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Electrochemical Redox Behaviour of Dithiocarbamates and Diselenocarbamates of Nickel, Palladium and Platinum

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An electrochemical study of $M(dtc)_2$ complexes, M = Pd, Pt, established that these complexes can be reduced to the unstable $M(dtc)_2^-$ species and irreversibly oxidized to the tris complexes, $M(dtc)_3^+$, although in low yields. A detailed study of the redox behaviour of the platinum tris compound, $Pt(dtc)_3^+$, revealed that a two electron transfer process occurred, with a very rapid decomposition of the reduced species, according to

$$Pt(dtc)_3^+ \rightarrow Pt(dtc)_3^- \rightarrow Pt(dtc)_2 + dtc^-$$

The electrochemical behaviour of the diseleno complexes, $M(dsc)_2$ and electrochemically generated $M(dsc)_3^+$, M = Ni, Pd, Pt, closely parallels that of their dtc congeners.

Introduction

The oxidation–reduction behaviour of metal dithiocarbamates has attracted wide attention [1] and much effort has recently been made to elucidate the electrochemical behaviour of these complexes [2]. From the nickel triad only the nickel dithiocarbamates have been studied in detail [3], while the palladium and platinum derivatives have hardly attracted attention [4]. During their investigations on the chemical oxidation of the biscomplexes $M(n\text{-}Bu_2dtc)_2$, M = Pd, Pt, Willemse and Cras isolated two types of metal(IV) compounds, *i.e.* the tris complexes $M(dtc)_3^+$ [5] and the iodo compounds $Pd(dtc)_2I_2$ and *cis*- and *trans*-$Pt(dtc)_2I_2$ [6]. In general the Pd(IV) dithiocarbamates are not very stable in solution.

An interesting feature of the $M^{n+}R_2dtc^-$ system of the nickel triad is the occurrence of an oxidation state III for nickel in $Ni(dtc)_3$ [3, 7] and $Ni(dtc)_2I$ [8]. Compounds of Pd(III) and Pt(III) have not been reported so far. Therefore, an electrochemical investigation concerning the occurrence of this oxidation state for palladium and platinum seems to be worthwhile.

In this paper we describe the electrochemical redox behaviour of the bis complexes, $M(R_2dtc)_2$ and the tris complexes $M(R_2dtc)_3^+$ M = Pd, and Pt. The redox behaviour of the diselenocarbamates, $M(R_2dsc)_2$ and $M(R_2dsc)_3^+$, M = Ni, Pd and Pt, will also be reported.

TABLE I. Electrochemical Data for the Reduction of $Pd(R_2dtc)_2$ and $Pt(R_2dtc)_2$.[a]

Complexes		Normal Pulse Polarography		AC Voltammetry		Cyclic Voltammetry		
		$E_{1/2}$ (V)	$E_{3/4} - E_{1/4}$ (mV)	E_p (V)	$\Delta E_{1/2}$[b] (mV)	$E_p^{cat.}$ (V)	ΔE_p[c] (mV)	$\frac{i_{cat.}}{i_{anod.}}$
$Pd(R_2dtc)_2$	R							
	i-Pr	−1.60	68	−1.59	143	−1.64	108	1.1
	Et	−1.50	88	−1.48	155	−1.56	131	1.5
	n-Bu	−1.50	68	−1.50	133	−1.56	114	1.3
	Ph	−1.44	58	−1.44	118	−1.47	72	1.4
	Bz	−1.39	56	−1.37	113	−1.40	76	1.2
$Pt(R_2dtc)_2$								
	Et					−2.09		
	Bu	−2.08				−2.13		
	i-Pr					−2.12		

[a] In acetone *vs.* a Ag/AgCl (0.1 *M* LiCl–acetone) reference electrode. [b] Width at half peak height. [c] Cathodic to anodic peak potential separation.

TABLE II. Electrochemical Data for the Oxidation of $Pd(R_2dtc)_2$ and $Pt(R_2dtc)_2$.[a]

Complexes		Normal Pulse Polarography			Cyclic Voltammetry $E_p^{anod.}$ (V)
		$E_{1/2}$ (V)	$E_{3/4} - E_{1/4}$ (mV)	i_l/conc. (mA/mol)	
$Pd(R_2dtc)_2$	R				
	i-Pr	1.31	90	58	1.40
	Et	1.31	115	67	1.40
	Bu	1.35	83	62	1.44
	Ph	1.37	80	40	1.44
	Bz	1.49	78	54	1.55
$Pt(R_2dtc)_2$					
	i-Pr	1.02	115	69	1.09
	Et	1.09	138	49	1.20
	Bu	1.12	118	80	1.19
	Ph	1.16	130	75	1.19
	Bz	1.22	108	54	1.30

[a] In CH_2Cl_2 solutions *vs.* a saturated calomel electrode.

Results and Discussion

Reduction of $Pd(R_2dtc)_2$ and $Pt(R_2dtc)_2$

The palladium complexes undergo a reduction at a quite negative potential (–1.34 to –1.60 V), Table I. The experimental data obtained with the various applied techniques are in good agreement with each other. In the cyclic voltammograms anodic peaks are observed, indicating that formed $Pd(R_2dtc)_2^-$ can be re-oxidized. The ratio of cathodic to anodic peak currents, well above unity suggests that the formed palladium(I) species $Pd(R_2dtc)_2^-$ has only a moderate stability in acetone solution, although no free ligand oxidation peak is observed. From these observations it can be concluded that the reduction behaviour of the palladium complexes resembles that of the nickel compounds [3].

For the platinum bis complexes a reduction was observed at very low potentials. Cyclic voltammetry showed no associated oxidation peak. With the reduction loss of ligand occurs, because a ligand oxidation peak is observed at 0.15 V [3]. Further detailed study is severely hindered by the low reduction potential, at the limit of the potential range of the solvent.

Oxidation of $Pd(R_2dtc)_2$ and $Pt(R_2dtc)_2$

The electrochemical oxidation of both these complexes has been studied in CH_2Cl_2 solutions (Table II). These oxidations occur at relatively high potentials, 1.10 V for $Pt(R_2dtc)_2$ and 1.35 V for $Pd(R_2dtc)_2$. Because of these high potentials acetone is less suitable to study the oxidation of the palladium complexes; furthermore the probably formed $Pd(dtc)_3^+$ is not very stable in solution, so electrolysis experiments were only carried out with the platinum complexes.

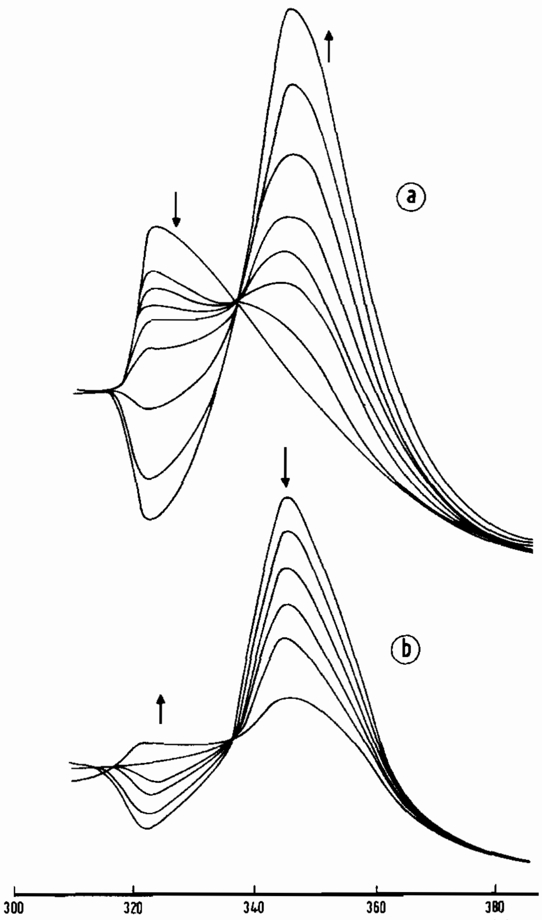

Fig. 1. Electrolysis in acetone solutions (0.1 *M* Bu_4NClO_4) followed spectrophotometrically. (a) Oxidation of $Pt(n\text{-}Bu_2dtc)_2$. (b) Reduction of $Pt(i\text{-}Pr_2dtc)_3ClO_4$.

Controlled potential coulometry of $Pt(Bu_2dtc)_2$ at a potential of 1.35 V in acetone at a gold electrode

TABLE III. Electrochemical Reduction of $Pd(R_2dtc)_3^+$ and $Pt(R_2dtc)_3^+$.[a]

Compound	Normal Pulse Polarography		Cyclic Voltammetry			
	$E_{1/2}$ (V)	$E_{3/4} - E_{1/4}$ (mV)	$E_p^{cat.}$	Other Waves		
				b	c	d
$Pd(Bu_2dtc)_3^+$	0.11	53	0.12		1.55	−1.56
$Pt(Et_2dtc)_3^+$	−0.47	53	−0.55	0.16	1.38	−2.11
$Pt(Bu_2dtc)_3^+$	−0.48	53	−0.55	0.17	1.33	−2.10
$Pt(i\text{-}Pr_2dtc)_3^+$	−0.58	53	−0.65	0.04	1.31	−2.12

[a] In acetone *vs.* Ag/AgCl electrode. [b] Oxidation of the released free ligand. [c] Oxidation of the formed bis complex, $M(R_2dtc)_2$. [d] Reduction peak of the bis complex.

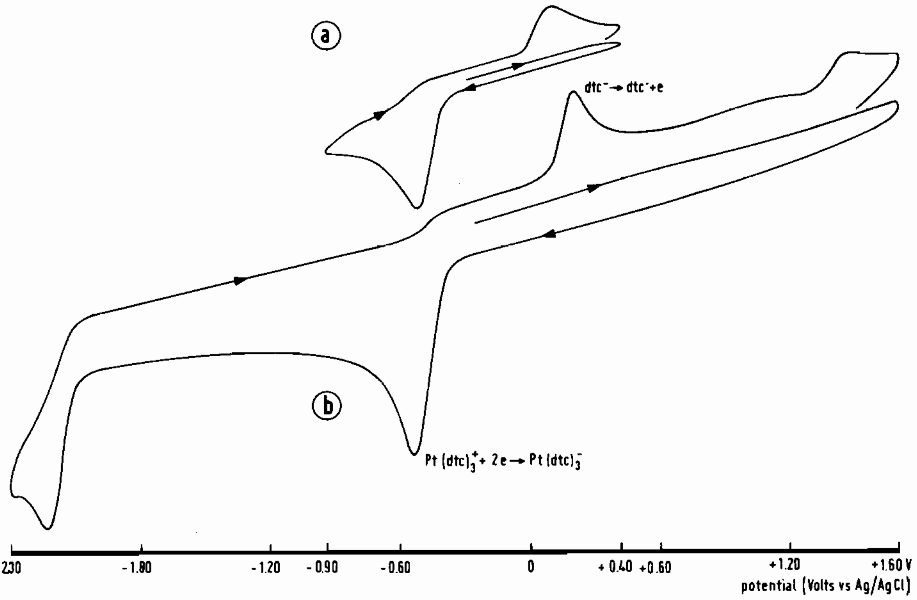

Fig. 2. Cyclic voltammograms of $Pt(n\text{-}Bu_2dtc)_3ClO_4$ in acetone. (a) Potential range −0.90 to 0.40 and (b) −2.30 to 1.60 V.

afforded *n* values of 0.82, 0.82 and 0.86 and $Pt(Et_2dtc)_2$ gave values of 0.88 and 0.94. With a platinum electrode no reliable results could be obtained, due to absorption of oxidation products.

Cyclic voltammograms recorded after the electrolysis showed that the tris complex was present in a low concentration. No free ligand was detected in the solution. Spectrophotometric monitoring of the electrolysis (Fig. 1) showed also the development of the Pt(IV) species at the expense of $Pt(R_2dtc)_2$.

From these data it is concluded that the oxidation of $M(R_2dtc)_2$, M = Pd, Pt, follows a complex electrode process, in which the oxidation products are decomposed. This in contrast to the electrochemical oxidation of $Ni(R_2dtc)_2$ at 0.90 V, for which in the overall process a stoichiometric amount (3:2) of $Ni(R_2dtc)_3^+$ was obtained [3].

Reduction of $Pd(Bu_2dtc)_3^+$

From chemical reaction studies [6] it is known that compounds containing this cation are not very stable in solution, so no detailed study can be made. The compound exhibits a relatively facile reduction at 0.11 V (Table III). Cyclic voltammograms show that the decomposition product is mainly the bis complex $Pd(Bu_2dtc)_2$. We therefore suggest the following reduction sequence:

$$Pd(dtc)_3^+ + e \rightarrow Pd(dtc)_3^0 \rightarrow Pd(dtc)_2 + \text{products}$$

Reduction of $Pt(R_2dtc)_3^+$

The tris complexes $Pt(R_2dtc)_3ClO_4$ show only one reduction at about −0.50 V *vs.* Ag/AgCl electrode (Table III). A detailed cyclic voltammetric study of this reduction was made to elucidate the electrochem-

TABLE IV. Electrochemical Reduction of Metal Diselenocarbamates.[a]

Complexes	Normal Pulse Polarography		AC Voltammetry		Cyclic Voltammetry		
	$E_{1/2}$ (V)	$E_{3/4} - E_{1/4}$ (mV)	E_p (V)	$\Delta E_{1/2}$[b] (mV)	$E_p^{cat.}$ (V)	ΔE_p[c] (mV)	$\frac{i_p^{cat.}}{i_p^{anod.}}$
$Ni(Et_2dsc)_2$	−1.34	55	−1.36	123	−1.43	148	1.3
$Ni(Bu_2dsc)_2$	−1.38	71	−1.36	123	−1.42	105	1.2
$Pd(Et_2dsc)_2$	−1.54	55	−1.53[d]	98	−1.59	111	1.9
$Pd(Bu_2dsc)_2$	−1.56	55	−1.54[d]	122	−1.60	101	1.4
$Pt(Et_2dsc)_2$	−1.87				−1.90		
$Pt(Bu_2dsc)_2$	−2.10				−2.04		

[a] In acetone *vs.* Ag/AgCl electrode. [b] Width at half peak height. [c] Cathodic to anodic peak potential separation. [d] AC frequency 35 Hz.

ical reaction process. Starting at 0.0 V in anodic direction (potential range −0.90 to 0.40 V) only in the second scan, not in the first one, an oxidation peak at 0.17 V was observed (Fig. 2a) which is ascribed to the oxidation of free dtc^-. This indicates that after the reduction of $Pt(dtc)_3^+$ loss of ligand occurs. Extension of the potential range (−2.30 to +1.60 V) showed that also the bis complex $Pt(dtc)_2$ is generated, for in the voltammograms peaks appeared at 1.33 and −2.10 V which were also observed for the bis complexes (Fig. 2b). Coulometric reduction at −0.75 V *vs.* Ag/AgCl electrode in acetone afforded *n* values of 2.0 for $Pt(Bu_2dtc)_3ClO_4$, 1.8 for $Pt(Bu_2dtc)_3Cl$ and 2.1 for $Pt(i\text{-}Pr_2dtc)_3ClO_4$. These controlled potential electrolyses were performed at a gold electrode, because with a platinum electrode irreproducible results were obtained. Spectrophotometric monitoring of the reduction of $Pt(i\text{-}Pr_2dtc)_3^+$ showed that the absorption peak at 323 nm disappeared and an intense peak at 343 nm appeared, indicating that the $Pt(i\text{-}Pr_2dtc)_2$ concentration increased at the expense of the tris complex, $Pt(i\text{-}Pr_2dtc)_3ClO_4$ (Fig. 1).

From these observations it is concluded that a two electron reduction takes place according to the equation

$$Pt(R_2dtc)_3^+ + 2e \rightarrow Pt(R_2dtc)_3^- \rightarrow Pt(R_2dtc)_2 + R_2dtc^-$$

followed by a rapid dissociation of the Pt(II) species, $Pt(R_2dtc)_3^-$, into the bis complex and free ligand. Even with high scan rates (up to 20 V sec^{-1}) no indication of a re-oxidation of the reduced species could be detected in the voltammograms. Hence, it can be concluded that this anionic species is very unstable in acetone solutions and dissociates immediately in this solvent.

These results differ completely from what is observed [3] for the electrochemical reduction of the similar nickel complexes, $Ni(R_2dtc)_3^+$, for which it has been established that the reduction products, $Ni(R_2dtc)_3^0$ and $Ni(R_2dtc)_3^-$, although also unstable, are still detectable at rather low scan rates (200 mV sec^{-1}).

TABLE V. Electrochemical Oxidation of Metal Diselenocarbamates.[a]

	Normal Pulse Voltammetry		Cyclic Voltammetry
	$E_{1/2}$ (V)	$E_{3/4} - E_{1/4}$ (mV)	$E_p^{anod.}$ (V)
$Ni(Et_2dsc)_2$	0.60	95	0.82
$Ni(Bu_2dsc)_2$	0.58	78	0.76
$Pd(Et_2dsc)_2$	0.95	70	1.09
$Pd(Bu_2dsc)_2$	0.95	90	1.07
$Pt(Et_2dsc)_2$	0.73	75	0.86
$Pt(Bu_2dsc)_2$	b	b	0.74

[a] In acetone *vs.* Ag/AgCl electrode. [b] Too insoluble for reliable data.

Diselenocarbamates

Reduction of $M(R_2dsc)_2$

The electrochemical data for the reduction of $M(R_2dsc)_2$, M = Ni, Pd and Pet, R = Et and Br are summarised in Table IV.

In their reduction behaviour the diseleno complexes closely parallel the dtc complexes and nearly the same half-wave potentials are found. $Ni(dsc)_2$ and $Pd(R_2dsc)_2$ are reduced in a one electron step. Cyclic voltammetry shows the reoxidations of the reduced species. The formed species, $M(R_2dsc)_2^-$, M = Ni, Pd, are only moderately stable in acetone as indicated by the ratio of cathodic to anodic peak currents. The platinum complexes are reduced at the

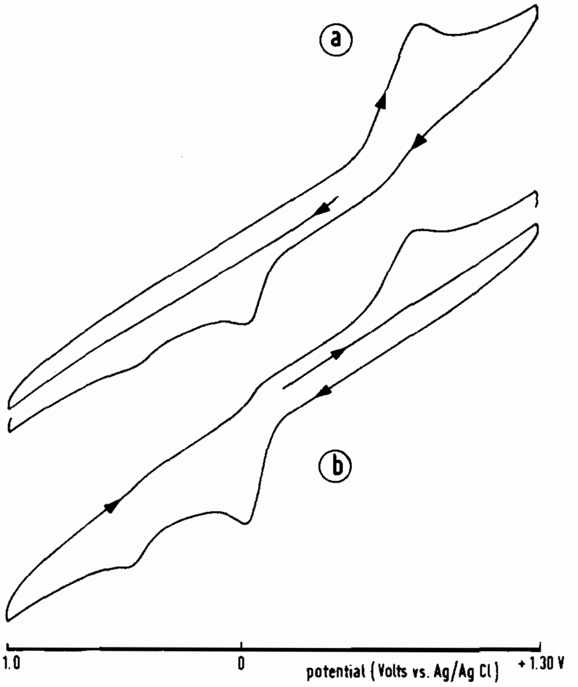

Fig. 3. Oxidative electrolysis of $Ni(Etdsc)_2$ in acetone (0.1 *M* Bu_4NClO_4). Voltammetric curves: (a) before and (b) after the electrolysis.

lower limit of the potential range of the solvent, so only the half-wave potentials could be determined.

Oxidation of $M(R_2dsc)_2$; electrochemical generation of $M(R_2dsc)_3^+$, M = Ni, Pd, Pt

The metal bis diselenocarbamates are all oxidized at a platinum electrode in acetone solution at clearly lower potentials as compared with the analogous dithiocarbamates (Table V).

Controlled potential electrolysis at 0.62 V affords for the oxidation of $Ni(Bu_2dsc)_2$ *n* values of 1.37 and 1.40, indicating that the same oxidation reaction mechanism is operating as reported for the dithiocarbamato complex [3]:

$$3Ni(R_2dsc)_2 \rightarrow 2Ni(R_2dsc)_3^+ + Ni^{2+} + 4e$$

The solution obtained after complete oxidation was subjected to a detailed cyclic voltammetric investigation (Fig. 3). The formed tris complex exhibits a reduction wave at 0.03 V and in the voltammogram an indication for a further reduction is found at −0.48 V (at a scan rate of 200 mV s^{-1}). When the scan rate is increased (up to 18 V s^{-1}) a much better resolved anodic peak for the reoxidation of $Ni(R_2dsc)_3^0$ appeared and the ratio of the anodic to cathodic peak currents approaches 1.0. The subsequent reduction of $Ni(R_2dsc)_3^0$ is now also demonstrated at these high scan rates by a well resolved peak at −0.48 V.

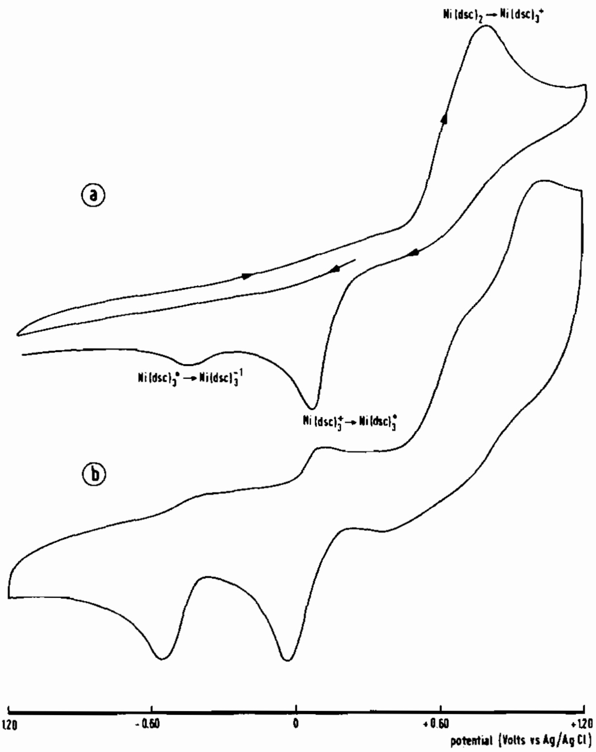

Fig. 4. Cyclic voltammetric generation of $Ni(Et_2dsc)_3^+$ with a scan rate of (a) 0.40 V/sec and (b) 24.0 V/sec.

TABLE VI. Redox Potentials for Electrochemical Generated $M(R_2dsc)_3^+$ Complexes.[a]

Complexes[b]	$E_p^{cathodic}$ (V)	
$Ni(Et_2dsc)_3^+$	0.03	−0.48
$Ni(Bu_2dsc)_3^+$	0.08	−0.42
$Pd(Et_2dsc)_3^+$	−0.09	
$Pd(Bu_2dsc)_3^+$	−0.10	
$Pt(Et_2dsc)_3^+$	−0.61	
$Pt(Bu_2dsc)_3^+$	−0.64	

[a] Data obtained by cyclic voltammetry. [b] $M(R_2dsc)_3^+$ complexes generated by cyclic voltammetric oxidation of the analogous bis complexes, $M(R_2dsc)_2$.

The bis complex, $Ni(R_2dsc)_2$, appeared to be a decomposition product of the reduced species, $Ni(R_2dsc)_3^0$ or $Ni(R_2dsc)_3^-$, because in the second scan (not in the first one) the oxidation wave of the bis complex appeared at 0.79 V.

The same experimental results are obtained by a careful cyclic voltammetric investigation of the bis complexes, $M(R_2dsc)_2$. By a continuous repeated anodic–cathodic scan the $Ni(R_2dsc)_2$ is oxidised to the tris compound in sufficient concentrations to

TABLE VII. Comparison of the Redox Behaviour of Dithiocarbamates and Diselenocarbamates of Ni, Pd, Pt, Cu and Au.[a]

$M(R_2dtc)_2$ and $M(R_2dsc)_2$			$M(R_2dtc)_3^+$ and $M(R_2dsc)_3^+$		
	Oxidation $E_{1/2}$, V	Reduction $E_{1/2}$, V		Reduction $E_p^{cathodic}$, V	
$Ni(Et_2dtc)_2$	0.89	−1.34	$Ni(Et_2dtc)_3^+$	0.36	−0.20
$Ni(Et_2dsc)_2$	0.60	−1.34	$Ni(Et_2dsc)_3^+$	0.09	−0.48
$Pd(Et_2dtc)_2$	1.49[b]	−1.50	$Pd(Et_2dtc)_3^+$	0.13	
$Pd(Et_2dsc)_2$	0.98	−1.54	$Pd(Et_2dsc)_3^+$	−0.06	
$Pt(Et_2dtc)_2$	1.26[b]	−2.09	$Pt(Et_2dtc)_3^+$	−0.45	
$Pt(Et_2dsc)_2$	0.73	−1.87	$Pt(Et_2dsc)_3^+$	−0.58	
$Cu(Et_2dtc)_2$[c]	0.68[b]	−0.40[b]			
$Cu(Et_2dsc)_2$[c]	0.51[b]	−0.39[b]			
$Au(Et_2dtc)_2^+$[d]		−0.08[b]			
$Au(Et_2dsc)_2^+$[d]		−0.25[b]			

[a] In acetone *vs.* Ag/AgCl electrode. [b] Corrected for measurements in CH_2Cl_2: $E_{1/2}$(acetone, Ag/AgCl) − $E_{1/2}$(CH_2Cl_2, SCE) = 0.18 V. [c] Ref. 9. [d] Ref. 10.

develop the two reduction peaks of $Ni(R_2dsc)_3^+$ at the same potentials as noted above (Fig. 4).

In the same way (by cyclic voltammetry) it was possible to generate electrochemically the palladium and platinum tris complexes to study their reduction behaviour. For each of the compounds only one reduction peak was observed, at −0.10 V for $Pd(R_2dsc)_3^+$ and at −0.61 V for $Pt(R_2dsc)_3^+$ (Table VI). No ligand oxidation peak was observed, which may be due to a low, undetectable concentration.

Conclusions

The most important parameters resulting from this study are summarised in Table VII, together with some data for copper [9] and gold [10] complexes.

The ease of reduction for metal bis dithiocarbamates as well as diselenocarbamates of the nickel triad follows the order (for $E_{1/2}$) Ni > Pd > Pt. All the nickel and palladium complexes undergo a quasi reversible reduction. Surprisingly, for one defined metal the same reduction potential is observed for both dtc and dsc complexes. This was also noted earlier for $Cu(dtc)_2$ and $Cu(dsc)_2$. Extended Hückel calculations made on $Cu(dtc)_2$ and $Cu(dsc)_2$ [11] reveal that the highest occupied molecular orbital has at most 60% metal character. Other important energy terms (like *e.g.* the reorganisation energy) seem to influence the reduction potentials in such a way that coincidently the same $E_{1/2}$ values for dtc and dsc compounds are found. This is not the case for the oxidation potentials.

For both $M(dtc)_2$ and $M(dsc)_2$ the ease of oxidation follows the order (for $E_{1/2}$) Ni < Pt < Pd. The diselenocarbamates are more readily oxidized, at lower potentials than those of the analogous dithiocarbamates. In all cases the tris complexes are formed, although for the various compounds in different yields. Only the nickel bis complexes are quantitatively converted.

The reduction of the tris compounds, $M(dtc)_3^+$ and $M(dsc)_3^+$, becomes more difficult going down the group, $E_{1/2}$ follows the order Ni < Pd < Pt. In this case, however, the dithiocarbamates are easier reduced, $E_{1/2}$(dtc) > $E_{1/2}$(dsc). Both $Ni(dtc)_3^+$ and $Ni(dsc)_3^+$ are reduced in two successive reversible steps, forming unstable complexes with nickel in the oxidation state III and II. While the re-oxidation of $Ni(dsc)_3$ can only be observed at high scan rates this compound is apparently less stable than $Ni(dtc)_3$. The $Pt(dtc)_3^+$ is directly reduced to the very unstable Pt(II) complex, $Pt(dtc)_3^-$, in a two electron transfer process.

In contrast with nickel not even a trace of a palladium or platinum complex in the oxidation state III could be detected.

Experimental

Electrochemical

All measurements were made with a three electrode Bruker E 310 modular polarograph with platinum working and auxiliary electrodes. Measurements were made on *ca.* 5×10^{-4} mol dm^{-3} depolariser in 0.1 mol dm^{-3} $[NBu_4][ClO_4]$–Me_2CO or CH_2Cl_2 solutions with potentials referred to a Ag–AgCl–0.1 mol dm^{-3} LiCl–Me_2CO electrode [12] or in CH_2Cl_2 referred to a saturated calomel electrode. Normal pulse voltammograms were obtained at a scan rate of 5 mV s^{-1} with a pulse frequency of 2.0 pulses

s^{-1}. Cyclic voltammograms at a scan speed greater than 200 mV s^{-1} were displayed on a Tektronix 564 B storage oscilloscope. AC voltammograms were recorded with a scan rate of 5 mV s^{-1} at a frequency of 77.5 Hz and a 10 mV peak to peak amplitude. All solutions were degassed with N_2 saturated with the appropriate solvent.

Electrolyses were carried out at potentials up to 200 mV beyond the $E_{1/2}$ value of the redox couple of interest, with a Wenking LB 75 M potentiostat and a Birtley electronic integrator. Acetone was passed over molecular sieve 4A and refractionated before use. Electronic spectra were obtained with a Beckman model 25 spectrophotometer.

Synthesis

Metal complexes used in this work were prepared and purified by standard literature methods.

$M(R_2dtc)_2$, M = Pd, Pt and R = Et, i-Pr, n-Bu, Ph and Bz [1, 13]. $M(R_2dsc)_2$, M = Ni, Pd, Pt and R = Et, n-Bu [14, 15]. $Pt(R_2dct)_3ClO_4$, R = Et, i-Pr, n-Bu, were prepared by exchange of the chloride ion in $Pt(R_2dtc)_3Cl$ for the perchlorate ion with an anion exchange resin (Amberlite IRA-400) in acetonitrile as described [16]. $Pt(R_2dtc)_3Cl$ complexes were prepared by the reaction of K_2PtCl_4 with thiuramdisulfide [6].

Anal. $Pt(Et_2dtc)_3Cl$; found C, 26.3; H, 4.5; N, 6.2; Pt $C_{15}H_{30}N_3S_6Cl$ requires C, 26.7; H, 4.5; N, 6.3. $Pt(i\text{-}Pr_2dtc)_3Cl$; found, C, 32.8; H, 5.4; N, 5.3; Pt $C_{21}H_{42}N_3S_6Cl$ requires C, 33.2; H, 5.6; N, 5.5. $Pt(i\text{-}Pr_2dtc)_3ClO_4$; found, C, 30.9; H, 5.2; N, 5.3; Pt $C_{21}H_{42}N_3S_6O_4Cl$ requires C, 30.6; H, 5.1; N, 5.1. $Pt(n\text{-}Bu_2dtc)_3ClO_4$; found, C, 36.2; H, 6.2; N, 4.5; Pt $C_{27}H_{54}N_3S_6ClO_4$ requires C, 35.7; H, 6.0; N, 4.6.

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