readily accessed alternate oxidation states, perhaps the ease of electron transfer in the radical steps is responsible for the apparent rate difference.

In summary, a detailed study of the thermolysis of group IA propiolate salts permits the thermolysis behavior of more complex transition-metal propiolates to be predicted and rationalized. The approximate gas product ratios and the tendency to form coupled products or carbonates can be judged from the decomposition temperatures alone of the salts.

Acknowledgment. We are grateful to Professor Bruce M. Foxman of Brandeis University for supplying several samples of propiolate salts and calling our attention to their interesting behavior. We are grateful to Morton-Thiokol, Inc., for financial support, and, especially, to Dr. David A. Flanigan for his willingness to let us continue the study of metal complexes.

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UV Photochemistry of *trans*-Cyanothiocyanatotetraamminechromium(III). Communication between Charge-Transfer and Ligand-Field States

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Irradiation (at 295 and 250 nm) of the charge-transfer (CT) bands of *trans*-$Cr(NH_3)_4(CN)(NCS)^+$ in 1 × 10^{-3} M $HClO_4$/0.10 M $NaClO_4$ solution results in aquation of all three types of ligands. With respect to ligand-field (LF) photolysis, Φ_{NH_3} and Φ_{CN^-} decrease by 20%, while Φ_{NCS^-} increases up to 5-fold. The photoreactions are partially quenched by $Cr(C_2O_4)_3^{3-}$, which also completely quenches the LF doublet-state emission. The limiting unquenchable quantum yields differ from the LF ones, and from comparison of the two quenching patterns, the efficiency for CT → LF internal conversion is determined to be $\eta_{IC} = 0.6$. This is confirmed by the wavelength dependence of the relative phosphorescence quantum yields. Also, the intrinsic CT photoreactivity is evaluated ($\Phi^\circ_{CT} = 0.05$–0.09). The predominance of NCS^- loss is consistent with the NCS-to-Cr CT transition, and primary photoredox activity is demonstrated by Cr(II) scavenging.

The charge-transfer (CT) photochemistry of chromium(III) complexes has not received as much attention as the ligand-field (LF) photochemistry. This is not surprising, since LF excited states, hence photosubstitution reactions,[1-3] have been the focus of all photolysis models.[3-9] That CT states of chromium(III) have their own chemistry is indicated by a number of changes observed on passing from LF to CT excitation. The quantum yields for aquation of one or more ligands often increase considerably.[10-14] New reaction modes may take place.[15-21] Redox products are sometimes revealed by flash photolysis[17,18,21-27] or Cr(II) scavenging.[16,17,24,28] However, little quantitative information is available on such chemistry, as it is generally superimposed on LF reactivity, consequent to CT → LF internal conversion. Because of the high reducing power of Cr(II), the primary CT redox products either partially or totally end up as substitutional species, often indistinguishable from those originated in the lower lying LF states. Related to this problem is the lack of knowledge on the efficiency of communication between the CT and LF manifolds.

Some chromium(III) systems do exhibit peculiar LF properties, as doublet-state emission and quenchability of photosubstitutions, which may be taken advantage of to unambiguously separate the CT from the LF photobehavior. Several features make the *trans*-$Cr(NH_3)_4(CN)(NCS)^+$ ion suitable for this kind of approach. (i) Easy access to CT states is provided by a band-rich UV spectrum, spread over a wide wavelength range. (ii) The well-characterized LF photochemistry consists of three simultaneous and comparably efficient reactions.[29] (iii) Reasonably intense and long-lived phosphorescence is emitted under photolysis conditions.[29]

Experimental Section

The *trans*-$[Cr(NH_3)_4(CN)(NCS)](ClO_4)$ salt was synthesized as already reported.[29] Besides the LF maxima at 466 (ϵ 80.0 M^{-1} cm^{-1}) and 355 nm (ϵ 51, shoulder), the absorption spectrum in aqueous medium exhibits intense CT bands at 298 (ϵ 3700), 252 (ϵ 2800, sh), 228 (ϵ 8400), and 210 nm (ϵ 6700, shoulder), as illustrated in Figure 1. $K_3[Cr(C_2$-

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Table I. Quantum Yields[a] for the Charge-Transfer Photolysis of *trans*-$Cr(NH_3)_4(CN)(NCS)^+$ in 1 × 10^{-3} M $HClO_4$/0.10 M $NaClO_4$ Aqueous Solution at 20 °C

λ_{irrn}, nm	$[Cr(C_2O_4)_3^{3-}]$, M	Φ_{NH_3}	Φ_{CN^-}	Φ_{NCS^-}
465[b]	0	0.254 ± 0.007	0.082 ± 0.005	0.019 ± 0.001
295	0	0.200 ± 0.011 (4)	0.063 ± 0.007 (4)	0.059 ± 0.007 (4)
	1.5×10^{-4}	0.167 ± 0.013 (4)[c]	0.056 ± 0.004 (2)	0.057
	3.4×10^{-4}	0.117 ± 0.012 (3)	0.042 ± 0.003 (4)	0.056 ± 0.003 (2)
	8.8×10^{-4}	0.097	0.035	
	1.8×10^{-3}	0.083 ± 0.008 (5)	0.027 ± 0.002 (5)	0.053 ± 0.002 (4)
250	0	0.207 ± 0.007 (3)	0.059 ± 0.003 (2)	0.104 ± 0.006 (6)
	2.9×10^{-4}	0.116	0.039 ± 0.001 (2)	
	1.8×10^{-3}	0.094 ± 0.003 (2)	0.024 ± 0.002 (2)	0.098 ± 0.004 (4)

[a] Number of independent determinations in parentheses. The uncertainties are usually standard deviations, except for the data based on two runs, for which the range of results is given. [b] Data from ref 29. [c] Inclusive of quenching results with $Cr(CN)_6^{3-}$.

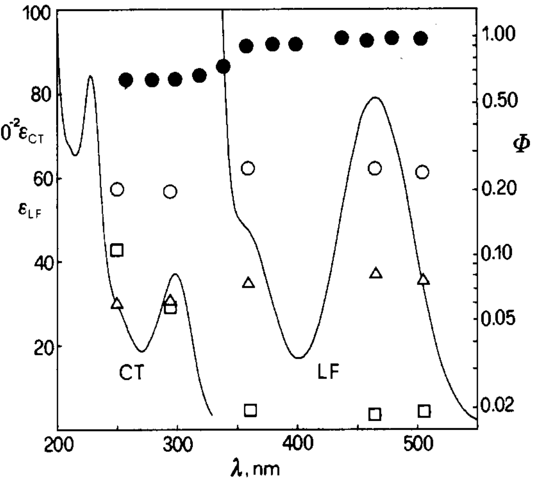

Figure 1. Charge-transfer (ϵ_{CT}) and ligand-field (ϵ_{LF}) absorption spectrum of *trans*-$Cr(NH_3)_4(CN)(NCS)^+$ in 1 × 10^{-3} M $HClO_4$ solution (left scale) and wavelength dependence for the photoaquation quantum yields (right scale) of NH_3 (○), CN^- (△), and NCS^- (□) and for the relative phosphorescence quantum yields, Φ_λ/Φ_{465} (●), at 20 °C.

$O_4)_3]\cdot3H_2O$,[30] $K_3[Cr(CN)_6]$,[31] and $[Co(NH_3)_5F](ClO_4)_2$[32] were prepared by standard methods.

The apparatus and procedures were essentially those described earlier.[29] Photolyses were performed at 20.0 ± 0.5 °C on aqueous samples (3–5) × 10^{-3} M in complex in 1 × 10^{-3} M $HClO_4$/0.10 M $NaClO_4$, both in the absence and in the presence of $Cr(C_2O_4)_3^{3-}$. At this temperature and acidity, thermal CN^- aquation was sufficiently slow (k_{obsd} ca. 6 × 10^{-6} s^{-1}) to minimize analytical interferences. In the Cr^{2+}-scavenging experiments the complex was 8 × 10^{-3} M and $Co(NH_3)_5F^{2+}$ was 1 × 10^{-2} M. In the quenching experiments $Cr(C_2O_4)_3^{3-}$ was 1.5 × 10^{-4} to 1.8 × 10^{-3} M. Correction for mixed light absorption by the quencher was at the most 7% at 295 nm (ϵ 685) and 13% at 250 nm (ϵ 1120). In the UV region light absorption was always complete. Ferrioxalate actinometry[33] was employed. When necessary, solutions were either deaerated by argon bubbling or saturated with oxygen for 30 min prior to photolysis.

Free NH_3 and CN^- were determined potentiometrically at pH 12, by use of selective electrodes. NCS^- was measured spectrophotometrically as the Fe(III) complex, and as already mentioned, its separation from reaction mixtures was necessary.[29] In the present study, anion exchange was found more convenient than cationic chromatography for processing samples with μ = 0.10 M. These were adsorbed on 3 × 0.5-cm columns of Sephadex QAE-A25 resin in the ClO_4^- form. After elution of all cationic complexes with 1 × 10^{-3} M $HClO_4$, NCS^- was displaced by 0.5 M $NaClO_4$/1 × 10^{-3} M $HClO_4$; $Cr(C_2O_4)_3^{3-}$, if present, was also displaced, but it did not hinder analysis. Co^{2+} was determined spectrophotometrically at 625 nm (ϵ 1650) by the thiocyanate–acetone method.[34]

Relative phosphorescence quantum yields were obtained as ratios of the intensities, I_λ, emitted at 709 nm by a given sample irradiated with light of different λ's. Saturated solutions of the complex (ca. 0.05 M in 1 × 10^{-3} M $HClO_4$) were employed in a 10-mm, square cuvette. Absorbances were sufficiently high (A > 4 in the LF region; A > 30 in the CT region) that virtually all the emission occurred from the front window of the cell. The standard fluorometer sample holder was modified so that part of such emission was reflected into the detector by a mirror not interfering with the exciting beam. The incident light intensity at the various wavelengths was determined by use of a thermopile. Care was taken to minimize the occurrence of photoproducts, some of which may act as quenchers. Narrow-band excitation was possible, thanks to the relatively strong emission. In addition, periodical stirring renewed the irradiated volume.

Results

The medium and temperature chosen for the UV photolysis of *trans*-$Cr(NH_3)_4(CN)(NCS)^+$ were the same as in the earlier LF investigation,[29] so as to allow direct comparison. Excitation at 295 and 250 nm was in correspondence of the two CT absorption maxima, shown in Figure 1. Analyses of uncoordinated ligands indicated concurrent, zero-order photorelease of NH_3, CN^-, and NCS^-. The quantum yields, generally obtained from 2 to 6 independent experiments for each entry, are collected in Table I. The values did not change appreciably within error limits when samples were either deaerated or oxygen-saturated. This invariance was ascertained particularly for NCS^- photoaquation.

Some irradiations of the low-energy CT band were performed on oxygen-free solutions, in the presence of 1 × 10^{-2} M $Co(NH_3)_5F^{2+}$ as potential Cr^{2+} scavenger.[35] At 295 nm the spectral maximum of the Cr(III) complex (ϵ 3700) matches the minimum of the Co(III) species (ϵ 9.5), so that fractional light absorption by the latter was less than 0.5%. Co^{2+} was produced with a quantum yield of (3.0 ± 0.5) × 10^{-3} (four determinations). Correction for direct photodecomposition was negligible: independent photolyses of $Co(NH_3)_5F^{2+}$ at 295 nm gave $\Phi_{Co^{2+}}$ = 0.018. No such experiments were possible at 250 nm, because of the higher direct photoredox yield ($\Phi_{Co^{2+}}$ = 0.17) and the unfavorable mixed light absorption. When the above mixtures were irradiated at 465 nm, no Co^{2+} was detected.

CT band excitation under the same experimental conditions induced phosphorescence from $^2A_1/^2B_1$, the characteristics of which (λ_{max} = 709 nm; τ = 30 μs at 20 °C) are known.[29] The wavelength dependence of the relative emission efficiencies is displayed in Figure 1. The Φ_λ/Φ_{465} ratios were found to be constant, within experimental error, inside both the LF and the CT regions: 0.99 ± 0.04 between 500 and 400 nm and 0.65 ± 0.03 between 330 and 250 nm, with a regular variation in the intermediate range.

The emission and the photochemistry were quenched by $Cr(C_2O_4)_3^{3-}$, with linear Stern–Volmer plots for intensity quenching, as upon LF irradiation. Phosphorescence was completely quenched by sufficiently high concentrations of tris(oxalato)chromate(III), while the photoreactions were quenched only in part. Table I lists the quenching results for the three photosubstitution modes at both CT excitation wavelengths. No differences in NH_3 quenching were observed when $Cr(CN)_6^{3-}$ was employed in place of $Cr(C_2O_4)_3^{3-}$. Figure 2 shows the plots of Φ/Φ° vs I/I° for each reaction, compared with the corresponding LF quenching data.

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Table II. Limiting Unquenchable Quantum Yields[a] for Aquation of *trans*-$Cr(NH_3)_4(CN)(NCS)^+$ and Derived Quantities[b]

released ligand	Φ^q_{LF}[c]	295 nm[d] Φ^q_{CT}[e]	295 nm[d] Φ°_{CT}	295 nm[d] η_{IC}	250 nm[d] Φ^q_{CT}[e]	250 nm[d] Φ°_{CT}	250 nm[d] η_{IC}
NH_3	0.064 (0.25)	0.076 (0.38)	0.035	0.65	0.078 (0.38)	0.036	0.67
CN^-	0.021 (0.25)	0.024 (0.38)	0.011	0.63	0.022 (0.38)	0.010	0.60
NCS^-	0.005 (0.25)	0.051 (0.85)	0.048	0.59	0.096 (0.92)	0.093	0.59

[a] In parentheses are the fractions Φ^q/Φ of unquenched photochemistry, corresponding to the intercepts of Figure 2; Φ are the quantum yields of Table I at zero quencher concentration. [b] See text. [c] Data from ref 29. [d] Irradiation wavelengths. [e] Uncertainties estimated from least-squares extrapolation: NH_3, ±8%; CN^-, ±5%; NCS^-, ±4%.

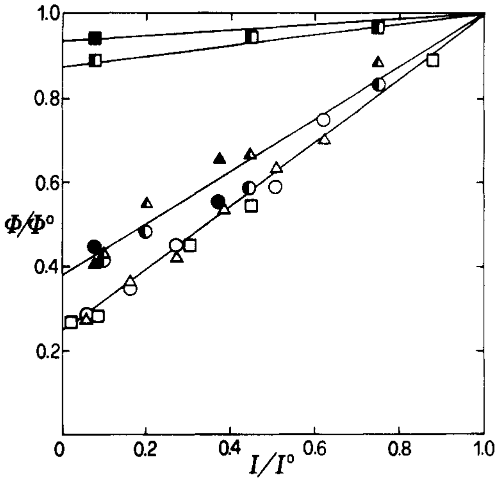

Figure 2. Quenching of the three photoaquation reactions of *trans*-$Cr(NH_3)_4(CN)(NCS)^+$ by $Cr(C_2O_4)_3^{3-}$ vs phosphorescence quenching: (○) NH_3; (△) CN^-; (□) NCS^-. Open, half-full, and full symbols refer to 465- (data from ref 29), 295-, and 250-nm photolyses, respectively.

Linearity indicates that in all cases photochemistry and emission are quenched in parallel. The unquenchable reaction components, extrapolated at infinite quencher concentration, Φ^q_{CT}, are given in Table II. Although, of necessity, the standard deviations for the NCS^- mode often overlap, the trend of the average Φ_{NCS^-} values denotes a small, but real, quenching effect.

Discussion

The previously studied LF photobehavior[29] may be thus summarized. (1) The equatorial (NH_3) and axial (CN^- and NCS^-) photosubstitutions are comparably efficient, in agreement with the small separation (ca. 300 cm^{-1}) evaluated[8] between the photochemically relevant, lowest quartet excited states, $^4B_2$ and ^4E. (2) The quantum yields, reported in Table I, are essentially wavelength independent. (3) On complete doublet quenching, one-fourth of the photoreactivity is unquenched. (4) The unquenchable and quenchable contributions exhibit the same Φ_{NH_3}:Φ_{CN^-}:Φ_{NCS^-} = 3:1:0.2 ratios, suggesting a unique LF reactive precursor, hence, doublet deactivation mainly via back-intersystem-crossing.

In Figure 1, differences between the CT and LF spectral regions are quite evident for both the photochemistry and the emission. At both 295 and 250 nm, Φ_{NH_3} and Φ_{CN^-} decrease to about 80% of their LF values, their 3:1 distribution being unaffected. By contrast, Φ_{NCS^-} increases by a factor of ca. 3 at 295 nm and ca. 5 at 250 nm. The latter substantial increments imply an inherent CT photoreactivity.

Partial internal conversion of CT into LF states is immediately apparent from the phosphorescence promoted by CT excitation; the wavelength profile of the Φ_λ/Φ_{465} ratio, alone, gives the efficiency of such a process: η_{IC} = 0.65 ± 0.03. However, much more independent information on this point is provided by the photolysis quenching—another intrinsic LF feature—which also enables quantification of the CT reactivity. It should be preliminarily noticed that the constancy of Φ_λ/Φ_{465} between 400 and 500 nm indicates virtually unit efficiency of conversion to the lowest quartet and doublet excited state(s), within the LF manifold, congruent with the constancy of the quantum yields for the three photoaquation modes.

Table II and Figure 2 show that also the quenching behavior changes considerably on passing from LF to CT irradiation. In general, photoaquation quenching becomes less effective for all ligands; moreover, there are again differences between the NCS^- mode and the two other reactions. NH_3 and CN^- are quenched to the same extent, within error limits, at both CT wavelengths, while the fractions of NCS^- quenching are much smaller. However, the proportion of the three quenchable quantum yields consistently remains 3:1:0.2.

Our findings may be analyzed as follows. For each ligand at a given CT excitation wavelength, the quantum yields in the absence (Φ_{CT}) and in the presence of a quencher (Φ^q_{CT}) can be expressed by eq 1 and 2, where Φ°_{CT} refers to the processes

$$\Phi_{CT} = \Phi^\circ_{CT} + \eta_{IC}\Phi^\circ_{LF} \qquad (1)$$

$$\Phi^q_{CT} = \Phi^\circ_{CT} + \eta_{IC}\Phi^q_{LF} \qquad (2)$$

originating directly in the CT state(s) and Φ°_{LF} and Φ^q_{LF} are the known LF photoreaction efficiencies.[29] The limiting Φ^q_{LF} values are included in Table II. Note that Φ°_{CT} is not affected by LF doublet quenching. The Φ°_{CT} and η_{IC} quantities, determined by combining the two relations, are given in Table II. η_{IC} is thus evaluated from six independent sets of data. The averages are 0.62 ± 0.03 at 295 nm and 0.62 ± 0.04 at 250 nm, in excellent agreement with the emission results.

Only two other η_{IC} values have been obtained for chromium(III) species, from the wavelength dependence of emission: ca. 0.7 for *trans*-$Cr(en)_2(NCS)_2^+$[28] and 0.40 for *trans*-$Cr(NH_3)_4(CN)Cl^+$.[36] No systematization is yet possible, but the available data suggest that efficient CT → LF conversion may be fairly common. Some role in enhancing η_{IC} may be played by the heavy-atom effect of NCS^-, as was proposed for cobalt(III)–ammine complexes.[37]

Differently from the LF photochemistry, the CT reactivity (Φ°_{CT}) involves mainly thiocyanate labilization, consistent with the assignment of the UV absorption bands to a $\pi(NCS) \rightarrow e_g^*(Cr)$ charge shift.[38,39] The nature of the transition suggests primary homolytic Cr–NCS bond cleavage, and scavenging experiments indeed demonstrate redox activity. Yet, substitutional products are ultimately observed. Even though not exhaustive, the available Φ°_{CT} data warrant some interpretation in light of current photolysis models.[40] Equations 3 and 4 provide a simple, but reasonable, picture.

$$\begin{tikzcd}
\{Cr(NH_3)_4(CN)^+, H_2O, {}^\bullet NCS\} \arrow[r] \arrow[dr] & Cr(NH_3)_4(H_2O)(CN)^{2+} + NCS^- \quad (3) \\
& Cr(aq)^{2+} + 4NH_3 + CN^- + {}^\bullet NCS \quad (4)
\end{tikzcd}$$

Following CT excitation, those radical pair species not undergoing primary recombination (to yield the reactant, not necessarily trans) and including the solvent in the cage may competitively diffuse apart with (eq 3), or without (eq 4), back electron transfer to ${}^\bullet NCS$. Since Cr(II) is a strong reductant, process 3 is expected to be highly efficient, so that most of the released NCS^-

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would be associated with formation of a Cr(III) cyano aquo complex. Identification of this species was precluded, however, by the complexity of the system, that is, by the simultaneous occurrence of other (LF) aquation products. The increase of Φ_{NCS^-} with decreasing irradiation wavelength is in line with excess energy preventing primary recombination of the cage partners. This variation may be alternatively explained by intervention of two reactive states, as the CT absorption (Figure 1) consists of two distinct bands.

Some NH_3 and CN^- photorelease must be also related to CT reactivity, as inferred, beyond experimental error, from the lower degree of quenchability of their total CT quantum yields (Figure 2). These minor amounts are envisaged as fragments of coordinatively unsaturated, labile Cr(II) species breaking apart in eq 4, in conjunction with cage escape of the $^{\bullet}NCS$ radical. Although the small Φ°_{CT} values for NH_3 and CN^- are necessarily affected by large percentage errors, their 3.5:1 ratio (close to 4:1) is compatible with this picture. The implication is an efficiency of 0.01 for pathway 4, ca. 10–20% of that for pathway 3. $\Phi_{Co^{2+}} = 0.003$ then indicates that scavenging of $Cr(aq)^{2+}$ by $Co(NH_3)_5F^{2+}$ is, naturally, incomplete.

Escaped $^{\bullet}NCS$ is very likely to gain stability by interaction with free NCS^- produced in reaction 3, to give $(NCS)_2^-$ ($k = 7 \times 10^9$ M^{-1} s^{-1}; $K = 2 \times 10^5$ M^{-1}),[41] subsequently decomposing to $(NCS)_2$ (and its hydrolysis products) and more NCS^-.[37,41] Also, bulk solution recombination with $Cr(aq)^{2+}$, leading to either $Cr(H_2O)_6^{3+} + NCS^-$ or $Cr(H_2O)_5(NCS)^{2+}$, should be considered in principle. However, these stabilization processes would involve but a small fraction ($\Phi \leq 0.01$) of totally released thiocyanate. Deaeration and O_2-saturation experiments show that oxygen competition in Cr(II) scavenging, hence in altering the overall Φ_{NCS^-} values, if any, is certainly small and obscured by experimental uncertainty.

To summarize, in the explored region the efficiency of CT chemical deactivation ranges between 0.05 and 0.09. By difference, the CT states result to relax about 25–35% of the time directly to the ground state, without populating the lower energy LF levels.

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Registry No. *trans*-$Cr(NH_3)_4(CN)(NCS)^+$, 108561-55-3; NH_3, 7664-41-7; CN^-, 57-12-5; NCS^-, 302-04-5.

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Differences in the Nature and Stability of Cadmium Complexes with Group 15/Group 16 Donor Ligands As Determined by Multinuclear (^{31}P, ^{77}Se, ^{113}Cd) Magnetic Resonance and Electrochemical Techniques

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Multinuclear (^{31}P, ^{77}Se, ^{113}Cd) magnetic resonance and electrochemical studies have been carried out to investigate the nature and stability of cadmium complexes with $Ph_2PCH_2P(E)Ph_2$ [E = S (dpmS), Se (dpmSe)] and $Ph_2P(E)CH_2P(E)Ph_2$ [E = S (dpmS$_2$), Se (dpmSe$_2$)] in dichloromethane solution. The NMR studies indicate a cadmium preference for selenium or sulfur rather than phosphorus coordination in the dpmE complexes but are limited in scope with the NMR technique to examination of the 1:2 cadmium to ligand stoichiometry due to the labile nature of the systems in the presence of excess ligand. Cadmium–selenium coupling is observed in some cases. The electrochemical reductions of both $[Cd(dpmE)_2]^{2+}$ and $[Cd(dpmE_2)_2]^{2+}$ at a mercury electrode are reversible two-electron processes. The variations in half-wave potential of these processes as a function of ligand concentration have been measured in order to calculate the number of moles of coordinated ligand and the stability constants of the resultant compounds in excess of 1:2 cadmium to ligand stoichiometry. Ligand coordination numbers of 4 and 6 are attained with the dpmE complexes, but the dpmE$_2$ complexes have a maximum ligand coordination number of 4 even at very high ligand to metal concentration ratios. The magnitudes of the calculated stability constants suggest that all of the dpmE and dpmE$_2$ complexes of cadmium(II) are essentially nondissociated in solution. The use of a Cd(Hg) amalgam electrode allows examination of the voltammetry of these cadmium systems in the presence of substoichiometric ligand concentrations and reemphasizes the high stability of the dpmE and dpmE$_2$ complexes. The preference of cadmium for the group 16 donor atoms rather than phosphorus in the dpmE complexes is confirmed by an investigation of the interactions of cadmium perchlorate with PPh_3 and PPh_3Se and by suitable mixing experiments.

Introduction

Few NMR studies on phosphine chalcogenide complexes of cadmium(II) have been reported in the literature.[3–6] Dean and co-workers[5,6] characterized a range of cadmium complexes with monodentate, bidentate, and potentially tridentate phosphine sulfides and phosphine selenides by phosphorus-31 NMR spectroscopy in liquid SO_2. In all cases, the maximum coordination number for cadmium was 4 although 6-coordination was observed with phosphine oxide ligands.[6] Cadmium-113 NMR spectroscopy has been used extensively to investigate solution structures of compounds of the type $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ and $[X_4Cd_{10}(SPh)_{16}]^{4-}$ (X = S, Se)[7] and other systems.[8]

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