solid was $Na_2[B_9H_{13}]$, while the remaining material consisted of $Na[B_9H_{14}]$,[9] $Na[BH_4]$,[17] and $Na[B_6H_9]$[18] as determined by their characteristic boron-11 NMR spectra. Prolonging the reaction time increased the amount of the impurities present.

Acknowledgment. This work was supported by the Army Research Office through Grant DAAG29-85-k0187. We thank the NSF for a grant (CHE84-11630) for an X-ray diffractometer. NMR spectra were obtained at The Ohio State University Campus Chemical Instrument Center (funded in part by NSF Grant 79-10019 and NIH Grant 1 S10 PRO140518-01A).

Registry No. $K[B_9H_{14}]$, 39296-28-1; $Na[B_9H_{14}]$, 70865-40-6; $Na_2[B_9H_{13}]$, 119391-53-6; $Na[NH_2]$, 7782-92-5; KH, 7693-26-7; $K_2[B_9H_{13}]$, 119391-51-4; $Ti(C_5H_5)_2Cl_2$, 1271-19-8; $[B_9H_{12}]^-$, 12430-26-1; $Si(CH_3)_2Cl_2$, 75-78-5; n-$B_{18}H_{22}$, 21107-56-2; NaH, 7646-69-7; $[(Krypt2.2.2)K]_2[B_9H_{13}]$, 119391-52-5.

Supplementary Material Available: Listings of bond distances, bond angles, positional parameters of H atoms, and anisotropic thermal parameters and ORTEP drawings of $[(Krypt2.2.2)K]^+$ (16 pages); a table of calculated and observed structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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NMR and Electrochemical Investigation of the Redox and Exchange Reactions of Tellurium(II) and Tellurium(IV) Dithiocarbamate Complexes

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Tellurium-125 NMR and electrochemical data at mercury and platinum electrodes show that tellurium(IV) dithiocarbamate (dtc) complexes $Te(dtc)_4$ are unstable in solution with respect to an internal redox reaction, producing the tellurium(II) complex $Te(dtc)_2$ and thiuram disulfide (tds). The rate at which the equilibrium $Te(dtc)_4 \rightleftharpoons Te(dtc)_2 + tds$ is established and the equilibrium position appear to be solvent dependent. NMR data reveal that intermolecular dithiocarbamate exchange occurs more rapidly in the tellurium(II) complexes than it does in the tellurium(IV) analogues. At mercury electrodes, in addition to the intermolecular ligand-exchange processes identified by ^{125}Te NMR, the exchange reactions $Te(Et_2dtc)_2 + Hg \rightleftharpoons Hg(Et_2dtc)_2 + Te$ and $Te(Et_2dtc)_4 + Hg \rightleftharpoons Hg(Et_2dtc)_2 + Te(Et_2dtc)_2$ are important. Reduction at mercury and platinum electrodes occurs with the same overall equation $Te(Et_2dtc)_n + ne^- \rightleftharpoons Te + nEt_2dtc^-$ (n = 2, 4) but via electrode-dependent pathways. Oxidation at mercury electrodes produces $[Hg_3(Et_2dtc)_4]^{2+}$ and tellurium metal whereas at platinum electrodes different products are obtained.

Introduction

The compounds $Te(Morphdtc)_2$,[3] $Te(Morphdtc)_4$,[4] $Te(Et_2dtc)_2$,[5] and $Te(Et_2dtc)_4$[6] (Et_2dtc = diethyldithiocarbamate and Morphdtc = 4-morpholinecarbodithioate) have been well characterized in the solid state by X-ray crystal structural analysis. However, little is known about the nature and reactivity of these compounds in solution except that solutions of the Te(IV) compound appear to be unstable with time.[6] With a ligand such as dithiocarbamate, dtc^-, which is itself redox active, being readily oxidized to thiuram disulfide, tds, there exists the possibility of an intimate relationship between the two oxidation states of tellurium and the oxidized and reduced forms of the ligand. If equilibria in solution involve either metal- or ligand-based redox reactions, then electrochemical techniques should provide considerable information on the nature of such reactions. However, electrochemical techniques may perturb the system whereas, in contrast, spectroscopic techniques such as nuclear magnetic resonance, NMR, may monitor the species present in the unperturbed situation. NMR and electrochemical techniques therefore should provide complimentary means of investigating the redox-related reactions between tellurium(II) and tellurium(IV) dithiocarbamate complexes in solution.

It has recently been shown by ^{125}Te NMR that organotellurium(IV) complexes containing dithiolate ligands such as diethyldithiocarbamate, ethyl xanthate (S_2COEt) and diethyl dithiophosphate ($S_2P(OEt)_2$), undergo both inter- and intramolecular exchange processes in solution.[7] To date only very few electrochemical studies have been reported for any class of Te(II) and Te(IV) complexes.[8] In the case of dithiocarbamate complexes, no data are available at mercury electrodes but some data exist for the electrochemistry of such complexes at platinum, gold and glassy-carbon electrodes.[9] The presence of a mercury electrode can substantially modify the course of redox processes of labile complexes compared with inert electrode materials such as platinum,[10] and a comparison of data at the different electrode surfaces can provide valuable information on the solution chemistry.

In this paper we report NMR data for $Te(Et_2dtc)_2$, $Te(Et_2dtc)_4$, and $Te(Morphdtc)_2$ in a variety of solvents and an electrochemical investigation at mercury and platinum electrodes of $Te(Et_2dtc)_2$ and $Te(Et_2dtc)_4$ in dichloromethane in order to provide further information on the nature of the redox and exchange processes that may occur between the different oxidation states of tellurium.

Experimental Section

Syntheses. The compounds $Te(Et_2dtc)_n$[11,12] and $Te(Morphdtc)_n$[13,14] (n = 2, 4) were prepared by previously published methods.[8]

Instrumentation. NMR spectra were routinely recorded by using a JEOL FX 100 spectrometer with broad-band decoupling. A JEOL NM 5471 controller was used for temperature control; the temperatures in the probe were measured with a calibrated platinum resistance thermometer. ^{125}Te spectra were recorded at 31.4 MHz, usually on a 20-kHz spectral window, by using external ^7Li lock; the pulse width was 22 μs and the

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Table I. ^{125}Te Chemical Shifts for Tellurium(II) and Tellurium(IV) Dithiocarbamate Complexes in Various Solvents

species	solvent	temp, °C	δ(^{125}Te)
Te(Et$_2$dtc)$_2$	dichloromethane	3	−930
Te(Morphdtc)$_2$	dichloromethane	30	−853
Te(Morphdtc)(Et$_2$dtc)	dichloromethane	−40	−946
Te(Et$_2$dtc)$_4$	benzene	30	−2332
Te(Et$_2$dtc)$_4$	tetrahydrofuran	30	−2309
Te(Morphdtc)$_4$	tetrahydrofuran	30	−2287
Te(Morphdtc)$_3$(Et$_2$dtc)	tetrahydrofuran	30	−2291
Te(Morphdtc)$_2$(Et$_2$dtc)$_2$	tetrahydrofuran	30	−2296
Te(Morphdtc)(Et$_2$dtc)$_3$	tetrahydrofuran	30	−2302

pulse delay 50 ms. Spectra were recorded in the presence of Cr(acac)$_3$ to reduce relaxation times. ^{125}Te chemical shifts were referenced against 0.7 M K$_2$TeO$_3$ in water.

Voltammetric measurements in dichloromethane (0.1 M Bu$_4$NClO$_4$) at 20 °C were made by using a Princeton Applied Research Corp. (PAR, Princeton, NJ) Model 174A polarographic analyzer with a dropping-mercury electrode or a polished platinum-disk working electrode. For experiments with a rotating platinum-disk electrode a Metrohm electrode assembly was used. A platinum wire served as the auxiliary electrode while the reference electrode was Ag/AgCl (saturated LiCl in ethanol) separated from the test solution by a salt bridge containing the solvent. The potential of [(C$_5$H$_5$)$_2$Fe]$^+$/(C$_5$H$_5$)$_2$Fe redox couple was measured frequently by oxidation of a 5 × 10^{-4} M solution of (C$_5$H$_5$)Fe to provide an internal check on the stability of the reference electrode. The reversible half-wave potential of the ferrocene oxidation process in dichloromethane is 0.48 V versus the Ag/AgCl reference electrode used in this work.

Controlled-potential electrolysis experiments were performed at either a mercury pool or at a platinum-gauze working 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 the same as used for voltammetry.

Results and Discussion

The tellurium-125 NMR results are reported first since they establish the various exchange processes present in the Te(IV) and Te(II) oxidation states.

Solution NMR Studies of Tellurium(II) and Tellurium(IV) Dithiocarbamates. The ^{125}Te{^{1}H} spectrum of Te(Et$_2$dtc)$_2$ in CH$_2$Cl$_2$ at room-temperature consists of a single sharp resonance at δ(^{125}Te) −930 ppm (Table I). The corresponding ^{13}C{^{1}H} spectrum contains three sharp resonances [δ(^{13}C) 12.3, 48.1, 194.4 ppm], attributed to the methyl, methylene, and dithio (i.e. S$_2$*C*−) carbons respectively. Similarly, the ^{125}Te{^{1}H} spectrum of Te(Morphdtc)$_2$ in CH$_2$Cl$_2$ at room temperature consists of a sharp signal [δ(^{125}Te) −853 ppm], while the ^{13}C{^{1}H} spectrum shows three sharp resonances [δ(^{13}C) 50.5, 66.7, 198.4 ppm]. Mixing equimolar amounts of Te(Et$_2$dtc)$_2$ and Te(Morphdtc)$_2$ in CH$_2$Cl$_2$ at room temperature results in the observation of an extremely broad ^{125}Te{^{1}H} resonance [δ(^{125}Te) approximately −914 ppm; $w_{1/2}$ = 1500 Hz], suggesting that the complexes are in rapid exchange under these conditions. Lowering the temperature to −40 °C causes this broad resonance to separate into three sharp signals [δ(^{125}Te) −904, −946, −989 ppm] of relative intensities 1:8:12 (Figure 1). The outer two resonances [δ(^{125}Te) −904, −989 ppm] are assigned to the species Te(Morphdtc)$_2$ and Te(Et$_2$dtc)$_2$, while the central ^{125}Te{^{1}H} resonance [δ(^{125}Te) −946 ppm] is assigned to the mixed-ligand species, Te(Et$_2$dtc)(Morphdtc). The compound Te(Morphdtc)$_2$ is only slightly soluble in CH$_2$Cl$_2$, which may account for the nonstatistical distribution of the complexes. The simultaneous observation of all three species confirms that intermolecular exchange of the dithiocarbamate ligands is slow relative to the NMR time scale at −40 °C.

Interestingly, McWhinnie et al.[15] report the ^{125}Te{^{1}H} shift of the tellurium(IV) analogue Te(Et$_2$dtc)$_4$ in CDCl$_3$ to be near −900 ppm [i.e., δ(^{125}Te) is 841.2 ppm relative to Me$_2$Te], which is very close to the position of the resonance that we assigned as due to Te(Et$_2$dtc)$_2$ [δ(^{125}Te) −930 ppm in CH$_2$Cl$_2$]. In fact, the ^{125}Te spectrum of a sample of Te(Et$_2$dtc)$_4$, freshly prepared according to literature methods,[12] dissolved in dichloromethane gives only a single resonance at −930 ppm. However the originally yellow solution begins to darken after approximately 30 min and suggests that the formation of Te(Et$_2$dtc)$_2$ may occur via a redox reaction

$$\mathrm{Te(Et_2dtc)_4 \rightleftharpoons Te(Et_2dtc)_2 + Et_4tds} \qquad (1)$$

and that the previously published NMR data may not have been correctly assigned.

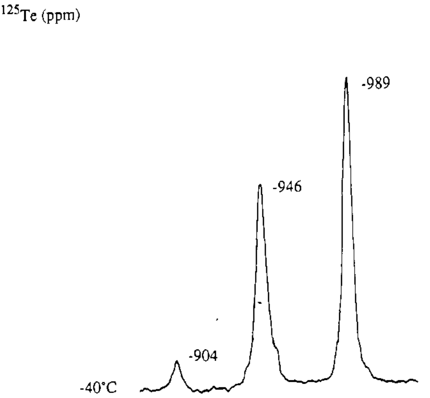

Figure 1. Tellurium-125 spectrum for an equimolar mixture of Te(Et$_2$dtc)$_2$ and Te(Morphdtc)$_2$ in dichloromethane solution at −40 °C.

In an endeavor to slow the rate at which this proposed equilibrium may be established, a solid sample of Te(Et$_2$dtc)$_4$ was dissolved in CH$_2$Cl$_2$ at −70 °C and the solution immediately examined by ^{125}Te. No ^{125}Te resonances were observed at this very low temperature, but the ^{13}C{^{1}H} spectrum indicated that a reaction had occurred, with Te(Et$_2$dtc)$_2$ apparently being one of the products. The presence of Te(Et$_2$dtc)$_2$ was supported by an experiment in which methyl iodide was added to a solution of Te(Et$_2$dtc)$_4$ in CH$_2$Cl$_2$. The ^{125}Te{^{1}H} spectrum of this mixture (at −40 °C) consists of a single resonance [δ(^{125}Te) −1907 ppm] at the chemical shift position previously assigned to the tellurium(IV) species MeTe(I)(Et$_2$dtc)$_2$.[16]

At room temperature, the ^{125}Te{^{1}H} spectrum of Te(Et$_2$dtc)$_4$ dissolved in benzene consists of a single sharp resonance [δ(^{125}Te) −2332 ppm] (Table I) that is attributed to the species Te(Et$_2$dtc)$_4$. The corresponding ^{13}C{^{1}H} spectrum contains only three sharp resonances [δ(^{13}C) 12.2, 49.4, 202.8 ppm] and these are assigned to the dithiocarbamate ligands. The ^{13}C{^{1}H} resonance at 202.8 ppm is due to the dithio (i.e. S$_2$*C*−) carbon. To confirm the ^{125}Te{^{1}H} assignments, an equimolar ratio of Te(Et$_2$dtc)$_4$ and Te(Et$_2$dtc)$_2$ dissolved in benzene was examined. The ^{125}Te{^{1}H} spectrum of this solution at room temperature consists of two resonances [δ(^{125}Te) −885.0, −2331.4 ppm] that may now be unambiguously assigned to the species Te(Et$_2$dtc)$_2$ and Te(Et$_2$dtc)$_4$, respectively. At least in benzene, the equilibrium position of eq 1 can be established to lie well to the left and be insufficiently fast to give rise to a redox-based exchange process on the NMR time scale.

Solutions of Te(Morphdtc)$_4$ also rapidly decompose in CH$_2$Cl$_2$ to give the reduced compound Te(Morphdtc)$_2$ [δ(^{125}Te) −851 ppm]. No ^{125}Te resonance could be detected for solutions of Te(Morphdtc)$_4$ dissolved in CS$_2$. The compound Te(Morphdtc)$_4$ is almost totally insoluble in benzene. However, it is soluble in tetrahydrofuran, and the ^{125}Te{^{1}H} spectrum of Te(Morphdtc)$_4$ in tetrahydrofuran at room temperature contains a single sharp resonance at δ(^{125}Te) −2287 ppm (Table I) that is attributed to the species Te(Morphdtc)$_4$. The ^{125}Te{^{1}H} spectrum at room temperature of a THF solution containing equimolar portions of Te(Et$_2$dtc)$_4$ and Te(Morphdtc)$_4$ consists of five resonances [δ(^{125}Te) −2286, −2291, −2296, −2302, −2309 ppm] (Table I) of relative intensities 1:4:6:4:1 (Figure 2). The outer two resonances correspond to chemical shift positions of the species Te(Morphdtc)$_4$

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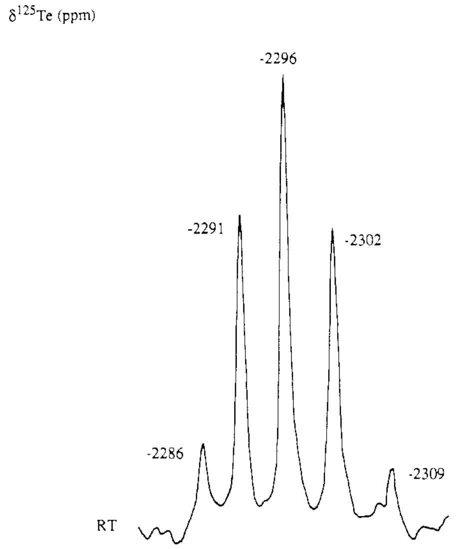

Figure 2. Tellurium-125 spectrum for an equimolar mixture of $Te(Et_2dtc)_4$ and $Te(Morphdtc)_4$ in tetrahydrofuran solution at room temperature.

and $Te(Et_2dtc)_4$ respectively. The inner three resonances [$\delta(^{125}Te)$ −2291, −2296, −2302 ppm] are attributed to the mixed species $Te(Morphdtc)_3(Et_2dtc)$, $Te(Morphdtc)_2(Et_2dtc)_2$, and $Te(Morphdtc)(Et_2dtc)_3$, respectively. Although the dithiocarbamate ligands are labile on the preparative time scale, ligand exchange is slow on the NMR time scale, thus allowing observation of all five possible mixed species in an apparent statistical distribution.

It is interesting that ligand exchange in the above compounds with tellurium in oxidation state (IV) is stopped at room temperature, relative to the NMR time scale, whereas in the tellurium(II) compounds $Te(Et_2dtc)_2$ and $Te(Morphdtc)_2$, cooling to −40 °C is required before ligand exchange slows. In order to gauge qualitatively the size of the barrier to ligand exchange, equal proportions of $Te(Et_2dtc)_4$ and $Te(Morphdtc)_4$ were examined in benzene solution. The $^{125}Te\{^1H\}$ spectrum at room temperature contains only four resonances [$\delta(^{125}Te)$ −2312, −2318, −2323, −2332 ppm]. The $^{125}Te\{^1H\}$ resonance at −2332 ppm is due to the compound $Te(Et_2dtc)_4$ with the other resonances [$\delta(^{125}Te)$ −2323, −2318, −2312 ppm] due to $Te(Morphdtc)(Et_2dtc)_3$, $Te(Morphdtc)_2(Et_2dtc)_2$, and $Te(Morphdtc)_3(Et_2dtc)$, respectively. The resonance for $Te(Morphdtc)_4$ itself is not observed at this temperature due to the limited solubility of the compound in benzene. Warming the solution to 60 °C results in some broadening of the four $^{125}Te\{^1H\}$ resonances, but they are still clearly separated and well resolved from each other, indicating that ligand exchange is still slow at this temperature.

Apparently, the tellurium(IV) dithiocarbamate complexes are unstable with respect to decomposition to their oxidation state(II) counterparts and thiuram disulfide in chlorinated hydrocarbons but are more stable in benzene or THF solutions. The relative instability of $Te(dtc)_4$ in chlorinated solvents may be due to interaction with the chloro groups. The $^{125}Te\{^1H\}$ spectrum of an equimolar mixture of $Te(Et_2dtc)_4$ and $Te(Morphdtc)_4$ in CH_2Cl_2 at room temperature shows a very broad resonance centered in the region [$\delta(^{125}Te) = -900$ ppm]. Lowering the temperature to −60 °C results in the broad resonance [$\delta(^{125}Te) = -900$ ppm] separating into three sharp resonances [$\delta(^{125}Te)$ −921, −962, −1004 ppm] of relative intensities 1:2:1. These resonances are identical with those observed for the species $Te(Morphdtc)_2$, $Te(Morphdtc)(Et_2dtc)$, and $Te(Et_2dtc)_2$ respectively, indicating that the original tellurium(IV) compounds had decomposed to the tellurium(II) analogues. In view of these results it appears that the single ^{125}Te resonance reported[15] for the chemically similar mixture of $Te(Et_2dtc)_4$ and $Te(Benzyldtc)_4$ is probably due to the fast ligand exchange within the reduced species $Te(Et_2dtc)_2$ and $Te(Benzyldtc)_2$.

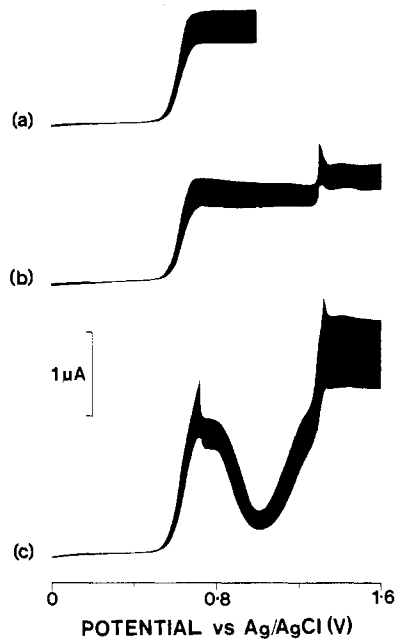

Figure 3. Reductive dc polarograms for 5×10^{-4} M (a) $Hg(Et_2dtc)_2$, (b) $Te(Et_2dtc)_2$, and (c) $Te(Et_2dtc)_4$ in dichloromethane (0.1 M Bu_4NClO_4; drop time = 0.5 s) at 20 °C.

Both compounds $Te(Et_2dtc)_2$ and $Te(Et_2dtc)_4$ are relatively stable and soluble in dimethylformamide. In this solvent, the $^{125}Te\{^1H\}$ spectrum of a mixture of the compounds at −40 °C gives sharp resonances [$\delta(^{125}Te)$ −936, −2354 ppm] corresponding to $Te(Et_2dtc)_2$ and $Te(Et_2dtc)_4$, respectively. Due to the relative stability of both compounds in dimethylformamide, an excess of tetraethylthiuram disulfide (Et_4tds) can be added to a solution of $Te(Et_2dtc)_2$ and the NMR spectra recorded over lengthy periods of time. The $^{125}Te\{^1H\}$ spectrum indicates that initially only $Te(Et_2dtc)_2$ is present in solution. However the ^{125}Te spectrum of the same sample 2 weeks later shows two $^{125}Te\{^1H\}$ resonances (at −40 °C) at $\delta(^{125}Te)$ −946 and −2353 ppm, indicating that oxidative addition of tetraethylthiuram disulfide to $Te(Et_2dtc)_2$ does occur. Therefore it appears that both the rate at which equilibrium between $Te(Et_2dtc)_4$ and $Te(Et_2dtc)_2$ is established and the equilibrium position is largely controlled by the nature of the solvent.

Electrochemical Behavior of $Te(Et_2dtc)_2$ and $Te(Et_2dtc)_4$. NMR data demonstrate the importance of intermolecular reactions and the presence of a redox equilibrium between $Te(dtc)_4$ and $Te(dtc)_2$ in solution. Consequently, electrochemical studies should be rather complex and should involve exchange processes at mercury electrodes and other reactions at platinum electrodes. These aspects have been examined in detail in dichloromethane to ascertain if data are consistent with information derived from the NMR experiments. Radiotracer studies have shown the existence of the exchange process $Et_4tds \rightleftharpoons 2Et_2dtc^-$.[17]

Mercury Electrodes. (a) Reduction. The complex dc polarographic reduction responses in dichloromethane for freshly prepared solutions of both $Te(Et_2dtc)_2$ and $Te(Et_2dtc)_4$ are shown in Figure 3. The response for $Hg(Et_2dtc)_2$ under the same conditions is also included for comparison in this figure. The reduction wave observed at mercury electrodes in the presence of 5×10^{-4} M $Te(Et_2dtc)_2$ (Figure 3b) has a half-wave potential, $E_{1/2}$, of −0.62 V, which is the same as for the mercury complex (Figure 3a). The limiting currents per unit concentration for both $Te(Et_2dtc)_2$ and $Hg(Et_2dtc)_2$ are also similar with small differences being attributable to slightly different diffusion coefficients. Also seen for the tellurium(II) complex is a small "spike" at −1.3 V, which is not seen when the concentration is lowered to 1×10^{-4} M; the spike does not therefore appear to be attributable to a faradaic process. For $Te(Et_2dtc)_4$, the response (Figure 3c) is more complex with current suppression over a well-defined potential range being an obvious feature. The polarographic response of

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the fresh solution of $Te(Et_2dtc)_4$ is essentially that of $Te(Et_2dtc)_2$ and unreacted $Te(Et_2dtc)_4$ as expected from the NMR data. The reduction wave prior to the potential at which current suppression occurs has an $E_{1/2}$ value of −0.63 V, which is close to that for either the $Te(Et_2dtc)_2$ or $Hg(Et_2dtc)_2$ complexes. The total limiting current per unit concentration (measured at −1.4 V) is twice the limiting current for $Te(Et_2dtc)_2$ or $Hg(Et_2dtc)_2$. Studies on $Te(Et_2dtc)_4$ at 5×10^{-5} M show that the current suppression phenomena are greatly diminished at low concentration, suggesting that this suppression occurs because of adsorption or surface-based processes. The results for the faradaic component of the electrode process indicate that reduction of both $Te(Et_2dtc)_2$ and $Te(Et_2dtc)_4$ is dominated by exchange reactions with electrode mercury as observed for other metal dithiocarbamate complexes.[18] These mercury exchange reactions are rapid (diffusion controlled), since reduction potentials and the current–voltage curves are similar to that observed for the corresponding mercury complex $Hg(Et_2dtc)_2$. Cyclic voltammograms for both tellurium complexes also include chemically reversible responses which are similar to that for $Hg(Et_2dtc)_2$. For $Te(Et_2dtc)_2$, eq 2a and 2b describe the

$$Te(Et_2dtc)_2 + Hg \rightleftharpoons Hg(Et_2dtc)_2 + Te \qquad (2a)$$

$$Hg(Et_2dtc)_2 + 2e^- \rightleftharpoons Hg + 2Et_2dtc^- \qquad (2b)$$

electrode processes at mercury electrodes, with the overall process being that described by eq 2c.

$$Te(Et_2dtc)_2 + 2e^- \rightarrow Te + 2Et_2dtc^- \qquad (2c)$$

This scheme was confirmed by carrying out reductive controlled-potential electrolysis for a dichloromethane solution of $Te(Et_2dtc)_2$ at a mercury pool electrode with an applied potential of −0.8 V. The transfer of 2.0 ± 0.1 faraday/mol was noted, and the resulting solution contains only the products from the breakdown of diethyldithiocarbamate in dichloromethane. The mercury working electrode was covered in a black/brown film of mercury(II) telluride.

For $Te(Et_2dtc)_4$ an extended sequence of reactions is indicated in addition to those given for $Te(Et_2dtc)_2$. Each of the species present in the equilibrium reaction identified by NMR (eq 1) undergoes exchange processes at the mercury electrode

$$Te(Et_2dtc)_4 + Hg \rightarrow Hg(Et_2dtc)_2 + Et_4tds + Te \qquad (3a)$$

$$Te(Et_2dtc)_2 + Hg \rightarrow Hg(Et_2dtc)_2 + Te \qquad (3b)$$

$$Et_4tds + Hg \rightarrow Hg(Et_2dtc)_2 \qquad (3c)$$

$$Hg(Et_2dtc)_2 + 2e^- \rightarrow Hg + 2Et_2dtc^- \qquad (3d)$$

$$Et_4tds + 2e^- \rightarrow 2Et_2dtc^- \qquad (3e)$$

The fact that the equilibrium in eq 1 (i.e., $Te(Et_2dtc)_4 \rightleftharpoons Te(Et_2dtc)_2 + Et_4tds$) does not lie totally to the left is clearly illustrated by Figure 3c. If the reaction formed 100% $Te(Et_2dtc)_2$, then the resultant polarogram would be the same as in Figure 3b but with twice the limiting current. That is, the result contained in Figure 3b provides definitive proof that reaction 3a is involved in the reduction scheme and confirms the NMR result that an equilibrium reaction does exist between the complexes in the two oxidation states. Irrespective of the actual pathway, the overall process involves four electrons, according to eq 4.

$$Te(Et_2dtc)_4 + 4e^- \rightarrow Te + 4Et_2dtc^- \qquad (4)$$

(b) Oxidation. The dc polarographic responses for both the tellurium(II) and tellurium(IV) dithiocarbamate complexes, at positive potentials, are shown in Figure 4a,b. For $Te(Et_2dtc)_2$ (Figure 4a) the oxidation process at the mercury electrode proceeds by an overall process that is complicated by adsorption. A similar (but not identical) dc polarographic response was observed for $Te(Et_2dtc)_4$ (Figure 4b). The half-wave potential determined in each case was approximately 0.48 V. Cyclic voltammetry (Figure 4c,d) show that certain aspects of oxidation process are chemically reversible in both cases, but again important differences are observed in the fine detail.

Table II. Voltammetric Data for Reduction of 5×10^{-4} M $Te(Et_2dtc)_2$ and $Te(Et_2dtc)_4$ at Mercury and Platinum Electrodes in Dichloromethane (0.1 M Bu_4NClO_4) at 20 °C

compd	dc polarography[a] $E_{1/2}$, V[d]	cyclic voltammetry[b] $E_p^{red}(1)$, V[d]	$E_p^{red}(2)$, V[d]	$E_p^{ox}(1)$, V[d]	$E_p^{ox}(2)$,[c] V[d]
$Te(Et_2dtc)_2$	−0.62	−0.68		−0.23	0.08
$Te(Et_2dtc)_4$	−0.63	−0.78	−1.51	−0.23	0.08

[a] Dropping mercury electrode; drop time = 0.5 s; $E_{1/2}$ = half-wave potential. [b] Platinum disk electrode; scan rate = 500 mV s^{-1}. $E_p^{red}(n)$ = peak potential of primary reduction process for *n*th process (*n* = 1, 2); E_p^{ox} = oxidation potentials of processes observed on reverse oxidative scan of cyclic voltammogram. [c] Corresponds to process for oxidation of Et_2dtc^-. [d] Vs Ag/AgCl.

Table III. Voltammetric Data for Oxidation Processes Observed in the Presence of 5×10^{-4} M $Te(Et_2dtc)_2$ and $Te(Et_2dtc)_4$ at Mercury and Platinum Electrodes in Dichloromethane (0.1 M Bu_4NClO_4) at 20 °C

compd	dc polarography[a] $E_{1/2}$, V[c]	cyclic voltammetry[b] E_p^{ox}, V[c]	E_p^{red}, V[c]
$Te(Et_2dtc)_2$	0.48	0.85	0.34
$Te(Et_2dtc)_4$	0.48	0.97	0.20

[a] Dropping mercury electrode; drop time = 0.5 s. [b] Platinum disk electrode; scan rate = 500 mV s^{-1}. [c] Vs Ag/AgCl. Other symbols and nomenclature are as in Table II.

In order to characterize the products of the oxidation process, oxidative controlled-potential electrolysis experiments were performed by using a mercury-pool electrode and an applied potential of 0.6 V. As shown in ref 19 this potential is sufficient to convert $Hg(Et_2dtc)_2$ to $[Hg_3(Et_2dtc)_4]^{2+}$.

For $Te(Et_2dtc)_2$, the transfer of 1.05 ± 0.1 faraday/mol was noted and the resulting solution contained only elemental tellurium and $[Hg_3(Et_2dtc)_4]^{2+}$, the latter being the product of one-electron oxidation of $Hg(Et_2dtc)_2$ in the presence of mercury.[19] The species $[Hg_3(Et_2dtc)_4]^{2+}$ was characterized by its color and reductive voltammetry at a platinum electrode.[19] Thus in a manner entirely analogous to the reduction process, $Te(Et_2dtc)_2$ undergoes an exchange reaction with elemental mercury to form the mercury complex, which is immediately oxidized at this potential. The overall reaction is described by eq 5.

$$2Te(Et_2dtc)_2 + 3Hg \rightarrow 2Te + [Hg_3(Et_2dtc)_4]^{2+} + 2e^- \qquad (5)$$

The response for the tellurium(IV) complex is once again based on the fact that this species can coexist with $Te(Et_2dtc)_2$ and Et_4tds. That is, at the electrode surface, eq 6a takes place followed by eq 5.

$$Te(Et_2dtc)_4 \rightleftharpoons Te(Et_2dtc)_2 + Et_4tds \qquad (6a)$$

As a consequence of eq 6a, the following reactions also take place at the electrode surface:

$$2Et_4tds + 3Hg \rightarrow [Hg_3(Et_2dtc)_4]^{2+} + 2e^- \qquad (6b)$$

$$Et_4tds + Hg \rightarrow Hg(Et_2dtc)_2 \qquad (6c)$$

$$Hg(Et_2dtc)_2 + \tfrac{1}{2}Hg \rightarrow \tfrac{1}{2}[Hg_3(Et_2dtc)_4]^{2+} + e^- \qquad (6d)$$

$$Te(Et_2dtc)_4 + 3Hg \rightarrow Te + [Hg_3(Et_2dtc)_4]^{2+} + 2e^- \qquad (6e)$$

That is, Et_4tds forms $Hg(Et_2dtc)_2$ at the mercury electrode surface, and hence the ultimate fate of all diethyldithiocarbamate under oxidizing conditions in the presence of mercury is the formation of products derived from $Hg(Et_2dtc)_2$. Data for the oxidation processes of tellurium dithiocarbamates are collected

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[18] (a) Bond, A. M.; Casey, A. T.; Thackeray, J. R. *Inorg. Chem.* **1973**, *12*, 887. (b) Bond, A. M.; Wallace, G. G. *Inorg. Chem.* **1984**, *23*, 1858.

[19] Bond, A. M.; Colton, R.; Hollenkamp, A. F.; Hoskins, B. F.; McGregor, K. *J. Am. Chem. Soc.* **1987**, *109*, 1969.

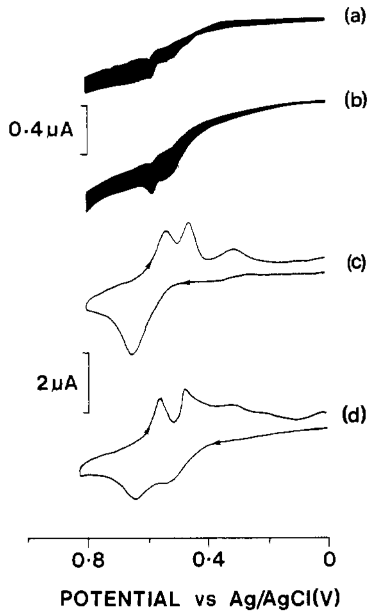


Figure 4. Oxidative responses observed at mercury electrodes for 5 × 10^{-4} M $Te(Et_2dtc)_2$ (curves a and c) and $Te(Et_2dtc)_4$ (curves b and d): (a, b) dc polarograms (drop time = 0.5 s); (c, d) cyclic voltammograms (slowly growing mercury drop electrode; scan rate = 500 mV s^{-1}) in dichloromethane (0.1 M Bu_4NClO_4) at 20 °C.

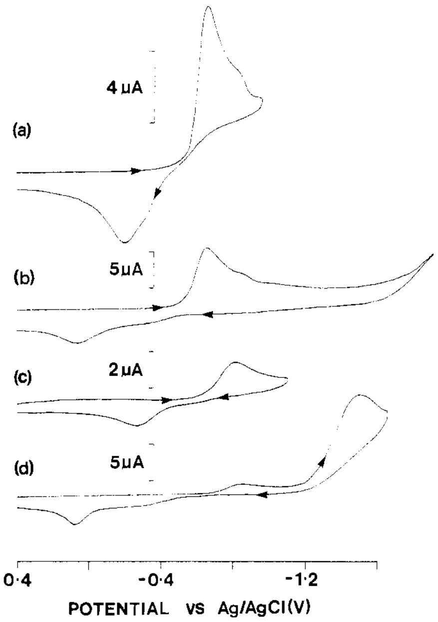


Figure 5. Reductive cyclic voltammograms at a platinum electrode for 5 × 10^{-4} M $Te(Et_2dtc)_2$ (curves a and b) and $Te(Et_2dtc)_4$ (curves c and d). Scan rate = 500 mV s^{-1} in dichloromethane (0.1 M Bu_4NClO_4) at 20 °C.

in Table III. The oxidation processes observed at mercury electrodes again confirm the importance of the redox reaction involving tellurium(IV) and tellurium(II) dithiocarbamate complexes and exchange reactions.

Platinum Electrode. (a) Reduction. The reductive processes of $Te(Et_2dtc)_2$ and $Te(Et_2dtc)_4$ at platinum electrodes in several solvents have been described.[9] However, no detailed knowledge of the behavior in dichloromethane is available. In this paper only a brief description of voltammetry at platinum electrodes in dichloromethane is given to provide a comparison with the behavior at the mercury electrode and a comparison with data available in ref 9. Figure 5 shows the reductive cyclic voltammograms for dichloromethane solutions of the tellurium diethyldithiocarbamate complexes at a platinum electrode. For a 5 × 10^{-4} M solution of $Te(Et_2dtc)_2$ (Figure 5a), one reduction peak is seen at −0.68 V with an oxidation peak on the reverse (oxidative) scan at −0.23 V. Shoulders are present on the major waves. Figure 5b shows that no other reduction processes are present at more negative potentials, but on the oxidative scan, the peak at −0.23 V is greatly diminished and the appearance of a new oxidation peak at 0.08V is observed. The latter corresponds to the oxidation of free diethyldithiocarbamate. These results are similar to those reported at a gold electrode in dimethylformamide.[9]

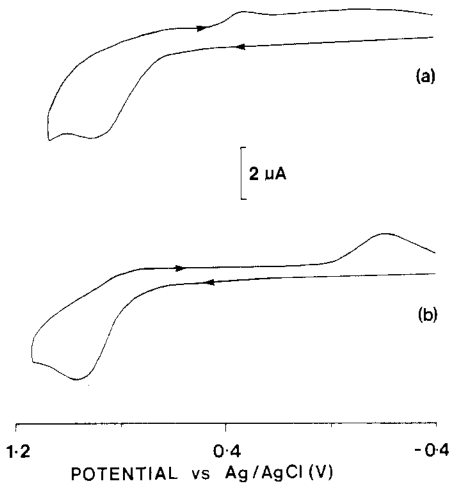


Figure 6. Oxidative cyclic voltammograms at a platinum electrode at a scan rate of 500 mV s^{-1} for 5 × 10^{-4} M (a) $Te(Et_2dtc)_2$ and (b) $Te(Et_2dtc)_4$ in dichloromethane (0.1 M Bu_4NClO_4) at 20 °C.

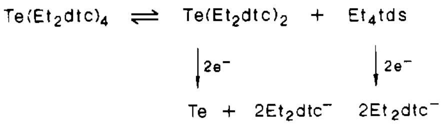
Reductive controlled-potential electrolysis in dichloromethane at a platinum electrode yields diethyldithiocarbamate and elemental tellurium as the only products with 2.0 ± 0.1 faraday/mole transferred, which is also the case in more coordinating solvents.[9] The amount of tellurium produced was assayed by dissolution in aqueous 1 M NaOH followed by polarographic detection using standard addition[20] and corresponds to that present initially as the complex. The overall reaction for reduction of $Te(Et_2dtc)_2$ is therefore formulated as in eq 7, which is the same as the overall

$$Te(Et_2dtc)_2 + 2e^- \rightarrow Te + 2Et_2dtc^- \qquad (7)$$

equation for reduction at mercury electrodes. The exchange reactions available at mercury electrodes provide an alternative reduction pathway.

Presumably, a zerovalent complex $[Te(Et_2dtc)_2]^{2-}$ is formed as an intermediate[9] in dichloromethane as is the case in other solvents, although this could not be detected in the present work. The reduction of $Te(Et_2dtc)_4$ is characterized by two processes at −0.78 and −1.51 V (Figure 5c). The height of the process at −0.78 V, which occurs in the potential range where $Te(Et_2dtc)_2$ is reduced, increases in magnitude with time. The process at −1.51 V occurs at a potential very similar to that for the reduction of Et_4tds.[21]

The reduction scheme for $Te(Et_2dtc)_4$ is summarized in eq 8.


$$\begin{array}{ccccc} Te(Et_2dtc)_4 & \rightleftharpoons & Te(Et_2dtc)_2 & + & Et_4tds \\ & & \downarrow{\scriptstyle 2e^-} & & \downarrow{\scriptstyle 2e^-} \\ & & Te + 2Et_2dtc^- & & 2Et_2dtc^- \end{array} \qquad (8)$$

The overall reduction process at the platinum electrode is given in eq 9 and is identical with that observed at the mercury electrode and in other solvents.[9]

$$Te(Et_2dtc)_4 + 4e^- \rightarrow Te + 4Et_2dtc^- \qquad (9)$$

The time-dependent nature of the response at the platinum electrode is again consistent with the NMR evidence that the reaction given in eq 1 is important when the tellurium(IV) complex is dissolved in CH_2Cl_2.

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(20) Zhdanov, S. I. In *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Ed.; Marcel Dekker: New York, 1975; Vol. IV, p 393.

(21) Labuda, J.; Mocak, J.; Bustin, D. I. *Chem. Zvesti* **1982**, *36*, 633.

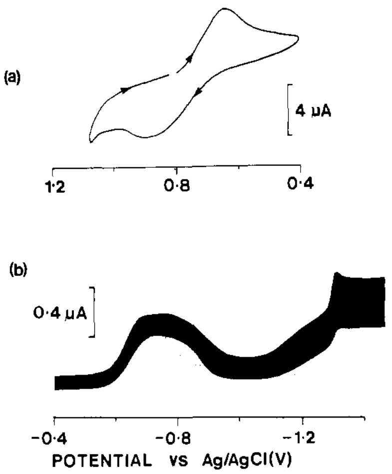

Figure 7. Reductive (a) cyclic voltammogram at a platinum electrode using a scan rate of 500 mV s^{-1} and (b) dc polarogram at a mercury electrode using a drop time of 0.5 s for 5 × 10^{-4} M Te(Et$_2$dtc)$_2$ after oxidative electrolysis (platinum electrode) in dichloromethane (0.1 M Bu$_4$NClO$_4$) at 20 °C.

Data for reduction of Te(Et$_2$dtc)$_2$ and Te(Et$_2$dtc)$_4$ at platinum electrodes are summarized in Table II.

(b) Oxidation. Unlike the case for reduction, it is impossible for the overall oxidation process to be the same at both Hg and Pt electrodes. Figure 6 shows the cyclic voltammetric responses under oxidizing conditions at platinum electrodes, for which data are summarized in Table III. For the cyclic voltammogram of Te(Et$_2$dtc)$_2$, Figure 6a shows that a single oxidation peak is observed with a peak potential at 0.85 V with one major reduction peak, at 0.34 V, on the reverse reductive scan. Figure 6b is for the same concentration of Te(Et$_2$dtc)$_4$ under the same conditions, and again a single oxidation response is seen at moderately positive potentials (E_p^{ox} = 0.97 V). On the reductive scan only one reduction peak is seen, at −0.20 V.

Oxidative controlled-potential electrolysis was carried out for Te(Et$_2$dtc)$_2$ at 1.0 V with a platinum-gauze electrode and resulted in the transfer of more than 1 faraday/mol. Near the point at which 1 faraday/mol had been passed, the current had fallen to its lowest point, which was still, however, above the true background level. Thus follow-up chemical reactions that generate other electroactive species are indicated although it appears that the primary oxidation process consists of a one-electron charge-transfer step. The voltammetric responses at platinum and mercury electrodes for the oxidatively electrolyzed solution are shown in Figure 7. Surprisingly, in the reductive cyclic voltammogram at a platinum electrode (Figure 7a), it can be noted that there is a reduction process at E_p^{red} = 0.64 V that regenerates the starting material (E_p^{ox} = 0.85 V). This is confirmed by scanning to more negative potentials and observing the existence of a reduction wave with a peak potential corresponding to Te(Et$_2$dtc)$_2$. This implies that on the controlled-potential-electrolysis time scale some rearrangement of the initial oxidation product takes place with the final voltammetrically detected (Figure 7a) species only being formed after a long period of time.

Figure 7b is the reductive dc polarogram after oxidative controlled-potential electrolysis at the platinum electrode. The polarographic limiting current (reduction) is virtually the same as that recorded for reduction of the original solution of Te(Et$_2$dtc)$_2$. Presumably, the reduction current is based on the amount of dithiocarbamate present and this has not changed. Equation 10

$$\mathrm{Te(Et_2dtc)_2} \rightarrow \mathrm{[Te(Et_2dtc)_2]^{2+}} + 2e^-$$

$$\mathrm{[Te(Et_2dtc)_2]^{2+}} + \mathrm{Te(Et_2dtc)_2} \rightarrow \mathrm{[Te_2(Et_2dtc)_2(Et_4tds)]^{2+}} \rightarrow \mathrm{Te(Et_2dtc)_4} + \mathrm{Te^{2+}} \quad (10)$$

is consistent with the above observations; however, we are unable to determine whether the primary electron transfer process is metal or ligand based. The polarogram after electrolysis is indistinguishable from that for Te(Et$_2$dtc)$_4$ at the concentration predicted from the reaction scheme given in eq 10.

The potential for oxidation of Te(Et$_2$dtc)$_4$ (Figure 6b) is very similar to that for Et$_4$tds.[16] The oxidation of Te(Et$_2$dtc)$_4$ is believed to be ligand based but was not investigated further.

Conclusions

Te(R$_2$dtc)$_2$ reacts with tetraalkylthiuram disulfide, R$_4$tds, to give a solvent-dependent equilibrium mixture containing Te(R$_2$dtc)$_4$. Te(R$_2$dtc)$_4$ dissolved in a solvent attains the same equilibrium position. For the first time the tellurium(IV) species has been unambiguously identified by ^{125}Te NMR spectroscopy. Mixtures of tellurium(II) dithiocarbamates undergo intermolecular ligand exchange at room temperature that is slow on the NMR time scale at low temperatures. In contrast, the tellurium(IV) analogues are not labile on the NMR time scale at room temperature. The voltammetric data are completely consistent with the NMR results. Not only is ligand exchange rapid between tellurium centers but also it is facile between Hg and Te.

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Registry No. Te(Et$_2$dtc)$_2$, 15080-52-1; Te(Morphdtc)$_2$, 30978-31-5; Te(Morphdtc)(Et$_2$dtc), 119455-93-5; Te(Et$_2$dtc)$_4$, 20941-65-5; Te(Morphdtc), 119480-24-9; Te(Morphdtc)$_2$(Et$_2$dtc)$_2$, 119455-94-6; dtc, 392-74-5; tds, 97-77-8; Hg(Et$_2$dtc)$_2$, 14239-51-1; Te, 13494-80-9; Hg, 7439-97-6; Pt, 7440-06-4; ^{125}Te, 14390-73-9.