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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The electrochemical reduction of cadmium complexes at mercury electrodes is almost invariably a two-electron process involving the formation of a cadmium amalgam with no indication of the formation of a Cd(I) intermediate. This process can be described by the reaction

$$[\mathrm{CdL}_x]^{2+} + 2\mathrm{e}^- \overset{\mathrm{Hg}}{\rightleftharpoons} \mathrm{Cd(Hg)} + x\mathrm{L} \qquad (1)$$

where L is a neutral ligand. If the process is completely reversible, then measurement of the half-wave potential as a function of ligand concentration relative to the value for the noncomplexed $[\mathrm{Cd}]^{2+}$ cation provides information on the nature and stability of the cadmium complexes formed. It has been shown recently[9] that oxidation of a Cd(Hg) amalgam electrode in dichloromethane in the presence of a noncomplexing electrolyte such as $\mathrm{Bu_4NPF_6}$ produces a reversible reaction

$$\mathrm{Cd(Hg)} \rightleftharpoons [\mathrm{Cd}]^{2+} + \mathrm{Hg} + 2\mathrm{e}^- \qquad (2)$$

and the reversible half-wave potential for $[\mathrm{Cd}]^{2+}$ is now available in this solvent. Therefore, a method is now available for studying the thermodynamics of labile cadmium complexes in dichloromethane via a combination of polarographic and amalgam electrode techniques.

In this paper we describe the use of NMR (^{31}P, ^{77}Se, ^{113}Cd) and electrochemical techniques to investigate the nature and stability of cadmium complexes of the mixed group 15/group 16 ligands $\mathrm{Ph_2PCH_2P(E)Ph_2}$ [E = S (dpmS), Se (dpmSe)] and the group 16 ligands $\mathrm{Ph_2P(E)CH_2P(E)Ph_2}$ [E = S ($\mathrm{dpmS_2}$), Se ($\mathrm{dpmSe_2}$)].

Experimental Section

Materials. All solvents and reagents used were of AR grade. The dichloromethane used for the electrochemical experiments was dried over $\mathrm{CaH_2}$ and distilled prior to use. In order to avoid any contamination by water, freshly activated alumina was present in the voltammetric cell during all experiments. Tetrabutylammonium hexafluorophosphate, $\mathrm{Bu_4NPF_6}$, used as the supporting electrolyte for electrochemical studies in $\mathrm{CH_2Cl_2}$ was obtained from Southwestern Analytical and was dried under vacuum at 70 °C. The Cd(Hg) amalgam (5×10^{-4} M Cd) was prepared as described in the literature.[9] The dpmE and $\mathrm{dpmE_2}$ ligands were prepared as described previously.[10,11]

Preparation. *Caution*! Although no difficulties have been experienced in the preparation and handling of these complexes, care should always be exercised in the use of perchlorate salts. The complexes $[\mathrm{Cd(dpmE)_2}][\mathrm{ClO_4}]_2$ and $[\mathrm{Cd(dpmE_2)_2}][\mathrm{ClO_4}]_2$ were prepared by stirring the ligands in approximately 1:1 proportions with solid $\mathrm{Cd(ClO_4)_2{\cdot}6H_2O}$ in dichloromethane at room temperature. This procedure ensures that the final product does not contain excess ligand. After reaction, the solution was filtered to remove excess $\mathrm{Cd(ClO_4)_2{\cdot}6H_2O}$ and evaporated to dryness, and the resulting solid was recrystallized from dichloromethane/*n*-hexane.

$[\mathrm{Cd(DMSO)_6}][\mathrm{CF_3SO_3}]_2$ was prepared by the interaction of 2 mol of $\mathrm{CF_3SO_3H}$ with 1 mol of $\mathrm{Cd(CO_3)_2}$ in dimethyl sulfoxide, DMSO (>6 mol). The excess DMSO was evaporated by heating, and the solution was then cooled to allow crystallization. The colorless product was recrystallized from DMSO and washed with tetrahydrofuran.

The complexes $[\mathrm{Cd(dpmE)_2}][\mathrm{CF_3SO_3}]_2$ and $[\mathrm{Cd(dpmS_2)_2}][\mathrm{CF_3SO_3}]_2$ were prepared by stirring $[\mathrm{Cd(DMSO)_6}][\mathrm{CF_3SO_3}]_2$ in 1:2 proportions with the appropriate ligand in dichloromethane at room temperature. The solvent was removed under vacuum, and the resulting solid was recrystallized from dichloromethane/*n*-hexane.

Instrumentation. NMR spectra of approximately 0.1 M solutions were recorded by using a JEOL FX 100 spectrometer with external ^{7}Li lock. Phosphorus-31 NMR spectra were recorded at 40.26 MHz (reference external 85% $\mathrm{H_3PO_4}$), selenium-77 spectra at 18.99 MHz (external 1 M $\mathrm{H_2SeO_3}$ in $\mathrm{H_2O}$[12] used as a secondary reference), and cadmium-113 spectra at 22.09 MHz (external 4.5 M $\mathrm{Cd(NO_3)_2}$ in $\mathrm{H_2O}$, which is 73 ppm to low frequency of 0.1 M $\mathrm{Cd(ClO_4)_2}$[8]). The convention used is that chemical shifts to high frequency are positive. A JEOL NM 5471 controller was used for temperature control, and temperatures in the probe were measured with a calibrated platinum resistance thermometer.

Infrared spectra were recorded on a Jasco A-320 instrument.

Voltammetric measurements were made with a Princeton Applied Research Corp. (PAR) (Princeton, NJ) Model 174A polarographic analyzer with a dropping-mercury or dropping-Cd(Hg) amalgam electrode. For cyclic voltammetry, a sweep delay of 1 s was introduced to allow uniform growth of the mercury or Cd(Hg) amalgam drop for each experiment. A platinum wire served as the auxiliary electrode, while the reference electrode was Ag/AgCl (saturated LiCl in $\mathrm{CH_2Cl_2}$) separated from the test solution by a salt bridge containing $\mathrm{CH_2Cl_2}$ (0.2 M $\mathrm{Bu_4NPF_6}$). The potential of the $[\mathrm{(C_5H_5)_2Fe}]^+/\mathrm{(C_5H_5)_2Fe}$ ($\mathrm{Fc^+/Fc}$) redox couple was measured frequently vs Ag/AgCl via monitoring of the oxidation of ferrocene, and all data are reported relative to this couple rather than Ag/AgCl. All measurements were made at 25 °C in $\mathrm{CH_2Cl_2}$ (0.2 M $\mathrm{Bu_4NPF_6}$).

Results and Discussion

NMR Studies. (a) dpmE Complexes. The phosphorus-31 NMR spectrum of $[\mathrm{Cd(dpmSe)_2}][\mathrm{ClO_4}]_2$ in dichloromethane at 25 °C consists of two overlapping doublets centered at δ 38.9 and a broad resonance at δ −7.5, which suggests that two species are present in solution and that some exchange mechanism is operating. On cooling of the solution to −80 °C, the exchange slows on the NMR time scale and the spectrum consists predominantly of two doublets of approximately equal intensity at δ 40.7 and −8.9. Upon spectral expansion, both doublets are resolved into doublets of doublets. The low-frequency doublet has broad, unresolved cadmium-111 and cadmium-113 satellites, while the other doublet has selenium-77 satellites ($^1J_{\mathrm{Se,P}}$ = 590 Hz). The phosphorus–selenium coupling constant is reduced from that of the free ligand value (732 Hz),[10] indicating selenium coordination.[11] The low-frequency phosphorus resonance is well shifted from the P(III) resonance of free ligand, and this observation, together with the large coupling constant to cadmium, indicates phosphorus coordination. The appearance of both phosphorus resonances as doublet of doublets shows that two dpmSe ligands are chelated to cadmium on the NMR time scale.[13] The phosphorus atoms constitute an AA′XX′ spin system, but unlike the corresponding spectrum[14] for $[\mathrm{Hg(dpmSe)_2}]^{2+}$, it does not completely simplify to an $\mathrm{A_2X_2}$ system due to the significantly different phosphorus–phosphorus coupling constants involved. The corresponding cadmium-113 NMR spectrum recorded at −80 °C is a triplet with a coupling constant equal to that observed in the phosphorus-13 NMR spectrum and indicates a cadmium atom coordinated to two equivalent phosphorus atoms. The coupling constant of 1550 Hz compares well with values of 1350–1635 Hz in a series of bis(phosphine) complexes of $\mathrm{CdX_2}$ (X = Cl, Br, I) in dichloromethane at low temperatures.[15] The selenium-77 NMR spectrum of $[\mathrm{Cd(dpmSe)_2}][\mathrm{ClO_4}]_2$ at −80 °C is a doublet flanked by a pair of superimposed cadmium-111 and cadmium-113 satellites ($^1J_{\mathrm{Cd,Se}}$ = 195 Hz), which account for about 25% of the total signal intensity. NMR data for this system are given in Table I.

All the spectral data at low temperature for the major species in solution are consistent with the chelation of two dpmSe ligands to give, presumably, a tetrahedral $\mathrm{CdSe_2P_2}$ core. The NMR data for $[\mathrm{Cd(dpmSe)_2}][\mathrm{ClO_4}]_2$ at −80 °C are comparable with the room-temperature data for the analogous mercury complex, $[\mathrm{Hg(dpmSe)_2}][\mathrm{ClO_4}]_2$.[14] The phosphorus–selenium coupling constant remains reduced relative to that of the free ligand in the exchange-averaged NMR spectrum at room temperature. This shows that the Cd–Se bond is not extensively dissociated at room temperature. If it were, the exchange-averaged coupling constant would approach that of the free ligand. It is known that the cadmium–phosphorus bond is considerably weaker than the mercury–phosphorus bond.[16] The relative strengths of cadmium–selenium and mercury–selenium bonds are unknown, but the tentative indication from the NMR work is that cadmium is more

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Table I. NMR Data in Dichloromethane for the dpmE Ligands and Their Derivatives of $Cd(ClO_4)_2{\cdot}6H_2O$ and $[Cd(DMSO)_6][CF_3SO_3]_2$

compd	$\delta(^{31}P)$	$\delta(^{77}Se)^a$	$\delta(^{113}Cd)$	couplings, Hz	temp, °C
dpmSe	30.4 (d) −27.7 (d)	−315 (d)		$^2J_{P,P} = 85$ $^1J_{Se,P} = 732$	25
$[Cd(dpmSe)_2][ClO_4]_2$	40.7 (dd) −8.9 (dd)	−315 (d)	670 (t)	$^2J_{P,P} = 56$ $^3J_{P,P} = 12$ $^1J_{Se,P} = 590$ $^1J_{Cd,P} = 1550$ $^1J_{Cd,Se} = 195$	−80
$[Cd(dpmSe)_2(DMSO)_x]^{2+\,b}$	33.9 (m) −18.9 (m)	*d*	400 (t)	$^1J_{Se,P} = 630$ $^1J_{Cd,P} = 1030$	−80
$[Cd(\eta^2\text{-dpmSe})(\eta^1\text{-dpmSe})(DMSO)_x]^{2+\,c}$	31.3 (d) −29.5 (d) 36.6 (d) −19.0 (d)	*d*	280 (d)	$^2J_{P,P} = 90$ $^1J_{Cd,P} = 1530$	−80
dpmS	40.0 (d) −28.5 (d)			$^2J_{P,P} = 78$	25
$[Cd(dpmS)_2][ClO_4]_2$	49.0 (dd) −10.4 (dd)		636 (t)	$^2J_{P,P} = 39$ $^3J_{P,P} = 20$ $^1J_{Cd,P} = 1785$	−80
$[Cd(dpmS)_2(DMSO)_x]^{2+\,b}$	40.7 (t) −22.0 (t)		*d*	$^3J_{P,P} = 20$ $^1J_{Cd,P} = 1255$	−80
$[Cd(\eta^2\text{-dpmS})(\eta^1\text{-dpmS})(DMSO_x]^{2+\,c}$	41.0 (d) −30.5 (d) 43.7 (d) −22.0 (d)		*d*	$^2J_{P,P} = 80$ $^2J_{P,P} = 49$ $^4J_{Cd,P} = 1700$	−80

[a] Versus Me_2Se, assuming δ for H_2SeO_3 is +1282 ppm.[12] [b] $x = 1, 2$. Counteranion = $[CF_3SO_3]^-$. [c] $x = 1–3$. Counteranion = $[CF_3SO_3]^-$. [d] Not observed due to solubility problems. d = doublet, dd = doublet of doublets, t = triplet, and m = multiplet.

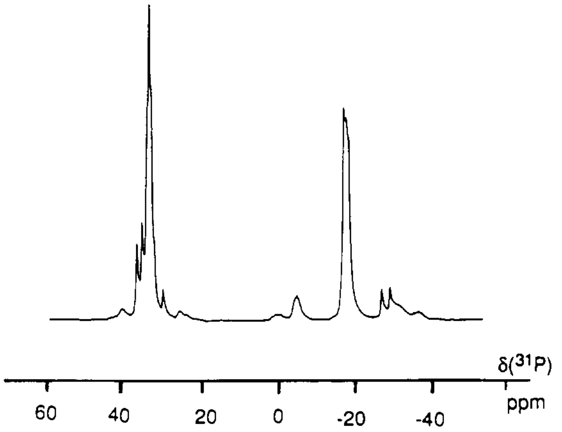

Figure 1. ^{31}P NMR spectrum at −80 °C of a dichloromethane solution of $[Cd(dpmSe)_2][CF_3SO_3]_2$.

strongly bonded to selenium than to phosphorus in the dpmSe complex and that the broadening of the phosphorus-31 NMR spectrum at 25 °C may be due to cadmium–phosphorus bond dissociation. This hypothesis will be confirmed by further NMR and electrochemical measurements described later.

Addition of a small excess of dpmSe to $[Cd(dpmSe)_2][ClO_4]_2$ in dichloromethane solution causes a rapid exchange process that cannot be slowed down on the NMR time scale within the accessible temperature range, so that NMR studies of solutions containing more than 2 mol equiv of dpmSe/cadmium are uninformative.

The phosphorus-31 NMR spectrum of $[Cd(dpmSe)_2][CF_3SO_3]_2$ in dichloromethane at 25 °C contains a sharp doublet at δ 33 with selenium satellites ($^1J_{P,Se} = 655$ Hz) and a broad doublet at δ −17.9. On cooling of the solution to −80 °C, the phosphorus-31 NMR spectrum shown in Figure 1 is obtained. This spectrum is dominated by two multiplets at δ 33.9 and −18.9, which are similar to those of $[Cd(dpmSe)_2][ClO_4]_2$ but at different chemical shifts. The low-frequency resonance has broad, unresolved cadmium-111 and cadmium-113 satellites ($^1J_{Cd,P} = 1030$ Hz) and the high-frequency signal has selenium-77 satellites, indicating chelation of the dpmSe ligands as before. In addition, two doublets of low intensity occur at δ −29.5 and 31.3 ($^2J_{P,P} = 90$ Hz), the latter signal being obscured by the intense resonance at δ 33.9. The chemical shifts of these doublets resemble those of free dpmSe (Table I). There is also a doublet at δ 36.6 associated with a P(Se) phosphorus atom, but its selenium satellites are not observed. The accompanying P(III) resonance is hidden beneath the intense resonance at δ −18.9, but its cadmium satellites are visible ($^1J_{Cd,P} = 1530$ Hz).

The apparent differences between the phosphorus-31 NMR spectra of $[Cd(dpmSe)_2]^{2+}$ as the perchlorate and the triflate complexes are due to the presence of some DMSO in the latter originating from the starting material, $[Cd(DMSO)_6][CF_3SO_3]_2$. The presence of DMSO was confirmed by proton NMR spectroscopy in $CDCl_3$, and the addition of DMSO to a solution of $[Cd(dpmSe)_2][ClO_4]_2$ produces this same type of spectrum. It is envisaged that in this system the complex formed with two chelated dpmSe ligands is $[Cd(dpmSe)_2(DMSO)]^{2+}$ or $[Cd(dpmSe)_2(DMSO)_2]^{2+}$ with expansion of the coordination number to 5 or 6, as previously observed[6] with oxygen donors, so that its chemical shifts are different from those of $[Cd(dpmSe)_2]^{2+}$ seen as the perchlorate. As noted above, there are two weak doublets whose chemical shifts are similar to those of free dpmSe and which, in the absence of other data, would certainly be assigned to free ligand. However, the electrochemical experiments described later demonstrate very high stability constants for the dpmSe complexes, and thus, a detectable concentration of free dpmSe is unlikely to be present in the solution. A monodentate dpmSe coordinated through selenium would be expected to have phosphorus-31 NMR parameters very similar to those of dpmSe itself, since the nature of both phosphorus atoms is almost unperturbed from those of the free ligand. Thus, the weak phosphorus resonances described above for the triflate salt are consistent with the presence of some $[Cd(\eta^2\text{-dpmSe})(\eta^1\text{-dpmSe})(DMSO)_x]^{2+}$ ($x = 1–3$, but the value is unknown), which is also consistent with the electrochemical results presented later in this paper.

The cadmium-113 NMR spectrum of $[Cd(dpmSe)_2][CF_3SO_3]_2$ at −80 °C consists of a broad triplet, a doublet, and a broad singlet. The triplet and doublet are assigned to $[Cd(dpmSe)_2(DMSO)_x]^{2+}$ and $[Cd(\eta^2\text{-dpmSe})(\eta^1\text{-dpmSe})(DMSO)_x]^{2+}$ (η^1-dpmSe is Se-bonded), respectively, by their cadmium–phosphorus coupling constants, while the singlet is due to an unidentified cadmium species. The phosphorus-31 and cadmium-113 NMR spectra of $[Cd(dpmS)_2]^{2+}$ are similar to those of $[Cd(dpmSe)_2]^{2+}$, and data are given in Table I.

(b) dpmE$_2$ Complexes. The phosphorus-31 NMR spectrum of $[Cd(dpmSe_2)_2][ClO_4]_2$ in dichloromethane at −80 °C consists of a singlet at δ 28.5 ppm with both selenium and cadmium satellites. The cadmium-113 NMR spectrum at −80 °C is a quintet at δ 195 ppm consistent with four equivalent phosphorus atoms about

Table II. Infrared Data[a] for the dpmE and dpmE$_2$ Ligands and Their Respective Cadmium Complexes

complex	ν(P=Se), cm^{-1}	ν(P=S), cm^{-1}
dpmSe	529	
[Cd(dpmSe)$_2$][ClO$_4$]$_2$	520	
[Cd(dpmSe)$_2$][CF$_3$SO$_3$]$_2$	525[b]	
	520[b]	
dpmS		600
[Cd(dpmS)$_2$][ClO$_4$]$_2$		590[b]
[Cd(dpmS)$_2$[]CF$_3$SO$_3$]$_2$		585[b]
dpmSe$_2$	520	
[Cd(dpmSe$_2$)$_2$][ClO$_4$]$_2$	518[b]	
dpmS$_2$		592
[Cd(dpmS$_2$)$_2$][CF$_3$SO$_3$]$_2$		585[b]

[a] KBr disk. [b] Broad.

the cadmium(II) center, but selenium-77 satellites are not resolved due to the poor signal to noise ratio. The selenium-77 NMR spectrum is a doublet at δ −310 ppm with superimposed cadmium-111 and cadmium-113 satellites. In all cases coupling constants are equal in the respective spectra. All of the spectroscopic data are consistent with the chelation of two dpmSe$_2$ ligands to cadmium. Dean[5] prepared [Cd(dpmSe$_2$)$_2$]$^{2+}$ in situ by the interaction of Cd(SbF$_6$)$_2$ and dpmSe$_2$ in liquid SO$_2$, and the reported phosphorus-31 NMR data at −50 °C agree well with those given here. Addition of a small excess of dpmSe$_2$ to [Cd(dpmSe$_2$)$_2$][ClO$_4$]$_2$ in dichloromethane solution causes a rapid exchange process that cannot be slowed down on the NMR time scale within the accessible temperature range.

The phosphorus-31 NMR spectrum at 25 °C of [Cd(dpmS$_2$)$_2$]$^{2+}$ as the perchlorate is a sharp singlet. On cooling of the solution to −80 °C, the singlet collapses to give, usually, two broad signals at δ 39.5 and 33.8, but the relative intensity of the signals varies. Upon spectral expansion, cadmium satellites ($^2J_{\mathrm{Cd,P}}$ = 35 Hz) become apparent for the singlet at δ 39.5. It is assumed that this phosphorus-31 NMR signal is due to [Cd(dpmS$_2$)$_2$][ClO$_4$]$_2$ by a comparison of the data for [Hg(dpmS$_2$)$_2$][ClO$_4$]$_2$.[14] The broad resonance at δ 33.8 is very close to that for free dpmS$_2$. However, the electrochemical experiments described later demonstrate a very high stability constant for dpmS$_2$ complexes of cadmium, and thus, a significant concentration of free dpmS$_2$ is unlikely to be present in the solution. Therefore, the signal at δ 33.8 may be due to a second cadmium species in which the dpmS$_2$ ligands are still exchanging at −80 °C. The cadmium-113 NMR spectrum at −80 °C consists of a broad multiplet at δ 415, but the multiplicity of this resonance is not clear due to the poor signal to noise ratio.

The NMR spectra of [Cd(dpmS$_2$)$_2$][CF$_3$SO$_3$]$_2$ are also difficult to interpret and do not provide sufficient information to clearly identify the species in solution. However, the cadmium-113 NMR spectrum at −80 °C consists of two multiplets at δ 340 and 220. This clearly demonstrates that there are at least two cadmium species in solution, which is consistent with the electrochemical results for this system (see later).

In summary, the NMR studies show the cadmium complexes to be labile on the NMR time scale at room temperature, although this does not necessarily indicate complete dissociation of the bidentate ligands from the metal. Reversible bidentate–monodentate coordination would be consistent with the observations, but NMR studies alone are not sufficient to fully characterize these systems, expecially in those cases where the ligand:metal concentration ratios exceed 2:1.

Infrared Studies. The infrared spectra of all of the compounds isolated were examined in the P=S and P=Se region. In all cases the frequency observed was lower than that of the free ligand and this is confirmation of coordination of the group 16 atoms.[11] Infrared data are given in Table II.

Electrochemical Studies. (a) dpmE Systems. Figure 2 shows a current-sampled dc polarogram for the reduction of 5 × 10^{-4} M [Cd(dpmSe)$_2$][CF$_3$SO$_3$)]$_2$ in dichloromethane (0.2 M Bu$_4$NPF$_6$) solution (polarogram i). One oxidation wave (process I) and one reduction wave (process II) are observed as shown by the line of zero current (i = 0). The oxidation process is associated with the formation of a mercury complex involving dpmSe. However, the half-wave potential of this response is not the same as that for the oxidation of mercury in the presence of free dpmSe[14] according to the equation

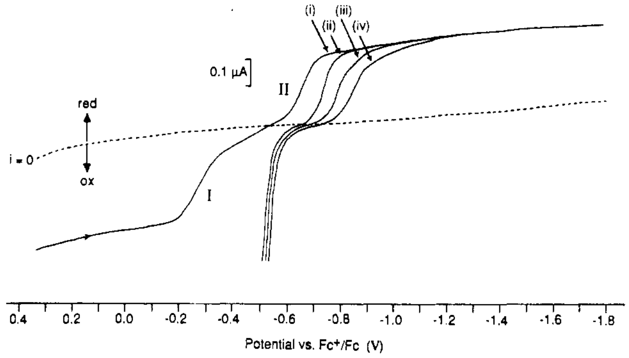

Figure 2. Current-sampled dc polarograms at a drop time of 0.5 s for the reduction of 5 × 10^{-4} M [Cd(dpmSe)$_2$][CF$_3$SO$_3$]$_2$ at a mercury electrode in dichloromethane (0.2 M Bu$_4$NPF$_6$) solution at 25 °C in the presence of (i) no added dpmSe, (ii) 5 × 10^{-3} M dpmSe, (iii) 2 × 10^{-2} M dpmSe, and (iv) 5 × 10^{-2} M dpmSe.

$$\mathrm{Hg} + 2\mathrm{dpmSe} \rightleftharpoons [\mathrm{Hg(dpmSe)_2}]^{2+} + 2e^- \qquad (3)$$

This suggests that process I is not due to free dpmSe in solution but rather that the cadmium complex, [Cd(dpmSe)$_2$]$^{2+}$, is interacting with the mercury electrode. The previously described NMR data reveal that at room temperature the cadmium–phosphorus bond in [Cd(dpmSe)$_2$]$^{2+}$ cleaves very rapidly, and therefore, mercury can interact with the pendent phosphorus atom in this labile complex to produce process I.

Figure 2 also shows that as free dpmSe is progressively added to the solution of [Cd(dpmSe)$_2$]$^{2+}$ the reduction process II shifts toward more negative potentials but its limiting current is almost independent of ligand concentration in the range 5 × 10^{-3} to 5 × 10^{-2} M (polarograms ii–iv). The oxidation process I associated with the presence of the ligand does of course increase in height as a function of ligand concentration. Data obtained from dc polarography and cyclic voltammetry for the reduction of [Cd(dpmSe)$_2$]$^{2+}$ in the presence of varying quantities of excess dpmSe are summarized in Table III. Uncompensated resistance effects are not entirely absent, but since the ligands are neutral and do not affect the conductivity, the effect of iR drop on the half-wave potential, $E_{1/2}$, is essentially constant. Consequently, the shifts in $E_{1/2}$ still reflect the thermodynamics of complex formation.

Cyclic voltammograms indicate that chemical reversibility of the cadmium system is essentially maintained for all ligand concentrations. Data described below obtained for the oxidation of a Cd(Hg) amalgam electrode in the presence of dpmSe show a similar $E_{1/2}$ value for oxidation as for the above described reduction process, establishing the reversibility of the process in a more fundamental sense.

The variation in half-wave potential as a function of ligand concentration can be used to calculate the number of moles of coordinated ligand and the stability constants of the resultant compounds. If only one complex is formed with an equilibrium constant, β_x, for the reaction

$$[\mathrm{Cd}]^{2+} + x\mathrm{dpmSe} \overset{\beta_x}{\rightleftharpoons} [\mathrm{Cd(dpmSe)}_x]^{2+} \qquad (4)$$

then β_x is related to $E^{\mathrm{r}}_{1/2}$ by the relationship

$$E^{\mathrm{r}}_{1/2}(\text{complex}) - E^{\mathrm{r}}_{1/2}(\text{free}) = -2.303RT/nF \log \beta_x - 2.303RT/nF \log\,[\mathrm{dpmSe}]^x \qquad (5)$$

assuming equal diffusion coefficients for the "free" and the complexed metal ions.[17-20] This assumption is not completely justified,

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(17) Heyrovský, J.; Kůta, J. *Principles of Polarography*; Academic Press: New York, 1966.

Table III. Electrochemical Data for the Reduction of 5×10^{-4} M $[Cd(dpmE)_2]^{2+}$ in the Presence of Varying Quantities of dpmE at a Dropping-Mercury Electrode in Dichloromethane (0.2 M Bu_4NPF_6) at 25 °C

added dpmE concn, M	dc polarography[a]		cyclic voltammetry[b]	
	$E_{1/2}$,[c] V	i_d, μA	E_p^{red}, V	E_p^{ox}, V
	(a) dpmSe			
	−0.645	0.60	−0.71	−0.63
5.0×10^{-3}	−0.745	0.50		
1.0×10^{-2}	−0.785	0.50		
1.5×10^{-2}	−0.815	0.53		
2.0×10^{-2}	−0.835	0.53		
3.0×10^{-2}	−0.855	0.45		
4.0×10^{-2}	−0.885	0.43		
5.0×10^{-2}	−0.915	0.40		
7.5×10^{-2}	−0.945	0.40		
1.0×10^{-1}	−0.965	0.33	−1.01	−0.95
	(b) dpmS			
	−0.620	0.72	−0.67	−0.60
5.0×10^{-3}	−0.710	0.53		
1.0×10^{-2}	−0.740	0.50		
1.5×10^{-2}	−0.760	0.40		
2.0×10^{-2}	−0.780	0.43		
3.0×10^{-2}	−0.815	0.40		
4.0×10^{-2}	−0.850	0.35		
5.0×10^{-2}	−0.865	0.31		
7.5×10^{-2}	−0.900	0.31		
9.0×10^{-2}	−0.925	0.31		

[a] Drop time t = 0.5 s. [b] Scan rate = 500 mV s^{-1}. [c] All potentials are relative to $E_{1/2}(Fc^+/Fc)$. $E_{1/2}(Fc^+/Fc)$ vs Ag/AgCl (saturated LiCl in CH_2Cl_2) = 0.470 V.

since the diffusion-controlled limiting current of process II decreases at higher ligand concentrations. While corrections could be made for this term, they are smaller than other experimental errors and are therefore not included. It is also assumed that the concentration of ligand is in considerable excess to that of the metal, which is true for much of the data. If more than one complex is formed at a given ligand concentration, the DeFord–Hume equation[17] is applicable. However, use of this equation requires very accurate and reproducible data, which are not readily acquired in dichloromethane. The simpler treatment of the data is therefore preferred.

A value for $E^{f}_{1/2}$(free) in the absence of dpmSe may be obtained from measurements made at a Cd(Hg) amalgam electrode.[9] Dc polarograms, cyclic voltammograms, and differential-pulse polarograms obtained at a Cd(Hg) amalgam (5×10^{-4} M Cd) dropping electrode under oxidative conditions for a 0.2 M Bu_4NPF_6 solution in dichloromethane show that this oxidative process is reversible and can be described by the reaction

$$Cd(Hg) \xrightleftharpoons{E^{f}_{1/2}} [Cd]^{2+} + Hg + 2e^- \qquad (6)$$

This process provides a measure of the potential of the cadmium ion in the absence of dpmSe and is 345 mV less negative than the half-wave potential found for the reduction of 5×10^{-4} M $[Cd(dpmSe)_2]^{2+}$. This large potential shift implies that the Cd–dpmSe complexes are extremely strong and that $[Cd(dpmSe)_2]^{2+}$ is not dissociated to any significant extent in solution. It is this result which leads to the conclusion that the weak doublets observed in the phosphorus-31 NMR spectrum of $[Cd(dpmSe)_2][CF_3SO_3]_2$ are due to selenium-bonded monodentate dpmSe rather than to free dpmSe.

It follows from eq 5 that a plot of $E^{f}_{1/2}$(complex) − $E^{f}_{1/2}$(free) versus log [dpmSe] should be linear and of slope $-x(2.303RT/nF)$ with intercept $-2.303RT/nF \log \beta_x$. However, the plot is nonlinear (Figure 3), but the limiting slopes of the curve correspond to $x = 4$ at the low concentration range and $x = 6$ in the presence of large ligand concentrations. This suggests that a mixture of complexes with values of x in the range 4–6 exist in the presence of high ligand to metal concentration ratios. With potentially bidentate ligands an ambiguity exists as to whether the ligand is acting as a monodentate or didentate species. Thus, when $x = 4$, the following equilibria, among others, are possible:

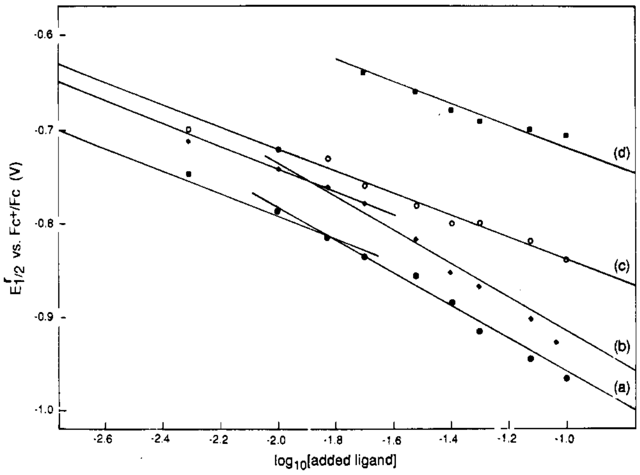

Figure 3. Plot of $E^{f}_{1/2}$ vs log [added ligand] for the reduction of the (a) dpmSe, (b) dpmS, (c) $dpmSe_2$, and (d) $dpmS_2$ complexes of cadmium. Experimental conditions and parameters are as for Figure 2.

$$[Cd]^{2+} + 4dpmSe \xrightleftharpoons{\beta_4} [Cd(\eta^2\text{-}dpmSe)_2(\eta^1\text{-}dpmSe)_2]^{2+} \qquad (7)$$

or

$$[Cd]^{2+} + 4dpmSe \xrightleftharpoons{\beta_4} [Cd(\eta^1\text{-}dpmSe)_4]^{2+} \qquad (8)$$

assuming cadmium(II) cannot take on a coordination number higher than 6. The overall stability constant calculated for the case where $x = 4$ is $\log \beta_4 = 25.3$, and at high ligand concentrations a value of $\log \beta_6 = 28.6$ is obtained for the equilibrium

$$[Cd]^{2+} + 6dpmSe \xrightleftharpoons{\beta_6} [Cd(\eta^1\text{-}dpmSe)_6]^{2+} \qquad (9)$$

At intermediate concentrations, various forms of $[Cd(\eta^1\text{-}dpmSe)_5]^{2+}$ are probably present in equilibrium with the complexes mentioned in eq 7–9. The decrease in limiting current observed at higher ligand concentrations is consistent with the higher coordination complexes having a different diffusion coefficient.

The electrochemical data for the dpmS system parallel those for the dpmSe system, and data are given in Table III. It is apparent that $E_{1/2}$ values for the same ligand concentration are significantly less negative for dpmS than for dpmSe. This implies that the dpmS complexes of cadmium(II) are weaker than the corresponding dpmSe complexes and is reflected in the calculated values of $\log \beta_4 = 23.1$ and $\log \beta_6 = 26.8$, which are both lower than the corresponding values obtained for the dpmSe complexes. This result also suggests that the group 16 element is dominant in bonding to cadmium, as little difference would be expected between the stability constants of $[Cd(\eta^1\text{-}dpmSe)_6]^{2+}$ and $[Cd(\eta^1\text{-}dpmS)_6]^{2+}$ if the ligands were P-bonded. Thus, the electrochemical data show that a coordination number of 6 may be attained with phosphine selenide and sulfide ligands (analogous to the phosphine oxide complexes) but only at high ligand to metal concentration ratios. This is the regime where NMR measurements are uninformative due to lability of the complexes.

(b) $dpmE_2$ Systems. The current-sampled dc polarograms for the reduction of 5×10^{-4} M $[Cd(dpmSe_2)_2]^{2+}$ in dichloromethane (0.2 M Bu_4NPF_6) solution in the presence of various ligand concentrations show maxima at high ligand concentrations, but the limiting current for the reduction process is essentially independent of ligand concentration. The data obtained from various electrochemical techniques are summarized in Table IV. The reduction process is essentially reversible for all ligand concentrations, and a plot of $E_{1/2}$ vs log [added $dpmSe_2$] is linear with a slope corresponding to $x = 4$, with no evidence for a complex

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(18) Heyrovský, J.; Ilkovic, D. *Collect. Czechoslov. Chem. Commun.* **1935**, *7*, 198.
(19) Stackelberg, M. v.; Freyhold, H. v. *Z. Elektrochem.* **1940**, *46*, 120.
(20) Lingane, J. J. *J. Chem. Rev.* **1941**, *29*, 1.

Table IV. Electrochemical Data for the Reduction of 5×10^{-4} M $[Cd(dpmE_2)_2]^{2+}$ in the Presence of Varying Quantities of $dpmE_2$ at a Dropping-Mercury Electrode in Dichloromethane (0.2 M Bu_4NPF_6) at 25 °C

added $dpmE_2$ concn, M	dc polarography[a] $E_{1/2}$,[c] V	dc polarography[a] i_d, μA	cyclic voltammetry[b] E_p^{red}, V	cyclic voltammetry[b] E_p^{ox}, V
	(a) $dpmSe_2$			
	−0.580	1.13	−0.67	−0.56
5.0×10^{-3}	−0.690	1.15		
1.0×10^{-2}	−0.695	1.20		
1.5×10^{-2}	−0.705[d]	1.25		
2.0×10^{-2}	−0.735[d]	1.30		
3.0×10^{-2}	−0.750[d]	1.25		
4.0×10^{-2}	−0.770[d]	1.25		
5.0×10^{-2}	−0.775[d]	1.08		
7.5×10^{-2}	−0.800[d]	1.13		
1.0×10^{-1}	−0.805[d]	1.00		
	(b) $dpmS_2$			
	−0.515	1.48	−0.62	−0.46
5.0×10^{-3}	−0.670	1.08		
1.0×10^{-2}	*e*	1.13		
1.5×10^{-2}	*e*	0.95		
2.0×10^{-2}	−0.615	1.08		
3.0×10^{-2}	−0.620	1.03		
4.0×10^{-2}	−0.665	0.95		
5.0×10^{-2}	−0.670	0.90		
7.5×10^{-2}	−0.675	0.78		
1.0×10^{-1}	−0.690	0.75		

[a] Drop time t = 0.5 s. [b] Scan rate = 500 mV s^{-1}. [c] All potentials are relative to $E_{1/2}(Fc^+/Fc)$. $E_{1/2}(Fc^+/Fc)$ vs Ag/AgCl (saturated LiCl in CH_2Cl_2) = 0.470 V. [d] Complicated by maxima. [e] Complicated by a second response.

of the type $[Cd(\eta^1\text{-}dpmSe_2)_6]^{2+}$ observed (Figure 3). The half-wave potential of the $[Cd(dpmSe_2)_2]^{2+}$ system is shifted from $E_{1/2}$(free) by much less than that of the $[Cd(dpmSe)_2]^{2+}$ system for each equivalent addition of ligand. Consequently, it can be concluded that the cadmium complexes containing $dpmSe_2$ are weaker than those with dpmSe and dpmS. A stability constant of log β_4 = 22.2 is obtained for $[Cd(\eta^2\text{-}dpmSe_2)_2(\eta^1\text{-}dpmSe_2)_2]^{2+}$ or $[Cd(\eta^1\text{-}dpmSe_2)_4]^{2+}$, which, although lower than the corresponding values for the dpmSe and dpmS cadmium complexes, still suggests that the $dpmSe_2$ complexes are still almost completely nondissociated in solution.

The reduction of $[Cd(dpmS_2)_2]^{2+}$ differs from the previously described systems because two reduction responses are evident at low ligand to metal concentration ratios, both of which are chemically reversible. It has already been established by NMR studies that there are at least two complexes present when the $dpmS_2$ concentration is the same order of magnitude as the cadmium ion concentration. These two reduction waves become well resolved as the concentration of dpmS increases to a ligand to metal ratio of 10:1. However, above 2×10^{-2} M in ligand, the polarograms are essentially well defined with a single response and are similar to those obtained for the previously described systems. The data obtained from various electrochemical techniques are summarized in Table IV. The shift in half-wave potential is far less than for all the other cadmium complexes, demonstrating that $dpmS_2$ forms the weakest complexes with cadmium(II). Over the added ligand concentration range from 2×10^{-2} to 1×10^{-1} M the electrochemical data satisfactorily fit eq 5 with a value of x = 4 and log β_4 = 18.1 (Figure 3).

The calculated stability constants clearly demonstrate that the dpmE complexes are stronger than those with $dpmE_2$. In turn, the selenium-containing ligands form stronger complexes with cadmium than do their sulfur analogues. These results completely vindicate the findings of competition studies between binary mixtures of diphosphine diselenides and diphosphine disulfides for coordination to cadmium(II) conducted by Dean.[5] The calculated stability constants also reflect the fact that the reduction $E_{1/2}$ potentials for the dpmS and $dpmS_2$ cadmium complexes are less negative than those for the corresponding selenium analgoues. This order of reduction $E_{1/2}$ potentials for sulfur and selenium ligand complexes is now well established, being observed[14] for $[Hg(dpmE)_2]^{2+}$ and $[Hg(dpmE_2)_2]^{2+}$ and the diseleno- and dithiocarbamate complexes of mercury.[21]

Table V. Dc Polarographic[a] Data for the Oxidation of the Cd(Hg) Amalgam (5×10^{-4} M Cd) in the Presence of Varying Quantities of dpmSe in Dichloromethane (0.2 M Bu_4NPF_6) at 25 °C

dpmSe concn, M	$E_{1/2}$,[b] V	i_d, μA	dpmSe concn, M	$E_{1/2}$,[b] V	i_d, μA
5.0×10^{-4}	−0.705	1.10	3.5×10^{-3}	−0.725	7.00
1.0×10^{-3}	−0.715	2.10	4.0×10^{-3}	−0.730	7.50
1.5×10^{-3}	−0.720	3.00	4.5×10^{-3}	−0.725	8.50
2.0×10^{-3}	−0.710	3.55	5.0×10^{-3}	−0.730	8.75
2.5×10^{-3}	−0.720	4.35	1.0×10^{-2}	−0.740	12.00
3.0×10^{-3}	−0.720	5.70			

[a] Drop time t = 0.5 s. [b] All potentials are relative to $E_{1/2}(Fc^+/Fc)$. $E_{1/2}(Fc^+/Fc)$ vs Ag/AgCl (saturated LiCl in CH_2Cl_2) = 0.470 V.

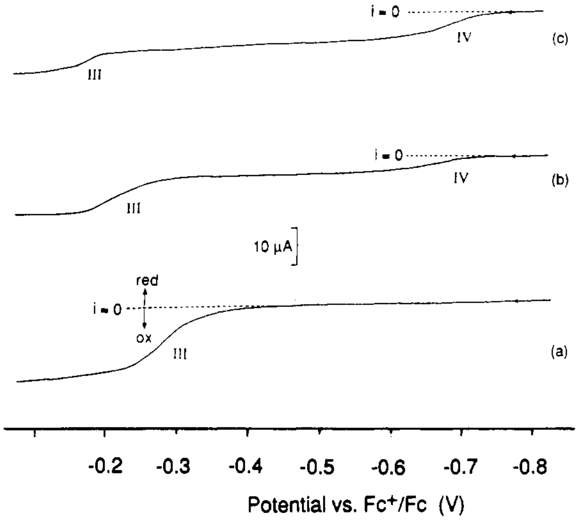

Figure 4. Current-sampled dc polarograms at a drop time of 0.5 s for the oxidation of a Cd(Hg) amalgam (5×10^{-4} M Cd) in dichloromethane (0.2 M Bu_4NPF_6) solution at 25 °C in the presence of (a) no added dpmSe, (b) 2×10^{-3} M dpmSe, and (c) 3.5×10^{-3} M dpmSe.

(c) Oxidation of Cd(Hg) Amalgam in the Presence of Ligand. The use of a Cd(Hg) amalgam electrode allows the examination of the voltammetry of the Cd–dpmE and –$dpmE_2$ systems in the presence of substoichiometric ligand concentrations. All relevant data are summarized in Table V and Tables S-I–S-III (supplementary material). Figure 4a shows a typical current-sampled dc polarogram obtained at a Cd(Hg) amalgam (5×10^{-4} M Cd) dropping electrode under oxidative conditions in dichloromethane (0.2 M Bu_4NPF_6) solution. The oxidation process (process III)

$$Cd(Hg) \rightleftharpoons [Cd]^{2+} + Hg + 2e^- \qquad (10)$$

is observed at −0.3 V vs Fc^+/Fc. Upon introduction of ligand, a new oxidation wave (process IV) becomes apparent at a more negative potential (Figure 4b), which increases in height with increasing ligand concentration (Figure 4c). Concomitantly, the limiting current of process III decreases. When the cadmium to ligand ratio is approximately 1:8, process III has disappeared; that is, no evidence of $[Cd]^{2+}$ existing at the electrode surface can be obtained for ligand concentrations in excess of the cadmium to ligand ratio 1:8. At these high concentrations, the remaining oxidation process (process IV) has a half-wave potential that is similar to that for the reduction process (process II) of an equivalent solution (comprising the appropriate cadmium complex and added ligand) at a dropping-mercury electrode. This result suggests that process IV is reversible on the polarographic

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[21] Bond, A. M.; Colton, R.; Dillon, M. L.; Hollenkamp, A. F.; Moir, J. E. *Inorg. Chem.* **1985**, *24*, 1591.

(dropping-mercury electrode) time scale. Cyclic voltammograms demonstrate the processes are chemically reversible.

If the electrode process IV simply involved the reaction

$$Cd(Hg) \rightleftharpoons [Cd]^{2+} + Hg + 2e^- \qquad (11)$$

$$[Cd]^{2+} + 6L \rightleftharpoons [CdL_6]^{2+}$$

$$L = \text{neutral ligand}$$

and the complex is extremely strong and the only complex present, then it could have been anticipated that process III would have disappeared at a molar ratio of 1:6 rather than 1:8. In the present situation it is probable that at these relatively low ligand:metal concentration ratios a range of complexes is present in significant concentrations. Thus, a sharp change in the limiting current is not necessarily expected at the 6:1 concentration ratio. Additionally, in dichloromethane the anion of the electrolyte, Bu_4NPF_6, which is present in very large molar excess, can also act as a ligand. Bond et al.[9] have shown that the anions $[BF_4]^-$ and $[ClO_4]^-$, which are often regarded as noncoordinating in solution, are in fact quite strong ligands relative to $[PF_6]^-$ when complexed to cadmium. Nevertheless, formation of a bare cadmium ion is unlikely in the presence of $[PF_6]^-$ and so it can be assumed that the Cd(Hg) amalgam oxidation process does actually result in the formation of a cadmium hexafluorophosphate complex. Thus, addition of ligand, L, results in a competitive equilibrium between $[PF_6]^-$ and L, and it is only in the presence of a small excess of L that all the cadmium is fully complexed by L and a single oxidation wave is observed. The limiting current of this response (process IV) is virtually independent of ligand concentration, but its half-wave potential becomes more negative with increasing ligand concentration. If the $[PF_6]^-$ anion coordinates to cadmium, then it follows that the calculated stability constants of log β_x ($x = 4, 6$) are all relative to the formation of a cadmium hexafluorophosphate complex; that is, the dpmE and $dpmE_2$ complexes of cadmium are even more stable than the calculated values would suggest.

The fact that two oxidation responses (processes III and IV) are seen at low ligand concentrations reemphasizes the high stability of these cadmium complexes. Philp[22,23] et al. have developed simulations that allow calculation of differential-pulse polarographic and cyclic voltammetric curves for reversibly reduced complexes in the presence of low (substoichiometric) ligand concentration. The same argument can be applied to amalgam oxidation, which is simply the reverse of the reduction process. It was reported by Philp et al. that, for a single 1:2 complex, a splitting of the differential-pulse polarographic wave is predicted at substoichiometric ligand concentrations for log β_2 values greater than about 10. The simulations suggest that such systems exhibit one response at around $E°$ for the uncomplexed metal process and a second response at a more negative potential. The Cd–dpmE and Cd–$dpmE_2$ systems do indeed exhibit two responses at substoichiometric ligand concentrations, one for the "free" cadmium and a second at a more negative potential related to the presence of the dpmE or $dpmE_2$ cadmium complex. The simulations also predict a single response above stoichiometric ligand concentrations whose potential shifts with β_x in a predictable manner, and this is also observed in the systems described here.

Additional Experiments. In order to confirm the suggestion that Cd–E bonds are stronger than Cd–P bonds, some additional experiments were conducted.

(a) Cadmium(II) Complexes with PPh_3 and PPh_3Se. The oxidation of a Cd(Hg) amalgam (5×10^{-4} M Cd) in the presence of these simple ligands and the reductions of the corresponding cadmium complexes are all, unfortunately, electrochemically irreversible. Consequently, no thermodynamic significance can be placed on the values of the half-wave potentials and a quantitative calculation of stability constants is precluded. Nevertheless, some qualitative observations can be made. In the case of low concentrations of PPh_3 in dichloromethane (0.2 M Bu_4NPF_6) at a Cd(Hg) amalgam dropping electrode only one, rather than two or more, response(s) involving cadmium amalgam electrode oxidation is observed. Furthermore, the potential remains in the vicinity of that for the Cd/$[Cd]^{2+}$ uncomplexed couple. This result immediately suggests that PPh_3 complexes of cadmium(II) are relatively weak.[22,23]

Dichloromethane (0.2 M Bu_4NPF_6) solutions of PPh_3Se at a Cd(Hg) amalgam dropping electrode under oxidative conditions produce two clearly distinct cadmium-related oxidation waves, showing that PPh_3Se forms stronger complexes with cadmium than does PPh_3. At a concentration ratio of Cd:PPh_3Se = 1:8, the process due to the formation of free $[Cd]^{2+}$ (process III) disappears and the limiting current of the process due to the formation of $[Cd(PPh_3Se)_x]^{2+}$ becomes almost constant. The stoichiometry at which the response due to free cadmium disappears is similar to that found for the chelate dpmE and $dpmE_2$ systems, implying that the PPh_3Se complexes are very strong. Polarographic reductions of the cadmium complexes with PPh_3 and PPh_3Se are complicated by the existence of adsorption effects and electrochemical irreversibility. Thus, although no quantitative data is available from the results of these studies, the results are consistent with PPh_3Se complexes of cadmium being stronger than those of PPh_3. The electrochemical data for these systems are given as supplementary material (Tables S-IV–S-VII).

These conclusions obtained from electrochemical studies are confirmed by NMR studies which show that the PPh_3 system is labile at all accessible temperatures, indicating that the complexes are weak, although others[24] have reported coupling in this system. The interaction between cadmium perchlorate and PPh_3Se in 1:2 molar proportions in dichloromethane generates $[Cd(PPh_3Se)_4]^{2+}$ (which has been previously observed in liquid SO_2[5]), as evidenced by ^{31}P, ^{77}Se, and ^{113}Cd NMR spectroscopy. It is immediately apparent that PPh_3Se forms stronger cadmium complexes than PPh_3.

The NMR and electrochemical data for these cadmium complexes therefore support the concept that selenium is more strongly coordinated to cadmium(II) than phosphorus.

(b) Competitive Reactions. Reaction between equimolar quantities of $[Hg(dpe)_2]^{2+}$ (dpe = $Ph_2PCH_2CH_2PPh_2$) and $[Hg(dpmSe)_2]^{2+}$ at room temperature leads to a phosphorus-31 NMR spectrum containing broad peaks, indicating ligand exchange. On cooling of the solution to −80 °C, the resulting phosphorus-31 NMR spectrum not only contains the expected singlet at δ 22.6 with mercury-199 satellites due to $[Hg(dpe)_2]^{2+}$ but also contains signals due to $[Hg(dpmSe)_2]^{2+}$, $dpeSe_2$, dpeSe, dpe, dpmSe, dpm, and possibly mixed-ligand complexes.[10,14] A similar spectrum is obtained when 2 mol of dpmSe is added to a dichloromethane solution of $[Hg(dpe)_2]^{2+}$ and 2 mol of dpe is added to $[Hg(dpmSe)_2]^{2+}$. It is known that phosphine selenides are labile,[10,25] and it is apparent that $[Hg(dpe)_2]^{2+}$ abstracts selenium from any available source, whether it be free dpmSe or a monodentate phosphorus-bonded η^1-dpmSe ligand present as a result of a ligand exchange process in $[Hg(dpmSe)_2]^{2+}$.

In contrast, the phosphorus-31 NMR spectrum of a dichloromethane solution containing equimolar proportions of $[Hg(dpe)_2][ClO_4]_2$ and $[Cd(dpmSe)_2][ClO_4]_2$ cooled to −80 °C shows no evidence that any reaction occurs. This result is important as it shows that selenium in $[Cd(dpmSe)_2]^{2+}$ is not available to react with $[Hg(dpe)_2]^{2+}$. The dpmE and $dpmE_2$ complexes of cadmium(II) are labile on the NMR time scale at room temperature so that if dissociation of the selenium atom of dpmSe were involved in the ligand exchange process, $[Cd(dpmSe)_2]^{2+}$ would be a source of monodentate, phosphorus-bonded dpmSe ligands. Consequently, addition of $[Cd(dpmSe)_2]^{2+}$ to a solution of $[Hg(dpe)_2]^{2+}$ should result in the abstraction of selenium by dpe as in the interactions between $[Hg(dpe)_2]^{2+}$ and $[Hg(dpmSe)_2]^{2+}$ and the other reactions given above. The fact that

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this does not occur shows that selenium is not available for abstraction because it is all strongly coordinated to cadmium, thus confirming the conclusions drawn earlier that it is the cadmium–phosphorus bond which is labile in $[Cd(dpmSe)_2]^{2+}$.

Conclusions

The results presented in this paper clearly support the concept of the group 16 donor atoms, sulfur and selenium, being more strongly coordinated to cadmium(II) than phosphorus, in contrast to the earlier conclusions[14] that mercury prefers coordination to phosphorus.

There is an apparent anomaly in that stability constants calculated for the dpmE and $dpmE_2$ complexes of cadmium(II) by the use of electrochemical methods in dichloromethane show that the dpmE ligands, which are capable of forming Cd–P bonds, form the most stable complexes. However, a consideration of the ligand geometries resolves this anomaly. DpmE ligands are not as flexible as the $dpmE_2$ ligands, and consequently, the dpmE ligands form chelates much more readily because when selenium or sulfur is coordinated, the phosphorus is close to the metal. The magnitude of these stability constants suggests that all of the dpmE and $dpmE_2$ complexes of cadmium(II) are completely nondissociated in solution.

The $dpmE_2$ complexes only possess a coordination number of 4 even at high cadmium to ligand ratios, whereas the stronger dpmE complexes have coordination numbers of 6 at high ligand concentrations. At these high cadmium to ligand ratios complexes of the type $[Cd(\eta^1\text{-dpmE})_6]^{2+}$ are assumed in which the ligand is coordinated in a monodentate fashion through the group 16 donor atom.

The calculated stability constants also reveal that the selenium-containing ligands form stronger complexes than their sulfur analogues. This is in accordance with other studies involving sulfur and selenium ligands, in particular that of $[Hg(dpmE)_2]^{2+}$ and $[Hg(dpmE_2)_2]^{2+}$, in which the sulfur derivatives are easier to reduce than their selenium analogues.[14]

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Registry No. dpmSe, 23176-19-4; dpmS, 54006-28-9; $dpmSe_2$, 16675-12-0; $dpmS_2$, 14633-92-2; $[Cd(dpmSe)_2][ClO_4]_2$, 123506-14-9; $[Cd(dpmS)_2][ClO_4]_2$, 123506-16-1; $[Cd(dpmSe)_2][CF_3SO_3]_2$, 123506-17-2; $[Cd(dpmS)_2][CF_3SO_3]_2$, 123506-18-3; $[Cd(dpmSe_2)_2][ClO_4]_2$, 123540-25-0; $[Cd(dpmS_2)_2][ClO_4]_2$, 123565-35-5; PPh_3, 603-35-0; PPh_3Se, 3878-44-2; $[Hg(dpe)_2][ClO_4]_2$, 123540-05-6; ^{77}Se, 14681-72-2; ^{113}Cd, 14336-66-4; $[Cd(\eta^1\text{-dpmSe})_6]^{2+}$, 123506-19-4; $[Cd(\eta^1\text{-dpmS})_6]^{2+}$, 123506-20-7; $[Cd(DMSO)_6][CF_3SO_3]_2$, 76703-11-2.

Supplementary Material Available: Tables S-I–S-VII, listing dc polarographic data for the oxidation of a Cd(Hg) amalgam electrode in the presence of $dpmE_2$, dpmS, PPh_3, and PPh_3Se and reduction of $[Cd(PPh_3)_x]^{2+}$ and $[Cd(PPh_3Se)_4]^{2+}$ at a dropping-mercury electrode (8 pages). Ordering information is given on any current masthead page.

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Similarities and Differences in the Structural and Electronic Properties of κ-Phase Organic Conducting and Superconducting Salts

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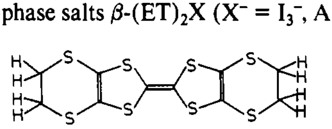
We have examined the similarities and differences in the crystal and band electronic structures of four κ-phase tetrathiafulvalene-based organic conducting salts κ-$(BEDT\text{-}TTF)_2X$ ($X^- = Cu(NCS)_2^-, I_3^-$), κ-$(MDT\text{-}TTF)_2AuI_2$, and κ-$(BMDT\text{-}TTF)_2Au(CN)_2$. Donor dimers have a bond-over-ring arrangement in the superconducting salts κ-$(BEDT\text{-}TTF)_2X$ ($X^- = Cu(NCS)_2^-, I_3^-$) and κ-$(MDT\text{-}TTF)_2AuI_2$ but a bond-over-bond arrangement in the nonsuperconducting salt κ-$(BMDT\text{-}TTF)_2Au(CN)_2$, so that the intradimer spacing is considerably larger in the nonsuperconducting than in the superconducting κ-phases. The terminal ethylene groups of BEDT-TTF have a staggered arrangement in the "high-T_c" salts κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ (T_c = 10.4 K) and β*-$(BEDT\text{-}TTF)_2I_3$ (T_c = ~ 8 K) but are eclipsed in the "low-T_c" salts κ-$(BEDT\text{-}TTF)_2I_3$ (T_c = 3.6 K), β-$(BEDT\text{-}TTF)_2AuI_2$ (T_c = 5.0 K), and β-$(BEDT\text{-}TTF)_2IBr_2$ (T_c = 2.8 K). All the Fermi surfaces of the κ-phases can be described in terms of overlapping "distorted circles" and hence are essentially two-dimensional in nature. However, the Fermi surface of the nonsuperconducting κ-phase, κ-$(BMDT\text{-}TTF)_2Au(CN)_2$, exhibits a partial nesting, in contrast to the case of the superconducting κ-phases, which is probably responsible for the metal–insulator transition at ~60 K.

Organic electron-donor molecules derived from tetrathiafulvalene lead to charge-transfer salts that are metals, semiconductors, and superconductors.[1] The superconducting salts formed with bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or simply ET, **1**) include the β-phase salts β-$(ET)_2X$ ($X^- = I_3^-$, AuI_2^-, and IBr_2^-, for which T_c = 1.4,[2] 5.0,[3] and 2.8 K,[4] respectively), γ-$(ET)_3(I_3)_{2.5}$ (T_c = 2.5 K),[5] θ-$(ET)_2I_3$ (T_c = 3.6 K),[6] and the κ-phase salts κ-$(ET)_2X$ ($X^- = I_3^-$ and $Cu(NCS)_2^-$, for which T_c = 3.6[7] and 10.4 K,[8] respectively). Surprisingly, the *un*symmetrical electron-donor



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