necessarily have some metal character, which causes the wave to be reversible, behavior which is not characteristic of the free ligand, and to occur at lower energies (more positive potentials) than the free ligand reduction. The first two reductions in each complex may be considered as "ligand-assisted-metal reductions" in that the metal is effectively reduced to oxidation states which would not be stable without the presence of the ligands. In view of the known characteristics of the Cr(I) and Cr(0) complexes given above, the Cr(I) → Cr(0) reduction is probably best considered to be an intermediate case, though for the complexes considered here it seems to follow the same pattern as the first two reductions. Following the terminology introduced above the fourth reduction wave appears to be better classified as a "metal-assisted ligand reduction".

On the basis of the data presented here, it is not possible to describe accurately the nature of the metal–ligand interaction which produces the unusual redox behavior of the formal Cr(0)–Cr(−I) couple. One possibility which suggests itself is that the metal, which in a complex such as $Cr(bipy)_3{}^0$ is actually in some intermediate positive oxidation state, can function as an electron acceptor to the ligand anions in the complex, lowering the energy of the redox orbital which is localized primarily on the ligands, and making the next reduction easier, i.e., occur at lower energies. The ligand which would be expected to show this effect to the greatest extent would be the one which appears to be the poorest at stabilizing low formal oxidation states, in this case phenanthroline, followed by bipyridine and then terpyridine. This would explain the observed inversion of the reduction potentials for the fourth wave as compared to the first three.

Registry No. $Cr(terpy)_2{}^{3+}$, 54984-99-5; $Cr(terpy)_2{}^{2+}$, 30596-50-0; $Cr(terpy)_2{}^{+}$, 59302-04-4; $Cr(terpy)_2$, 15009-46-8; $Cr(terpy)_2{}^{-}$, 59302-05-5; $Cr(bipy)_3{}^{3+}$, 15276-15-0; $Cr(bipy)_3{}^{2+}$, 17632-84-7; $Cr(bipy)_3{}^{+}$, 34424-07-2; $Cr(bipy)_3$, 14751-89-4; $Cr(bipy)_3{}^{-}$, 55297-25-1; $Cr(phen)_3{}^{3+}$, 15276-16-1; $Cr(phen)_3{}^{2+}$, 47836-39-5; $Cr(phen)_3{}^{+}$, 59302-06-6; $Cr(phen)_3$, 14767-25-0; $Cr(phen)_3{}^{-}$, 59302-07-7.

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Electron Spin Resonance on Powders of Chromium(III) Complexes of the Type $[Cr(NH_3)_5X]Z$ and *cis*-$[Cr(NH_3)_4XY]Z$

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The spin Hamiltonian parameters of $[Cr(NH_3)_5X]Z$, where X is H_2O, Cl^-, Br^-, NCS^-, or NO_3^-, and of *cis*-$[Cr(NH_3)_4XY]Z$, where XY is H_2O–Cl^- or $C_2O_4^{2-}$, have been determined at 295 and 77 K. Some complexes showed considerable variations in the parameters with temperature. For $[Cr(NH_3)_5H_2O]Z_3$, where Z is NO_3^- or ClO_4^-, the effect of the counterion on the parameters was investigated. It appeared that the counterion had a considerable influence. Within a tetragonal ligand field model the spin Hamiltonian parameters were calculated by means of second-order perturbation theory. It was found that there was reasonable agreement between the calculated and experimental axial zero-field parameter D if the ligands did not have large spin–orbit constants.

Introduction

In electron spin resonance studies of transition metal complexes the experimental spin Hamiltonian parameters are often compared with those calculated from experimental optical parameters.[1–4] Often the parameters from the optical spectrum are obtained from solution spectra, while the spin Hamiltonian parameters are calculated from doped powder or single-crystal spectra. In ESR measurements it is often impossible to obtain well-resolved spectra from frozen solutions, and in vis–uv measurements it is often impossible to solve the optical spectrum of the paramagnetic ion from that of the diamagnetic host lattice. One purpose of the present work was to get an impression about the influence of environmental effects on the spin Hamiltonian parameters. As a result of peak broadening[5] no accurate values for the spin Hamiltonian parameters could be obtained from frozen-solution spectra. Therefore the effect of the temperature and of the counterion was investigated on powders in order to create different environments for the paramagnetic complexes. To get accurate values for the parameters the X-band and Q-band spectra had to be analyzed together.[6] Another purpose of this investigation was to compare the experimental values with the calculated ones. For some nearly tetragonal pentaamminechromium complexes the spin Hamiltonian parameters were calculated by a second-order perturbation method[7] within a tetragonal ligand field model.

Experimental Section

All pure Cr and analogous Co complexes were prepared by standard literature methods.[8–11] The compounds were identified by their ir spectra.[12–16] For some powders the usual procedure for growing crystals from an aqueous solution failed, either due to decomposition or due to insolubility of one or both compounds. In these cases alternative procedures were followed to obtain measurable powders.

Co/$[Cr(NH_3)_5NCS](SCN)_2$. A solution of a mixture of 2 wt % $[Cr(NH_3)_5H_2O](NO_3)_3$ in $[Co(NH_3)_5H_2O](NO_3)_3$ was treated with excess KSCN at 50 °C. The precipitate consisted of crystallites which contained the desired Cr complex.

Co/$[Cr(NH_3)_5Br]Br_2$. A solution of $[Cr(NH_3)_5H_2O](NO_3)_3$ and the analogous Co complex was converted into the bromine complex by means of concentrated HBr.

Co/$[Cr(NH_3)_5NO_3](NO_3)_2$. This powder was prepared by the thermal matrix method. A diluted powder of Co/$[Cr(NH_3)_5H_2O](NO_3)_3$ was heated at 70 °C for 1 week to expel the water molecule.

ESR spectra were recorded on X and on Q band on a Varian V4052 spectrometer. The magnetic field strengths were measured with an AEG gaussmeter. The microwave frequency was measured with a Takeda Riken 5502A counter equipped with a 5023 frequency converter.

Results

For most complexes ESR spectra were recorded at room temperature and at liquid nitrogen temperature. The parameters were determined from the combined results of X- and Q-band spectra. The results have been summarized in Table I for the pentaamminechromium complexes and in Table II for the tetraammine complexes. The complexes could be divided into two groups with respect to their behavior at low temperature. For the first group the line widths decreased with decreasing temperature. However, the second group exhibited an anomalous behavior as the peaks broadened with decreasing temperature. To this group belonged all investigated aquapentaamminechromium(III) complexes with the counterions NO_3^-, ClO_4^-, Cl^-, and Br^-. The isothiocyanato pentaammine complex also exhibited this behavior.

The counterion effect was investigated for the aquapentaamminechromium(III) complex. Besides the complex with the NO_3^- anion, also the Cl^-, Br^-, and ClO_4^- complexes were prepared and the powder spectra of 2% doped analogous Co complexes recorded. The spectra of the aqua complexes with Cl^- or Br^- as counterions were obscured partly by the strong signals of the $[Cr(NH_3)_5Cl]^{2+}$ and $[Cr(NH_3)_5Br]^{2+}$ species, respectively. This prohibited an accurate determination of the spin Hamiltonian parameters. The ClO_4^- complex at room temperature showed rather broad peaks but at 373 K the peaks were small enough to permit an accurate determination of the parameters. Unfortunately for the NO_3^- complex the parameters could not be determined at the same temperature as decomposition of the complex into $[Cr(NH_3)_5NO_3](NO_3)_2$ occurred. Therefore, a temperature effect may not be excluded entirely on comparison of the parameters, but it is estimated that this is of minor importance. Thus, we may conclude that for this complex there exists evidence for a considerable influence of the counterion on the parameters. For $[Cr(NH_3)_5Cl]Cl_2$ the sign of D was determined. On