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Investigation of Exchange and Redox Reactions of Mercury Dithiocarbamate Complexes by Electrochemical Techniques at Mercury Electrodes, Mercury-199 Nuclear Magnetic Resonance Spectrometry, and Mass Spectrometry

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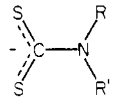
Electrochemical techniques of polarography, cyclic voltammetry, and controlled-potential electrolysis at mercury electrodes, in conjunction with spectroscopic methods, have enabled a detailed investigation to be made of the exchange and redox reactions associated with mercury dithiocarbamate complexes, $Hg(RR'dtc)_2$, in dichloromethane. Mass spectrometric measurements show that mixed-ligand mercury dithiocarbamate complexes are formed after reaction of mercury dithiocarbamate complexes containing different ligands. The ligand exchange possibly occurs in the solid state. ^{199}Hg NMR spectra of mixtures of different complexes demonstrate that exchange processes in solution to form mixed-ligand complexes are extremely fast. Dimer formation, as an intermediate step, is believed to account for the observation of these exchange processes. The lability of the mercury(II) complexes and their rapid interaction with elemental mercury and mercury(I), together with dimer formation, also strongly influence the nature of both electrochemical reduction and oxidation processes observed at mercury electrodes. Reduction of $Hg(RR'dtc)_2$ at a mercury electrode occurs in an overall two-electron step as $Hg(RR'dtc)_2 + 2e^- \rightleftharpoons Hg + 2[RR'dtc]^-$ although mercury(I) is implicated as an intermediate. Substituent effects correlate with those for reduction of other metal dithiocarbamate complexes. Surprisingly, two reversible one-electron-oxidation steps are also observed at mercury electrodes. These are not metal or ligand based as is the case with other metal dithiocarbamate complexes, but rather they are believed to be associated with oxidation of the mercury electrode to produce multinuclear cationic mercury dithiocarbamate complexes.

Introduction

Metal dithiocarbamate complexes have been used and studied extensively because of their importance in a number of areas of chemistry. For example, in the field of analytical chemistry dithiocarbamate complexes have been used to concentrate metals into organic solvents (solvent extraction) as a preliminary to elemental analysis using techniques such as atomic absorption spectrometry.[3,4] Commercially, dithiocarbamate complexes are widely used.[5] In the field of inorganic chemistry, the occurrence of many unusual and interesting structural features, magnetic properties, and the ability to stabilize high oxidation states has attracted substantial interest.[5-8] Consequently, for many reasons, chemical characterization of dithiocarbamate complexes have been regarded as important.

Mercury(II) dithiocarbamate complexes have been known for many years[5-9] and have been widely used as fungicides.[10] A number of their chemical, physical, and spectroscopic properties have been examined.[5-8] Usually, they are isolated as complexes with the empirical formula $Hg(RR'dtc)_2$, where RR'dtc represents the dithiocarbamate ligand (I).



I

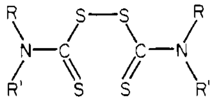
Structurally, $Hg(RR'dtc)_2$ complexes can be monomeric or dimeric[6-9,11-14] in the solid state. In organic solvents, available information would suggest that they are predominantly monomeric complexes.[15,16] A brief report of the nuclear magnetic resonance behavior[16] (NMR) of *N,N*-dialkyldithiocarbamate complexes suggests that $Hg(R_2dtc)_2$ complexes are kinetically labile, with exchange reactions presumed to occur via a monomer–dimer equilibrium. Reduction of $Hg(R_2dtc)_2$ has been examined at mercury electrodes[17,18] for a small number of *N,N*-dialkyldithiocarbamate ligands, and the overall process is

$$Hg(R_2dtc)_2 + 2e^- \rightleftharpoons Hg + 2[R_2dtc]^- \quad (1)$$

with mercury(I) intermediates, which are presumed to disproportionate, as part of the reaction scheme. At platinum electrodes the oxidation process has been examined briefly.[19] It has been assumed that the process

$$Hg(R_2dtc)_2 \rightarrow Hg^{2+} + (R_2dtc)_2 + 2e^- \quad (2)$$

occurs, but firm evidence on the nature of this electrode process has yet to be presented. In eq 2, $(R_2dtc)_2$ is the thiuram disulfide formed by oxidation of $[R_2dtc]^-$. The more general structure $(RR'dtc)_2$ is shown in structure II.



II

The oxidation of $Hg(RR'dtc)_2$ has therefore been proposed to be ligand rather than metal based in contrast to oxidation of $Fe(RR'dtc)_3$[20] or $Cu(RR'dtc)_2$,[21] which is clearly a metal-based process.

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In summary, while some of the redox properties of Hg(RR′dtc)$_2$ complexes are known, for a limited range of ligands, the detailed understanding of the redox properties in relation to other properties has yet to be presented. In this publication, electrochemical investigations in dichloromethane at mercury electrodes with a wide variety of Hg(RR′dtc)$_2$ complexes are described. Additionally, the influence of the dynamic nature of the complexes on electrochemical, ^{199}Hg NMR, and mass spectrometric properties of the complexes are considered.

Experimental Section

Synthesis. Mercury dithiocarbamate complexes were prepared by using standard methods.[6] Stoichiometric amounts of sodium or tetrabutylammonium hydroxide, carbon disulfide, and the appropriate amine were combined in water to form the sodium or tetrabutylammonium salt of the dithiocarbamate ligand. Mercury(II) nitrate was then added to this solution to form the mercury(II) dithiocarbamate complex. Hg(RR′dtc)$_2$ complexes were purified by Soxhlet extraction with chloroform and subsequent recrystallization.

Instrumentation. Polarographic measurements were made with a Princeton Applied Research Corp., PAR (Princeton, NJ), Model 174A polarographic analyzer. A dropping-mercury working electrode, Ag/AgCl (saturated LiCl/dichloromethane) reference electrode, and platinum-wire auxiliary electrode were used for all polarographic measurements. All measurements were made at 22 ± 1 °C in dichloromethane containing 0.1 M Bu_4NClO_4. Dichloromethane was HPLC grade. Experiments undertaken in the presence of alumina or deliberately added water (up to 1%) demonstrated that electrochemical measurements for mercury complexes are insensitive to traces of water impurity. Consequently all measurements could be made on an open bench without need to carefully dry the solvent and the electrolyte. Oxygen was removed by degassing solutions with high-purity nitrogen. Unless otherwise stated, the concentration of Hg(RR′dtc)$_2$ compounds used was 5×10^{-4} M.

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

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, 1600 kV; pressure, $(3-5) \times 10^{-6}$ torr. The complexes were introduced via a solids probe with spectra obtained at probe temperatures of 200–350 °C.

The NMR spectra of the mercury dithiocarbamate complexes in dichloromethane solution were recorded on a JEOL FX 100 pulsed Fourier transform spectrometer at 17.82 MHz on a 20-kHz spectral window (acquisition time 0.2 s, recycle time 0.7 s, 8192 data points). Proton noise decoupling was used and tris(acetylacetonate)chromium(III) was added to solutions to reduce the relaxation time of the ^{199}Hg nuclei. An external ^{7}Li lock was used, and chemical shifts were referenced against 1 M phenylmercury acetate in dimethyl sulfoxide by using the high-frequency positive convention. A JEOL NM 5471 variable-temperature controller was used and calibrated against a platinum resistance thermometer.

Results and Discussion

The interpretation of the electrochemical processes requires an understanding of the dynamic properties of the Hg(RR′dtc)$_2$ complexes. Information gained from mass spectra and ^{199}Hg NMR spectra are invaluable in this context. Consequently, data from these spectroscopic techniques are presented first.

A. Mass Spectrometry. Table I summarizes data obtained for Hg(RR′dtc)$_2$ complexes. For ease of representation, the abbreviations HgL_2 etc., where L = RR′dtc, is used in the tables and figures describing mass spectra. The molecular ion corresponding to the species $[Hg(RR'dtc)_2]\cdot^+$ was always observed in the mass spectrum although usually at an intensity of only about 2% of the base peak. This molecular ion showed the characteristic mass distribution expected for the isotopic composition of mercury. Apart from an m/e value corresponding to the formula $[L_2HNCS]^+$ observed in all but one complex, the remainder of the mass spectrum consisted of peaks corresponding to the ligand $[RR'dtc]^+$ and its subsequent fragmentation. That is, $[Hg(RR'dtc)_2]\cdot^+$ breaks down to Hg(RR′dtc) and $[RR'dtc]^+$, with the remaining breakdown pattern being that expected from $[RR'dtc]^+$. Interestingly, on no occasion was the ion $[Hg(RR'dtc)]^+$ observed, implying that Hg(RR′dtc) is very unstable. This is consistent with electrochemical data obtained in solution where this species disproportionates at a very fast rate (see later). The breakdown pattern for the ligand RR′dtc is similar to that reported by other workers who studied the mass spectra of $[RR'dtc]^-$, $Ni(RR'dtc)_2$, and $Zn(RR'dtc)_2$.[22-24]

The ion having the highest m/e value below that of $[Hg(RR'dtc)_2]^+$ did not have the characteristic isotopic distribution associated with mercury and has been assigned the formula $[(RR'dtc)_2HNCS]^+$. It is not clear how this species could be obtained from monomeric Hg(RR′dtc)$_2$. However, since dimeric species are known to be formed in the solid state, the single ion monitoring mode was used to look for evidence of dimers in the mass spectrum. The mass spectrometer used has an upper detection limit of m/e 800, so species of formula $[Hg_2(RR'dtc)_4]^+$ could not be detected, even if they exist. However, evidence was obtained for m/e values corresponding to $[Hg_2(RR'dtc)_3]^+$, an obvious fragmentation product of a dimer. Dimer formation could account for the formation of the species assigned as $[(RR'dtc)_2HNCS]^+$. There has been a report of the detection of $Zn_2(RR'dtc)_4$ dimers in the gas phase by mass spectrometry.[24] In the crystalline state, mercury dithiocarbamate dimers are structurally related to zinc dithiocarbamates, so this postulate seems reasonable. Consequently, in Table I, it is not certain whether $[Hg(RR'dtc)_2]\cdot^+$ is the parent derived from the monomer or a breakdown product resulting from a dimer. The unassigned m/e value also corresponds to $[CoL_2]^+$. Interaction of HgL_2 with metallic cobalt contained in the metal components of the mass spectrometer could result in formation of a cobalt dithiocarbamate complex. In subsequent discussion this m/e value is referred to as arising from $[L_2HNCS]^+$ but attention should be drawn to this possible alternative explanation.

Mass spectra were also recorded on mixtures of dithiocarbamate complexes obtained in different ways. One mixture was prepared in the solid state by mixing equimolar quantities of different Hg(RR′dtc)$_2$ complexes, subsequently referred to as HgL_2 and HgL'_2 ($L \neq L'$). Analysis of the mass spectrum obtained from this solid mixture showed molecular ions corresponding to $[ML_2]\cdot^+$, $[MLL']\cdot^+$, and $[ML'_2]\cdot^+$ as shown in Figure 1. Also, in the spectra of the mixtures, three peaks corresponding to $[L_2HNCS]^+$, $[LL'HNCS]^+$, and $[L'_2HNCS]^+$ were observed. Other mixtures obtained from equimolar proportions of the sodium salts of two dithiocarbamates and mercury nitrate also produced the same mass spectrum as did dichloromethane solutions of mixtures of HgL_2 and HgL'_2. These results indicate that exchange reactions must be occurring in the solid state on the probe of the mass spectrometer. It is postulated that the exchange reactions occur via dimer formation in accordance with Scheme I.

Some metal acetylacetonate complexes show dimer formation under mass spectrometric conditions and exhibit similar exchange behavior.[25] Exchange reactions in the solid state

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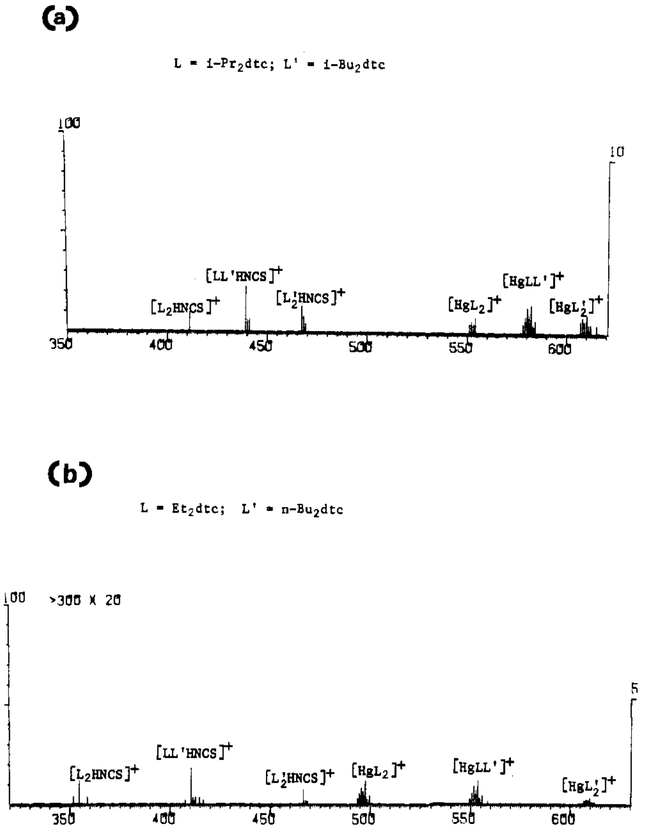
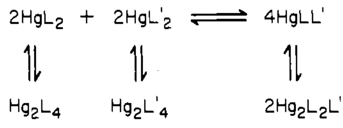


Figure 1. Mass spectra of mixtures of HgL_2 and HgL'_2: (a) Hg(i-$Pr_2dtc)_2$ + Hg(i-$Bu_2dtc)_2$; (b) $Hg(Et_2dtc)_2$ + Hg(n-$Bu_2dtc)_2$.

Scheme I



have been observed in other systems.[26]

A thin-layer chromatographic separation of synthetically prepared equimolar HgL_2 and HgL'_2 mixtures in dichloromethane produced only two bands, which proved to be pure HgL_2 and HgL'_2 according to mass spectral analysis. However, NMR data imply that HgLL′ species are present in a solution of a mixture of HgL_2 and HgL'_2[16] (also see later). Thus, the process

$$HgL_2 + HgL'_2 \rightleftharpoons 2HgLL' \qquad (3)$$

must be very rapid. On the chromatographic plate, as separation of HgLL′ from HgL_2 and HgL'_2 is attempted, any removal of HgL_2 immediately requires that the equilibrium position of eq 3 shifts to the left. If this occurs, then only HgL_2 and HgL'_2 can be prepared. This kind of phenomenon has been noted in analytical application employing the chromatography of kinetically labile nickel(II) dithiocarbamate complexes[27] and in studies of iron(III) dithiocarbamates.[28]

B. Mercury-199 NMR Data. ^{199}Hg NMR data have been previously reported for a limited range of mercury *N*,*N*-dialkyldithiocarbamates.[16] ^{199}Hg has a spin of $^1/_2$, and mercury complexes generally exhibit sharp NMR signals.[29] Spectra have to be recorded at close to saturated solutions in dichloromethane to provide adequate sensitivity for a number of the mercury complexes. Table II summarizes data for those complexes that were sufficiently soluble to obtain ^{199}Hg NMR spectra with an acceptable signal to noise ratio of 10:1 or better.

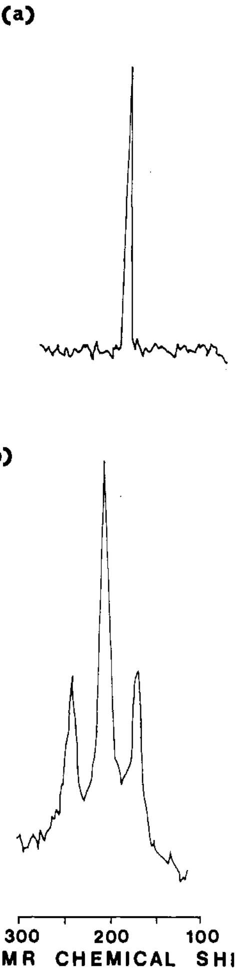


Figure 2. ^{199}Hg NMR spectra of a mixture of Hg(i-$Pr_2dtc)_2$ and Hg(i-$Bu_2dtc)_2$ in CH_2Cl_2: (a) 30 °C; (b) −110 °C.

Mass spectrometry studies imply that exchange reactions occur in the solid state. To establish that the same phenomena occur in solution, approximately equimolar solutions of HgL_2 and HgL'_2 were mixed and the ^{199}Hg NMR spectra recorded at 30 °C. A single resonance was observed approximately midway between the resonances for HgL_2 and HgL'_2. Data from these experiments are summarized in Table III and confirm that Hg(RR′dtc)$_2$ complexes are extremely labile in solution for the dithiocarbamate ligands studied.

Figure 2 shows a comparison of NMR spectra for mixtures of Hg(i-$Pr_2dtc)_2$ and Hg(i-$Bu_2dtc)_2$ at 30 and −110 °C. A single-exchange averaged spectrum was seen at 30 °C, but at −110 °C the rate of exchange had been slowed down sufficiently to enable identification of individual species. The three resonances at −110 °C are due to the almost statistical distribution of Hg(i-$Bu_2dtc)_2$, Hg(i-Bu_2dtc)(i-Pr_2dtc), and Hg(i-$Pr_2dtc)_2$. That is, the redistribution reaction

$$Hg(i\text{-}Bu_2dtc)_2 + Hg(i\text{-}Pr_2dtc)_2 \rightleftharpoons 2Hg(i\text{-}Bu_2dtc)(i\text{-}Pr_2dtc) \qquad (4)$$

does occur in solution. However, for other mixtures of HgL_2 and HgL'_2, broadening of the exchange average resonances occurred at low temperature, but individual responses were not observed. The rapid exchange process probably occurs via dimer formation as is proposed in the solid state. Data ob-

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Table I. Mass Spectral Data for Hg(RR'dtc)$_2$ Complexes[a]

		fragments																
R	R'	$[HgL_2]^+$	$[L_2\text{-}HNCS]^{+b}$	$[LH]^+$	$[L]^+$	$[LH\text{-}S]^+$	$[L\text{-}S]^+$	$[L\text{-}S_2]^+$	$[LH\text{-}S\text{-}R]^+$	$[L\text{-}S\text{-}R]^+$	$[L\text{-}CS_2]^+$	$[R]^+$	$[H_2NCS]^+$	$[CS_2]^+$	$[CS]^+$	$[S_2]^+$	$[CSH]^+$	$[Hg]^+$
Me	Me	2	2	21	80	4	100	7	2	12	43			9	43	1	4	3
Et	Et	2	4	33	100	7	81		44	4	65	73	42	5	58	3	2	4
i-Pr	*i*-Pr	<1	6	23	100	4	31		32	42	10	23	36	6	8	6	2	8
n-Bu	*n*-Bu	2	2	33	100	11	66	8	22	2	55	69	9	4	8	2	2	8
i-Bu	*i*-Bu	1	6	35	100	6	39	2	6	3	18	72	7	8	2	3	1	6
n-Pe	*n*-Pe	3	22	18	88	13	63	7	37	3	27	53	7	9	45	4	4	7
n-Hx	*n*-Hx	<1	<1	18	88	9	52	3	35	6	38	37	2	4	13			3
Me	*n*-Bu	<1	6	20	42	4	47		83	8	12	54	18	25	100	6	87	5
Et	*n*-Bu	2	5	31	100	8	75	1	50	5	4	100	23	12	48	4	5	6
n-Bu	*t*-Bu	2		7	26	1	9		20	20	1	73	7	20	9	6	5	5
c-Hx	*c*-Hx	≪1	≪1	9	30	1	10	1	30	15	5	46	3	4	1	1	1	1
Me	Ph	1	<1	11	41	16	100	2	4	22	18	73		4	2		2	10
Et	Ph	2	4	22	48	7	63		100	35	43	59	7	18	10		1	10
i-Pr	Ph	2	3	22	60	5	40	1	45	20	41		11	13	8	5	1	10

	fragments													
N heterocyclic deriv	$[HgL_2]^+$	$[L_2HNCS]^+$	$[LH]^+$	$[L]^+$	$[LH\text{-}S]^+$	$[L\text{-}S]^+$	$[L\text{-}S_2]^+$	$[L\text{-}CS_2]^+$	$[H_2NCS]^+$	$[CS_2]^+$	$[CS]^+$	$[S_2]^+$	$[CSH]^+$	$[Hg]^+$
pip	3	3	25	28	7	60		100	2	21	4	2	1	3
2-Mepip	2	10	25	52	4	56	2	10	2	4	7	1		6
3-Mepip	1	3	52	62	14	100	1	32	3	11	11	5	2	9
4-Mepip	2	13	53	60	12	100		6	4	13	8		3	4
2,6-dimepip	1	2	43	95	10	72	1	100	5	14	13	6	2	6
morph	2	1	30	40	12	100	2	33	44	34	20	17	23	10
pyrr	2	6	54	52	9	100		4	6	2	3		1	9

[a] All measurements are percent relative intensity to the base peak. [b] Could also be $[CoL_2]^+$; see text.

Table II. ^{199}Hg NMR Data for Hg(RR'dtc)$_2$ Complexes in Dichloromethane at 30 °C[a]

Hg(RR'dtc)$_2$			Hg(RR'dtc)$_2$		
R	R'	$\delta(^{199}Hg)$	R	R'	$\delta(^{199}Hg)$
Me	Me	179.8	Et	*n*-Bu	193.7
Et	Et	176.5	*n*-Bu	*t*-Bu	200.0
i-Pr	*i*-Pr	224.4	Me	Ph	123.6
n-Bu	*n*-Bu	173.4	Et	Ph	170.7
i-Bu	*i*-Bu	143.3	*i*-Pr	Ph	187.7
c-Hx	*c*-Hx	199.5			

N heterocyclic deriv	$\delta(^{199}Hg)$	N heterocyclic deriv	$\delta(^{199}Hg)$
pip	177.6	4-Mepip	156.2
2-Mepip	196.2	2,6-dimepip	202.6
3-Mepip	163.6		

[a] Values are reported relative to 1 M phenylmercury acetate in dimethyl sulfoxide.

Table III. ^{199}Hg NMR Data for Mixtures of Hg(RR'dtc)$_2$ Complexes at 30 °C in CH_2Cl_2[a]

		NMR chem shift	
compd	$\delta(^{199}Hg)$	average δ	mixed δ
Hg(*i*-Bu$_2$dtc)$_2$ Hg(3-Mepip)$_2$	143.9 161.4	152.6	154.0
Hg(*i*-Bu$_2$dtc)$_2$ Hg(*n*-Bu$_2$dtc)$_2$	143.9 166.1	155.0	155.1
Hg(*i*-Bu$_2$dtc)$_2$ Hg(Et$_2$dtc)$_2$	143.9 173.7	158.8	161.1
Hg(3-Mepip)$_2$ Hg(*i*-Pr$_2$dtc)$_2$	161.4 225.0	193.2	196.8
Hg(*n*-Bu$_2$dtc)$_2$ Hg(*i*-Pr$_2$dtc)$_2$	166.1 225.0	195.5	198.4
Hg(Et$_2$dtc)$_2$ Hg(*i*-Pr$_2$dtc)$_2$	173.7 225.0	199.3	195.4
Hg(*i*-Bu$_2$dtc)$_2$ Hg(*i*-Pr$_2$dtc)$_2$	143.9 225.0	184.5	187.0

[a] Shifts are measured relative to 1 M phenylmercury acetate in dimethyl sulfoxide.

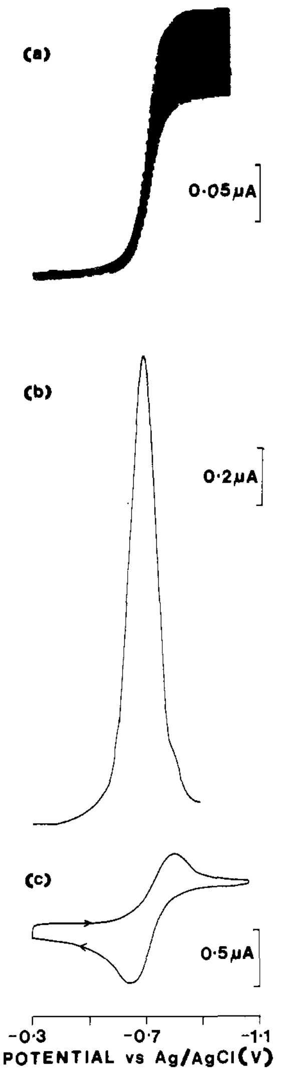

Figure 3. Reduction of Hg(n-$Bu_2dtc)_2$ at the mercury electrode in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 22 °C: (a) dc polarogram; (b) differential-pulse polarogram; (c) cyclic voltammogram.

tained with dialkyldithiocarbamates[16] are now shown to be generally true for other ligands.

C. Electrochemical Reduction at Mercury Electrodes in Dichloromethane. Figure 3 shows a dc polarogram, differential-pulse polarogram, and cyclic voltammogram for reduction of Hg(n-$Bu_2dtc)_2$ in the noncoordinating solvent dichloromethane. Cyclic voltammograms at mercury electrodes are those expected for a chemically reversible electrode process. Controlled-potential electrolysis of Hg(n-$Bu_2dtc)_2$ at a mercury pool electrode gave an n value of 2.03 ± 0.01 (average of three determinations). Polarograms of (Bu_4N)(RR′dtc) showed oxidation waves with the same $E_{1/2}$ value as found for reduction of the mercury complex. Unfortunately, tetrabutylammonium dithiocarbamate salts are not completely stable in dichloromethane, and quantitative measurements with the ligands were not possible. The more stable sodium salts are insoluble in CH_2Cl_2. However, the data provide convincing evidence that in CH_2Cl_2 the overall electrode process is

$$\mathrm{Hg(RR'dtc)_2 + 2e^- \rightleftharpoons Hg + 2[RR'dtc]^-} \qquad (5)$$

Table IV summarizes the polarographic data at mercury electrodes. A substantial substituent effect can be noted. Figure 4 shows a plot of $E_{1/2}$ for $Hg(RR'dtc)_2$ vs. that for the reduction of $Cu(RR'dtc)_2$. This shows that substituent effects are related to those found with other metal dithiocarbamate complexes. However, a plot of ^{199}Hg NMR chemical shift vs. $E_{1/2}$ shows no obvious correlation. Structural factors clearly influence electrochemical and ^{199}Hg NMR data in a different fashion. Relationships of $E_{1/2}$ with other spectroscopic parameters for other dithiocarbamate complexes have also proved difficult to understand. When a wide range of $[RR'dtc]^-$ ligands are employed, both electronic and steric effects appear to be important.[28] Electronic (thermodynamic) effects play a dominant role in determining reversible $E_{1/2}$ values for reduction of $Hg(RR'dtc)_2$, the implication being that steric and other effects must have a pronounced effect on the NMR data.[30] ^{113}Cd NMR spectra of the related $Cd(Et_2dtc)_2$ compound have been reported as part of a survey of cadmium sulfur chelates.[31] Similarly, no generally systematic trends in ^{113}Cd NMR spectra were observed in this study. The authors of this study pointed out that many intermolecular effects may influence ^{113}Cd NMR parameters. The same would appear to be true for ^{119}Hg NMR in the sense that electronic effects have been shown not to be dominant, when a wide range of ligands are examined. To verify that the presence of 0.1 M Bu_4NClO_4 was not influencing correlations, NMR spectra were recorded in the presence of the electrochemical electrolyte. The same shifts were encountered within the limit of experimental error.

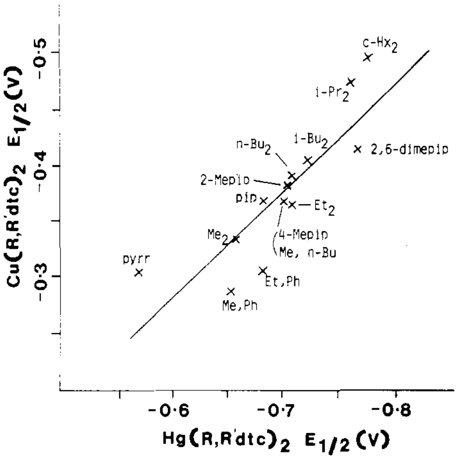

Figure 4. $E_{1/2}[Cu(RR'dtc)_2]$ in acetone vs. $E_{1/2}[Hg(RR'dtc)_2]$ in CH_2Cl_2 for reduction (slope 0.955 ± 0.170; correlation coefficient 0.852; data for $Cu(RR'dtc)_2$ obtained from ref 21).

While the overall reduction step has been previously characterized in eq 5, the reaction pathway in dichloromethane has yet to be considered. In acetone,[17] the reduction has been reported to occur via a mercury(I) intermediate

$$\mathrm{Hg(RR'dtc)_2 + Hg \rightleftharpoons 2Hg(RR'dtc)} \qquad (6)$$

$$\mathrm{2Hg(RR'dtc) + 2e^- \rightleftharpoons 2Hg + 2(RR'dtc)^-} \qquad (7)$$

A plot of log $[(i_d - i)/i]$ vs. E obtained from dc polarograms in CH_2Cl_2 is close to linear with a slope of −57 mV for Hg(i-$Pr_2dtc)_2$, which is consistent with this mechanism. For other complexes, the slope varied from 50 to 90 mV. $E_{1/4} - E_{3/4}$ values in Table IV are close to that expected for a one-electron charge-transfer step for some complexes, although, for many compounds, values are greater than this. Concentration-dependence studies show the presence of strong adsorption, with pronounced maxima being evident at concentrations above 10^{-3} M. $E_{1/2}$ values were in fact slightly dependent on concentration, which is not expected from the proposed mechanism, although the presence of adsorption may account for this. The highly symmetrical differential-pulse polarograms and half-width values are approximately those expected for a one-

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Table IV. Data for Reduction of $Hg(RR'dtc)_2$ at the Mercury Electrode in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 22 °C

$Hg(RR'dtc)_2$		dc polarography[a]		differential-pulse polarography[b]		cyclic voltammetry[c]		
R	R'	$E_{1/2}$,[d] V	$E_{1/4} - E_{3/4}$, mV	E_p,[d] V	$w_{1/2}$, mV	E_p^{red},[d] V	E_p^{ox},[d] V	ΔE_p, mV
Me	Me	−0.660	75	−0.650	120	−0.735	−0.572	163
Et	Et	−0.710	68	−0.694	110	−0.825	−0.570	255
i-Pr	*i*-Pr	−0.762	80	−0.762	100	−0.850	−0.670	180
n-Bu	*n*-Bu	−0.709	60	−0.699	95	−0.785	−0.640	145
i-Bu	*i*-Bu	−0.723	60	−0.720	90	−0.790	−0.655	135
n-Hx	*n*-Hx	−0.728	65	−0.707	100	−0.875	−0.570	305
Me	*n*-Bu	−0.702	78	−0.685	110	−0.825	−0.565	260
Et	*n*-Bu	−0.732	65	−0.720	100	−0.815	−0.650	165
n-Bu	*t*-Bu	−0.830	60	−0.820	90	−0.905	−0.760	145
c-Hx	*c*-Hx	−0.778	60	−0.785	95	−0.850	−0.725	135
Me	Ph	−0.655	80	−0.645	130	−0.800	−0.535	265
Et	Ph	−0.683	100	−0.680	155	−0.825	−0.555	270
i-Pr	Ph	−0.682	92	−0.685	140	−0.775	−0.630	145

	dc polarography[a]		differential-pulse polarography		cyclic voltammetry		
N heterocyclic deriv	$E_{1/2}$,[d] V	$E_{1/4} - E_{3/4}$, mV	E_p,[d] V	$w_{1/2}$, mV	E_p^{red},[d] V	E_p^{ox},[d] V	ΔE_p, mV
pip	−0.685	85	−0.685	120	−0.840	−0.535	305
2-Mepip	−0.705	78	−0.695	110	−0.825	−0.560	265
3-Mepip	−0.700	60	−0.690	110	−0.825	−0.575	250
4-Mepip	−0.702	68	−0.685	110	−0.825	−0.580	245
2,6-dimepip	−0.770	65	−0.770	100	−0.860	−0.685	175
morph	−0.635	100	−0.625	180	−0.755	−0.505	250
pyrr	−0.572	70	−0.580	105	−0.685	−0.495	190

[a] drop time 0.5 s. [b] pulse amplitude 50 mV. [c] scan rate 500 mV s^{-1}. [d] Potential vs. Ag/AgCl.

electron charge transfer, although the position of $E_{1/2}$ relative to the differential-pulse peak position is not that expected theoretically for all compounds. On the time scale of cyclic voltammetry, E_p values indicate incomplete diffusion control, with rates of electron transfer being ligand dependent. This also accounts for larger values of $E_{1/4}$–$E_{3/4}$ than expected for a reversible charge-transfer step sometimes being observed in polarography.

Theoretical studies on the direct two-electron-reduction step $Hg(RR'dtc)_2 + 2e^- \rightleftharpoons Hg + 2[RR'dtc]^-$ led to a concentration dependence of $E_{1/2}$ as expected.[32] However, a plot of log $[(i_d - i)/i^2]$ should be linear with a slope of −29 mV. Experimentally determined slopes are much greater than this for all complexes. Differential-pulse polarographic half-widths $w_{1/2}$ are also far greater than expected theoretically for this mechanism.[32]

Thus, the reversible one-electron-transfer mechanism appears to more adequately describe the reduction process than a two-electron charge transfer, but obviously this is not a complete description with adsorption and slow electron transfer being present to a significant degree. The possibility of dimer formation having some influence on the electrode process may also need to be considered. ^{199}Hg NMR chemical shifts showed no concentration dependence although the concentration range available was very limited because of solubility problems at one extreme and the level of sensitivity at the other. Naturally, a mixture of mechanisms for reduction may be operative, as is the case with other mercury complexes.[33] We have conclusively confirmed the nature of the overall electrode process and ascertained that it is chemically reversible under conditions of dc polarography. The mechanism involving a one-electron charge-transfer step appears to be the dominant pathway.

In view of the mass spectrometry and NMR data on mixtures of HgL_2 and HgL'_2, an electrochemical examination of the influence of exchange reactions was performed in CH_2Cl_2.

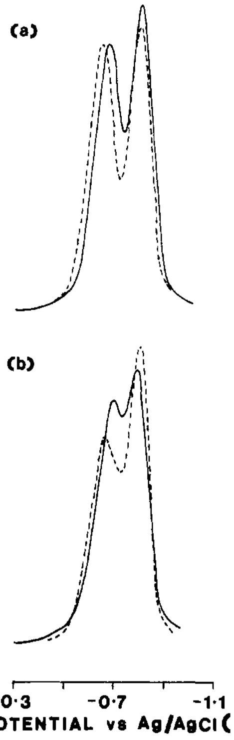

Figure 5. Differential-pulse polarograms for mixtures of (a) $Hg(Me_2dtc)_2$ and $Hg(n\text{-}Bu,t\text{-}Budtc)_2$ and (b) $Hg(pip)_2$ and $Hg(n\text{-}Bu,t\text{-}Budtc)_2$: (—) experimentally observed current for a mixture of 2.5×10^{-4} M HgL_2 and HgL'_2: (- -) arithmetic summation of current from individual 2.5×10^{-4} M solutions of HgL_2 and HgL'_2.

The resolution in electrochemistry is not as high as in spectroscopy. With dc polarography, the resolution was inadequate to undertake any useful studies. However, with use of combinations of the $Hg(RR'dtc)_2$ complexes with the most positive and most negative $E_{1/2}$ values, e.g. $Hg(Me_2dtc)_2$ and $Hg(n\text{-}Bu,t\text{-}Budtc)_2$, with differential-pulse polarography adequate resolution was achieved. Figure 5 shows the results for differential-pulse polarograms obtained by mixing 2.5×10^{-4} M

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HgL_2 and 2.5×10^{-4} M HgL'_2 compared with graphical summation of individual polarograms obtained from 2.5×10^{-4} M solutions of each complex. On the basis of rapid exchange observed in the NMR experiments, a single exchange-averaged response equivalent to 5×10^{-4} M HgLL′ may have been expected.[34] Clearly, this is not found, and the observed response is consistent with a small concentration of HgLL′ being present, the response being the summation of HgL_2, HgLL′, and HgL'_2.

This result is attributed to the special nature of this class of electrode process. In solution and prior to electrolysis the equilibrium

$$HgL_2 + HgL'_2 \rightleftharpoons 2HgLL' \qquad (8)$$

exists. If it is assumed that HgL_2 is more easily reduced than HgL'_2, with HgLL′ being exactly intermediate in terms of ease of reduction, then the reduction process for individual complexes would be

$$HgL_2 + 2e^- \rightleftharpoons Hg + 2L^- \qquad (E_{1/2})_1 \qquad (9)$$

$$HgLL' + 2e^- \rightleftharpoons Hg + L^- + L'^- \qquad (E_{1/2})_2 \qquad (10)$$

$$HgL'_2 + 2e^- \rightleftharpoons Hg + 2L'^- \qquad (E_{1/2})_3 \qquad (11)$$

where

$$(-E_{1/2})_1 < (-E_{1/2})_2 < (-E_{1/2})_3$$

$$(E_{1/2})_2 = [(E_{1/2})_1 + (E_{1/2})_3]/2$$

As the electrode potential is scanned toward more negative values, HgL_2 is the first species in the mixture to be reduced, generating L^- at the electrode surface. Loss of HgL_2 by reduction will of course cause HgLL′ to decrease in concentration since the equilibrium concentration in eq 8 will be shifted to the left, favoring generation of HgL_2 and HgL'_2. At more negative potentials, reduction of remaining HgLL′ occurs to generate L^- and L'^-. However generation of L'^- occurs where the rate of the process

$$2L'^- + Hg \rightleftharpoons HgL'_2 + 2e^- \qquad (12)$$

is close to diffusion controlled. Consequently, an electrochemical oxidation process will be operative in competition with eq 8, with the reduction current being partially nulled by an oxidation current, so that even if HgLL′ is present at $(E_{1/2})_2$ at the electrode surface or in the full solution, it may not necessarily give rise to a polarographic response. In the limiting case, polarographic reduction will appear to be that for reduction of HgL_2 and HgL'_2 even though HgLL′ may be present in the bulk solution. This result is similar to the thin-layer chromatographic work described earlier where only two bands of pure HgL_2 and HgL'_2 were detected by mass spectrometry, even though HgLL′ was present at the start of the experiment. Figure 5 does indicate the presence of a small current attributable to HgLL′. NMR data indicate that eq 8 occurs at a rapid, but less than diffusion-controlled, rate. Under this condition, the combination of eq 8–11 is responsible for the fact that polarographic responses of HgL_2 and HgL'_2 are not additive in mixtures. If eq 8 were diffusion controlled together with all other steps, a single electrochemical response would occur, which would be equivalent to the exchange-average value in NMR. Alternatively, if eq 8 were so slow as to be inoperative on the electrochemical time scale, then individual responses for each of the three complexes would be observed. The contrast between NMR and electrochemical measurement with respect to exchange reactions is interesting. As noted elsewhere,[30,34,35] correlations between the two techniques can provide a great deal of information relevant to both thermodynamic and kinetic aspects of electrochemical processes. This system is an excellent example of this suggestion.

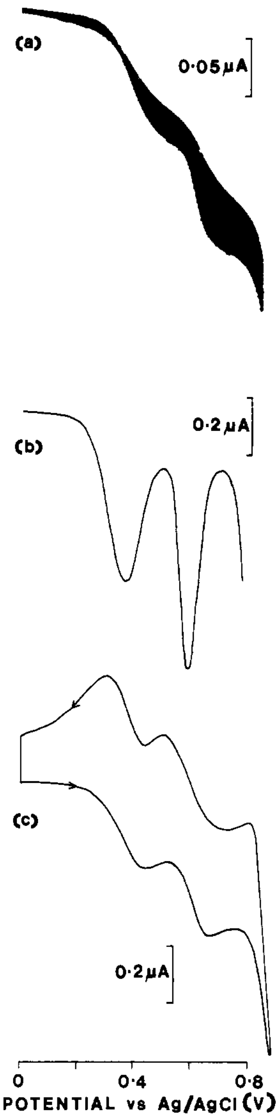

Figure 6. Oxidation of $Hg(n\text{-}Bu_2dtc)_2$ at a mercury electrode in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 22 °C: (a) dc polarogram; (b) differential-pulse polarogram; (c) cyclic voltammogram.

D. Electrochemical Oxidation at Mercury Electrodes in CH_2Cl_2. Perhaps surprisingly, two very well-defined oxidation waves were found under polarographic conditions for the $Hg(RR'dtc)_2$ complexes. Figure 6 shows a dc polarogram, differential-pulse polarogram, and cyclic voltammogram for the oxidation processes observed with $Hg(n\text{-}Bu_2dtc)_2$. Each oxidation process has a dc limiting current of approximately equal height, with the sum of the two steps being approximately equal to the limiting current of the two-electron-reduction process (compare Figures 3a and 6a). The oxidation limiting current for the combined processes was essentially diffusion controlled. The first oxidation process has an $E_{1/2}$ value in the range 0.36–0.42 V vs. Ag/AgCl. Compared with $E_{1/2}$ values for reduction, this is a very narrow range and the substituent dependence is very small. The second oxidation step was unresolved with some complexes, while with other complexes the second oxidation step had an $E_{1/2}$ value in the range 0.48–0.63 V vs. Ag/AgCl. Under conditions of differential-pulse polarography, resolution between the two ox-

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Table V. Data for Oxidation of $Hg(RR'dtc)_2$ at the Mercury Electrode in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 20 °C

$Hg(RR'dtc)_2$		dc polarography[a]		differential-pulse polarography[a]	
R	R′	$(E_{1/2})_1$,[b] V	$(E_{1/2})_2$,[c] V	$(E_p)_1$,[b] V	$(E_p)_2$,[c] V
Me	Me	0.390	0.480	0.370	0.468
Et	Et	0.390	0.570	0.361	0.550
i-Pr	*i*-Pr	0.405	0.600	0.365	0.585
n-Bu	*n*-Bu	0.380	0.595	0.365	0.585
i-Bu	*i*-Bu	0.390	0.630	0.370	0.615
n-Hx	*n*-Hx	0.420	0.560	0.420	0.550
Me	*n*-Bu	0.390	0.545	0.365	0.535
Et	*n*-Bu	0.370	0.565	0.350	0.550
n-Bu	*t*-Bu	0.385	0.600	0.335	0.585
c-Hx	*c*-Hx	0.360	0.560	0.340	0.550
Me	Ph	0.465[d]	*d*	0.415	0.480
Et	Ph	0.485[d]	*d*	0.410	0.490
i-Pr	Ph	0.495[d]	*d*	0.420	0.485

	dc polarography		differential-pulse polarography[a]	
N heterocyclic derivatives	$(E_{1/2})_1$,[b] V	$(E_{1/2})_2$,[c] V	$(E_p)_1$,[b] V	$(E_p)_2$,[c] V
pip	0.390	0.510	0.348	0.480
2-Mepip	0.390	0.550	0.355	0.510
3-Mepip	0.395	0.550	0.365	0.525
4-Mepip	0.390	0.535	0.370	0.515
2,6-dimepip	0.375	0.565	0.355	0.555
morph	0.425	0.510	0.400	0.495
pyrr	0.385[d]	*d*	0.340	0.400

[a] Potential vs. Ag/AgCl. [b] Least positive oxidation process. [c] Most positive oxidation process. [d] Unresolved.

idation steps was superior to that observed with the dc polarograms (Figure 6). Polarographic data for oxidation are summarized in Table V. Cyclic voltammograms indicate that both processes have a considerable degree of chemical reversibility (Figure 6c) for many but not all complexes. A substantial degree of adsorption accompanying the electrode process is indicated by concentration-dependent studies. Controlled-potential electrolysis experiments on the $Hg(n\text{-}Bu_2dtc)_2$ complex gave an *n* value of 2.03 ± 0.03 for the combined processes. After the mixtures were allowed to stand, polarograms obtained after controlled-potential electrolysis gave a composite reduction–oxidation response, with the zero of current essentially midway between the two processes. $E_{1/2}$ values for the two oxidation responses were unaltered compared with polarograms obtained prior to oxidative electrolysis.

At a platinum electrode, no oxidation response was observed at potentials near the oxidation step at mercury. A single irreversible response was noted at very much more positive potentials. This process may be related to that reported by Nieuwpoort et al. in acetone,[19] where it was suggested, without strong evidence, that ligand oxidation occurs to generate a thiuram disulfide type ligand and mercury(II) ions.

For most metal dithiocarbamates, reversible oxidation processes occur without gross structural change and give rise to unusually high oxidation states, e.g.

$$Cu(RR'dtc)_2 \rightleftharpoons [Cu(RR'dtc)_2]^+ + e^- \quad (13)$$

In the case of $Hg(RR'dtc)_2$, the chemically reversible oxidation steps *cannot* be assigned to the electron-transfer series

$$Hg(RR'dtc)_2 \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Hg(RR'dtc)_2]^+ \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Hg(RR'dtc)_2]^{2+}$$

since these processes should be observed at platinum as well as mercury electrodes and should show the same substituent dependence as for the reduction step. Elemental mercury appears to be involved in the oxidation step to produce polymeric cations. The process

$$Hg(RR'dtc)_2 + Hg \rightleftharpoons [Hg_2(RR'dtc)_2]^+ + e^- \quad (14)$$

would be the simplest example of an electrode process consistent with the observation of the first one-electron oxidation, with the second step then being

$$[Hg_2(RR'dtc)_2]^+ \rightleftharpoons [Hg_2(RR'dtc)_2]^{2+} + e^- \quad (15)$$

or

$$[Hg_2(RR'dtc)_2]^+ + Hg \rightleftharpoons [Hg_3(RR'dtc)_2]^{2+} + e^- \quad (16)$$

etc.

Other polymeric species such as $[Hg_3(RR'dtc)_4]^{2+}$ etc. could be formed as a product since a rapid equilibrium

$$2Hg(RR'dtc)_2 \rightleftharpoons Hg_2(RR'dtc)_4$$

is indicated to be important in solution.

An oxidation process

$$2Hg(RR'dtc)_2 \rightleftharpoons Hg_2(RR'dtc)_4 \quad (17)$$

$$Hg_2(RR'dtc)_4 + Hg \rightleftharpoons [Hg_3(RR'dtc)_4]^{2+} + 2e^- \quad (18)$$

could also explain the observed first one-electron oxidation. Attempts to isolate the product of controlled-potential electrolysis led to the isolation of $Hg(RR'dtc)_2$. Since all data indicate that elemental mercury, mercury(I), and mercury(II) form a dynamic system, this is not surprising. The suggestion that mercury(II) ion plus thiuram disulfide (eq 19) represents

$$Hg(RR'dtc)_2 \rightarrow Hg^{2+} + (RR'dtc)_2 + 2e^- \quad (19)$$

the overall process of controlled-potential electrolysis was examined. However, in a polarographic cell containing a mercury pool electrode, polarograms of $(RR'dtc)_2$ were identical with those for $Hg(RR'dtc)_2$. That is, eq 20 is operative.

$$Hg + (RR'dtc)_2 \rightarrow Hg(RR'dtc)_2 \quad (20)$$

The mechanism implied by eq 19 can therefore be ruled out because when eq 20 accompanies the reaction at a mercury pool electrode, coulometric *n* values of much greater than 2 would be predicted. Furthermore, the polarogram after controlled-potential electrolysis containing both oxidative and reductive components is not consistent with this hypothesis. The one-electron-oxidation product is relatively stable in solution, with the two-electron product being readily reduced back to this species via elemental mercury or via a radical pathway involving the solvent dichloromethane. Reduction of the electrolyzed solution produces $Hg(RR'dtc)_2$ as required for a reversible process.

It seems clear that oxidation steps at mercury electrodes are best considered as neither metal- nor ligand-based steps. Rather, they correspond to oxidation of mercury in the presence of $Hg(RR'dtc)_2$ to produce multinuclear cationic mercury dithiocarbamate complexes. The reduction process implies that the neutral mercury(I) complexes are kinetically very labile. Addition of mercury(I) perchlorate to $[RR'dtc]^-$ in dichloromethane shows that disproportionation to $Hg(RR'dtc)_2$ and elemental mercury occurs (electrochemical monitoring). However, multinuclear mixed mercury(II)/mercury(I) complexes may possibly have stability against disproportionation. Multinuclear mercury dithiocarbamate complexes have been well characterized when halides are incorporated in to the complexes.[6,36,37] Homopolyatomic cations such as Hg_3^{2+} and Hg_4^{2+} have been prepared in SO_2 solution, and redox properties related to those reported in this work are available in molten $AlCl_3$–$NaCl$[38] for the Hg_3^{2+} species. In

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our study, only the very weak perchlorate ligand is available for coordination and products are relatively unstable.

Conclusions

The lability of mercury dithiocarbamate complexes exerts considerable influence in the mass spectrometry, NMR, and electrochemical experiments. In mass spectrometry and NMR spectrometry, rapid dimer formation appears to be responsible for the observation of exchange process. The lability of the mercury(II) complexes and their rapid interactions with elemental mercury and mercury(I) together with dimer formation also influences the nature of electrode process occurring at mercury electrodes.

Acknowledgment. Financial assistance from the Australian Research Grants Scheme is gratefully acknowledged as is technical assistance in the area of mass spectrometry from G. R. Franklin and discussion on the electrochemistry with K. Hanck.

Appendix of Symbols and Abbreviations

E	potential
i	current
$E_{1/2}$	half-wave potential—defined by $i = {}^1/_2 i_{\rm d}$
$E_{1/4}-E_{3/4}$	difference in potential between $i = {}^1/_4 i_{\rm d}$ and $i = {}^3/_4 i_{\rm d}$
$i_{\rm d}$	limiting diffusion-controlled current
$E_{\rm p}$	peak position
$i_{\rm p}$	peak current
dc	direct current
$\Delta E_{\rm p}$	separation in forward and reverse scan potentials in cyclic voltammetry
$w_{1/2}$	differntial-pulse polarogram peak width at peak half-height
$E_{\rm p}^{\rm red}$	peak potential for reduction in cyclic voltammetry
$E_{\rm p}^{\rm ox}$	peak potential for oxidation in cyclic voltammetry
NMR	nuclear magnetic resonance
δ	NMR chemical shift
m/e	mass to charge ratio
average δ	arithmetic average $[\delta(\mathrm{HgL_2}) + \delta(\mathrm{HgL'_2})]/2$
mixed δ	experimentally observed shift for approximately equal concentrations of $\mathrm{HgL_2}$ and $\mathrm{HgL'_2}$
dtc	dithiocarbamate
L	RR′dtc ligand
Me	methyl
Et	ethyl
i-Pr	isopropyl
n-Bu	*n*-butyl
i-Bu	isobutyl
t-Bu	*tert*-butyl
c-Hx	cyclohexyl
Ph	phenyl
pipdtc	piperidine-*N*-carbodithioate
2-Mepipdtc	2-methylpiperidine-*N*-carbodithioate
3-Mepipdtc	3-methylpiperidine-*N*-carbodithioate
4-Mepipdtc	4-methylpiperidine-*N*-carbodithioate
2,6-dimepipdtc	2,6-dimethylpiperidine-*N*-carbodithioate
pyrrdtc	pyrrolidine-*N*-carbodithioate
morphdtc	morpholine-*N*-carbodithioate

Registry No. $\mathrm{Hg(Me_2dtc)_2}$, 15415-64-2; $\mathrm{Hg(Et_2dtc)_2}$, 14239-51-1; Hg(*i*-$\mathrm{Pr_2dtc)_2}$, 21439-57-6; Hg(*n*-$\mathrm{Bu_2dtc)_2}$, 21439-58-7; Hg(*i*-$\mathrm{Bu_2dtc)_2}$, 79001-48-2; Hg(*n*-$\mathrm{Hx_2dtc)_2}$, 21439-60-1; Hg(Me,*n*-$\mathrm{Budtc)_2}$, 91003-05-3; Hg(Et,*n*-$\mathrm{Budtc)_2}$, 79572-82-0; Hg(*n*-Bu,*t*-$\mathrm{Budtc)_2}$, 79572-80-8; $\mathrm{Hg(c\text{-}Hx_2dtc)_2}$, 21439-59-8; $\mathrm{Hg(Me,Phdtc)_2}$, 79572-86-4; $\mathrm{Hg(Et,Phdtc)_2}$, 78320-43-1; Hg(*i*-$\mathrm{Pr,Phdtc)_2}$, 91003-06-4; $\mathrm{Hg(pipdtc)_2}$, 21439-62-3; $\mathrm{Hg(2\text{-}Mepipdtc)_2}$, 79572-81-9; $\mathrm{Hg(3\text{-}Mepipdtc)_2}$, 79572-84-2; $\mathrm{Hg(4\text{-}Mepipdtc)_2}$, 79572-85-3; $\mathrm{Hg(2,6\text{-}dimepipdtc)_2}$, 79594-68-6; $\mathrm{Hg(morphdtc)_2}$, 14024-75-0; $\mathrm{Hg(pyrrdtc)_2}$, 41060-60-0; Hg(*n*-$\mathrm{Pedtc)_2}$, 91003-07-5; Hg, 7439-97-6; ^{199}Hg, 14191-87-8.

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Ground- and Excited-State Electron-Transfer Reactions: Photoinduced Redox Reactions of Poly(pyridine)ruthenium(II) Complexes and Cobalt(III) Cage Compounds

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Rate constants for the quenching of poly(pyridine)ruthenium(II) ($\mathrm{RuL_3^{2+}}$) excited states by caged cobalt(III) amine complexes ($\mathrm{Co(cage)^{3+}}$) range from 2×10^8 to 1×10^9 $\mathrm{M^{-1}\,s^{-1}}$ at 25 °C. The quenching process involves parallel energy transfer ($k_{\rm en} \sim 1 \times 10^8$ $\mathrm{M^{-1}\,s^{-1}}$) and electron transfer ($k_{\rm el} = (0.1\text{–}1) \times 10^9$ $\mathrm{M^{-1}\,s^{-1}}$) from $^*\mathrm{RuL_3^{2+}}$ to $\mathrm{Co(cage)^{3+}}$. The rate constants for electron-transfer quenching are consistent with expectations based on an adiabatic semiclassical model. The yields of electron-transfer products range from 0.3 to 1.0, increasing as the rate constants for the back-reaction of $\mathrm{RuL_3^{3+}}$ with $\mathrm{Co(cage)^{2+}}$ diminish. The relatively low magnitudes of the back-reaction rate constants, $(0.08\text{–}8) \times 10^8$ $\mathrm{M^{-1}\,s^{-1}}$, are consistent with the high yields of electron-transfer products and derive from poor coupling of the $\mathrm{RuL_3^{3+}}$ and $\mathrm{Co(cage)^{2+}}$ orbitals.

The redox properties of tris(2,2′-bipyridine)ruthenium(II) and its derivatives are currently being extensively investigated.[1] The reasons for this widespread interest include the use of these complexes as sensitizers in water photodecomposition studies,[1,2] as powerful reductants or oxidants to generate and characterize other reactive species,[3] and as probes of fundamental aspects of electron-transfer processes.[4]

The reduction potentials of the luminescent excited states of the $\mathrm{RuL_3^{2+}}$ complexes depend upon the nature of L. By subtle variations in L, the driving force for the redox reactions of $^*\mathrm{RuL_3^{2+}}$ with a substrate Q may be varied systematically. The change in electron-transfer rate resulting from such free

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