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^{207}Pb NMR, Mass Spectrometric, and Electrochemical Studies on Labile Lead(II) Dithiocarbamate Complexes: Formation of Mixed Mercury–Lead Complexes at a Mercury Electrode in Dichloromethane Solution

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^{207}Pb NMR spectra have been observed in dichloromethane for series of $Pb(RR'dtc)_2$ compounds (RR'dtc = dialkylthiocarbamate). The resonances are rather broad, and molecular weight determinations show that this is caused by polymerization reactions. Ligand exchange between different $Pb(RR'dtc)_2$ compounds is fast on the NMR time scale, and the complexes are therefore labile. The labile nature of the $Pb(RR'dtc)_2$ systems in the solid state is confirmed by mass spectrometric measurements on mixtures of different complexes. Electrochemical reduction of $Pb(RR'dtc)_2$ in dichloromethane (0.1 M Bu_4NClO_4) at mercury electrodes takes place in a single reversible two-electron step to give lead amalgam and free $[RR'dtc]^-$, the reversibility of this process further confirming the lability of the complexes. At platinum electrodes, initially an irreversible reduction occurs to generate elemental lead and $[RR'dtc]^-$. However, long-term behavior at platinum electrodes is complicated by the gradual coating of the electrode with elemental lead, thereby generating a lead electrode at which reversible responses are observed. Electrochemical oxidation processes at mercury electrodes are best described in terms of oxidation of the electrode in the presence of $Pb(RR'dtc)_2$. There are three oxidation steps; the product of the first oxidation step is a labile mixed mercury–lead species $[HgPb_2(RR'dtc)_4]^{2+}$, which is fully characterized in solution. Attempted isolation of the mixed-metal complex causes ligand redistribution, and $[Hg_5(RR'dtc)_8](ClO_4)_2$, $Pb(RR'dtc)_2$, and $Pb(ClO_4)_2$ are produced in the solid state. Controlled-potential electrolysis at the potential of the second oxidation process produces the known $[Hg_3(RR'dtc)_4]^{2+}$ species in solution. The electrochemistry in solution and the nature of the isolated products in the solid state indicate that when mercury and lead are competing for dithiocarbamate in a ligand deficient situation, then mercury is the successful element.

Introduction

Many metal dithiocarbamate complexes exhibit a wide range of redox reactions to generate complexes in unusual oxidation states.[3,4] However, many of these complexes are kinetically labile systems and exchange reactions can significantly effect the observed redox behavior. This has been particularly apparent in our electrochemical studies of dithiocarbamate complexes at mercury electrodes.[6–8] Recently, we have further elaborated on this theme of complex redox behavior observed for labile systems by comparing the electrochemical responses for $Hg(RR'dtc)_2$ (RR'dtc = dialkyldithiocarbamate or related carbodithioate ligand) compounds at reactive mercury and inert platinum electrodes.[9,10] The $Hg(RR'dtc)_2$ complexes show oxidation processes involving electrode mercury, producing mercury-rich polymeric species.[7,9,10] When the working electrode is platinum, oxidation of $Hg(RR'dtc)_2$ occurs at much more positive potentials but, significantly, the major product of oxidation is the same as that obtained at mercury, albeit by a less efficient pathway. At mercury electrodes the electrochemical behavior of $Cd(RR'dtc)_2$ compounds strongly parallels that of the corresponding $Hg(RR'dtc)_2$ compounds by virtue of exchange with electrode mercury to form the latter species[6] and mixed mercury–cadmium complexes.[6]

Lead(II) dithiocarbamates, $Pb(RR'dtc)_2$, are known to be labile,[3] suggesting that complex redox behavior similar to that observed for $M(RR'dtc)_2$ complexes (M = Hg, Cd, Zn) might be expected. However, few electrochemical studies on these complexes have been reported[11–13] and all have concentrated on the polarographic detection of metal dithiocarbamates after extraction from aqueous phases. Studies in polar solvents have established that $Pb(RR'dtc)_2$ complexes are reduced in a single diffusion-controlled two-electron step showing Nernstian behavior.[12,13] The products of reduction were said to be lead amalgam, Pb(Hg), and free dithiocarbamate ligand, although no evidence was offered to support this contention. The behavior of $Pb(Pyrrdtc)_2$ under oxidative conditions at mercury electrodes has been reported by Ichimura et al.[11] They observed a single two-electron process that was assigned to the process

$$Pb(RR'dtc)_2 + Hg \rightarrow Hg(RR'dtc)_2 + Pb^{2+} + 2e^- \quad (1)$$

although no evidence was offered to support this mechanism. This reaction is related to that reported by us for one of the oxidation processes observed at mercury electrodes in the presence of $Cd(RR'dtc)_2$ in dichloromethane[6] and is consistent with the labile nature of these systems.

In this paper we present detailed electrochemical studies of both the reduction and oxidation of $Pb(RR'dtc)_2$ systems in dichloromethane solution at both mercury and platinum electrodes. In addition, ^{207}Pb NMR spectroscopy, molecular weight measurements, and mass spectrometry provide additional information and evidence of the lability of these systems.

Experimental Section

Materials. All solvents and reagents used were of AR grade or better. The electrochemical supporting electrolyte Bu_4NClO_4 was obtained wet with water from South Western Analytical and was dried under vacuum at 70 °C.

Preparations. $Pb(RR'dtc)_2$ complexes were prepared according to standard literature methods,[3] which involved stirring together stoichiometric amounts of sodium hydroxide, carbon disulfide, and the appropriate secondary amine in water, followed by the addition of lead(II) nitrate. The resulting precipitate was filtered out, dried, and purified by Soxhlet extraction into dichloromethane.

Instrumentation. Voltammetric measurements were made with a Princeton Applied Research Corp. (PAR) (Princeton, NJ) Model 174A polarographic analyser with a dropping-mercury electrode or a polished platinum-disk electrode. For experiments with a platinum rotating-disk electrode either a Beckman or a Metrohm assembly was used. A platinum wire served as the auxiliary electrode, while the reference electrode was Ag/AgCl (saturated LiCl/EtOH) separated from the test solution by a salt bridge. The $[(C_5H_5)_2Fe]^+/(C_5H_5)_2Fe$ redox couple was measured frequently to provide an internal check on the stability of the

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Table I. Lead-207 NMR Data for $Pb(RR'dtc)_2$ Complexes at 20 °C[a]

R = R'	$\delta(^{207}Pb)$[b]	R = R'	$\delta(^{207}Pb)$[b]
Et	406	*i*-Bu	614
n-Pr	438	*n*-Pen	489
i-Pr	603	c-Hx	586
n-Bu	500		

[a] Saturated solution in dichloromethane. [b] Relative to neat $PbMe_4$.

Table II. Molecular Weight Data[a] for $Pb(RR'dtc)_2$ Compounds in Dichloromethane at 20 °C

		mol wt[b] at	
compd	fw	5×10^{-5} M	5×10^{-4} M
$Pt(Et_2dtc)_2$	504	500	1050
$Pb(c\text{-}Hx_2dtc)_2$	720	975	1800
$Pb(pipdtc)_2$[c]	528	540	1015

[a] Isopiestic method using benzil in dichloromethane as calibrant. [b] Concentrations were calculated by using formula weight. [c] Lead(II) bis(piperidine-1-carbodithioate).

reference electrode. The reversible half-wave potential of this process was 0.5 V vs Ag/AgCl. Unless otherwise stated all measurements were made at 20 °C with 0.1 M supporting electrolyte present.

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

A JEOL FX 100 spectrometer was used to record ^{207}Pb NMR spectra at 20.84 MHz, spectral width 20 KHz, 8196 data points with $Cr(Acac)_3$ used as a paramagnetic relaxant. Chemical shifts were referenced against external $PbMe_4$, and the high-frequency positive convention was used.

Electron impact positive ion mass spectra were obtained on a Finnigan 3200 series quadrupole mass spectrometer coupled to a Finnigan 6000 series interactive digital 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 (3–5) × 10^{-6} Torr. The compounds were introduced via a solids probe at temperatures of 200–350 °C.

Results and Discussion

Lead-207 NMR Studies. There have been no previous ^{207}Pb NMR studies of $Pb(RR'dtc)_2$ compounds. The spectra obtained from saturated dichloromethane solutions of the compounds are rather broad singlets ($w_{1/2}$ = 50–100 Hz) spanning a range of nearly 200 ppm. All data are given in Table I. Solutions containing two different $Pb(RR'dtc)_2$ compounds give only one signal at the exchange average position, showing that ligand exchange in these systems is fast on the NMR time scale. Variation of solvent (acetone, acetonitrile, *n*-butyronitrile) has little effect upon the chemical shifts, but temperature and concentration both have marked effects. With decreasing temperature the resonance for $Pb(Et_2dtc)_2$ shifts to lower frequency by 1.3 ppm/°C and a decrease in chemical shift is also observed with increasing concentration (570 ppm M^{-1} in the range 5–40 × 10^{-3} M for $Pb(Et_2dtc)_2$). This behavior suggests that $Pb(RR'dtc)_2$ complexes aggregate in solution, and this was confirmed by measuring the molecular weight of some of the complexes in dichloromethane as a function of concentration. The results are given in Table II, and it is apparent that monomeric species are present only at very low concentrations. At the concentration used for electrochemical studies (5 × 10^{-4} M) the compounds exist principally as dimers. At the considerably higher concentrations necessary for the NMR studies, aggregation involving higher polymers is very likely. It is the moderately fast exchange between the different forms of $Pb(RR'dtc)_2$ in solution that leads to the relatively broad ^{207}Pb NMR signals.

Mass Spectrometric Studies. The positive ion mass spectra of $Pb(RR'dtc)_2$ compounds commonly display a weak parent ion peak, but the base peak is always $[L - S]^+$, as has been observed for other metal dithiocarbamates.[6,7] Mass spectrometry has been previously used to monitor ligand exchange reactions in metal dithiocarbamates[6,7] and has been used to confirm the labile nature of the $Pb(RR'dtc)_2$ systems in the solid state. The mass spectrum of a mixture of $Pb(Et_2dtc)_2$ and $Pb(n\text{-}Bu_2dtc)_2$ shows the parent ion $[Pb(Et_2dtc)(Bu_2dtc)]^+$, confirming that ligand exchange has occurred in the mass spectrometer probe. Similar ligand exchange was observed to occur between $Hg(Et_2dtc)_2$ and $Pb(n\text{-}Bu_2dtc)_2$ by detection of both parent ions $[Hg(Et_2dtc)(n\text{-}Bu_2dtc)]^+$ and $[Pb(Et_2dtc)(n\text{-}Bu_2dtc)]^+$.

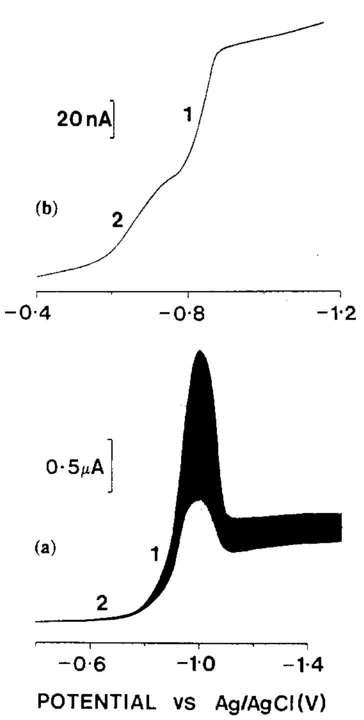

Figure 1. Dc polarograms (drop time 0.5 s) for the reduction of $Pb(Et_2dtc)_2$ in dichloromethane (0.1 M Bu_4NClO_4) at 20 °C: (a) 5 × 10^{-4} M; (b) 5 × 10^{-5} M.

Electrochemical Reduction Processes for $Pb(RR'dtc)_2$. (a) Mercury Electrodes. Figure 1 shows the dc polarographic reduction responses for dichloromethane solutions of $Pb(Et_2dtc)_2$. The dc polarogram (Figure 1a) (5 × 10^{-4} M solution) shows a major reduction wave (process 1) as well as a small prewave (process 2) at less negative potential. Process 1 exhibits a pronounced maximum due to adsorption effects. The maximum is substantially decreased at lower concentrations as shown in Figure 1b (5 × 10^{-5} M). It is also apparent that the current for process 2 greatly increases relative to that for process 1 at lower concentrations. However, the total limiting current for processes 1 and 2 is a linear function of $Pb(RR'dtc)_2$ concentration. Similar responses are observed for all the $Pb(RR'dtc)_2$ complexes studied, and data are given in Table III.

Reductive controlled-potential electrolysis at a mercury-pool electrode with the potential set in the limiting current region for process 1 resulted in the passage of 2.0 ± 0.1 faradays/mol of $Pb(RR'dtc)_2$ with the resulting solution containing only free dithiocarbamate (detected polarographically).[5,7] The presence of lead in the mercury electrode was confirmed by recording a cyclic voltammogram at a hanging-mercury-drop electrode taken as a sample from the mercury pool in aqueous 0.1 M KNO_3 and observing a well-defined reversible oxidation process due to

$$Pb(Hg) \rightleftharpoons Pb^{2+} + Hg + 2e^- \qquad (2)$$

Thus, if the formation of polymers is neglected, the overall reduction of $Pb(RR'dtc)_2$ in dichloromethane (0.1 M Bu_4NClO_4) at mercury electrodes is as given by eq 3.

$$Pb(RR'dtc)_2 + 2e^- \xrightarrow{Hg} Pb(Hg) + 2RR'dtc^- \qquad (3)$$

Figure 2 shows a cyclic voltammogram for a 5 × 10^{-4} M solution of $Pb(Et_2dtc)_2$ in dichloromethane (0.1 M Bu_4NClO_4) at a slowly growing dropping-mercury electrode, the scan being

Table III. Polarographic Data for the Reduction of Processes of 5×10^{-4} M $Pb(RR'dtc)_2$ in Dichloromethane (0.1 M Bu_4NClO_4) at 20 °C

	dc polarography[a]		cyclic voltammetry[b]			
	process 1	process 2	process 1		process 2	
R = R′	$E_{1/2}$, V[c]	$E_{1/2}$, V	E_p^{red}, V	E_p^{ox}, V	E_p^{red}, V	E_p^{ox}, V
Me	−0.830	−0.600	−0.880	−0.770	−0.630	−0.535
Et	−0.870	−0.620	−0.930	−0.800	−0.650	−0.580
n-Pr	−0.860	−0.625	−0.950	−0.755	−0.665	−0.600
i-Pr	−0.900	−0.660	−0.975	−0.815	−0.700	−0.605
n-Bu	−0.850	−0.610	−0.910	−0.770	−0.640	−0.580
i-Bu	−0.860	−0.620	−0.940	−0.800	−0.680	−0.610
n-Pen	−0.840	−0.620	−0.945	−0.785	−0.650	−0.570
i-Hx	−0.860	−0.650	−0.920	−0.780	−0.680	−0.575
c-Hx	−0.900	−0.735	−0.940	−0.845	−0.740	−0.670
pyrr[d]	−0.845	−0.565	−0.905	−0.750	−0.600	−0.400
pip[e]	−0.870	−0.680	−0.920	−0.765	−0.695	−0.610

[a] Drop time 0.5 s. [b] *n* Mercury-drop electrode; scan rate 500 mV s^{-1}. [c] Potential vs Ag/AgCl. [d] Pyrrolidine-1-carbodithioate. [e] Piperidine-1-carbodithioate.

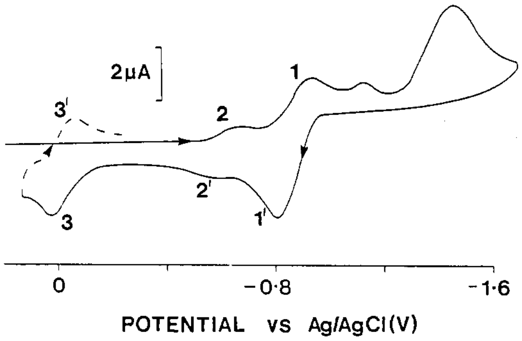

Figure 2. Reductive cyclic voltammogram (scan rate 500 mV s^{-1}) for a 5×10^{-4} M solution of $Pb(Et_2dtc)_2$ in dichloromethane (0.1 M Bu_4NClO_4) at 20 °C.

recorded on one drop. Several responses are seen, with those at potentials more negative than −1.0 V vs Ag/AgCl being attributed to adsorption phenomena. On the first scan in the negative potential direction, a reduction response is seen (process 1) and the corresponding oxidation peak (process 1′) on the reverse scan establishes the chemical reversibility of process 1. An additional reversible couple seen prior to process 1 is characterized by processes 2 and 2′ and is identified[7,9] as being due to the formation of $Hg(Et_2dtc)_2$ at the electrode surface. These results indicate that an exchange reaction takes place between $Pb(Et_2dtc)_2$ and mercury at the electrode surface to form $Hg(Et_2dtc)_2$.

$$Pb(Et_2dtc)_2 + Hg \rightleftharpoons Hg(Et_2dtc)_2 + Pb(Hg) \qquad (4)$$

The remaining feature in Figure 2 is the oxidation process 3 and the corresponding reduction step (process 3′) seen on the second scan. A response at the same potential as for process 3 is obtained when lead amalgam in a hanging-mercury-drop electrode is subjected to electrochemical oxidation in dichloromethane (0.1 M Bu_4NClO_4), and thus process 3 is due to oxidation (eq 2) of the lead (amalgam) produced by the exchange reaction (eq 4).

It is now possible to discuss the variation of the relative magnitudes of processes 1 and 2 (Figure 1). It is seen in Figure 1a that at a concentration of 5×10^{-4} M the current for process 2 is small relative to that for process 1. This is true for all the $Pb(RR'dtc)_2$ complexes and indicates that the exchange via eq 4 is limited by kinetically and/or thermodynamically controlled processes. The presence of a kinetically controlled step was verified by recording dc polarograms at varying drop times. As the drop time (and hence the time available for exchange) increases, so does the current for process 2 relative to that for process 1. As detailed earlier, at the concentration employed for electrochemistry, the $Pb(RR'dtc)_2$ complexes exist largely as dimers and as the concentration is lowered, dissociation takes place. The above results suggest that the monomer of $Pb(RR'dtc)_2$ reacts with mercury much faster than the dimer, but even its exchange reaction with mercury is rather slow on the time scale of dc polarography.

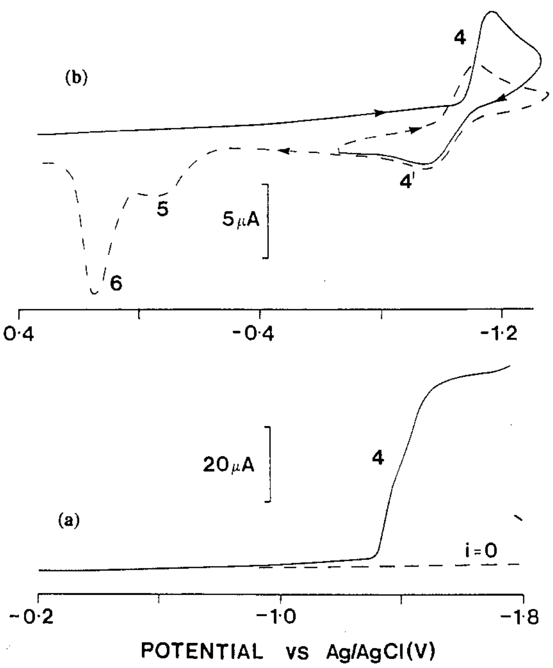

Figure 3. (a) Voltammogram at a rotating platinum-disk electrode (rotation rate 2000 revolutions min^{-1}) for 5×10^{-4} M $Pb(n\text{-}Pr_2dtc)_2$ in dichloromethane (0.1 M Bu_4NClO_4). (b) Cyclic voltammogram (scan rate 500 mV s^{-1}) at a platinum-disk electrode for the same solution. Temperature = 20 °C.

The fact that all the electrode processes are reversible on the electrochemical time scale is a reflection of the lability of the system in solution as was ascertained from the NMR data.

(b) Platinum Electrodes. Figure 3a is a voltammogram recorded at a rotating platinum-disk electrode for a 5×10^{-4} M solution of $Pb(n\text{-}Pr_2dtc)_2$ in dichloromethane (0.1 M Bu_4NClO_4) and shows a complex reduction step (process 4). Controlled-potential electrolysis at −1.6 V vs Ag/AgCl (limiting current region) using a platinum-gauze working electrode resulted in the transfer of 2.0 ± 0.2 faradays/mol. Polarographic analysis of the resulting solution showed that only the products of decomposition of free dithiocarbamate[9] are present in the solution. Soaking the platinum electrode in dilute nitric acid and subsequent polarographic analysis of the resulting solution showed that all the lead originally in solution as $Pb(n\text{-}Pr_2dtc)_2$ has been deposited onto the working electrode during electrolysis. Thus, the reaction at platinum electrodes

$$Pb(RR'dtc)_2 + 2e^- \rightarrow Pb + 2RR'dtc^- \qquad (5)$$

is similar to that at mercury electrodes with elemental lead rather than lead amalgam being produced. However, close inspection of Figure 3a reveals that the reduction response is not as straightforward as indicated by eq 5. It is apparent that at the foot of the voltammetric wave there is a very broad prewave, as evidenced by the current in this potential region being greater than the background level ($i = 0$), and that the main part of the voltammetric response consists of two components. These data have parallels with that obtained for the reduction of $Hg(RR'dtc)_2$ at a platinum electrode[9] and suggest that analogous processes are occurring. That is, reduction of $Pb(RR'dtc)_2$ involves deposition of elemental lead onto the platinum surface and part of the reduction process takes place at what is essentially a lead-coated platinum electrode. Thus, a distinct change in the electrode reaction is observed as the surface potential is changed.

Figure 3b shows cyclic voltammograms at a platinum electrode for the reduction of $Pb(n\text{-}Pr_2dtc)_2$. On the first scan a reduction peak (process 4) and an oxidation peak (process 4′) are seen. On

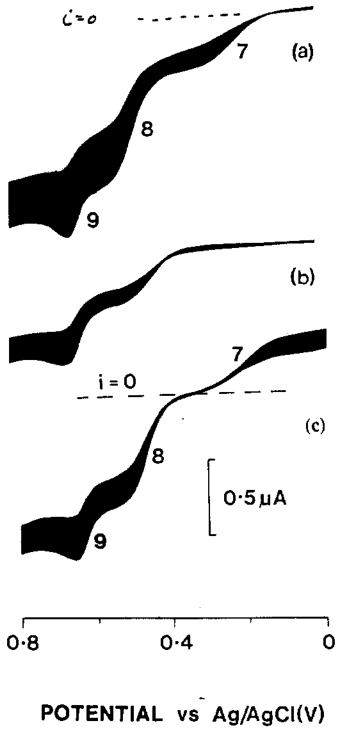

Figure 4. Oxidative dc polarograms (drop time 0.5 s) obtained in dichloromethane (0.1 M Bu$_4$NClO$_4$) at 20 °C for 5 × 10^{-4} M solutions of (a) Pb(Et$_2$dtc)$_2$, (b) Hg(Et$_2$dtc)$_2$, and (c) Pb(Et$_2$dtc)$_2$ after controlled-potential electrolysis.

the second cycle, process 4 is shifted to less negative potentials, while the potential of process 4′ remains unchanged. During the first cyclic scan elemental lead is deposited onto the platinum electrode, which results in an increase in the reversibility of the reduction process. This is entirely analogous to the reduction of Hg(RR′dtc)$_2$ at platinum under the same conditions,[9] and the similarity in behavior is remarkable. Figure 3b also shows two other oxidation processes (5 and 6) on the positive potential scan of the second cycle. Process 5 is for the oxidation of free [n-Pr$_2$dtc]$^-$ released via process 4, while the ireversible process 6 is due to the oxidation of elemental lead deposited during the reduction step. A response identical with process 6 is observed when a platinum-disk electrode coated with a small amount of lead is used as the working electrode for oxidative cyclic voltammetry in dichloromethane (0.1 M Bu$_4$NClO$_4$).

Comparison of Figure 3a,b shows that the major reduction process occurs at significantly more negative potentials under the conditions of rotating-disk voltammetry than is the case with cyclic voltammetry. Clearly, the surface of the electrode and the mass transport are important in determining the nature of the reduction process at platinum electrodes. It is conceivable that a soluble zerovalent lead dithiocarbamate complex is observed as an intermediate in the reduction process at lead electrodes.

Electrochemical Oxidation Processes for Pb(RR′dtc)$_2$. (a) Mercury Electrodes. Figure 4a shows the dc polarographic oxidation response in the presence of 5 × 10^{-4} M solution of Pb(Et$_2$dtc)$_2$ in dichloromethane (0.1 M Bu$_4$NClO$_4$). Three well-defined waves, labeled processes 7–9, are observed with limiting currents in the ratios 1:2:1, respectively. A comparison of the limiting current per unit concentration for each process with the overall two-electron reduction (sum of processes 1 and 2) for the same compound shows that processes 7 and 9 are one-electron steps, while process 8 is a two-electron step. Similar responses are observed for all the Pb(RR′dtc)$_2$ complexes, and data are given in Table IV. Figure 4b shows oxidation responses under the same conditions for Hg(Et$_2$dtc)$_2$,[7,9] and comparison with Figure 4a reveals that processes 8 and 9 correspond closely in potential to the first and second oxidation steps of the mercury complex on the polarographic time scale, indicating that ligand exchange between Pb(Et$_2$dtc)$_2$ and electrode mercury has occurred, as was noted in the reduction studies. However, process 8 is a two-electron step for Pb(Et$_2$dtc)$_2$ solutions, while each mercury oxidation step is a one-electron step. In addition, process 8 is shifted in all cases (by 20–100 mV, Table IV) in the positive direction compared to that for corresponding mercury complex. Cyclic voltammograms show a high degree of chemical reversibility for all three oxidation processes.

Oxidative controlled-potential electrolysis at a mercury-pool electrode at a potential of 0.38 V vs Ag/AgCl (limiting current region for process 7) resulted in the transfer of 1.0 ± 0.1 faraday/mol of Pb(Et$_2$dtc)$_2$ and yielded a light green solution. The voltammetric responses recorded after electrolysis are shown in Figure 4c. Waves for processes 7–9 are still present with the total limiting current being similar to that observed before electrolysis. However, process 7 now corresponds to a reduction process, since the response for solvent and supporting electrolyte alone (i = 0) passes through a point midway between processes 7 and 8. This confirms that process 7 is reversible and that the product of

Table IV. Polarographic and Voltammetric Data for the Oxidation Processes Observed in the Presence of 5 × 10^{-4} M Pb(RR′dtc)$_2$ and Hg(RR′dtc)$_2$ Complexes in Dichloromethane (0.1 M Bu$_4$NClO$_4$) at 20 °C[a]

	$E_{1/2}$, V from dc polarography[b]			E_p^{ox}, V from cyclic voltammetry[c]	
R = R′	process 7[d]	process 8	process 9	process 10	process 11
Me	0.230	0.500 (0.410)	*e* (0.505)	1.03	1.30
Et	0.220	0.480 (0.405)	0.625 (0.605)	1.04	1.35
n-Pr	0.210	0.475 (0.455)	0.650 (0.655)	1.10	1.30
i-Pr	0.200	0.455 (0.425)	0.650 (0.640)	1.04	1.30
n-Bu	0.240	0.485 (0.390)	0.705 (0.675)	1.20	1.42
i-Bu	0.210	0.475 (0.450)	0.710 (0.710)	1.15	1.40
n-Pen	0.245	0.475 (0.450)	0.650 (0.625)	1.20	1.40
n-Hx	0.240	0.450 (0.420)	0.665 (0.655)	1.25	1.40
c-Hx	0.230	0.455 (0.410)	0.640 (0.625)	1.05	1.30
pyrr	0.230	0.445 (0.400)	0.585 (*e*)	1.20	1.45
pip	0.220	0.490 (0.445)	0.610 (0.610)	1.08	1.35

[a] Data for mercury complexes in parentheses. [b] Drop time 0.5 s. [c] Platinum electrode; scan rate 500 mV s^{-1}; E_p^{ox} = oxidation potential. [d] Potential versus Ag/AgCl (saturated LiCl/EtOH) based on $E_{1/2}$[(C$_5$H$_5$)$_2$Fe$^+$/(C$_5$H$_5$)$_2$Fe] = 0.500 V vs Ag/agCl. [e] Process poorly defined.

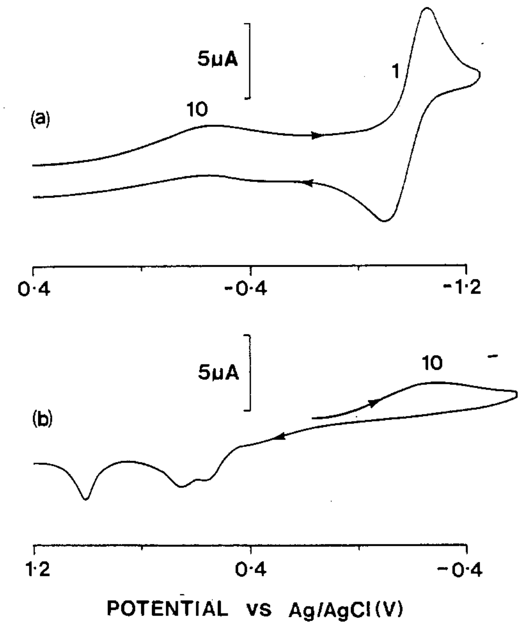

Figure 5. Reductive cyclic voltammograms at a platinum electrode (scan rate 500 mV s^{-1}) for 5 × 10^{-4} M Pb(Et$_2$dtc)$_2$ in dichloromethane (0.1 M Bu$_4$NClO$_4$) at 20 °C (a) including processes 10 and 1 and (b) switching potential scan direction immediately after process 10.

oxidation is stable on the coulometric time scale.

Figure 5a shows a reductive cyclic voltammogram at a platinum electrode for the oxidized solution prepared as above. A broad reduction step (process 10) is observed followed by the reversible reduction response for $Pb(Et_2dtc)_2$ (process 1). Switching the potential scan direction immediately following process 10 produces the oxidation responses shown in Figure 5b. The response at 1.0 V vs Ag/AgCl is due to the oxidative stripping of elemental mercury. Thus, process 10 is the deposition of mercury onto the platinum electrode and the release of $Pb(Et_2dtc)_2$, which gives rise to process 1, which corresponds to reduction of $Pb(Et_2dtc)_2$ at a *mercury* electrode. The responses in the range 0.2–0.8 V vs Ag/AgCl in Figure 5b can therefore correspond to processes 7–9 because a mercury electrode has been generated in situ. No oxidative responses are observed when the positive potential scan is commenced at potentials more positive than process 10. This experiment confirms that the mercury is released by process 10.

The stoichiometry of the oxidation product was determined by reductive controlled-potential electrolysis of the oxidized solution at −0.6 V vs Ag/AgCl (prior to the onset of process 2) with a platinum-gauze working electrode. A transfer of 1.0 ± 0.1 faraday/mol of $Pb(Et_2dtc)_2$ is observed. The amount of mercury deposited on the electrode (by weight) is 1 mol/2 mol of $Pb(Et_2dtc)_2$ generated, and the amount of $Pb(Et_2dtc)_2$ generated in solution was the same as originally present before the electrolysis (electrochemical determination). Thus, the empirical formula of the product of process 7 is established as $[HgPb_2(Et_2dtc)_4]^{2+}$ and it is produced according to eq 6 with process 10 being the reverse

$$2Pb(Et_2dtc)_2 + Hg \rightarrow [HgPb_2(Et_2dtc)_4]^{2+} + 2e^- \quad (6)$$

of this reaction. Similar observations were made for the other lead dithiocarbamate complexes. The mercury in $[HgPb_2(RR'dtc)_4]^{2+}$ complexes is reactive in the sense that addition of 2 mol of free $[RR'dtc]^-$ gives a solution containing both $Pb(RR'dtc)_2$ and $Hg(RR'dtc)_2$ (determined electrochemically) in the ratio 2:1. This reaction also confirms the stoichiometry of the oxidation product.

At this stage attention is drawn to the remarkable similarities between $[HgPb_2(RR'dtc)_4]^{2+}$ and the previously characterized $[Hg_3(RR'dtc)_4]^{2+}$. The complexes are produced in analogous reactions, they show very similar electrochemical responses, and they react with free dithiocarbamate in the same way.[9] The solid isolated from solutions of $[Hg_3(Et_2dtc)_4]^{2+}$ was $[Hg_5(Et_2dtc)_8](ClO_4)_2$, but unfortunately, all attempts to isolate lead–mercury complexes from solutions of $[HgPb_2(RR'dtc)_4]^{2+}$ failed. Rapid isolation techniques, such as addition of water to an acetonitrile (0.1 M Et_4NClO_4) solution of the oxidation product, caused dissociation according to the eq 7, while slow

$$[HgPb_2(Et_2dtc)_4]^{2+} \rightarrow Hg(Et_2dtc)_2 + Pb(Et_2dtc)_2 + Pb^{2+} \quad (7)$$

evaporation techniques from dichloromethane solution yielded $[Hg_5(Et_2dtc)_8](ClO_4)_2$, which, as already noted, is the solid product obtained from solutions of $[Hg_3(Et_2dtc)_4]^{2+}$. In addition, both $Pb(Et_2dtc)_2$ and Pb^{2+} are produced according to eq 8.

$$5[HgPb_2(Et_2dtc)_4]^{2+} \rightarrow [Hg_5(Et_2dtc)_8]^{2+} + 6Pb(Et_2dtc)_2 + 4Pb^{2+} \quad (8)$$

These results serve to reemphasise the point made previously[9] that the relatively simple electrochemical results belie the complex nature of the species in solution and illustrate the competition between mercury and lead when there is a deficiency of dithiocarbamate ligand available. Clearly, mercury complexes more strongly with the ligand than lead and it is then the kinetics and thermodynamics of the mercury dithiocarbamate system that determine the actual product isolated according to the experimental conditions.

As noted earlier (Figure 4), process 8 is a two-electron process and oxidative controlled-potential electrolysis of $Pb(Et_2dtc)_2$ at a mercuy-pool electrode at 0.56 V (between processes 8 and 9) results in the transfer of 2.9 ± 0.2 faradays/mol, which is the summation of process 7 (1e) and process 8 (2e). A light green solution is obtained (some cloudiness visible) that is stable, so the techniques used to identify $[HgPb_2(Et_2dtc)_4]^{2+}$ can also be used in this case. The results show that upon reduction of the oxidized solution 1.5 mol of mercury is liberated/mol of $Pb(Et_2dtc)_2$. That is, for each 1 mol of $[HgPb_2(Et_2dtc)_4]^{2+}$ produced via process 7 a further 2 mol of mercury is incorporated. Thus, process 8 may be represented empirically by eq 9. However, the UV/visible

$$[HgPb_2(Et_2dtc)_4]^{2+} + 2Hg \rightleftharpoons [Hg_3Pb_2(Et_2dtc)_4]^{6+} + 4e^- \quad (9)$$

spectrum of the solution is identical[9] with that of $[Hg_3(Et_2dtc)_4]^{2+}$ and eq 10 may be better written as

$$[HgPb_2(Et_2dtc)_4]^{2+} + 2Hg \rightleftharpoons [Hg_3(Et_2dtc)_4]^{2+} + 2Pb^{2+} + 4e^- \quad (10)$$

which is consistent with the previously noted superiority of mercury over lead to complex with the available dithiocarbamate. The cloudiness in the electrolyzed solution may then be due to suspended $Pb(ClO_4)_2$, yet the fact that the potential for process 8 is shifted to positive potentials compared to the analogous $Hg(Et_2dtc)_2$ process suggests that other species are present in equilibrium with those given in eq 10.

Oxidative controlled-potential electrolysis of $Pb(Et_2dtc)_2$ in dichloromethane (0.1 M Bu_4NClO_4) at a potential more positive than process 9 (Figure 4) results in the transfer of 3.8 ± 0.2 faradays/mol. The product is an intractable insoluble white powder, which has not been identified but which appears to be the same as that obtained by the two-electron oxidation of $Hg(Et_2dtc)_2$.[9] This is not surprising, since in both the lead and mercury systems it is believed that $[Hg_3(Et_2dtc)_4]^{2+}$ is the precurser.

(b) Platinum Electrodes. Oxidative voltammograms at a rotating platinum-disk electrode for a 5×10^{-4} M solution of $Pb(Et_2dtc)_2$ in dichloromethane (0.1 M Bu_4NClO_4) show two responses at $E_{1/2}$ = 1.04 V (process 11) and 1.35 V vs Ag/AgCl (process 12), and comparison with the known two-electron step (process 4) shows each to be a one-electron step. Cyclic voltammograms show both processes to be irreversible over the temperature range +25 to −70 °C and scan rates up to 50 V s^{-1}. Electrochemical data are included in Table IV. Oxidative controlled-potential electrolysis of $Pb(Et_2dtc)_2$ in dichloromethane (0.1 M Bu_4NClO_4) at 1.14 V vs Ag/AgCl (limiting current region for process 11) results in the transfer of more than 3 faradays/mol of $Pb(Et_2dtc)_2$, with a small residual current persisting. Electrochemical measurements show that the resulting cloudy solution contains the products of ligand oxidation, many of which are unstable in dichloromethane,[9] and the precipitate is identified as $Pb(ClO_4)_2$. On the repeating of the electrolysis with the potential set at 1.0 V vs Ag/AgCl, corresponding to the foot of the wave, the passage of charge is slower, as anticipated. After the transfer of 1.0 faraday/mol the limiting current at the rotating-disk electrode remains above background but the solution is still clear. A dc polarogram of this solution shows responses very similar to those in Figure 4c. This indicates that the product(s) of the oxidation at platinum interact with the mercury electrode to form $[HgPb_2(Et_2dtc)_4]^{2+}$. A complex containing coordinated thiuram disulfide, the oxidized dimer of $[RR'dtc]^-$, would be expected to have this characteristic.

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