Inorganica Chimica Acta, 160 (1989) 11–21

Electrochemistry of Tellurium(II) and Tellurium(IV) Dithiocarbamates at Solid Electrodes in Non-aqueous Solvents

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(Received July 11, 1988)

Abstract

The electrochemistry of several tellurium(II) and tellurium(IV) dithiocarbamates has been examined in non-aqueous solvents at solid electrodes. The reduction of $Te(R_2NCS_2)_2$ compounds was observed to involve an overall two-electron process on the cyclic voltammetry time scale. The electrode reduction processes were found to be complex and highly dependent on both the solvent and the electrode, but under the conditions of electrolysis a simple reduction to tellurium metal was observed.

$$Te(R_2NCS_2)_2 + 2e \longrightarrow Te^0 + 2R_2NCS_2^-$$

The reduction of the $Te(R_2NCS_2)_4$ compounds occurred at more negative potentials compared to those of the tellurium(II) analogues and involved a four-electron reduction on the coulommetric time scale via the formation of the intermediate $Te(R_2NCS_2)_2$. The initial process is consistent with a ligand mediated reduction in contrast with the metal based reduction of $Te(R_2NCS_2)_2$.

Introduction

The electrochemistry of transition metal dithiocarbamates has been investigated by various researchers [1–13] of whom Martin, Bond and coworkers have published most extensively on this subject. The redox processes of these compounds are regarded as metal-based [2] and perturbed by the electronic effects of the ligand substituent groups [3–6]. They are noted for the stability of high metal oxidation states (eg. Fe(IV), Co(IV), Ni(III) and Cu(III)) [5–7, 12] and to a lesser extent low metal oxidation states (eg. Fe(II), Co(I), Ni(I) and Cu(I)) [5–8, 14–16].

Although tellurium(II) [17] and tellurium(IV) [18] dithiocarbamates have been known for some considerable time, the electrochemistry of these compounds has previously not been reported. The superior stability of these compounds relative to the xanthate and thiolate analogues [17, 19] adds to their attraction as an avenue for the exploration of the electrochemistry of tellurium. The use of tellurium dioxide in the curing of thiol-terminated polysulfide sealants [20] and the application of tellurium dithiocarbamates as accelerators in the curing of rubber [21, 22] together with the increasing importance of tellurium semiconductors [23] and organic conductors [24] is also motivation for interest in this subject.

In this work the electrochemistry of some common tellurium dithiocarbamates is examined in non-aqueous media at solid electrodes and comparisons are made with transition metal analogues.

Experimental

Preparations

Bis(dithiocarbamato)tellurium(II) compounds were prepared from sodium telluropentathionate and the appropriate sodium dithiocarbamate as described by Foss [17] and the products were recrystallized from carbon disulfide or carbon disulfide/ethanol depending upon the solubility of the compounds.

Tetrakis(dithiocarbamato)tellurium(IV) compounds were prepared by the addition of an aqueous solution of the appropriate sodium dithiocarbamate to an 0.1 M solution of potassium tellurite in pH 8.4 buffer [18] (19.05 g borax, 7.0 g potassium dihydrogen phosphate in 500 ml distilled water). The products were recrystallized from toluene/petroleum ether (60–80 °C fraction).

All compounds gave satisfactory elemental analyses.

Electrochemistry

An EG & G PAR model 173 potentiostat was used in conjunction with an EG & G PARC model 175 Universal Programmer for cyclic voltammetry and an EG & G PAR model 179 Digital Coulometer for controlled potential electrolysis. A Metrohm model 628 rotating disc electrode was used when required. All electrochemical measurements were

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performed with a three-electrode system, working disc electrode, auxiliary wire electrode (gold) and a reference electrode (saturated calomel electrode for dimethylformamide solutions and silver wire in 1×10^{-3} M $AgNO_3$/acetonitrile [25] for other solvents). Controlled potential electrolysis was carried out on 50 ml solutions (approximately 1×10^{-3} M in tellurium dithiocarbamate) at a platinum gauze electrode using a coiled platinum auxiliary electrode isolated from the bulk solution in a compartment with a glass frit. Potentials were determined relative to the ferrocenium/ferrocene (Fc^+/Fc) redox couple as an internal standard [26] (SCE = +0.48 V, Ag/Ag^+ = +0.06 V). Ferrocene (2×10^{-3} M) was added to the electrochemical cell at the end of each cyclic voltammetry experiment. Concentrations of tellurium dithiocarbamates were 2×10^{-3} M in 10 ml of 0.1 M supporting electrolyte/solvent unless otherwise stated. All electrochemical experiments were conducted under an atmosphere of dry argon.

Dimethylformamide was purified by stirring the analytical grade solvent with barium oxide overnight then decanting the solvent on to activated 4A molecular sieves under dry nitrogen. After being allowed to stand for 48 h the solvent was again decanted and distilled at 60 °C under vacuum and then stored under dry nitrogen at 4 °C. Analytical grade acetone and acetonitrile were dried over activated 4A molecular sieves and distilled and then stored under dry nitrogen. Analytical grade dichloromethane was used without further purification.

Supporting electrolytes were recrystallized and dried at 60 °C under vacuum and stored under dry nitrogen prior to use.

Results and Discussion

Reduction of $Te(R_2NCS_2)_2$

The bis(dithiocarbamato)tellurium(II) compounds exhibit only one faradaic reduction process at negative potentials with respect to the ferrocinium/ferrocene (Fc^+/Fc) couple at a gold electrode (Fig. 1A). At a rotating gold disc electrode the limiting current for reduction of $Te(Et_2NCS_2)_2$ was found to be twice that of an equimolar solution of $Cu(Et_2NCS_2)_2$ which is known to undergo a one-electron reduction [7]. Assuming equal diffusion coefficients for both compounds, the overall reduction may be defined as a two-electron process. This is also supported by the coulometric data (Table 1).

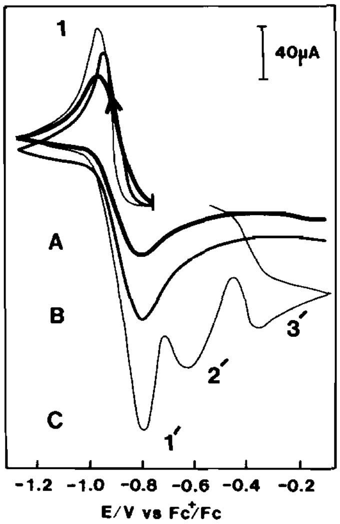


Fig. 1. Cyclic voltammetry of the reduction of $Te(Et_2NCS_2)_2$ at a gold disc electrode in acetonitrile/Bu_4NBF_4 (0.1 M) at 200 mV s^{-1} scan rate. Curve A represents 2.1×10^{-3} M $Te(Et_2NCS_2)_2$. Curves B and C were derived in the presence of 2.1×10^{-3} M and 7.9×10^{-3} M Et_2NCS_2Na respectively.

$$Te(R_2NCS_2)_2 + 2e \longrightarrow [Te(R_2NCS_2)_2]^{2-} \qquad (1)$$

The cyclic voltammetry experiments show that only minor changes in reduction potentials are brought about by altering the dithiocarbamate substituent group (Table 2). This dependency is slightly less than that observed for the reduction of some transition metal analogues [4–8]. It also appears that the solvent effect on the reduction of $Te(R_2NCS_2)_2$ compounds has a more profound impact than changing the substituent group. Similar solvent effects have been observed in the case of $Mo(R_2NCS_2)_4$ compounds [27]. These observations are consistent with the minor contributions of the

TABLE 1. Controlled potential electrolysis of $Te(R_2NCS_2)_2$ and $Te(R_2NCS_2)_4$ compounds

Compound	Electrolysis potential (V)	Solvent	Number of electrons (*n*) transferred per molecule
$Te(Et_2NCS_2)_2$	−0.85 (*vs.* SCE)	dimethylformamide	2.07
	−1.20 (*vs.* $Ag/AgNO_3$)	acetonitrile	1.97
		acetone	1.53
$Te(i\text{-}Pr_2NCS_2)_2$	−1.20 (*vs.* $Ag/AgNO_3$)	acetonitrile	1.95
$Te(Et_2NCS_2)_4$	−1.70 (*vs.* $Ag/AgNO_3$)	acetonitrile	3.8
	−1.40 (*vs.* SCE)	dimethylformamide	4.0

TABLE 2. Cyclic voltammetric reduction of $Te(R_2NCS_2)_2$ in various solvents at a gold disc electrode at 25 °C[a]

Compound	Solvent	Scan rate ($mV\ s^{-1}$)	E/V vs. Fc^+/Fc				ΔEp^e (mV)	ΔEp, Fc^+/Fc^f (mV)
			$E_{1/2}$	$Ep^{red\ b}$	$Ep^{ox\ c}$	$ip^{ox}/ip^{red\ d}$		
$Te(Et_2NCS_2)_2$	dimethylformamide	500	−0.94	−1.02	−0.86	1.00	160	115
		20	−0.93	−0.98	−0.87	0.85	110	115
	dichloromethane	500	−1.01	−1.21	−0.81	1.06	400	340
		20	−0.99	−1.09	−0.89	0.69	200	150
	acetonitrile	500	−0.91	−0.98	−0.83	0.80	150	120
		20	−0.89	−0.96	−0.82	0.66	140	95
	acetone	500	−0.99	−1.10	−0.88	0.97	230	150
		20	−0.99	−1.06	−0.91	0.63	150	90
$Te(n\text{-}Pr_2NCS_2)_2$	acetonitrile	500	−0.91	−0.97	−0.84	0.84	130	
		20	−0.89	−0.95	−0.82	0.68	130	
	acetone	500	−1.05	−1.26	−0.84	0.99	420	
		20	−1.04	−1.17	−0.91	0.74	260	
$Te(i\text{-}Pr_2NCS_2)_2$	acetonitrile	500	−0.98	−1.07	−0.89	0.85	180	
		20	−0.97	−1.04	−0.90	0.64	140	
	acetone	500	−1.09	−1.25	−0.92	0.82	330	
		20	−1.07	−1.15	−0.98	0.61	170	
$Te(i\text{-}Bu_2NCS_2)_2$	acetonitrile	500	−0.91	−1.00	−0.82	0.83	180	
		20	−0.91	−0.97	−0.85	0.63	120	
	acetone	500	−1.00	−1.21	−0.79	0.83	420	
		20	−1.00	−1.11	−0.88	0.63	230	
$Te(Bz_2NCS_2)_2$[g]	acetone	500	−0.93	−1.12	−0.73	0.91	390	
		20	−0.84	−1.02	−0.65	0.55	370	

[a] Supporting electrolyte in DMF and acetonitrile, 0.1 M Et_4NClO_4; dichloromethane and acetone, 0.1 M Bu_4NBF_4. [b] Peak potential for the reduction process. [c] Peak potential for the corresponding oxidation process. [d] Ratio of peak currents according to R. S. Nicholson, ref. 29. [e] Separation of peak potentials. [f] Separation of peak potentials for the Fc^+/Fc couple in the same solvent. [g] Not sufficiently soluble in acetonitrile.

dithiocarbamate substituent groups to the ^{125}Te NMR chemical shifts which are comparable with the solvent shifts [28].

Cyclic voltammetry of $Te(Et_2NCS_2)_2$ at concentrations of 2×10^{-3} M in dimethylformamide, acetonitrile, acetone and dichloromethane shows ip^{ox}/ip^{red} approaching unity at fast scan rates (Table 2) indicating that the reduction process is chemically reversible. Large peak separations, ΔEp, (Table 2) compared with the value of $60/n$ mV for a reversible couple [29] are also observed. However, in non-aqueous media, particularly with low polarity solvents, the effect of uncompensated iR drop results in an increase in these values [30].

Under conditions of low iR drop (low $Te(Et_2NCS_2)_2$ concentrations and high supporting electrolyte concentration) ΔEp values approach the expected value of 60 mV for a reversible one-electron transfer in highly polar solvents such as dimethylformamide and acetonitrile (Table 3). However, it is uncertain whether the reduction process involves a quasi-reversible two-electron reduction or two sequential one-electron reductions at similar potentials. The latter may be quasi-reversible in one or both of the one-electron processes

$$Te(R_2NCS_2)_2 + 2e \overset{k_s}{\rightleftharpoons} [Te(R_2NCS_2)_2]^{2-} \qquad (2)$$

$$Te(R_2NCS_2)_2 + e \overset{k_s}{\rightleftharpoons} [Te(R_2NCS_2)_2]^{-} \qquad (3)$$

$$[Te(R_2NCS_2)_2]^{-} + e \overset{(k_s)}{\rightleftharpoons} [Te(R_2NCS_2)_2]^{2-} \qquad (4)$$

where k_s is the heterogeneous charge-transfer constant.

When the temperature was reduced to −60 °C, the voltammogram of $Te(Et_2NCS_2)_2$ in dimethylformamide, at a gold disc electrode, was largely unaffected while significant increases in ΔEp were observed in acetonitrile and acetone solutions at −40 and −55 °C respectively (Fig. 2). The results are consistent with slow electron transfer processes in the latter two solvents which are accentuated at low temperatures.

Large ΔEp values are also observed at the platinum electrode in dimethylformamide, acetonitrile and acetone compared with those obtained at the gold electrode at 25 °C (Table 3). This effect is even more pronounced at the glassy carbon electrode (Fig. 3). Thus, the heterogeneous charge-transfer constant for $Te(Et_2NCS_2)_2$ appears to be both solvent and electrode dependent.

TABLE 3. Cyclic voltammetry of the reduction of $Te(Et_2NCS_2)_2$ at various solid electrodes and solvents

Scan rate (mV s^{-1})	*E*/*V* *vs.* Fc^+/Fc			ΔEp (mV)	ip^{ox}/ip^{red}	ΔEp, Fc^+/Fc (mV)
	$E_{1/2}$	Ep^{red}	Ep^{ox}			
Gold disc electrode in dimethylformamide[a]						
500	−0.90	−0.95	−0.84	110	0.92	80
100	−0.91	−0.95	−0.87	80	0.90	70
20	−0.91	−0.94	−0.87	70	0.80	70
Platinum disc electrode in dimethylformamide						
500	−0.87	−0.97	−0.77	200	0.85	
100	−0.89	−0.97	−0.80	170	0.86	
20	−0.89	−0.95	−0.83	120	0.84	
Glassy carbon electrode in dimethylformamide						
500	−0.96	−1.51	−0.41	1100		
100	−0.89	−1.33	−0.44	890		
20	−0.83	−1.20	−0.45	750		
Gold disc electrode in acetonitrile[b]						
500	−0.87	−0.90	−0.84	60	0.88	
100	−0.87	−0.89	−0.84	50	0.85	
20	−0.85	−0.89	−0.81	80	0.69	
Platinum disc electrode in acetonitrile						
500	−0.84	−0.91	−0.76	150	0.81	60
100	−0.83	−0.90	−0.76	140	0.77	60
20	−0.85	−0.90	−0.80	100	0.66	70
Glassy carbon disc electrode in acetonitrile						
500	−0.84	−0.95	−0.73	220	0.77	
100	−0.84	−0.97	−0.71	260	0.67	
20	−0.84	−0.91	−0.77	140	0.60	
Gold disc electrode in acetone[c]						
500	−0.91	−0.98	−0.83	150	0.93	65
100	−0.92	−0.98	−0.85	130	1.10	65
20	−0.88	−0.95	−0.84	110	0.70	70
Platinum disc electrode in acetone						
500	−0.88	−1.00	−0.75	250	0.83	
100	−0.87	−0.97	−0.77	200	0.64	
20	−0.88	−0.94	−0.81	130	0.69	
Glassy carbon disc electrode in acetone						
500	−0.91	−1.09	−0.73	360	0.95	
100	−0.92	−1.11	−0.73	380	0.81	
20	−0.92	−1.00	−0.83	170	0.60	
Gold disc electrode in dichloromethane[d]						
500	−0.91	−1.05	−0.77	280	0.87	130
100	−0.92	−1.04	−0.80	240	0.75	100
20	−0.94	−1.01	−0.86	150	0.69	80
Platinum disc electrode in dichloromethane						
500	−0.91	−1.08	−0.73	350	0.85	
100	−0.92	−1.05	−0.79	260	0.68	
20	−0.94	−1.01	−0.86	150	0.62	
Glassy carbon disc electrode in dichloromethane						
500	−0.90	−1.28	−0.51	770	0.50	
100	−0.88	−1.22	−0.54	680	0.84	
20	−0.91	−1.09	−0.72	370	0.21	

[a] $Te(Et_2NCS_2)_2 = 5 \times 10^{-4}$ M, $Et_4NClO_4 = 0.2$ M, ferrocene = 1×10^{-3} M. [b] $Te(Et_2NCS_2)_2 = 6 \times 10^{-4}$ M, $Et_4NClO_4 = 0.2$ M, ferrocene = 2×10^{-3} M. [c] $Te(Et_2NCS_2)_2 = 3.8 \times 10^{-4}$ M, $Bu_4NBF_4 = 0.2$ M, ferrocene = 5×10^{-4} M. [d] $Te(Et_2NCS_2)_2 = 7 \times 10^{-4}$ M, $Bu_4NBF_4 = 0.2$ M, ferrocene = 1×10^{-3} M.

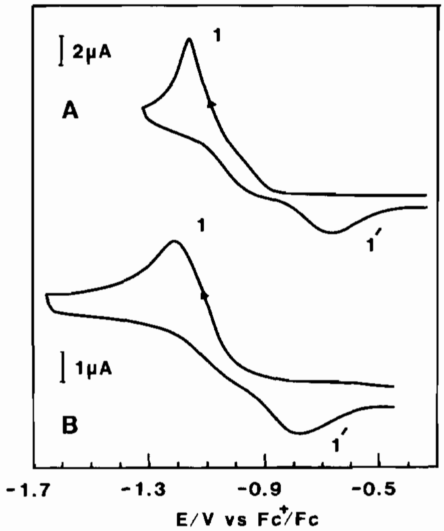


Fig. 2. Cyclic voltammetry of the reduction of $Te(Et_2NCS_2)_2$ at a gold disc electrode and at a scan rate of 50 mV s^{-1}. A, 9×10^{-4} M in acetonitrile/Et_4NClO_4 (0.1 M) at −43 °C; B, 4×10^{-4} M in acetone/Bu_4NBF_4 (0.2 M) at −58 °C.

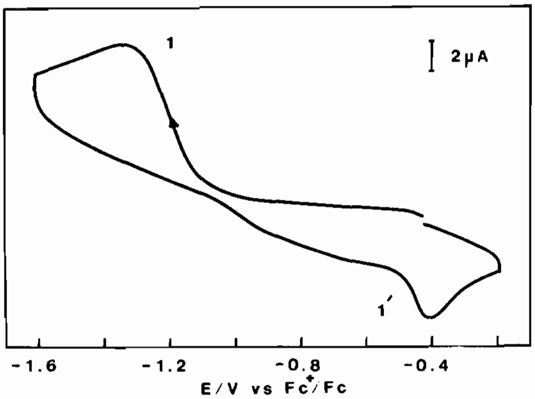


Fig. 3. Cyclic voltammetry of the reduction of $Te(Et_2NCS_2)_2$ (5×10^{-4} M) at a glassy carbon disc electrode in dimethylformamide/Et_4NClO_4 (0.2 M) at 25 °C and a scan rate of 100 mV s^{-1}.

At low scan rates (20 mV s^{-1}) the departure from unity in ip^{red}/ip^{ox} indicates that the reduced species is undergoing a chemical reaction (Tables 2 and 3). This is supported by the observation of a dark coating formed on the working electrode after the reduction process has been scanned. The overall redox process can therefore be more accurately described as

$$\mathrm{Te(R_2NCS_2)_2} + 2e \overset{k_s}{\rightleftharpoons} [\mathrm{Te(R_2NCS_2)_2}]^{2-} \xrightarrow{k_1} \mathrm{Te^0} + 2\mathrm{R_2NCS_2^-} \qquad (5)$$

where k_1 is the chemical rate constant for the decomposition of the reduced species. The scan rate dependency shows that the chemical reaction is slow.

In dimethylformamide solution, holding the potential subsequent to the reduction peak 1 does not result in an increase in peak 1′. However, this experiment gives rise to an increase in peak 4′ at more positive potentials (Fig. 4A) indicating this to be the anodic stripping peak for $\mathrm{Te^0}$ (eqn. (6))

$$\mathrm{Te^0} \longrightarrow \mathrm{Te^{2+}} + 2e \qquad (6)$$

Furthermore, peak 4′ current increases with a decrease in scan rate. This too is consistent with eqn. (5).

The addition of $\mathrm{Et_2NCS_2Na}$ inhibits the formation of $\mathrm{Te^0}$ subsequent to the reduction of $\mathrm{Te(Et_2NCS_2)_2}$. This suggests the existence of a chemical equilibrium involving the reduced species and the products of decomposition.

$$[\mathrm{Te(R_2NCS_2)_2}]^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Te^0} + 2\mathrm{R_2NCS_2^-} \qquad (7)$$

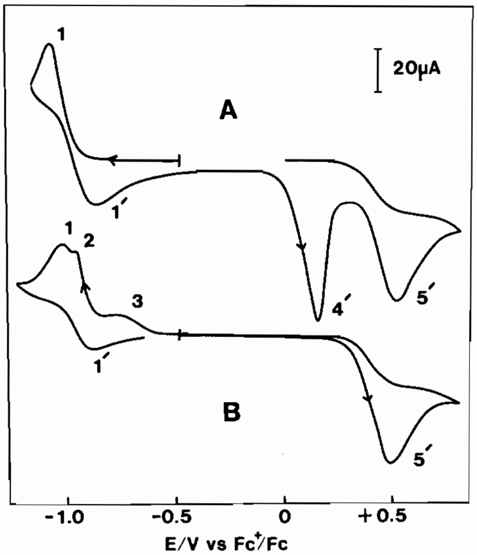


Fig. 4. Cyclic voltammetry of $\mathrm{Te(Et_2NCS_2)_2}$ in dimethylformamide/$\mathrm{Et_4NClO_4}$ (0.1 M) at a gold disc electrode and 100 mV s^{-1} scan rate: A, scanned towards negative potentials; B, scanned towards positive potentials.

However, cyclic voltammetry of a mixture of $\mathrm{Et_2NCS_2Na}$ and tellurium powder stirred in acetonitrile shows evidence of only a small quantity of $[\mathrm{Te(Et_2NCS_2)_2}]^{2-}$ being generated. This indicates that the equilibrium for eqn. (7) favours the decomposition of the reduced species. The other possible mechanism of $\mathrm{Te^0}$ inhibition by $\mathrm{Et_2NCS_2^-}$ is through its oxidation at the electrode and subsequent reaction of the disulfide with $\mathrm{Te^0}$.

$$\mathrm{Te^0} + \mathrm{(Et_2NCS_2)_2} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{Te(Et_2NCS_2)_2} \qquad (8)$$

In fact, $\mathrm{Te(Et_2NCS_2)_2}$ can be prepared in good yield by this reaction [28].

When an equimolar quantity of $\mathrm{Et_2NCS_2Na}$ is added to $\mathrm{Te(Et_2NCS_2)_2}$ (2.1×10^{-3} M) in acetonitrile at a scan rate of 100 mV s^{-1} and at a gold disc electrode, two oxidation peaks (−0.81 and −0.74 V *versus* $\mathrm{Fc^+/Fc}$) are observed on the reverse scan subsequent to the primary reduction process. At a faster scan rate (200 mV s^{-1}), only one such peak is observed. It occurs at a potential corresponding to the oxidation of $[\mathrm{Te(Et_2NCS_2)_2}]^{2-}$ (Fig. 1B). However, when the concentration of $\mathrm{Et_2NCS_2Na}$ is increased (7.9×10^{-3} M), three anodic peaks appear (−0.84, −0.67 and −0.37 V *versus* $\mathrm{Fc^+/Fc}$, Fig. 1C). When the scan rate is reduced to 20 mV s^{-1}, the peaks coalesce into a single broad peak at −0.74 V with a shoulder at −0.85 V (*versus* $\mathrm{Fc^+/Fc}$) as shown in Fig. 5.

A scan towards positive potentials, initiated just prior to the reduction process (peak 1, Fig. 1) shows only one oxidation peak (Fig. 6) at −0.34 V *versus* $\mathrm{Fc^+/Fc}$ which corresponds to peak 3′ in Fig. 1C. This is attributable to the oxidation of $\mathrm{Et_2NCS_2Na}$.

$$2\mathrm{Et_2NCS_2^-} \longrightarrow \mathrm{(Et_2NCS_2)_2} + 2e \qquad (9)$$

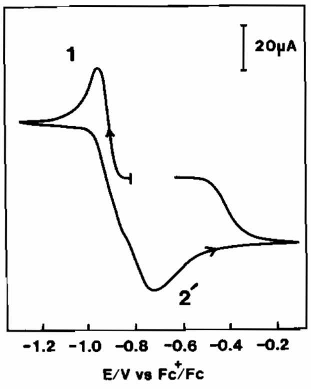


Fig. 5. Cyclic voltammetry of the reduction of $\mathrm{Te(Et_2NCS_2)_2}$ (2.1×10^{-3} M) in the presence of $\mathrm{Et_2NCS_2Na}$ (7.9×10^{-3} M) in acetonitrile/$\mathrm{Bu_4NBF_4}$ (0.1 M) at a gold disc electrode and 20 mV s^{-1} scan rate.

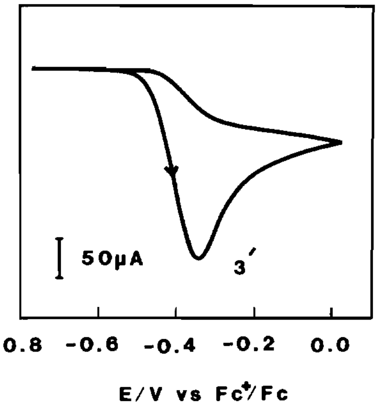
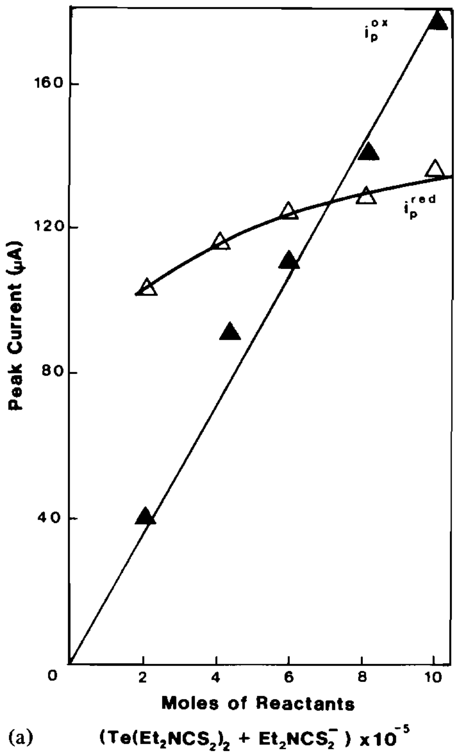
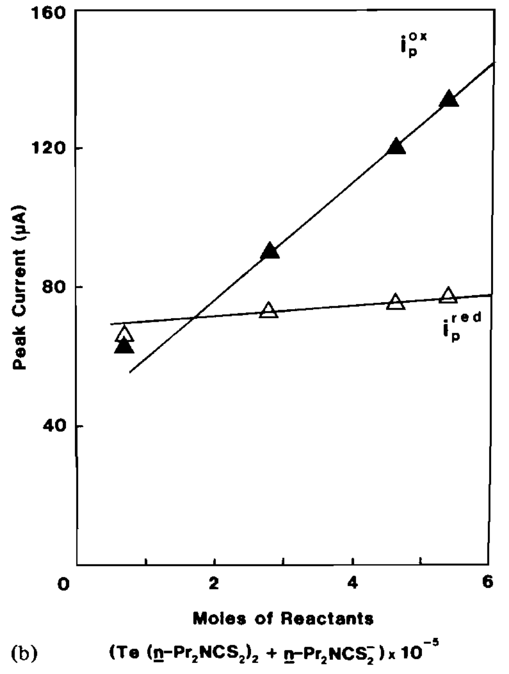


Fig. 6. Cyclic voltammetry of the reduction of a mixture of $Te(Et_2NCS_2)_2$ (1.9×10^{-3} M) and Et_2NCS_2Na (7×10^{-3} M) at a gold disc electrode in acetonitrile/Et_4NClO_4 (0.1 M) at 200 mV s^{-1} scan rate.

The voltammogram also confirms that peak 2′ (Fig. 1C) does not arise from the reaction of $Te(Et_2NCS_2)_2$ and Et_2NCS_2Na.

The variation of peak 1′ current shows a linear dependency on the concentration of $Te(Et_2NCS_2)_2$ and Et_2NCS_2Na (Fig. 7). A similar study of peak 1 currents shows only a minor dependence on these reactants. Comparable results were obtained by the addition of $n\text{-}Pr_2NCS_2Na$ to $Te(n\text{-}Pr_2NCS_2)_2$ (Fig. 7b) whereas the addition of $i\text{-}Bu_2NCS_2Na$ to $Te(i\text{-}Bu_2NCS_2)_2$ under identical conditions showed a much reduced dependency of peak 1′ current on the addition of $i\text{-}Bu_2NCS_2Na$ (Fig. 7c). In acetone solution only a broad peak 2′ is observed when excess $R_2NCS_2^-$ is added to $Te(i\text{-}Bu_2NCS_2)_2$.





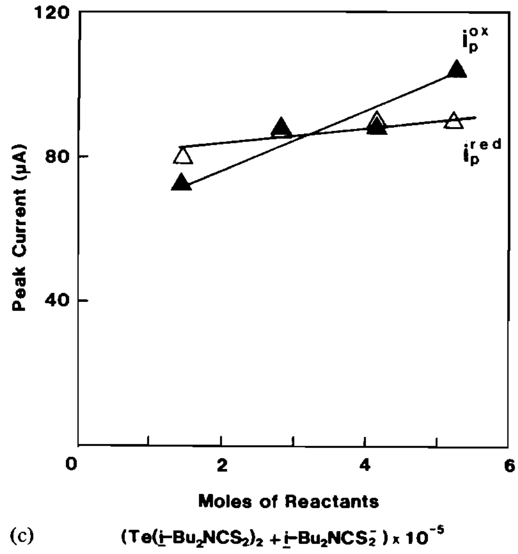


Fig. 7. Variation of peak current with the progressive addition of R_2NCS_2Na to $Te(R_2NCS_2)_2$ compounds as determined from cyclic voltammetry in acetonitrile/Bu_4NBF_4 (0.1 M) at a gold disc electrode and 200 mV s^{-1} scan rate. Initial peak currents correspond to $Te(R_2NCS_2)_2$ alone.

The results indicate that the dithiocarbamate is regenerating the reduced species subsequent to its reoxidation. As this reaction has little effect on the $Te(R_2NCS_2)_2$ reduction peak (1) it implies the existence of a reactive intermediate formed after the oxidation of $[Te(R_2NCS_2)_2]^{2-}$. This provides some evidence for the existence of the one-electron reduced intermediate species $[Te(R_2NCS_2)_2]^-$.

$$[Te(R_2NCS_2)_2]^{2-} \rightleftharpoons [Te(R_2NCS_2)_2]^- + e \qquad (10)$$

$$2[Te(R_2NCS_2)_2]^- + 2R_2NCS_2^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} 2[Te(R_2NCS_2)_2]^{2-} + (R_2NCS_2)_2 \qquad (11)$$

The stability of this species appears to depend on the substituent R group in the following order Et > n-Pr > i-Bu as observed in Fig. 7. At low scan rates (20 mV s^{-1}) peaks 1′, 2′ and 3′ merge into one broad peak (Fig. 5) which is consistent with the exchange process described in eqn. (11).

These reactions are also affected by the nature of the electrode. At the platinum electrode, at a scan rate of 100 mV s^{-1}, the narrow reduction peak 1 may be due to the presence of an electrode adsorption process (Fig. 8). In addition, peaks 1′ and 2′ observed at the gold electrode are replaced by a single peak at the platinum electrode while at the glassy carbon electrode there appears to be no interaction between the reduction products and Et_2NCS_2Na (Fig. 9). This may imply a two-electron reduction at the glassy carbon electrode.

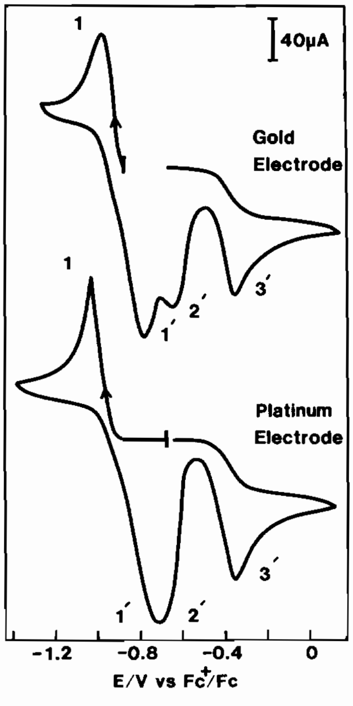


Fig. 8. Cyclic voltammetry of the reduction of $Te(Et_2NCS_2)_2$ (1.9×10^{-3} M) in the presence of Et_2NCS_2Na (7×10^{-3} M) in acetonitrile/Et_4NClO_4 (0.1 M) at 100 mV s^{-1} scan rate at gold and platinum electrodes.

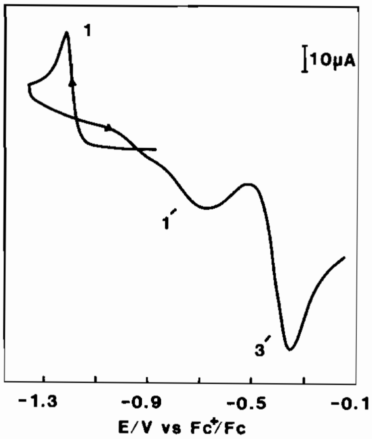


Fig. 9. Cyclic voltammetry of the reduction of $Te(Et_2NCS_2)_2$ (9×10^{-4} M) in the presence of Et_2NCS_2Na (3.8×10^{-3} M) in acetonitrile/Et_4NClO_4 (0.1 M) at a glassy carbon disc electrode and 100 mV s^{-1} scan rate.

Although there is electrochemical evidence to support the existence of a one-electron reduced species, $[Te(Et_2NCS_2)_2]^-$, it must be acknowledged that tellurium(I) is an unusual oxidation state for this type of compound and this species could be too short lived for unambiguous detection on the cyclic voltammetry time scale.

Oxidation Processes

Subsequent to the observation of the $Te(Et_2NCS_2)_2/[Te(Et_2NCS_2)_2]^{2-}$ couple, two oxidation peaks, 4′ and 5′, are observed in dimethylformamide at positive potentials with respect to Fc^+/Fc (Fig. 4, Table 4). A scan in a direction of increasingly positive potentials however, reveals only one oxidation peak 5′ at approximately +0.5 V *versus* Fc^+/Fc as peak 4′ is the Te^0 anodic stripping peak.

Peak 5′ represents a chemically irreversible oxidation process which is independent of any other electrode process. It is therefore assigned to the oxidation of $Te(Et_2NCS_2)_2$. Controlled potential electrolysis suggests the transfer of two electrons per molecule although the high background current near the potential limit of the solvent gave some uncertainty to this measurement. The assignment of a two-electron oxidation is supported by the observation of similar limiting currents for both the reduction process (eqn. (1)) and this oxidation process (eqn. (12)) as determined at a rotating gold disc electrode in dimethylformamide.

$$Te(Et_2NCS_2)_2 \longrightarrow [Te(Et_2NCS_2)_2]^{2+} + 2e \qquad (12)$$
$$\downarrow$$
$$\text{products}$$

TABLE 4. Oxidation of $Te(Et_2NCS_2)_2$ at a gold disc electrode at 25 °C

Solvent	Scan rate (mV s^{-1})	E/V vs. Fc^+/Fc			
		$Ep^{ox}(1)$	$Ep^{ox}(2)$	$Ep^{ox}(3)$	$Ep^{ox}(4)$
Dimethylformamide[a]	500	+0.11[b]		+0.56	
	200	+0.16[b]		+0.53	
	100	+0.16[b]		+0.52	
	50	+0.12[b]	+0.29[b]	+0.50	
	20	+0.10[b]	+0.26[b]	+0.48	
Acetonitrile[a,b]	500	+0.35		+0.78	+1.13
	200	+0.36		+0.75	+1.10
	100	+0.33		+0.74	+1.08
	50	+0.32	+0.64	+0.73	+1.08
	20	+0.30	+0.64		+1.06
Acetonitrile[a,c]	500	+0.32			
	200	+0.35			
	100	+0.36			
	50	+0.34			
	20	+0.32			
Acetone[b,d]	500	+0.30		0.54	+1.16
	200	+0.28		0.48	+1.10
	100	+0.28		0.45	+1.07
	50		+0.35		+1.05
	20		+0.35		+1.04
Acetone[c]	500	+0.49		+0.59	+1.17
	200	+0.48		+0.56	+1.11
	100	+0.48		+0.60	+1.08
	50	+0.47		+0.53	+1.04
	20	+0.44			+1.04

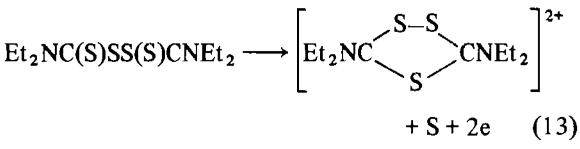
[a] Supporting electrolyte, 0.1 M Et_4NClO_4. [b] Peak(s) appears after scanning the $Te(Et_2NCS_2)_2/[Te(Et_2NCS_2)_2]^{2-}$ couple. [c] Positive scan direction. [d] Supporting electrolyte, 0.1 M Bu_4NBF_4.

The oxidation is followed by the formation of products which are subsequently reduced at peak 2 and 3 (Fig. 4). Peak 3 has also been observed in acetone under similar circumstances.

The exact nature of the products is not known but the potential of the reduction peak 2 indicates that at least one of the products is closely related to $Te(Et_2NCS_2)_2$ implying that the tellurium is in the +2 oxidation state.

In acetonitrile after scanning the $Te(Et_2NCS_2)_2/[Te(Et_2NCS_2)_2]^{2-}$ couple, the oxidation processes at positive potentials appear less clearly defined than in dimethylformamide and give rise to a number of chemically irreversible oxidation peaks (Table 4). There is also an absence of a well defined $Te(Et_2NCS_2)_2$ oxidation which occurs as a broad peak at approximately +0.35 V (*versus* Fc^+/Fc). While in acetone this oxidation, depending on the scan rate, appears as one or two small peaks (by comparison with those observed after scanning the reduction process) at approximately +0.5 V (*versus* Fc^+/Fc). A peak at approximately +1 V (*versus* Fc^+/Fc) is also evident. In acetonitrile the Te^0 stripping peak occurs between +0.73 and +0.78 V (*versus* Fc^+/Fc) while in acetone it lies between +0.3 and +0.4 V (*versus* Fc^+/Fc) depending on the scan rate.

The data is consistent with the oxidation of $(Et_2NCS_2)_2$ [2] at +1 V (*versus* Fc^+/Fc) as indicated by a cyclic voltammogram of Et_2NCS_2Na.


(13)

The presence of $(Et_2NCS_2)_2$ implies the decomposition of $Te(Et_2NCS_2)_2$ after oxidation.

Reduction of $Te(R_2NCS_2)_4$

The reduction of $Te(R_2NCS_2)_4$ compounds (Table 5) occurs at more negative potentials to those of $Te(R_2NCS_2)_2$, implying that the higher oxidation state is more thermodynamically stable if the reduction is metal based. Cyclic voltammetry at gold, platinum and glassy carbon electrodes indicates that this phenomenon is not electrode specific and tellurium-125 NMR studies confirmed the presence of $Te(R_2NCS_2)_4$ in acetone solution [28].

TABLE 5. Cyclic voltammetry of the reduction of $Te(R_2NCS_2)_4$ compounds in various solvents at a gold disc electrode and a scan rate of 200 mV s^{-1} at 25 °C

Compound	Solvent	$Ep^{red}(1)$	$Ep^{red}(2)$	$Ep^{ox}(1)$	$Ep^{ox}(2)$	$Ep^{ox}(3)$
$Te(Et_2NCS_2)_4$	dimethylformamide[a]	−1.63	−1.32	−0.79	−0.65	
	acetonitrile[b]	−1.63	−0.95	−0.78	−0.67	
	acetone[b,c]	−1.68		−0.85	−0.72	−0.49
	dichloromethane[b]	−1.99	−1.25	−0.74		−0.45
$Te(i\text{-}Pr_2NCS_2)_4$	acetonitrile[b]	−1.93	−1.10	−0.79		−0.56
	acetone[b]	−1.92	−1.32	−0.86	−0.63	
$Te(n\text{-}Pr_2NCS_2)_4$	acetonitrile[b]	−1.76	−0.95	−0.81	−0.68	
	acetone[b]	−1.84	−1.26	−0.87	−0.77	−0.51
$Te(Bz_2NCS_2)_4$[d]	acetone[b]		−0.99	−0.78		−0.37

[a] Supporting electrolyte, 0.1 M Et_4NClO_4. [b] Supporting electrolyte, 0.1 M Bu_4NBF_4. [c] 100 mV s^{-1} scan rate. [d] Insoluble in acetonitrile.

The reduction process is chemically irreversible in dimethylformamide, acetonitrile, acetone and dichloromethane leading to the formation of decomposition products (Fig. 10). Controlled potential electrolysis at a platinum gauze electrode indicates the transfer of four electrons per molecule on the coulometric time scale (Table 1).

$$Te(Et_2NCS_2)_4 + 4e \longrightarrow [Te(Et_2NCS_2)_4]^{4-} \longrightarrow \text{products} \qquad (14)$$

The steady increase of a reduction peak 1 at a similar potential to that of the reduction of $Te(Et_2NCS_2)_2$ indicates some chemical decomposition is occurring during the course of the electrochemistry experiments. NMR studies have shown this decomposition to be reversible [28].

$$Te(Et_2NCS_2)_4 \rightleftharpoons Te(Et_2NCS_2)_2 + (Et_2NCS_2)_2 \qquad (15)$$

In acetonitrile, the appearance of peaks 1′ and 2′ (Fig. 10) correspond to similarly designated peaks in Fig. 1. They are not dependent on the formation of $Te(Et_2NCS_2)_2$ from the decomposition of $Te(Et_2NCS_2)_4$ (eqn. (15)). However, in acetone, three oxidation peaks are observed at the gold electrode and only one peak, at −0.49 V (*versus* Fc^+/Fc) is observed at the platinum and glassy carbon electrodes (Table 5).

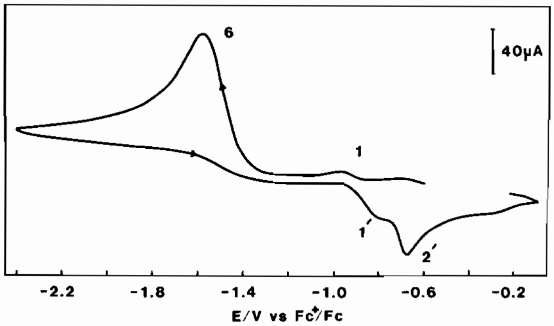


Fig. 10. Cyclic voltammetry of the reduction of $Te(Et_2NCS_2)_4$ at a gold disc electrode in acetonitrile/Bu_4NBF_4 (0.1 M) at 100 mV s^{-1} scan rate.

Holding the potential slightly negative to that of the reduction peak 6 does not give rise to a Te^0 stripping peak at positive potentials as observed in the case of $Te(Et_2NCS_2)_2$. This implies that Te^0 is not a product of the reduced species. However, it has already been shown that the deposition of Te^0 is inhibited in the presence of excess $R_2NCS_2^-$.

Consistent with this observation is the evidence of some $[Te(Et_2NCS_2)_2]^{2-}$ being formed at the gold electrode. Without taking into consideration the redox properties of $Te(Et_2NCS_2)_2$ the decomposition of the reduction product, on the coulometric time scale, may be expressed in the following simple terms

$$[Te(Et_2NCS_2)_4]^{4-} \longrightarrow [Te(Et_2NCS_2)_2]^{2-} + 2Et_2NCS_2^- \qquad (16)$$

These assignments are also supported by the presence of oxidation peaks at −0.65 and −0.4 V (*versus* Fc^+/Fc) observed in the cyclic voltammogram of an acetonitrile solution after exhaustive electrolysis of $Te(Et_2NCS_2)_4$. They correspond to peaks 1′ and 2′ in Fig. 1.

Taking into consideration the reduction potential of $Te(Et_2NCS_2)_2$, the data suggest that the reduction of $Te(Et_2NCS_2)_4$ proceeds via a two-electron step both on the cyclic voltammetry and electrolysis time scales to form $Te(Et_2NCS_2)_2$ which is spontaneously reduced in the manner described previously.

$$Te(Et_2NCS_2)_4 + 2e \longrightarrow Te(Et_2NCS_2)_2 + 2Et_2NCS_2^- \qquad (17)$$

The two-electron reduction is consistent with the decomposition of $Te(R_2NCS_2)_4$ compounds in solution by intramolecular electron transfer, observed during NMR studies, to form $Te(R_2NCS_2)_2$ and $(R_2NCS_2)_2$ (eqn. (15)) [28].

Similar behaviour has also been observed in the decomposition of tetrathiolate analogues [19].

$$Te(SR)_4 \longrightarrow Te(SR)_2 + RSSR \qquad (18)$$

The most intriguing aspect of the reduction of $Te(R_2NCS_2)_4$ compounds is that it occurs at a more negative potential than those of the $Te(R_2NCS_2)_2$ analogues although the thermal (and thermodynamic) stability of the Te(IV) compounds is lower than that of the Te(II) derivatives.

The possibility of reduction peak 6 (Fig. 10) arising from an exchange between $Te(R_2NCS_2)_4$ and the products of its decomposition, $Te(R_2NCS_2)_2$ and $(R_2NCS_2)_2$, was considered (eqn. (15)). If no exchange reaction takes place then the reduction peaks of the three components should be observed. However, if exchange occurs between two components then only one peak will arise at a potential dependent on the relative concentrations of the components [31].

The addition of $Te(Et_2NCS_2)_2$ (1.3×10^{-3} M) to $Te(Et_2NCS_2)_4$ (2×10^{-3} M) in dimethylformamide produced an identifiable $Te(Et_2NCS_2)_2$ reduction peak with the $Te(Et_2NCS_2)_4$ peak remaining unchanged. When the $Te(Et_2NCS_2)_2$ concentration was increased to 6.2×10^{-3} M the $Te(Et_2NCS_2)_4$ reduction peak gave the appearance of a narrow adsorption peak.

A mixture of $(Et_2NCS_2)_2$ (15×10^{-3} M) and $Te(Et_2NCS_2)_4$ (2×10^{-3} M) resulted in a broad composite reduction peak with at least two discernible peak potentials, -1.45 and -1.53 V (*versus* Fc^+/Fc) and a minor broad peak at -1.9 V (*versus* Fc^+/Fc). The latter peak corresponds to the reduction of $(Et_2NCS_2)_2$ and as the peak current was considerably smaller than that of the composite peak it indicates that most of the disulfide was being reduced at less negative potentials in the vicinity of -1.5 V (*versus* Fc^+/Fc). The results clearly indicate some interaction between $(Et_2NCS_2)_2$ and $Te(Et_2NCS_2)_4$ although no significant change occurs in the $Te(Et_2NCS_2)_4$ reduction peak potential. Thus the very negative reduction potential of the $Te(R_2NCS_2)_4$ compounds appears to be an intrinsic property rather than the result of a simple chemical reaction.

The decomposition of $Te(Et_2NCS_2)_4$ may be assisted by the relatively short interligand sulfur distances of 3.17 Å [32] and the electrochemical reduction may occur via the partially formed disulfide ligand. In the morpholinecarbodithiolate analogue [33] this distance is 3.39 Å and the compound shows a greater resistance to disulfide formation. The S–S bond length in free disulfide, $(Et_2NCS_2)_2$, is 1.999 Å [34] and the reduction potential is -2.22 V (*versus* Fc^+/Fc) at a scan rate of 100 mV s^{-1}, in acetone at a gold electrode which is at a considerably more negative potential than that of $Te(Et_2NCS_2)_4$. The proposed ligand based electrochemical reduction contradicts the general observation that the redox processes in metal dithiocarbamates are invariably metal based [2].

Conclusions

The reduction of $Te(R_2NCS_2)_2$ compounds proceeds via an overall two-electron reduction. However, on the cyclic voltammetry time scale, at the gold and platinum electrodes there is evidence for two chemically reversible one-electron reduction steps of which at least one is quasi-reversible in dimethylformamide, acetonitrile, acetone and polarity solvents such as acetone and dichloromethane. At the platinum electrode electron transfer appears to be slower than at the gold electrode in all these solvents while at the glassy carbon electrode a quasi-reversible two-electron reduction appears to occur.

The reduction of $Te(R_2NCS_2)_4$ compounds occurs at potentials more negative to those of tellurium(II) analogues and proceeds via a four-electron reduction on the coulometric time scale. Initially an irreversible two-electron reduction is involved in the formation of the intermediate $Te(R_2NCS_2)_2$. The reduction is thought to be ligand mediated although the details of the process are not known.

Acknowledgement

The author is grateful to Professor A. M. Bond for helpful discussions.

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