

So also is the cluster with NO and CN ligands $[\text{Mo}_4(\mu_3\text{-S})_4(\text{NO})_4(\text{CN})_8]^{8-}$, in which there are only two Mo-Mo bonds with a mean distance of 2.99 (5) Å.²⁹ The clusters in these compounds have 60 electrons. If we assume the same bonding orbitals for the Mo_4S_4 cluster as shown in Figure 2, clusters with up to 60 electrons will have six Mo-Mo bonds. Clusters with 68 electrons fill the antibonding orbitals ($a_1 + b_2 + e$) with 8 electrons, resulting in four net metal-metal bonding electrons. Thus, these clusters have two Mo-Mo bonds. Aside from the compounds listed in Table V, Dahl mentioned a Mo_4S_4 -containing cyclopentadienyl complex,³⁰ but no structural parameter is available in the literature.

Preliminary results for the title compound were published as a note.³¹

Since the structure of $\text{Mo}_2(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_6$ is unknown, it is rather difficult even to speculate on the mechanism for the formation of the title compound, but that remains an interesting problem.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

Supplementary Material Available: Listings of observed and calculated structure factors and a packing diagram (14 pages). Ordering information is given on any current masthead page.

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Reversible Electrode Processes Involving Multistep Mechanisms for Cadmium Dithiocarbamates and Diselenocarbamates at Mercury Electrodes

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The electrochemistry of cadmium dithio- and diselenocarbamate complexes ($\text{Cd}(\text{RR}'\text{dte})_2$ and $\text{Cd}(\text{RR}'\text{dsc})_2$, respectively) at mercury electrodes in dichloromethane solution is characterized by a series of chemically and electrochemically reversible processes. However, unlike the situation with other metal dithiocarbamates, the processes are not based solely on simple charge transfer, but rather on exchange reactions with electrode mercury and mercury(II) dithiocarbamates, and also involve dimer-monomer equilibria as well as formation of a bimetallic (Cd-Hg) species. The oxidation is an overall four-electron process consisting of the following reversible reactions: $\text{Cd}_2(\text{RR}'\text{dte})_4 \rightleftharpoons 2[\text{Cd}(\text{RR}'\text{dte})_2]$; $\text{Cd}(\text{RR}'\text{dte})_2 + \text{Hg} \rightleftharpoons \text{Hg}(\text{RR}'\text{dte})_2 + \text{Cd}^{2+} + 2e^-$; $\text{Hg}(\text{RR}'\text{dte})_2 + \text{Hg} \rightleftharpoons [\text{Hg}_2(\text{RR}'\text{dte})_2]^+ + e^-$; $[\text{Hg}_2(\text{RR}'\text{dte})_2]^+ + \text{Hg} \rightleftharpoons [\text{Hg}_3(\text{RR}'\text{dte})_2]^{2+} + e^-$. The reduction occurs in two major steps and is an overall two-electron process: $\text{Cd}(\text{RR}'\text{dte})_2 + \text{Hg} + 2e^- \rightleftharpoons \text{Cd}(\text{Hg}) + 2[\text{RR}'\text{dte}]^-$. The first reduction step is controlled kinetically by the exchange reaction $\text{Cd}(\text{RR}'\text{dte})_2 + \text{Hg} \rightleftharpoons \text{Hg}(\text{RR}'\text{dte})_2 + \text{Cd}(\text{Hg})$. In addition, the $\text{Cd}(\text{RR}'\text{dte})_2$ and $\text{Hg}(\text{RR}'\text{dte})_2$ species react with each other to produce a bimetallic complex that gives a reversible reduction response at potentials more positive than for reduction of either the cadmium or the mercury complex. ¹¹³Cd NMR data confirm that all the exchange reactions are rapid on the NMR time scale and are consistent with the chemically reversible and diffusion-controlled nature of the electrode processes. Both negative ion and positive ion mass spectra have been obtained for $\text{Cd}(\text{RR}'\text{dte})_2$ compounds, and all data again show evidence of ligand exchange. The electrochemistry of $\text{Cd}(\text{Et}_2\text{dsc})_2$ and $\text{Hg}(\text{Et}_2\text{dsc})_2$ parallels that of the dithiocarbamate analogues.

Introduction

The redox chemistry of dithiocarbamate complexes has been studied extensively³⁻⁵ and is noteworthy for the existence of unusually high oxidation states. In the case of $\text{Cd}(\text{RR}'\text{dte})_2$ (see Appendix for definition of symbols) the electrochemistry has received little attention with one of the few reports to date being that of Nieuwpoort et al.,⁶ who examined the oxidation processes that occur for $\text{Cd}(\text{Et}_2\text{dte})_2$ and $[\text{Cd}(\text{Et}_2\text{dte})_3]^-$ in acetone at a platinum electrode. Complex cyclic voltammograms were reported, but little discussion of mechanism was provided. Chemical oxidation of $\text{M}(\text{RR}'\text{dte})_2$ ⁷⁻⁹ with halogens leads to the formation

of $\text{M}(\text{R}_4\text{tds})\text{X}_2$ ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{R} = \text{Me}, \text{Et}$; $\text{tds} = \text{thiuram disulfide}$). By analogy with this reaction, products for the electrochemical oxidation processes were postulated without proof to be thiuram disulfide complexes and/or ligand oxidation products.⁶

To date, electrochemical studies of cadmium dithiocarbamates at mercury electrodes have been confined to brief reports of reduction waves in DMF¹⁰ and in ternary solvent mixtures.¹¹ In both cases only cursory discussion of possible mechanisms was presented. Furthermore, the selenium analogues, $\text{Cd}(\text{RR}'\text{dsc})_2$, have not been examined electrochemically and the influence of the substituent groups R and R' is unknown.

In the solid state the complexes $\text{Cd}(\text{Et}_2\text{dte})_2$ ^{12,13} and cadmium hexamethylenedithiocarbamate¹⁴ are dimeric, the cadmium environment being five-coordinate, with two bridging dithiocarbamate ligands. One Cd-S bond length is significantly longer

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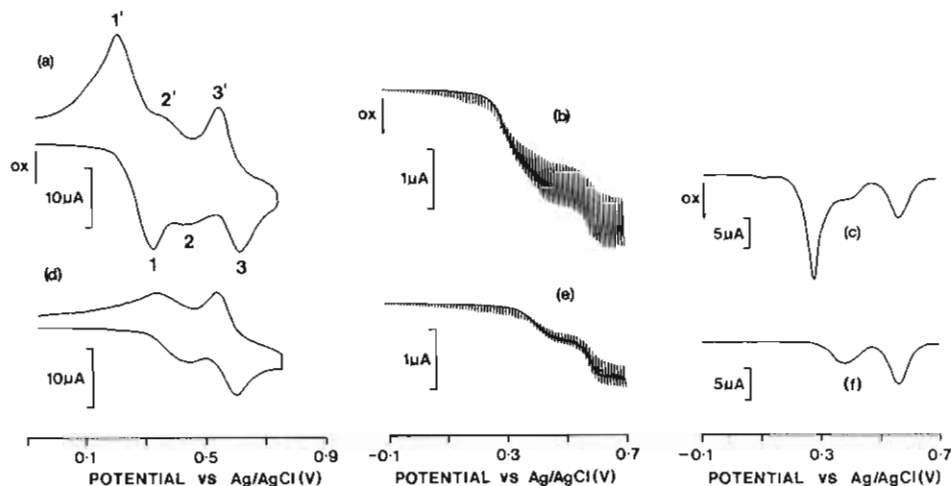
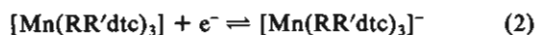


Figure 1. Cyclic voltammograms (a, d) at a HMDE (scan rate 500 mV s^{-1}), dc polarograms (b, e) (drop time 0.5 s), and differential pulse polarograms (c, f) (drop time 0.5 s, pulse amplitude 50 mV) for the oxidation process of (a–c) $\text{Cd}(\text{Et}_2\text{dsc})_2$ and (d–f) $\text{Hg}(\text{Et}_2\text{dsc})_2$, each $2.5 \times 10^{-4} \text{ M}$ in CH_2Cl_2 ($0.1 \text{ M Bu}_4\text{NClO}_4$) at 20°C .

than the remainder.¹² In solution the complexes are associated to varying degrees, depending on both R group and concentration.¹⁵ In general, $\text{Cd}(\text{RR}'\text{dsc})_2$ complexes are insoluble in common electrochemical solvents such as acetonitrile. However, they are moderately soluble in solvents such as chloroform and dichloromethane and electrochemical and other measurements should be possible in these media.

In this work oxidation and reduction processes at mercury electrodes are reported. NMR data, molecular weight determinations, and other physical measurements are used to help characterize the redox processes. As a corollary to this discussion the first detailed study of diselenocarbamate complexes of cadmium is reported. In order to interpret the electrochemical processes at mercury electrodes, the complexes $\text{Hg}(\text{RR}'\text{dsc})_2$ and $\text{Hg}(\text{RR}'\text{dsc})_2$ were also characterized as were mixed cadmium-mercury complexes.

In previous investigations of the redox behavior of metal dithiocarbamates, reversible processes have usually involved a lack of structural change,^{5,16–18} for example



In this present work, however, a novel feature is the observation of electrochemically and chemically reversible processes involving many fast reactions rather than just a simple electron transfer.

Experimental Section

Materials. Carbon diselenide was obtained from Strem Chemicals (Newbury Port, MA) and purified by column chromatography (alumina). All solvents were of HPLC or Analytical grade. The tetrabutylammonium perchlorate used as supporting electrolyte was of electrochemical grade, and all other chemicals used were of Analytical Reagent grade.

Preparations. (a) $\text{Cd}(\text{RR}'\text{dsc})_2$ and $\text{Hg}(\text{RR}'\text{dsc})_2$. These complexes were prepared as described in the literature.¹⁹ A solution of the sodium salt was produced by addition of CS_2 to a chilled aqueous mixture of sodium hydroxide and the corresponding secondary amine. To this solution was added either cadmium nitrate or mercury(II) nitrate. The resulting precipitates were filtered, dried, and then purified by Soxhlet extraction into chloroform.

(b) $\text{Cd}(\text{Et}_2\text{dsc})_2$ and $\text{Hg}(\text{Et}_2\text{dsc})_2$. These were prepared by a modification of the literature method.^{20,21} A solution of CSe_2 in diethyl ether

was added slowly, with stirring, to an ethereal solution of diethylamine in the mole ratio of 1:2. The compound diethylammonium diethyldiselenocarbamate formed as a yellow precipitate and was filtered immediately, dried, and taken up in water. Addition of an aqueous solution of either cadmium nitrate or mercury(II) nitrate to the suspension produced a precipitate of the metal diselenocarbamate. Soxhlet extraction of the dried precipitates with chloroform followed by recrystallization from dichloromethane gave the pure complexes.

Instrumentation. (a) Electrochemistry. Polarographic measurements were made with a Princeton Applied Research Corp. (Princeton, NJ) Model 174A Polarographic Analyzer. A dropping mercury electrode and a hanging mercury drop electrode were used as working electrodes with a platinum-wire auxiliary electrode and a Ag/AgCl (saturated LiCl in dichloromethane) reference electrode. The $(\text{C}_3\text{H}_5)_2\text{Fe}/(\text{C}_3\text{H}_5)_2\text{Fe}^+$ redox couple was also measured frequently to provide an internal check on the stability of the reference electrode. All measurements were made at 20°C in dichloromethane containing $0.1 \text{ M Bu}_4\text{NClO}_4$. Unless otherwise stated, the concentration of $\text{Cd}(\text{RR}'\text{dsc})_2$ and $\text{Hg}(\text{RR}'\text{dsc})_2$ compounds used was $5 \times 10^{-4} \text{ M}$.

Controlled-potential electrolysis experiments were performed at a mercury pool electrode with a PAR Model 173 potentiostat/galvanostat in conjunction with a Model 179 digital coulometer. The platinum-gauze auxiliary electrode was isolated from the test solution via a salt bridge, and the reference electrode was identical with that used for polarographic measurements.

(b) Mass Spectrometry. Electron impact positive ion mass spectra were obtained on a Finnigan 3200 series quadrupole mass spectrometer, coupled with a Finnigan 6000 series interactive data system. Spectra were obtained under the following conditions: electron energy 30–70 eV; filament emission current 0.5 mA; collector voltage 34.8 V; electron multiplier voltage 1.6 kV ; pressure $(3\text{--}5) \times 10^{-6}$ torr. The compounds were introduced via a solids probe with spectra obtained at probe temperature of 200–350 $^\circ \text{C}$. Chemical ionization negative ion mass spectra were obtained on a Vacuum Generators 7070F magnetic sector mass spectrometer, coupled to a Vacuum Generators 2235 data system. Spectra were acquired under the following conditions: ionizing energy 50 eV; reagent gas methane; trap current 1 mA; acquisition time 5 s/decade of mass, accelerating voltage 4 kV. The compounds were introduced via a solids probe into a constant-temperature environment maintained at 200°C .

(c) NMR Spectroscopy. The cadmium-113 NMR spectra of all complexes in dichloromethane were recorded with broad-band proton decoupling on a JEOL FX 100 spectrometer using an external ^7Li lock. Cadmium-113 NMR spectra were recorded at 22.04 MHz, with acquisition time 0.2 s, recycle time 0.7 s, and 8192 data points. Chemical shifts were referenced against aqueous 4.5 M cadmium nitrate; the high-frequency-positive convention is used. All spectra were recorded in the presence of $\text{Cr}(\text{acac})_3$ to reduce ^{113}Cd relaxation times. A JEOL NM 5471 controller was used for temperature control, and temperatures in the probe were measured with a calibrated platinum resistance thermometer.

(d) Other Physical Measurements. Molecular weights in dichloromethane solution were determined with a Hitachi-Perkin-Elmer Model 115 molecular weight apparatus. A linear response was obtained for concentrations of the calibrant (benzil) over the range 1×10^{-4} – $1 \times 10^{-2} \text{ M}$. Conductivity measurements were made in a conventional cell with

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Table I. Polarographic Data for the Oxidation Processes of Cd(RR'dtc)₂ and Hg(RR'dtc)₂^a Complexes at Mercury Electrodes in Dichloromethane (0.1 M Bu₄NClO₄) at 20 °C

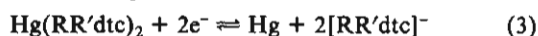
Cd(L) ₂		dc polarography ^b			differential pulse polarography ^b		
R	R'	E _{1/2} , V ^c			E _p , V ^c		
		process 1	process 2	process 3	process 1	process 2	process 3
RR'dtc Derivatives							
Et	Et	0.310	0.410 (0.390)	0.590 (0.580)	0.305	0.410 (0.380)	0.605 (0.570)
<i>n</i> -Pr	<i>n</i> -Pr	0.330	0.460 (0.440)	0.660 (0.640)	0.330	0.425 (0.435)	0.645 (0.635)
<i>i</i> -Pr	<i>i</i> -Pr	0.320	0.430 (0.425)	0.645 (0.625)	0.310	0.440 (0.440)	0.635 (0.615)
<i>n</i> -Bu	<i>n</i> -Bu	0.305	0.390 (0.375)	0.635 (0.590)	0.340	0.445 (0.430)	0.680 (0.650)
<i>i</i> -Bu	<i>i</i> -Bu	0.365	0.445 (0.435)	0.725 (0.695)	0.340	0.420 (0.460)	0.700 (0.680)
<i>c</i> -Hx	<i>c</i> -Hx	0.285 ^d	<i>d</i> (0.410)	0.570 (0.610)	0.340 ^d	<i>d</i> (0.400)	0.625 (0.600)
Bz	Bz	0.340	0.530 (0.475)	0.620 (0.590)	0.330	0.535 (0.495)	0.590 (0.570)
Me	<i>i</i> -Bu	0.380 ^d	<i>d</i> (0.430)	0.655 (0.625)	0.375 ^d	<i>d</i> (0.420)	0.635 (0.610)
N-Heterocyclic Derivatives							
	pip	0.380 ^d	<i>d</i> (0.445)	0.600 (0.595)	0.370 ^d	<i>d</i> (0.420)	0.585 (0.570)

^a Data for the corresponding Hg(RR'dtc)₂ oxidation processes are included in parentheses. ^b Dropping mercury electrode; *t* = 0.5 s. ^c E_{1/2}(C₅H₅)₂Fe/(C₅H₅)₂Fe⁺ = +0.485 V vs. Ag/AgCl (saturated LiCl in CH₂Cl₂). ^d Adjacent responses could not be resolved.

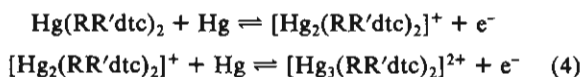
a Radiometer (Copenhagen) CDM 80 conductivity meter in conjunction with a Radiometer CDC 104 conductivity electrode.

Results and Discussion

Oxidation Processes for Cd(RR'dtc)₂ at Mercury Electrodes. Figure 1a shows a cyclic voltammogram at a HMDE for Cd(Et₂dtc)₂. Three well-defined chemically reversible processes are observed. With other Cd(RR'dtc)₂ compounds the three processes, labeled 1, 2, and 3, are always observed but with varying degrees of resolution. Figure 1b shows a dc polarogram for the same oxidation process in which the third step is frequently characterized by maxima at higher concentrations. The ratio of the limiting currents for the three processes is approximately 2:1:1. The reduction of Hg(RR'dtc)₂ in dichloromethane is known to be overall a two-electron process:²²



The summation for the limiting currents for the three oxidation processes for Cd(RR'dtc)₂ is almost exactly twice the limiting current of the known two-electron reduction for Hg(RR'dtc)₂ for equal concentrations. Process 1 is therefore defined as a two-electron step and processes 2 and 3 as one-electron steps. Figure 1c shows a differential pulse polarogram for Cd(Et₂dtc)₂. Figure 1d-f shows the corresponding oxidation responses observed for Hg(Et₂dtc)₂ at mercury electrodes. Within experimental error the two processes observed for Hg(RR'dtc)₂ are coincident with processes 2 and 3 for all Cd(RR'dtc)₂ complexes. The oxidation processes associated with Hg(RR'dtc)₂ have been reported elsewhere²² and, in dichloromethane, are attributed to the reactions



This suggests that the equation for process 1 consists of an exchange reaction coupled with electron transfer



and this mechanism is proved conclusively later in this paper. Molecular weight measurements (see later) indicate that the dimer-monomer equilibria Cd₂(RR'dtc)₄ = 2[Cd(RR'dtc)₂] also contribute to this process as does an exchange process between cadmium and mercury dithiocarbamate complexes (also see later).

A theoretical treatment of this exchange reaction (5) predicts that a graphical plot of *E* against log (*i*_d - *i*)/*i*² should be linear with a slope of -29 mV, and this is confirmed by experiment. Theory also shows that the half-wave potential (E_{1/2}) for process 1 should be concentration dependent, and this was also verified experimentally. The fact that reaction 5 is reversible is remarkable as it involves the transfer of two electrons and a number of exchange processes, one of which involves electrode mercury. Further

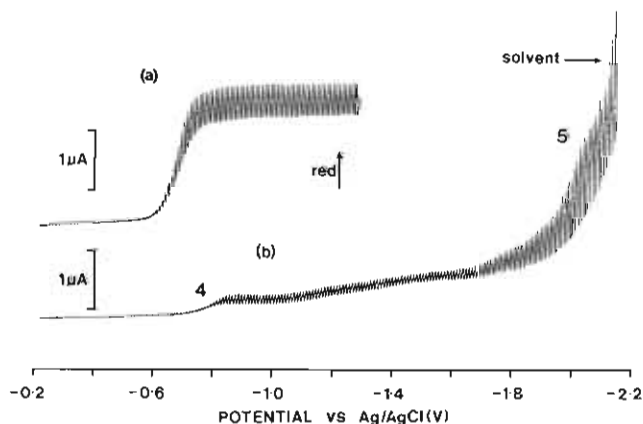
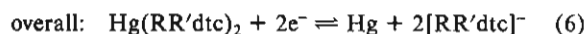
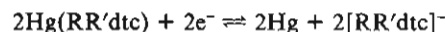


Figure 2. Dc polarograms (drop time 0.5 s) for the reduction processes of (a) Hg(Et₂dte)₂ and (b) Cd(Et₂dte)₂ in CH₂Cl₂ (0.1 M Bu₄NClO₄) at 20 °C.

proof of the validity of reaction 5 was obtained by exhaustive electrolysis at a potential just prior to the onset of process 2. The resulting solution from the two-electron oxidation gave a dc polarogram identical with that of the corresponding Hg(RR'dtc)₂ compound, and a solid, deposited during the electrolysis, was found to be cadmium perchlorate in accordance with the proposed mechanism. Table I summarizes data for a range of Cd(RR'dtc)₂ compounds and their mercury analogues.

Reduction Processes for Cd(RR'dtc)₂ at Mercury Electrodes. Figure 2a shows the well-defined polarographic two-electron reduction step for Hg(Et₂dte)₂, which follows the general reaction²²



The overall process will be used elsewhere in this paper to simplify the discussion.

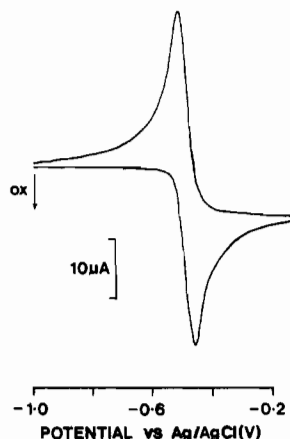
Figure 2b shows the dc polarograms for Cd(Et₂dte)₂, which consists of two major steps. For a range of Cd(RR'dtc)₂ compounds reduction process 4 occurs at potentials approximately 100 mV more negative than the reduction of the corresponding Hg(RR'dtc)₂ compound (Table II). While the summation of the reduction current for processes 4 and 5 is consistent with a two-electron reduction, the final reduction process is too close to the solvent limit for an accurate determination of the number of electrons involved via coulometry. Controlled-potential electrolysis does, however, show that the free dithiocarbamate ligand and cadmium amalgam are products of the reduction process. Polarograms of the reduced solutions are identical with those of authentic samples of *n*-Bu₄N(RR'dtc). At a HMDE electrolysis

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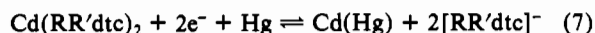
Table II. Polarographic Data for the Reduction Processes of Cd(RR'dtc)₂ and Hg(RR'dtc)₂ Complexes at Mercury Electrodes in Dichloromethane (0.1 M Bu₄NClO₄) at 20 °C

L		dc polarography ^a		
R	R'	HgL ₂	process 4	process 5
RR'dtc Derivatives				
Et	Et	-0.690	-0.820	-1.470
<i>n</i> -Pr	<i>n</i> -Pr	-0.635	-0.725	-1.375
<i>i</i> -Pr	<i>i</i> -Pr	-0.710	-0.820	-1.755
<i>n</i> -Bu	<i>n</i> -Bu	-0.695	-0.800	-1.505
<i>i</i> -Bu	<i>i</i> -Bu	-0.660	-0.750	-1.540
<i>c</i> -Hx	<i>c</i> -Hx	-0.720	-0.850	-1.800
Bz	Bz	-0.595	-0.725	-1.770
Me	<i>i</i> -Bu	-0.630	-0.765	-1.695
N-Heterocyclic Derivatives				
pip		-0.610	-0.760	-1.590

^a Dropping mercury electrode; $t = 0.5$ s. ^b $E_{1/2}((C_5H_5)_2Fe/(C_5H_5)_2Fe^+) = +0.485$ V vs. Ag/AgCl (saturated) LiCl in CH₂Cl₂.

**Figure 3.** Cyclic voltammogram in water (0.1 M KNO₃) at a HMDE previously used as the working electrode in controlled-potential electrolysis (reduction) of Cd(*n*-Bu₂dte)₂ in CH₂Cl₂ (0.1 M Bu₄NClO₄) at 20 °C and scan rate 500 mV s⁻¹.

in dichloromethane followed by transfer of the electrode to an aqueous electrolyte produces the well-known anodic stripping voltammograms for the Cd(Hg) = Cd²⁺ + 2e⁻ process (Figure 3). There seems, then, no doubt that the two main processes (4 and 5) correspond to an overall transfer of two electrons according to



For a range of Cd(RR'dtc)₂ compounds the magnitude of the current per unit concentration associated with process 4 was found to vary greatly, with the smallest values corresponding to ligands with large substituent R groups. The current for process 4 was measured at increasing drop times, and the dependence on time observed was typical of kinetically controlled processes. This information, as well as the facility of exchange between Cd(RR'dtc)₂ and electrode mercury implied in the oxidation data, suggests that the first reduction process is of the kind

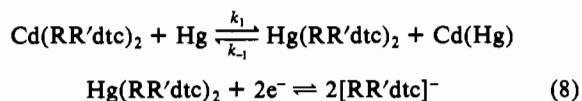
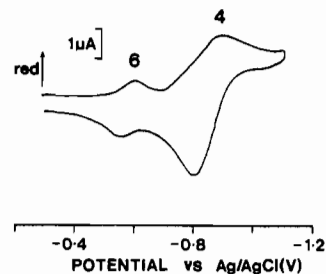


Figure 4 shows a cyclic voltammogram at a HMDE at potentials close to those of process 4 for Cd(Et₂dte)₂. A high degree of reversibility is apparent, and also a new reversible couple is seen at more positive potentials (process 6, Figure 4). The magnitude of process 6 depends on the time the electrode is held at the initial potential. It is not observed until second and subsequent scans of cyclic voltammograms recorded at the DME nor under conditions of dc polarography. The potential of this new process

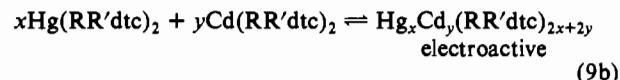
**Figure 4.** Cyclic voltammogram at potentials near reduction process 4 for Cd(Et₂dte)₂ at a HMDE in CH₂Cl₂ (0.1 M Bu₄NClO₄) at 20 °C and scan rate 500 mV s⁻¹.**Table III.** Voltammetric Data for the Reduction Processes of Cd(RR'dtc)₂ Complexes at Mercury Electrodes in Dichloromethane (0.1 M Bu₄NClO₄) at 20 °C

L		cyclic voltammetry ^a			
R	R'	process 4		process 6 (bimetallic complex)	
		E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{ox}
RR'dtc Derivatives					
Et	Et	-0.930	-0.810	-0.610	-0.525
<i>n</i> -Pr	<i>n</i> -Pr	-0.825	-0.725	-0.560	-0.505
<i>i</i> -Pr	<i>i</i> -Pr	-0.950	-0.880	-0.820	-0.725
<i>n</i> -Bu	<i>n</i> -Bu	-0.875	-0.775	-0.510	-0.395
<i>i</i> -Bu	<i>i</i> -Bu	-0.830	-0.735	-0.605	-0.555
<i>c</i> -Hx	<i>c</i> -Hx	-1.120	-0.900	-0.720	-0.500
Bz	Bz	-0.785	-0.685	-0.465	-0.370
Me	<i>i</i> -Bu	-0.845	-0.715	-0.565	-0.450
N-Heterocyclic Derivatives					
pip		-0.800	-0.705	-0.495	-0.390

^a Hanging mercury drop electrode; $v = 500$ mV s⁻¹.
^b $E_{1/2}((C_5H_5)_2Fe/(C_5H_5)_2Fe^+) = +0.485$ V vs. Ag/AgCl (saturated) LiCl in CH₂Cl₂.

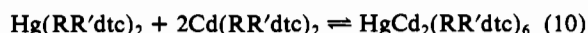
(Table III) is also more positive than that for the Hg(RR'dtc)₂ + 2e⁻ = Hg + 2[RR'dtc]⁻ couple. It would appear that an exchange process coupled with eq 8 is involved, which produces a compound that is not Hg(RR'dtc)₂. That is, eq 8 is an incomplete description.

A mechanism that may fit the observed behavior is



To confirm the existence of a bimetallic complex, a number of experiments were performed. The dc polarogram for a solution of Cd(RR'dtc)₂ that had remained in contact with a mercury pool for 2 h showed a small response at a potential identical with that for process 6. This new process was enhanced by addition of the corresponding Hg(RR'dtc)₂.

Figure 5 shows polarograms for a solution of Hg(*i*-Bu₂dte)₂ with varying amounts of Cd(*i*-Bu₂dte)₂ present. With increasing concentration of cadmium complex the wave due to Hg(*i*-Bu₂dte)₂ is replaced by the reversible reduction process 6 (a cyclic voltammogram is shown in Figure 6). When the mole ratio Cd(*i*-Bu₂dte)₂:Hg(*i*-Bu₂dte)₂ reaches 2:1, the response for the mercury complex has almost disappeared, allowing eq 9b to be rewritten as



Further addition of Cd(*i*-Bu₂dte)₂ causes the appearance of a reduction response for the cadmium complex. Equation 10 is written in the form of an equilibrium since differential pulse polarograms for solutions represented in Figure 5 show that all three species are actually present over a range of concentrations.

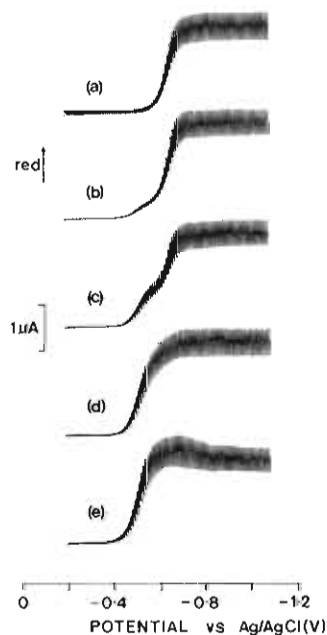


Figure 5. Dc polarograms (drop time 0.5 s) for the reduction responses of $\text{Hg}(i\text{-Bu}_2\text{dtc})_2$ (5×10^{-4} M) with $\text{Cd}(i\text{-Bu}_2\text{dtc})_2$ present at (a) 0, (b) 2.5×10^{-4} M, (c) 5×10^{-4} M, (d) 1×10^{-3} M, and (e) 2×10^{-3} M in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 20 °C.

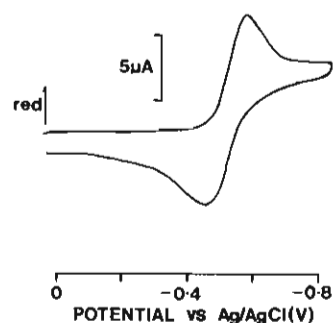
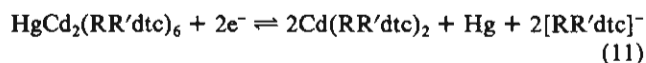


Figure 6. Cyclic voltammograms at a HMDE for the reduction response of a solution containing $\text{Hg}(i\text{-Bu}_2\text{dtc})_2$ (5×10^{-4} M) and $\text{Cd}(i\text{-Bu}_2\text{dtc})_2$ (1×10^{-3} M) in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 20 °C and scan rate 500 mV s^{-1} .

At a platinum working electrode no equivalent reversible responses are observed for the bimetallic complex. Likewise, no responses are observed for pure $\text{Cd}(\text{RR}'\text{dtc})_2$ and $\text{Hg}(\text{RR}'\text{dtc})_2$ compounds at platinum electrodes at potentials where waves are seen at mercury electrodes. The electrode process for the bimetallic complex must involve elemental mercury as is the case for cadmium and mercury dithiocarbamate complexes. Mixtures of $\text{Hg}(\text{RR}'\text{dtc})_2$ and $\text{Cd}(\text{RR}'\text{dtc})_2$ in solution with different dithiocarbamates also give a reduction process consistent with the formation of an equilibrium concentration of mixed-metal complexes. Controlled-potential electrolysis of a solution containing both $\text{Cd}(\text{RR}'\text{dtc})_2$ and $\text{Hg}(\text{RR}'\text{dtc})_2$ at a potential prior to the reduction processes for the pure compounds shows that two electrons are transferred overall. The products of electrolysis are $\text{Cd}(\text{RR}'\text{dtc})_2$ and free dithiocarbamate ligand (polarographic evidence). This process can therefore be written as



It has been mentioned previously that the bimetallic species $\text{HgCd}_2(\text{RR}'\text{dtc})_6$ is formed when a $\text{Cd}(\text{RR}'\text{dtc})_2$ solution is in contact with metallic mercury. The compound is also formed when $\text{Hg}(\text{II})$ ions (from $\text{Hg}(\text{ClO}_4)_2$) are present in a solution of the cadmium complex:

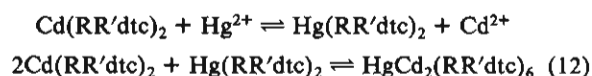


Table IV. Cadmium-113 Chemical Shifts^a for $\text{Cd}(\text{RR}'\text{dtc})_2$ Complexes in Dichloromethane at 25 °C

L		$\delta(^{113}\text{Cd})$	L		$\delta(^{113}\text{Cd})$
R	R'		R	R'	
RR'dtc Derivatives					
Et	Et	383	Me	<i>n</i> -Bu	374
<i>n</i> -Pr	<i>n</i> -Pr	381	Me	<i>i</i> -Bu	374
<i>i</i> -Pr	<i>i</i> -Pr	419	Et	<i>n</i> -Bu	384
<i>n</i> -Bu	<i>n</i> -Bu	386	<i>t</i> -Bu	<i>n</i> -Bu	407
<i>i</i> -Bu	<i>i</i> -Bu	389	<i>i</i> -Pr	<i>c</i> -Hx	423
<i>n</i> -Hx	<i>n</i> -Hx	384	Me	<i>n</i> -Oc	373
N-Heterocyclic Derivatives					
	pip	385		3-Mepip	384
	2-Mepip	397		2,6-Me ₂ pip	409

^a Chemical shifts are reported with respect to external 4.5 M $\text{Cd}(\text{NO}_3)_2(\text{aq})$.

Table V. Molecular Weight Data^a for $\text{Cd}(\text{RR}'\text{dtc})_2$ Complexes in Dichloromethane

L		concn, g dm^{-3}	M_x in soln	fw
R	R'			
RR'dtc Derivatives				
Et	Et	0.2	410	408.9
		3.2	780	
<i>n</i> -Pr	<i>n</i> -Pr	3.2	640	469.1
<i>n</i> -Bu	<i>n</i> -Bu	2.0	870	522.8
<i>i</i> -Bu	<i>i</i> -Bu	0.25	530	522.8
		2.0	800	
Bz	Bz	2.0	1030	655.2
Me	<i>i</i> -Bu	2.0	710	437.0
N-Heterocyclic Derivatives				
	pip	0.2	460	433.0
		2.0	870	

^a Data were obtained with use of an isopiestic method, comparing test solutions with standard solutions of benzil in dichloromethane.

Mixtures of $\text{Cd}(\text{RR}'\text{dtc})_2$ and $\text{Hg}(\text{RR}'\text{dtc})_2$ in solution were studied by other physical methods. The dichloromethane solutions were nonconducting, thus ruling out the formation of significant concentrations of charged species from the two complexes in the bulk solution. Molecular weight measurements in dichloromethane gave an average value for the species present and hence no indication of polymeric compounds. Thus, despite the fact that the equilibrium concentration of this complex is very small, a large reduction current can still be produced because the process has the most positive $E_{1/2}$ value of all the electroactive species involved and rate constants for formation of this complex are rapid.

In summary, the reduction process for $\text{Cd}(\text{RR}'\text{dtc})_2$ compounds at mercury electrode involves interaction with the electrode to form $\text{Hg}(\text{RR}'\text{dtc})_2$ and at least one other species. This species is formally written as $\text{HgCd}_2(\text{RR}'\text{dtc})_6$ although, since elementary mercury is present, a complex involving $\text{Hg}(\text{I})$, such as $\text{Hg}_2\text{Cd}_2(\text{RR}'\text{dtc})_6$, may also contribute. A solution containing $\text{Cd}(\text{RR}'\text{dtc})_2$ and $\text{Hg}(\text{RR}'\text{dtc})_2$ shows no unique response at positive potentials, merely a summation of the separate responses for each compound. This is consistent with the very small equilibrium concentration of the bimetallic complex present. Aggarwal et al.^{23,24} have shown that bimetallic dithiocarbamate complexes $\text{MM}'(\text{RR}'\text{dtc})_4$ can be formed with a wide range of metals (e.g. $\text{HgCo}(\text{RR}'\text{dtc})_4$). Thus, while no mercury-cadmium dithiocarbamate complexes have been previously reported, bimetallic dithiocarbamate complexes are well documented.

NMR Spectroscopy. Table IV shows cadmium-113 chemical shifts for a range of $\text{Cd}(\text{RR}'\text{dtc})_2$ compounds in dichloromethane.

(23) Aggarwal, R. C.; Singh, B.; Singh, M. K. *J. Indian Chem. Soc.* **1982**, *59*, 269.

(24) Aggarwal, R. G.; Singh, B.; Singh, M. K. *Indian J. Chem. Sect. A* **1983**, *22A*, 533.

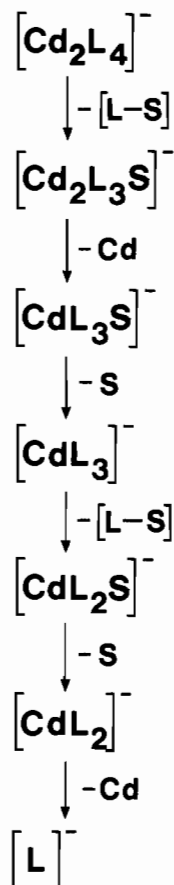
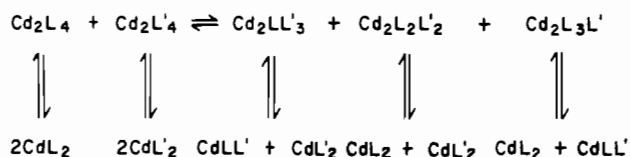
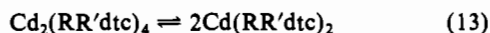


Figure 7. Mass spectral breakdown pattern for $\text{Cd}(\text{RR}'\text{dtc})_2$ compounds derived from CI/NI mass spectra.

Scheme I



Addition of the electrochemical supporting electrolyte had no effect on the chemical shifts. Table V provides data from molecular weight determinations of $\text{Cd}(\text{RR}'\text{dtc})_2$ compounds in dichloromethane at concentrations similar to those used for the NMR measurements, and the results show that a monomer-dimer distribution is operative in solution:



This equilibrium was found to be concentration dependent so that at the concentrations employed for electrochemical measurements the monomeric form predominates in solution, but at concentrations used for the NMR studies, the complexes are predominantly dimeric.

A solution containing two different $\text{Cd}(\text{RR}'\text{dtc})_2$ compounds gave only the average NMR signal even when the solution was cooled to -110°C . There data imply that the exchange reactions shown in Scheme I (where L and L' represent different RR'dtc ligands) are all fast on the NMR time scale. In addition it was shown, by mixing $\text{Cd}(n\text{-Pr}_2\text{dtc})_2$ with $\text{Hg}(i\text{-Pr}_2\text{dtc})_2$ and also $\text{Cd}(i\text{-Bu}_2\text{dtc})_2$ with $\text{Hg}(i\text{-Pr}_2\text{dtc})_2$, that the exchange average cadmium-113 NMR signal is obtained, identical with that observed by mixing the appropriate $\text{Cd}(\text{RR}'\text{dtc})_2$ complexes, thus confirming that ligand exchange between the metals is rapid on the NMR time scale. Electrochemical reversibility could only occur if all the exchange processes proceed at a diffusion-controlled rate. The NMR data are at least consistent with the hypothesis that the reactions are very fast.

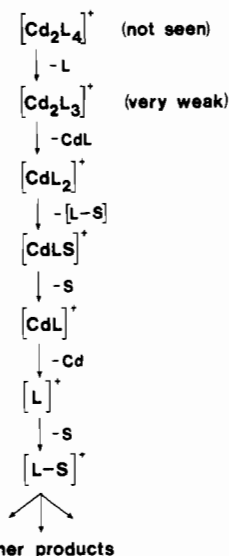


Figure 8. Mass spectral breakdown pattern for $\text{Cd}(\text{RR}'\text{dtc})_2$ compounds derived from EI/PI spectra.

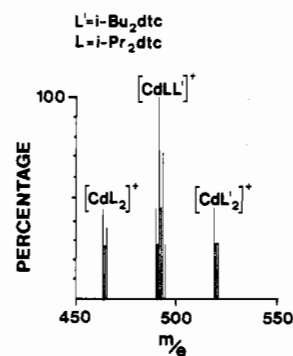


Figure 9. EI/PI mass spectrum for a mixture of $\text{Cd}(i\text{-Pr}_2\text{dtc})_2$ and $\text{Cd}(i\text{-Bu}_2\text{dtc})_2$.

Mass Spectrometry. Mass spectral studies of $\text{Cd}(\text{RR}'\text{dtc})_2$ compounds show relatively simple behavior with evidence of ligand-exchange reactions. According to the polarographic and NMR experiments, this would certainly be expected. When chemical ionization with negative ion detection (CI/NI) is used, the mass spectrum for $\text{Cd}(\text{Et}_2\text{dtc})_2$ confirms that in the solid state this species exists as a dimer. An m/e value corresponding to $[\text{Cd}_2(\text{Et}_2\text{dtc})_4]^-$ was observed, but the base peak is $[\text{Et}_2\text{dtc}]^-$ with $[\text{Cd}(\text{Et}_2\text{dtc})_2]^-$ appearing prominently. The breakdown pattern is shown in Figure 7. Unfortunately, the peaks for $[\text{Cd}_2(\text{RR}'\text{dtc})_4]^-$ were weak or even absent in other cases. When electron impact ionization with positive ion detection (EI/PI) is used, the mass spectra are generally as expected, but with the instrumentation available to us species having m/e values >800 could not be detected. The highest observed m/e value obtained by single-ion counting corresponds to $[\text{Cd}_2(\text{RR}'\text{dtc})_3]^+$ ($\text{RR}'\text{dtc} = \text{Me}_2\text{dtc}$) with the species $[\text{Cd}(\text{RR}'\text{dtc})_2]^+$ and $[\text{RR}'\text{dtc}]^+$ predominant, analogous to the CI/NI spectra. Tables S-I-S-II (supplementary information) show the EI/PI mass spectral data and Figure 8 shows the breakdown pattern.

Equimolar mixtures of two different $\text{Cd}(\text{RR}'\text{dtc})_2$ compounds (CdL_2 and CdL'_2) show m/e values corresponding to $[\text{CdL}_2]^+$, $[\text{CdLL}']^+$, and $[\text{CdL}'_2]^+$ (Figure 9) in the statistical proportions. The mass spectral behavior of $\text{Hg}(\text{RR}'\text{dtc})_2$ compounds has been described elsewhere.²² Mixtures of HgL_2 and CdL'_2 did not, however, show evidence of bimetallic species, but all the products of ligand exchange were observed: viz. $[\text{HgLL}']^+$, $[\text{HgL}'_2]^+$, $[\text{CdLL}']^+$, and $[\text{CdL}'_2]^+$ as well as peaks due to the starting materials. It is evident that exchange reactions occur in the solid state on the probe of the spectrometer as is believed to be the case for mixtures of the more kinetically inert cobalt dithiocarbamate complexes.²⁵

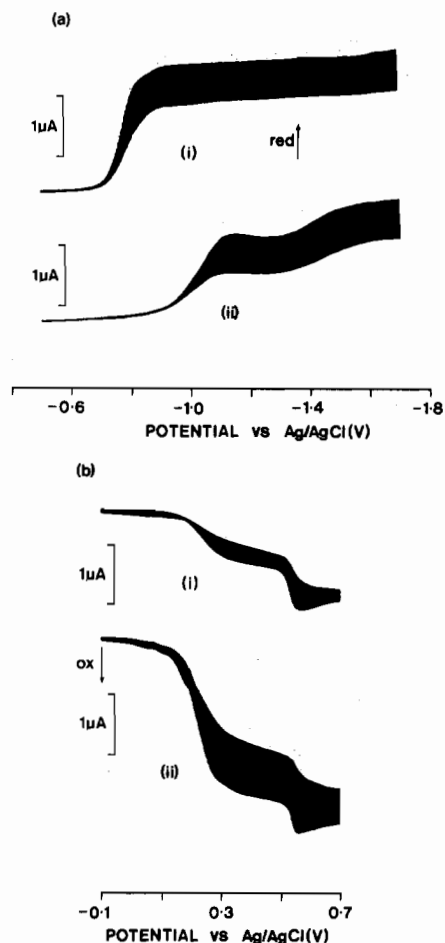


Figure 10. Dc polarograms (drop time 0.5 s) for (a) the reduction and (b) the oxidation processes of (i) Hg(Et₂dsc)₂ and (ii) Cd(Et₂dsc)₂ in CH₂Cl₂ (0.1 M Bu₄NClO₄) at 20 °C.

Cadmium and Mercury Diethyldiselenocarbamates. A brief examination of the electrochemical behavior of cadmium and mercury diselenocarbamates is reported for the first time. The reduction process for Hg(Et₂dsc)₂ (dc polarogram shown in Figure 10a) is entirely analogous to that for Hg(Et₂dsc)₂ with a fairly close correspondence for $E_{1/2}$ values ($E_{1/2}$ (Hg(Et₂dsc)₂) = -0.710 V, $E_{1/2}$ (Hg(Et₂dsc)₂) = -0.770 V vs. Ag/AgCl (saturated LiCl in dichloromethane)). In the case of Cd(Et₂dsc)₂, process 4 is very large and process 5 occurs at a potential more positive than for the sulfur analogue (Figure 10a). However, the summation of currents for the two reduction processes is close to the limiting current for an equivalent concentration of the mercury complex. This suggests that the mechanism for the reduction process is analogous to that described for Cd(RR'dtc)₂ compounds.

In a manner similar to Hg(RR'dtc)₂ compounds, the oxidation of Hg(Et₂dsc)₂ shows two single-electron steps (Figure 10b). Processes 1 and 2 for Cd(Et₂dsc)₂ (Figure 10b) are not resolved, but overall a four-electron process takes place. Clearly process 3 occurs at the same potential as the second oxidation step for Hg(Et₂dsc)₂. Therefore, exchange mechanisms to form Hg(Et₂dsc)₂, due to reaction with the electrode, appear to operate in both the reduction and oxidation of Cd(Et₂dsc)₂. Overall there are strong similarities between the electrochemical behavior of Cd(Et₂dsc)₂ and Cd(RR'dtc)₂ compounds.

Conclusions

The electrochemistry of cadmium dithio- and diselenocarbamates is characterized by chemically reversible processes.

These are, however, all multistep processes and do not simply involve charge transfer as is the case with most other metal dithiocarbamate complexes. Some of the important processes involved include exchange reactions with mercury analogues, and with the electrode material, and the formation of bimetallic complexes. The overall reversibility requires that all these processes be essentially diffusion controlled. Data from NMR and mass spectral experiments are consistent with these processes being extremely rapid.

Acknowledgment. We are grateful to Desma Page and Garry Franklin for technical assistance and for contribution to the discussion of experimental data. Grateful acknowledgement is made to the University of Tasmania (Hobart, Tasmania, Australia) for the recording of the negative ion mass spectra. We acknowledge financial support given by the Australian Research Grants Scheme.

Appendix of Symbols and Abbreviations

E	potential
i	current
$E_{1/2}$	half-wave potential, defined by $i = i_d/2$
i_d	limiting diffusion-controlled current
E_p	peak position
i_p	peak current
dc	direct current
E_p^{red}	peak potential for reduction in cyclic voltammetry
E_p^{ox}	peak potential for oxidation in cyclic voltammetry
k	rate constant
DME	dropping mercury electrode
HMDE	hanging mercury drop electrode
NMR	nuclear magnetic resonance
δ	NMR chemical shift
m/e	mass to charge ratio
EI/PI	electron impact ionization with positive ion detection
CI/NI	chemical ionization with negative ion detection
dsc	dithiocarbamate
dsc	diselenocarbamate
L	RR'dtc ligand
Me	methyl
Et	ethyl
EtOH	hydroxyethyl
<i>n</i> -Pr	normal propyl
<i>i</i> -Pr	isopropyl
<i>n</i> -Bu	normal butyl
<i>i</i> -Bu	isobutyl
<i>t</i> -Bu	<i>tert</i> -butyl
<i>n</i> -Hx	normal hexyl
<i>c</i> -Hx	cyclohexyl
<i>n</i> -Oc	normal octyl
Bz	benzyl
Ph	phenyl
pipdsc	piperidine- <i>N</i> -carbodithioate
2-Mepip	2-methylpiperidine- <i>N</i> -carbodithioate
3-Mepip	3-methylpiperidine- <i>N</i> -carbodithioate
4-Mepip	4-methylpiperidine- <i>N</i> -carbodithioate
2,6-Me ₂ pip	2,6-dimethylpiperidine- <i>N</i> -carbodithioate
pyrrdsc	pyrrolidine- <i>N</i> -carbodithioate
morphdsc	morpholine- <i>N</i> -carbodithioate

Registry No. Cd(Et₂dsc)₂, 14239-68-0; Cd(*n*-Pr₂dsc)₂, 55519-99-8; Cd(*i*-Pr₂dsc)₂, 31312-98-8; Cd(*n*-Bu₂dsc)₂, 14566-86-0; Cd(*i*-Bu₂dsc)₂, 69090-75-1; Cd(*c*-Hx₂dsc)₂, 92451-30-4; Cd(Bz₂dsc)₂, 26609-04-1; Cd(*i*-BuMedsc)₂, 95589-51-8; Cd(pipdsc)₂, 14949-59-8; Hg(Et₂dsc)₂, 14239-51-1; Hg(*n*-Pr₂dsc)₂, 21439-56-5; Hg(*i*-Pr₂dsc)₂, 21439-57-6; Hg(*n*-Bu₂dsc)₂, 21439-58-7; Hg(*i*-Bu₂dsc)₂, 79001-48-2; Hg(*c*-Hx₂dsc)₂, 21439-59-8; Hg(Bz₂dsc)₂, 21439-61-2; Hg(*i*-BuMedsc)₂, 95589-52-9; Hg(pipdsc)₂, 21439-62-3; Cd(3-Mepipdsc)₂, 79572-67-1; Cd(2,6-Me₂pipdsc)₂, 79716-29-3; Cd(Et₂dsc)₂, 19400-66-9; Hg(Et₂dsc)₂, 57349-79-8; ¹¹³Cd, 14336-66-4; Cd, 7440-43-9; Hg, 7439-97-6.

Supplementary Material Available: Tables S-I-S-III listing EI/PI mass spectral data for Cd(RR'dtc)₂ complexes (3 pages). Ordering information is given on any current masthead page.