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Contribution from the Division of Chemical and Physical Sciences, Deakin University, Waurn Ponds 3217, Victoria, Australia, and Research School of Chemistry, Australian National University, Canberra 2600, ACT, Australia

Electrochemical Reduction and Oxidation of Cobalt(III) Dithiocarbamates

A. M. BOND,*[1] A. R. HENDRICKSON,[2,3] R. L. MARTIN,[2,4] J. E. MOIR,[1] and D. R. PAGE[1]

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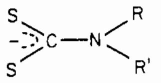
The literature describing the oxidation and reduction of cobalt(III) dithiocarbamate complexes, $Co(R_2dtc)_3$, and the chemistry of formally cobalt(II) and cobalt(IV) dithiocarbamate complexes contains substantially conflicting data. An extensive investigation of the electrochemical reduction and oxidation of $Co(R_2dtc)_3$ leads to the following conclusions: (i) In CH_2Cl_2 and for R = cyclohexyl, controlled-potential oxidative electrolysis at platinum electrodes produces a complex that appears to be the elusive cobalt(IV) complex $[Co(R_2dtc)_3]^+$ (or possibly $[Co_2(R_2dtc)_6]^{2+}$ or related species). In acetone, electrolysis of the cyclohexyl derivative at platinum electrodes produces the cobalt(III) dimer $[Co_2(R_2dtc)_5]^+$. At mercury electrodes, the oxidation process proceeds via a pathway different from that at platinum electrodes and $[Co_2(R_2dtc)_5]^+$ and mercury dithiocarbamate complexes are obtained as products. (ii) On the electrochemical time scale, oxidation of most $Co(R_2dtc)_3$ complexes is chemically reversible in CH_2Cl_2 but not always in acetone or acetonitrile, implying that $[Co(R_2dtc)_3]^+$ has a finite stability for many complexes, at least in CH_2Cl_2. However, with the exception of R = cyclohexyl, noted above, this complex is not obtained from electrolysis experiments. While $[Co_2(R_2dtc)_5]^+$ rather than $[Co(R_2dtc)_3]^+$ may be isolated from the oxidized solution in CH_2Cl_2, it is not formed at the electrode surface and results from a series of chemical reactions subsequent to electron transfer. (iii) Electrochemical reduction of $Co(R_2dtc)_3$ is extremely complex and depends markedly on the nature of the R group, solvent, and electrode. Formation of $[Co(R_2dtc)_3]^-$ is favored by solvents such as acetone or acetonitrile and is stabilized by adsorption on mercury electrodes. Thus, chemically reversible one-electron reduction steps are observed in some circumstances. By contrast, $Co(R_2dtc)_2$ appears to be significantly more stable in CH_2Cl_2 than $[Co(R_2dtc)_3]^-$, and chemically irreversible reduction is generally associated with this solvent at platinum electrodes. The nature of further electrochemical reduction steps, which ultimately produce cobalt metal and dissociated ligands, also depends on numerous variables.

Redox reactions of many dithiocarbamate complexes have been studied in considerable detail.[5-7] With a number of transition metals, unusually high oxidation states, e.g. Cu(III), Fe(IV), and Ni(IV), can be obtained. Electrochemical techniques[6,7] have proved to be extremely valuable in systematically studying the various oxidation states accessible with particular metals. Additionally, electrochemical methods enable substituent and related effects obtained by varying the nature of organic groups (R, R′) associated with the dithiocarbamate ligand $[RR'dtc]^-$ (I)[7] to be studied.



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The reported redox chemistry of the cobalt dithiocarbamates, unlike that for many of the other well-characterized transition-metal complexes, contains substantially conflicting data. Following the successful synthesis of $[Fe^{IV}(R_2dtc)_3]^+$ and $[Mn^{IV}(R_2dtc)_3]^+$ from oxidation of $M^{III}(R_2dtc)_3$ (M = Mn, Fe), Saleh and Straub attempted the oxidation of $Co(R_2dtc)_3$ in the presence of boron trifluoride.[8] Paramagnetic complexes formulated as $[Co(Et_2dtc)_3]BF_4$ and $[Co((C_6H_{11})_2dtc)_3]BF_4$ were said to be isolated. Using a similar method, Gahan and O'Connor however obtained what they reported as diamagnetic oligomeric cobalt(IV) complexes.[9] By contrast, Hendrickson and Martin, when using the same reaction, isolated the cobalt(III) dimeric species $[Co_2(R_2dtc)_5]BF_4$.[10,11] The reported UV–visible spectra for the claimed species $[Co_2(R_2dtc)_5]^+$ and $[Co(R_2dtc)_3]^+$ are essentially identical. Since a crystal structure is available for the $[Co_2(R_2dtc)_5]^+$ complex, doubt has been cast of the existence of the paramagnetic cobalt(IV) monomer.[5]

Cobalt(II) dithiocarbamate chemistry has been also slightly controversial. The $Co(R_2dtc)_2$ complexes are extremely easy to oxidize.[5,6] It has been stated that with $Co(Et_2dtc)_2$ oxidation to produce $Co(Et_2dtc)_3$ occurs even when considerable care is taken to remove oxygen.[12] This result appears to be in conflict with the claimed preparation of $Na[Co(Et_2dtc)_3]$.[13] Presumably, the alleged cobalt(II) anion was in fact the well-known tris cobalt(III) species $Co(Et_2dtc)_3$.[14] With large R groups some $Co(R_2dtc)_2$ species appear to be moderately stable and they are believed to be four-coordinate planar complexes.[15]

Electrochemical oxidation at platinum electrodes of $Co(R_2dtc)_3$ has been briefly reported in dimethylformamide,[16] acetone,[17] and acetonitrile.[9] Apart from reporting peak potentials[9,17] and some indication that a reversible one-electron couple may exist,[16] no other details are available on the oxidation pathway. Electrochemical reduction, predominantly at mercury electrodes, has led to very different interpretations of the chemical reactions. Patterson and Holm[16] refer to a single irreversible reduction step at platinum electrodes in dimethylformamide. In the same solvent, Toropova et al.[19] report three one-electron steps at the dropping-mercury electrode, the first being reversible and assigned to the reaction

$$Co(R_2dtc)_3 + e^- \rightleftharpoons [Co(R_2dtc)_3]^-$$

By contrast, in dimethyl sulfoxide a one-electron reduction step followed by a two-electron step is reported at mercury electrodes[18] with significantly different interpretations of data

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[1] Deakin University.
[2] Australian National University.
[3] Present address: Patents Trademarks & Design Office, Scarborough House, Phillip 2600, ACT, Australia.
[4] Present address: Monash University, Clayton 3168, Victoria, Australia.
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being offered compared to the Russian work.[7,19,20] All of the above electrochemical studies refer to a very limited range of R groups, and substituent effects are not well-known.

The present study describes a detailed electrochemical investigation at mercury and platinum electrodes of the reduction and oxidation of $Co(R_2dtc)_3$ in dichloromethane and acetone using an extensive range of substituents. A relatively small number of compounds were studied in acetonitrile. The aim of the work is to rationalize existing discrepancies in the literature and to extend the available knowledge of transition-metal dithiocarbamate redox reactions.

Experimental Section

$Co(R_2dtc)_3$ complexes were prepared by using standard literature methods.[5,21] Stoichiometric amounts of sodium hydroxide, amine, and carbon disulfide were reacted in cold aqueous solution to produce the sodium dithiocarbamate salt (NaR_2dtc). Solid cobalt(II) nitrate was then added to this mixture in the presence of air to form $Co(R_2dtc)_3$. Purification was carried out via Soxhlet extraction using chloroform or dichloromethane as the solvent. The cobalt complexes are generally obtained as dark green solids after solvent evaporation. The $Hg(R_2dtc)_2$ complexes used to verify part of the electrode mechanisms at mercury electrodes were synthesized in a manner similar to that for the cobalt complexes by reaction of mercury(II) nitrate and sodium dithiocarbamate.

Electrochemical measurements were carried out with either an EG & G Princeton Applied Research Corp. Model 174A polarographic analyzer or a Model 170 electrochemistry system. Both mercury and platinum working electrodes were used. A platinum auxiliary electrode was used for all measurements while the reference electrode was Ag/AgCl (satd LiCl; CH_2Cl_2) when dichloromethane (0.1 M Bu_4NClO_4) was the solvent or Ag/AgCl (0.1 M LiCl; acetone) when acetone (0.1 M Et_4NClO_4) or acetonitrile (0.1 M Et_4NClO_4) was the solvent.

Electrochemical measurements were made in solvent initially degassed with solvent-saturated nitrogen. During the course of making the measurements, a continuous stream of nitrogen was passed over the solutions.

Unless otherwise stated, all measurements were made under the following conditions: temperature 22 ± 1 °C; concentration of $Co(R_2dtc)_3$ 10^{-3} M; polarographic drop time 0.5 s; differential pulse amplitude ±50 mV; cyclic voltammetric scan rate 500 mV/s; alternating current polarography applied signal 10 mV p-p at 80 Hz.

Controlled-potential electrolysis experiments were monitored both electrochemically and spectrophotometrically with use of cells of our own design. Mercury was detected in solution after oxidative electrolysis experiments at mercury electrodes by using atomic absorption spectrometry (Varian AA6 atomic absorption spectrometer).

Abbreviations and symbols used are contained in an Appendix at the end of the text.

Results and Discussion

(i) Electrochemical Reduction of $Co(R_2dtc)_3$ in Dichloromethane. Reduction at a dropping-mercury electrode produces a very substituent-dependent result in dichloromethane. For some compounds two well-resolved dc polarographic reduction waves are observed. Figures 1 and 2 show this situation for reduction of $Co(Et,n\text{-}Budtc)_3$ and $Co(pipdtc)_3$, respectively. The second (more negative) reduction step in this well-resolved situation has a limiting current per unit concentration that is approximately twice that for the first (more positive) wave, and both limiting currents are diffusion controlled. The reduction processes for these complexes are therefore readily defined as

$$Co(III) + e^- \rightarrow Co(II) \qquad (1)$$

$$Co(II) + 2e^- \rightarrow Co(0) \qquad (2)$$

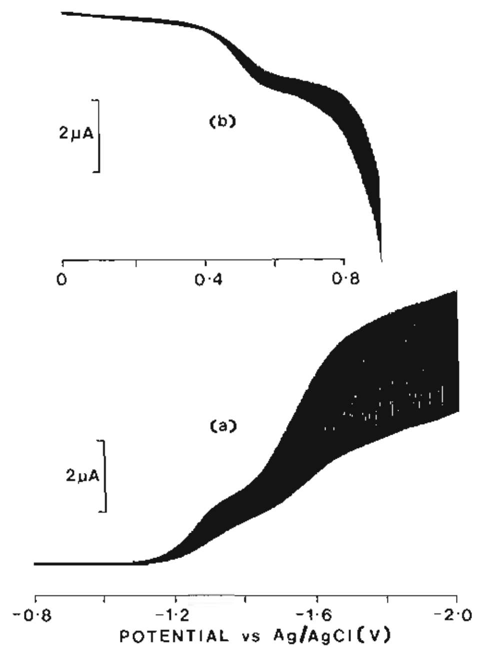

Figure 1. (a) Dc polarographic reduction and (b) oxidation of $Co(Et_2dtc)_3$ at the dropping-mercury electrode in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 22 °C.

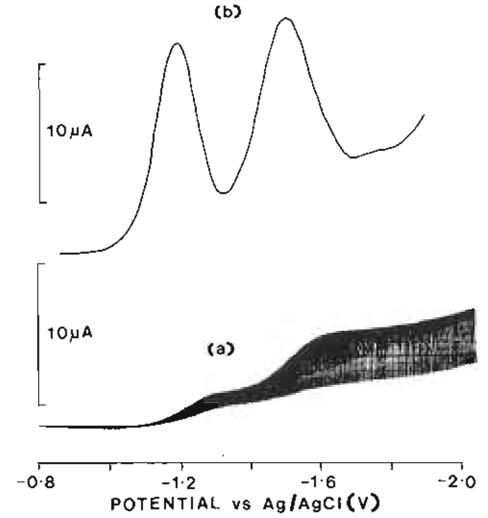

Figure 2. (a) Dc and (b) differential-pulse polarographic reductions of $Co(pipdtc)_3$ at the dropping-mercury electrode in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 22 °C.

Other compounds such as $Co(n\text{-}Bu,t\text{-}Budtc)_3$, however, exhibit only one wave (Figure 3); other compounds produce barely resolved processes. For most $Co(R_2dtc)_3$ complexes exhibiting a single unresolved step, the limiting current per unit concentration is approximately equal to the sum of the two steps for those complexes reduced according to eq 1 and 2 and therefore corresponds to a three-electron reduction (eq 3). Differential-pulse polarograms for reduction of Co-

$$Co(III) + 3e^- \rightarrow Co(0) \qquad (3)$$

$(pipdtc)_3$ and $Co(n\text{-}Bu,t\text{-}Budtc)_3$ are shown in Figures 2 and 3. Visual inspection of these curves and comparison with dc polarograms reveal that kinetic phenomena are operative. (Wave shape and peak current per unit concentration for differential-pulse polarograms are not values predicted for a reversible process.)

For a few complexes such as $Co(morphdtc)_3$ (Figure 4) the single well-defined process observed prior to reduction of solvent corresponds to a one-electron reduction.

Half-wave potentials, $E_{1/2}$, for dc polarographic reduction of the complexes are included in Table I, along with peak potentials obtained from differential-pulse polarography.

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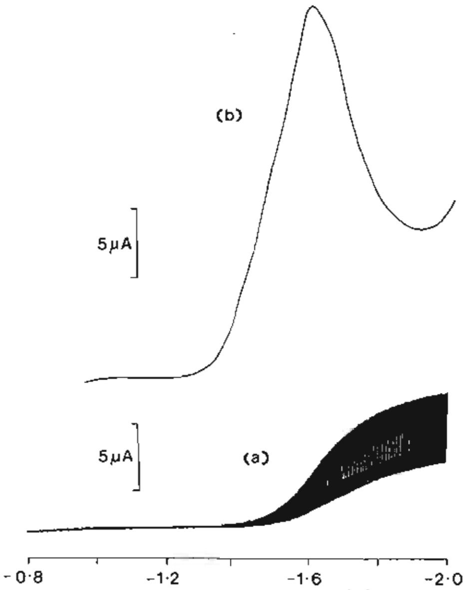

Figure 3. (a) Dc and (b) differential-pulse polarographic reductions of Co(*n*-Bu,*t*-Budtc)$_3$ at the dropping-mercury electrode in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 22 °C.

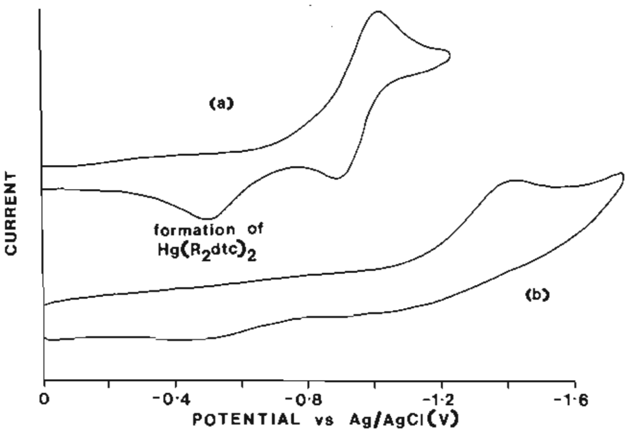

Figure 4. Comparison of cyclic voltammograms for reduction of Co(morphdtc)$_3$ at (a) mercury and (b) platinum electrodes in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 22 °C.

Cyclic voltammograms at both platinum and mercury electrodes confirm that the majority of reduction processes are chemically irreversible. However, for some complexes, some degree of chemical reversibility is noted at mercury electrodes for complexes exhibiting a response described by eq 1 but not at platinum (Figure 4). Dc $E_{1/2}$ and differential-pulse E_p values were essentially independent of concentration for concentrations less than 10^{-3} M. For the Co(III) + e$^-$ → Co(II) process, plots of E vs. log $[(i_d - i)/i]$ were linear with the slope generally in the range 100 ± 20 mV. At concentrations greater than 10^{-3} M, additional waves and evidence of adsorption were noted. The responses at platinum electrodes are more drawn out than at mercury electrodes, implying a slower rate of electron transfer, k_s, at platinum.

Table I. Polarographic Data for Reduction of Co(RR'dtc)$_3$ Complexes at Mercury Electrodes in Dichloromethane (0.1 M Bu_4NClO_4) at 22 °C

Co(RR'dtc)$_3$		technique			
		dc polarography $E_{1/2}$, V vs. Ag/AgCl		differential-pulse polarography E_p, V vs. Ag/AgCl	
R	R'	Co(III) + e$^-$ → Co(II)	Co(II) + 2e$^-$ → Co(0)	Co(III) + e$^-$ → Co(II)	Co(II) + 2e$^-$ → Co(0)
Me	Me	−1.15	−1.52	−1.13	−1.48
Et	Et	−1.21	−1.53	−1.20	−1.51
i-Pr	*i*-Pr	(−1.60)^a		−1.43	−1.58
n-Bu	*n*-Bu	(−1.61)^a		−1.34	−1.60
i-Bu	*i*-Bu	(−1.56)^a		(−1.58)^a	
n-Pe	*n*-Pe	(−1.58)^a		(−1.60)^a	
n-Hx	*n*-Hx	(−1.64)^a		−1.46	−1.65
n-Oc	*n*-Oc	(−1.64)^a		(−1.64)^a	
Me	*n*-Bu	−1.20	−1.55	−1.19	−1.52
Et	*n*-Bu	−1.25	−1.56	−1.25	−1.53
n-Bu	*t*-Bu	(−1.64)^a		(−1.64)^a	
Me	Ph	−1.23		−1.12	
Et	Ph	−1.19	−1.53	−1.16	−1.52
i-Pr	Ph	*b*		*b*	
n-Bu	Ph	*b*		*b*	
Me	Bz	−1.11	−1.45	−1.08	−1.44
Et	Bz	−1.16	−1.49	−1.13	−1.46
Bz	Bz	−1.13	−1.48	−1.08	−1.44
c-Hx	c-Hx	(−1.67)^a		(−1.64)^a	
i-Pr	c-Hx	(−1.61)^a		−1.45	−1.60
Et	*m*-tol	(−1.21)^a		−1.18	−1.48
N-heterocyclic derivatives					
pip		−1.21	−1.52	−1.18	−1.48
2-Mepip		−1.27	−1.60	−1.23	−1.53
3-Mepip		−1.22	−1.53	−1.19	−1.50
4-Mepip		−1.20	−1.50	−1.16	−1.48
2,6-Me$_2$pip		(−1.55)^a		−1.31	−1.55
pyrr		−1.07	−1.52	−1.03	−1.49
morph		−1.03		−1.02	

^{a} A single wave was observed but believed to correspond to Co(III) + 3e$^-$ → Co(0) or unresolved Co(III) + e$^-$ → Co(II) and Co(II) + 2e$^-$ → Co(0) processes. ^{b} Wave(s) too close to solvent limit to characterize; $E_{1/2}$ more negative than −1.8 V vs. Ag/AgCl.

Cyclic voltammograms at mercury and platinum electrodes confirm that ligand loss occurs after each reduction step (Figure 4a). The additional and reversible couple observed on second and subsequent scans at mercury is due to the electrode process[22] (eq 4 and 5).

$$2[R_2dtc]^- + 2Hg \rightleftharpoons 2HgR_2dtc + 2e^- \qquad (4)$$

$$2HgR_2dtc \rightleftharpoons Hg(R_2dtc)_2 + Hg \qquad (5)$$

Deliberate addition of Hg(R$_2$dtc)$_2$ to dichloromethane produced a response identical (allowing for current sign) with that found for the new wave observed on second and subsequent scans for reduction of the Co(R$_2$dtc)$_3$ species where resolved response attributed to eq 1 could be found. When resolved waves are evident, the second reduction step produced an enhanced response for $[R_2dtc]^-$ in cyclic voltammograms. Clearly, $[R_2dtc]^-$ is a product of both reduction steps.

On platinum electrodes, the reduction was found to be chemically and electrochemically irreversible for most complexes down to −78 °C, and evidence for loss of R_2dtc^- was found by noting the response for the oxidation to thiuram disulfide.[23] The more restricted solvent range available in the reduction direction and more drawn-out curves meant that reduction studies at platinum electrodes were more difficult to interpret. The single wave observed prior to the solvent limit at platinum electrodes generally appears to correspond to a one-electron reduction with loss of ligand.

(ii) Electrochemical Reduction of Co(R$_2$dtc)$_3$ in Other Solvents. The first one-electron reduction process for a number of complexes exhibits a considerable degree of chemical reversibility at both platinum and mercury electrodes in the more polar acetone solvent (Table II). Figure 5a shows a cyclic

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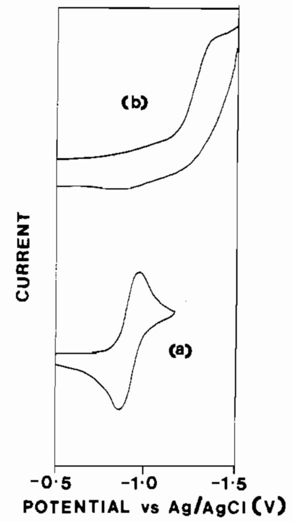

Figure 5. Cyclic voltammograms at a platinum electrode for reductions of (a) $Co(Me_2dtc)_3$ and (b) $Co(c\text{-}Hx_2dtc)_3$ in acetone (0.1 M Et_4NClO_4) at 22 °C.

Table II. Voltammetric Data for the Most Positive Reduction Process for $Co(RR'dtc)_3$ Complexes at Platinum Electrodes in Acetone (0.1 M Et_4NClO_4) at 22 °C

$Co(RR'dtc)_3$		normal-pulse voltammetry		ac voltammetry		cyclic voltammetry (scan rate 50 mV/s)	
R	R'	$E_{1/2}$, V	$E_{3/4} - E_{1/4}$, mV	E_p, V	width at half height, mV	ΔE_p, mV	$(i_p)_f/(i_p)_r$
Me	Me	−0.88	58	−0.89	92	69	1.2
Et	Et	−0.96	57	−0.94	96	80	1.5
i-Pr	*i*-Pr	−1.08	50	−1.11	98		*b*
n-Bu	*n*-Bu	−0.94	52	−0.95	130		*b*
i-Bu	*i*-Bu	−0.99	60	−0.94	*a*		*b*
c-Hx	c-Hx	−1.13	62	−1.14	126		*b*
Bz	Bz	−0.80	58	−0.80	92	107	1.2
Ph	Ph	−0.88	48	−0.88	95		*b*
Ph	Me	−0.89	50	−0.89	88		*b*
N-heterocyclic derivatives							
pyrr		−0.82	58	−0.82	93	162	1.8
pip		−0.92	53	−0.92	91		*b*
morph		−0.78	57	−0.80	90	123	1.2

[a] Complex electrode process. [b] Chemically irreversible process; no reverse peak for oxidation of $[Co(R_2dtc)_3]^-$.

voltammogram at platinum electrodes for reduction of $Co(Me_2dtc)_3$ in acetone. However, some complexes such as $Co(c\text{-}Hx_2dtc)_3$ that are reduced at very negative potentials on mercury electrodes in CH_2Cl_2 remain as irreversible electrode processes in acetone, as shown in Figure 5b. A limited number of complexes were also examined in acetonitrile (0.1 M Et_4NClO_4), and as in acetone, reversibility also was noted for the first one-electron reduction of complexes such as $Co(Me_2dtc)_3$ and $Co(Et_2dtc)_3$ at both platinum and mercury electrodes. Adsorption was noted at mercury electrodes in both acetone and acetonitrile. Electrode processes occurring at more negative potentials in these solvents, while noted, were not examined in detail.

(iii) Conclusions on the Electrochemical Reduction of $Co(R_2dtc)_3$. The above survey demonstrates that the reduction of $Co(R_2dtc)_3$ is very solvent and electrode dependent. In the nonpolar solvent CH_2Cl_2 the Co(III) + $e^- \rightarrow$ Co(II) step can be written as

$$Co(R_2dtc)_3 + e^- \overset{k_s,\ \alpha}{\rightleftharpoons} [Co(R_2dtc)_3]^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(R_2dtc)_2 + [R_2dtc]^- \quad (6)$$

Data imply that k_1 is very fast. The equilibrium constant, K, probably lies to the right in CH_2Cl_2 for the reaction

$$[Co(R_2dtc)_3]^- \overset{K}{\rightleftharpoons} Co(R_2dtc)_2 + [R_2dtc]^- \quad (7)$$

At mercury electrodes, adsorption of $[Co(R_2dtc)_3]^-$ may account for the chemical reversibility observed with some complexes. However, in a solvent of much higher dielectric constant such as acetone or acetonitrile, K may be smaller and $[Co(R_2dtc)_3]^-$ may be more stable than in CH_2Cl_2. There is also the possibility that $Co(R_2dtc)_2$ may have enhanced stability in CH_2Cl_2 due to polymer formation. In all cases examined, chemical irreversibility does not seem to be related to solvent displacement of a ligand but rather to the relative stability of $Co(R_2dtc)_2$ and $[Co(R_2dtc)_3]^-$ in the different solvents.

The extreme air sensitivity of cobalt(II) dithiocarbamate was confirmed by controlled-potential electrolysis experiments. Application of a potential where the Co(III) + $e^- \rightarrow$ Co(II) reduction process occurs produced solutions with electrochemical and spectrophotometric characteristics identical with those of $Co(R_2dtc)_3$. That is, any cobalt(II) species generated at the electrode surface immediately reacts with oxygen and regenerates the cobalt(III) species. At mercury electrodes when a very negative potential was applied, elemental cobalt and $[R_2dtc]^-$ were identified as products of controlled-potential electrolysis experiments. The second reduction step when observed as a resolved step is therefore characterized as being

$$[Co(R_2dtc)_3]^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(R_2dtc)_2 + [R_2dtc]^- \quad (8)$$

$$Co(R_2dtc)_2 + 2e^- \rightarrow Co + 2[R_2dtc]^- \quad (9)$$

Dc polarographic reduction[18] of $Co(R_2dtc)_3$ in Me_2SO at mercury electrodes (R = Me, Et, *n*-Bu, *i*-Bu) and $Co(pipdtc)_3$ and $Co(morphdtc)_3$ showed waves of relative height 1:2, as was the case for a number of complexes in this work in CH_2Cl_2.

Toropova et al.[19,20] have also examined the polarographic reduction of a limited range of cobalt(III) dithiocarbamates at mercury in dimethylformamide. In contrast to CH_2Cl_2 or Me_2SO, three one-electron reduction steps are found. The electrode processes are assigned by these authors as

$$Co(R_2dtc)_3 + e^- \overset{(E_{1/2})_1}{\rightleftharpoons} [Co(R_2dtc)_3]^- \quad (10a)$$

$$[Co(R_2dtc)_3]^- + e^- \overset{(E_{1/2})_2}{\rightleftharpoons} [Co(R_2dtc)_3]^{2-} \quad (10b)$$

$$[Co(R_2dtc)_3]^{2-} \rightleftharpoons [Co(R_2dtc)_2]^- + [R_2dtc]^- \quad (10c)$$

$$[Co(R_2dtc)_2]^- + e^- \xrightarrow{(E_{1/2})_3} Co(0) + 2[R_2dtc]^- \quad (10d)$$

Thus either one, two, or three reduction steps can be observed depending on the relative values of $(E_{1/2})_1$, $(E_{1/2})_2$, and $(E_{1/2})_3$ and on the k_s values for rate of electron transfer at the electrodes and the rate (or equilibrium) constants associated with the chemical steps

$$[Co(R_2dtc)_3]^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(R_2dtc)_2 + [R_2dtc]^- \quad (11a)$$

$$[Co(R_2dtc)_3]^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Co(R_2dtc)_2]^- + [R_2dtc]^- \quad (11b)$$

$$2[Co(R_2dtc)_2]^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Co(R_2dtc)_2 + Co(0) + 2[R_2dtc]^- \quad (11c)$$

etc.

Apparently, the thermodynamic and kinetic data for cobalt complexes are very dependent on the solvent, R group, and electrode material so that even an extremely wide range of

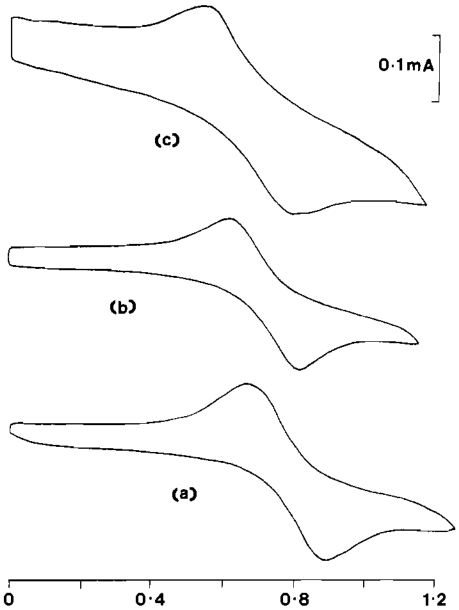

Figure 6. Cyclic voltammograms at a platinum electrode for oxidations of (a) Co(*n*-$Pe_2dtc)_3$, (b) Co(*i*-$Pr_2dtc)_3$, and (c) Co(*n*-Bu,*t*-$Budtc)_3$ in CH_2Cl_2 (0.1 M Bu_4NClO_4) at 22 °C. Scan rate was 500 mV s^{-1}.

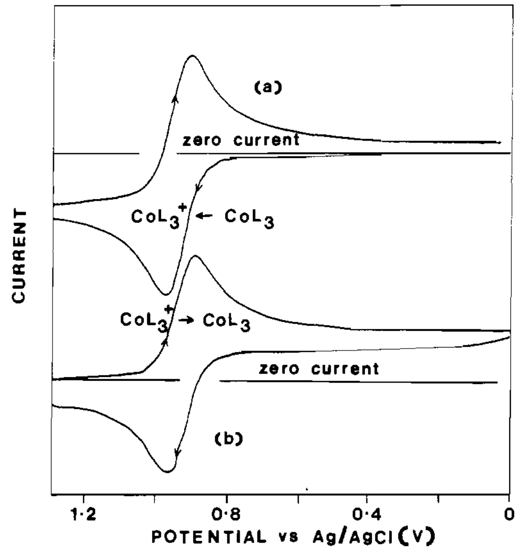

Figure 7. Cyclic voltammograms at a platinum electrode (a) before and (b) after controlled-potential electrolysis (oxidation at platinum gauze) of Co(c-$Hx_2dtc)_3$ in CH_2Cl_2 (satd Et_4NClO_4).

Table III. Voltammetric Data for Oxidation of Co(RR′dtc)$_3$ Complexes at Mercury and Platinum Electrodes in Dichloromethane (0.1 M Bu_4NClO_4) at 22 °C

Co(RR′dtc)$_3$		dc polarography[a]		differential-pulse polarography[a]	cyclic voltammetry at Pt electrodes	
R	R′	$E_{1/2}$, V	$E_{3/4} - E_{1/4}$, mV	E_p, V	$10^3 k_s$, cm s^{-1}	$E°$, V
Me	Me	0.510	85	0.465	1.4	0.838
Et	Et	0.490	90	0.460	3.1	0.770
i-Pr	*i*-Pr	0.450	80	0.380	2.1	0.676
n-Bu	*n*-Bu	0.475	90	0.460	2.2	0.784
i-Bu	*i*-Bu	0.520	95	0.485	1.4	0.758
n-Pe	*n*-Pe	0.500	85	0.470	2.5	0.769
n-Hx	*n*-Hx	0.500	80	0.475	2.8	0.784
n-Oc	*n*-Oc	0.465	110	0.460	2.0	0.779
Me	*n*-Bu	0.515	55	0.490	3.9	0.810
Et	*n*-Bu	0.495	80	0.470	2.5	0.779
n-Bu	*t*-Bu	0.490	65	0.480 0.640 } *b*	2.1	0.676
Me	Ph	0.565	80	0.530	2.2	0.874
Et	Ph	0.570	130	0.550	2.2	0.834
i-Pr	Ph	0.715	130	0.640 0.670 } *b*	*c*	*c*
n-Bu	Ph	0.705	80	0.645 0.675 } *b*	*c*	*c*
Me	Bz	0.550	70	0.520	0.28	0.894
Et	Bz	0.560	110	0.540	0.19	0.856
Bz	Bz	0.630[d]	*d*	0.600	0.31	0.930
c-Hx	c-Hx	0.590	70	0.500	0.18	0.633
i-Pr	c-Hx	0.440	70	0.412	0.28	0.665
Et	*m*-tol	*e*	*e*	0.590 0.670 } *b*	0.15	0.803
N-heterocyclic derivatives						
pip		0.470	80	0.450	1.8	0.793
2-Mepip		0.440	85	0.440	3.5	0.775
3-Mepip		0.460[d]	*d*	0.470	3.1	0.800
4-Mepip		0.470	85	0.460	2.5	0.769
2,6-Me_2pip		0.470[d]	*d*	0.445	3.5	0.725
pyrr		0.420[d]	*d*	0.415	4.5	0.825
morph		0.454[d]	*d*	0.520	2.2	0.934

[a] Dropping-mercury electrode. [b] Two peaks present—presence of adsorption indicated. [c] No reduction wave on reverse scan: electrode process not chemically reversible. [d] Maxima present; value uncertain. [e] Wave close to Hg oxidation limit; $E_{1/2} \sim 0.8$ V vs. Ag/AgCl.

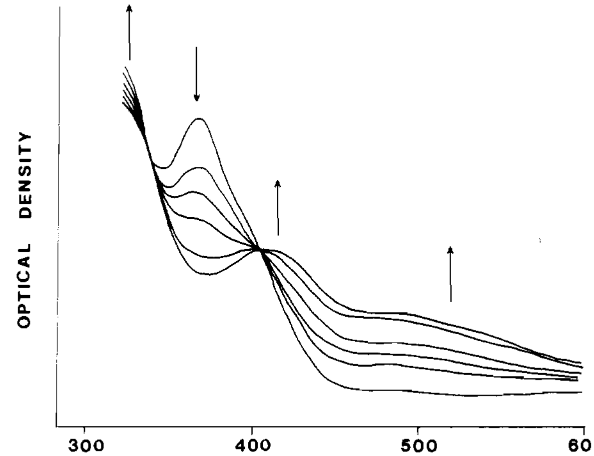

Figure 8. Spectrophotometric monitoring of the electrolysis experiment described in Figure 7.

responses can be observed for reduction of Co($R_2dtc)_3$.

(iv) Oxidation at Platinum Electrodes in CH_2Cl_2. Unlike the reduction steps, oxidation of Co($R_2dtc)_3$ at platinum electrodes in CH_2Cl_2 is straightforward. Figure 6 shows some representative examples and Table III summarizes the data. k_s and $E°$ values were calculated by theory based on digital simulation[24] of the electrode process

$$\mathrm{Co(R_2dtc)_3} \xrightleftharpoons{E^\circ,\ k_s,\ \alpha} [\mathrm{Co(R_2dtc)_3}]^+ + e^- \tag{12}$$

assuming $\alpha = 0.5$ and using diffusion coefficients obtained from dc polarographic limiting currents (Ilkovic equation).

The data imply the existence of a cobalt(IV) cation, $[Co^{IV}(R_2dtc)_3]^+$, analogous to $[Fe^{IV}(R_2dtc)_3]^+$ or $[Mn^{IV}(R_2dtc)_3]^+$.

Controlled-potential electrolysis of Co(c-$Hx_2dtc)_3$ at a platinum electrode in CH_2Cl_2 gave an *n* value of 1.0 ± 0.1 for the oxidation process. Figure 7 shows cyclic voltammograms recorded before and after electrolysis at a platinum electrode. A one-electron oxidation step is converted to a one-electron reduction step, and the reversibility of the process is substantiated. Spectrophotometric monitoring of the con-

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(24) S. W. Feldberg, *Electroanal. Chem.*, 3, 199–296 (1969).

Table IV. Voltammetric Data for Oxidation Process of Co(RR'dtc)$_3$ Complexes at Platinum Electrodes in Acetone (0.1 M Et$_4$NClO$_4$) at 22 °C

Co(RR'dtc)$_3$		normal-pulse voltammetry		ac voltammetry		cyclic voltammetry (scan rate 200 mV/s)	
R	R'	$E_{1/2}$, V	$E_{3/4} - E_{1/4}$, mV	E_p, V	width at half height, mV	ΔE_p, mV	$(i_p)_f/(i_p)_r$
Me	Me	1.10	52	1.09	84	80	1.1
Et	Et	1.07	52	1.07	88	63	1.5
i-Pr	*i*-Pr	0.97	52	0.97	91	67	1.2
n-Bu	*n*-Bu	1.10	54	1.09	90	67	1.4
i-Bu	*i*-Bu	1.07	52	1.07	95	60	1.2
c-Hx	c-Hx	0.96	50	0.96	86	65	1.1
Bz	Bz	1.22	46	1.22	86	64	1.2
Ph	Ph	1.18	52	1.19	89	70	1.6
Ph	Me	1.13	55	1.12	80	72	3.2
N-heterocyclic derivatives							
pyrr		1.06	41	1.06	85	68	1.1
pip		1.06	53	1.05	85	69	2.3
morph		1.17	52	1.16	84	78	2.1

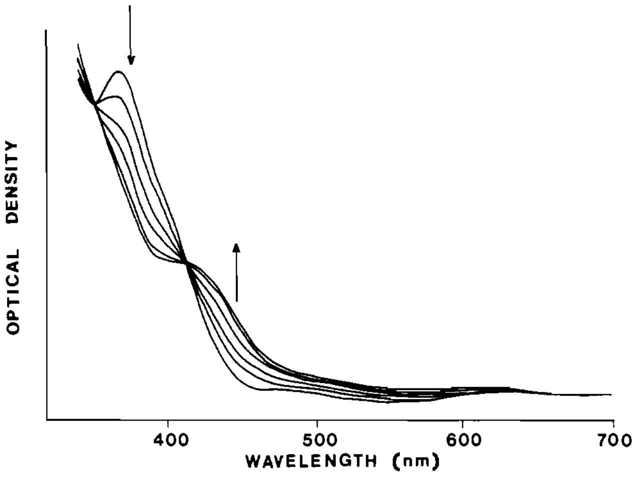

Figure 9. Spectrophotometric monitoring of the controlled-potential electrolysis of Co(c-Hx$_2$dtc)$_3$ in acetone (0.1 M Et$_4$NClO$_4$) at platinum electrodes.

trolled-potential electrolysis reaction produced the data shown in Figure 8. An isosbestic point is observed, and the final spectrum is attributed to [Co(c-Hx$_2$dtc)$_3$]$^+$. Controlled-potential electrolysis of Co(*i*-Pr$_2$dtc)$_3$ gave an *n* value of 0.9 ± 0.1. However, cyclic voltammograms of the product did not produce a reversible one-electron reduction wave as was the case for the cyclohexyl derivative. Thus, [Co(R$_2$dtc)$_3$]$^+$ does not appear to be stable with this derivative. A number of other oxidation reactions with other R groups were also attempted in CH$_2$Cl$_2$, but only with the cyclohexyl species could a product attributable to a cobalt(IV) cation be obtained. Species that appear to be [Co$_2$(R$_2$dtc)$_5$]$^+$ could be isolated from the reaction mixture by using synthetic and characterization methods described by Hendrickson et al.[10,11] However, this dimeric complex is not formed as a direct product of electrolysis. A further oxidation step near the solvent limit was not characterized.

(v) Oxidation at Platinum Electrodes in Acetone. Table IV summarizes voltammetric data for some of the complexes in acetone. The oxidation process is not chemically reversible in acetone as was frequently the case in CH$_2$Cl$_2$.

Spectrophotometric monitoring of the oxidation process for Co(c-Hx$_2$dtc)$_3$ in acetone produces the result shown in Figure 9. The spectrum after completion of the electrolysis is certainly not that for [Co(c-Hx$_2$dtc)$_3$]$^+$ but rather is identical with

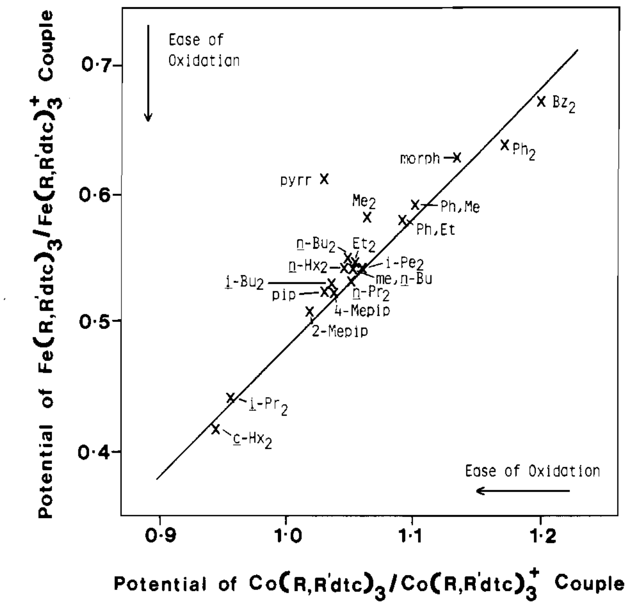

Figure 10. Plot of $E°$ for the Fe(RR'dtc)$_3$/Fe(RR'dtc)$_3$$^+$ couple vs. Co(RR'dtc)$_3$/[Co(RR'dtc)$_3$]$^+$ couple. Both sets of data were obtained in acetone (0.1 M Et$_4$NClO$_4$); iron dithiocarbamate data were obtained from ref 29. (Note: In this figure RR' also includes N-heterocyclic derivatives.)

the spectrum of an authentic sample of [Co$_2$(c-Hx$_2$dtc)$_5$]$^+$ prepared according to the method of Hendrickson and Martin.[10,11] Although the mechanistic details of the oxidation process in acetone are unknown, the isosbestic point in the spectroelectrochemical analysis of Figure 9 and product identification imply that the overall process is

$$2\mathrm{Co(c\text{-}Hx_2dtc)_3} \rightarrow [\mathrm{Co_2(c\text{-}Hx_2dtc)_5}]^+ + \text{oxidized dicyclohexyldithiocarbamate ligand} + 2e^- \qquad (13)$$

The oxidized ligand(s) may be the species characterized in other studies[23,25-27] and shown to be formed in the reaction between Ru(R$_2$dtc)$_3$ and BF$_3$/O$_2$ to produce [Ru$_2$(R$_2$dtc)$_5$]$^+$.[28]

(vi) Electrochemical Oxidation of Co(R$_2$dtc)$_3$ at Mercury Electrodes in CH$_2$Cl$_2$. Data in Table III and Figure 1 show that oxidation of Co(R$_2$dtc)$_3$ at mercury electrodes in CH$_2$Cl$_2$ occurs at a potential very different from that at platinum electrodes. Cyclic voltammetry at mercury electrodes also shows that the process is chemically irreversible, unlike the situation at platinum. Controlled-potential electrolysis experiments for a number of compounds were undertaken. The close proximity to the mercury oxidation limit prohibited reliable coulometric determinations of the number of electrons involved in the electrolysis. Atomic absorption spectrophotometric experiments indicated the presence of mercury in solutions after the electrolysis, and mercury dithiocarbamate could be detected as a product as could [Co$_2$(R$_2$dtc)$_5$]$^+$ after workup based on the method of Hendrickson and Martin.[10,11] However, neither the identified mercury or cobalt complexes were generated directly from the electrolysis reaction. The dc polarographic limiting current per unit concentration (ignoring sign difference) is the same as for the previously characterized Co(III) + e$^-$ → Co(II) one-electron reduction

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(25) P. T. Beurskens, W. P. J. H. Bosman, and J. A. Cras, *J. Cryst. Mol. Struct.*, **2**, 183 (1972).

(26) J. Willemse and J. J. Steggerda, *J. Chem. Soc. D*, 1123 (1969).

(27) J. Willemse, J. A. Cras, and P. J. H. A. M. van de Leemput, *Inorg. Nucl. Chem. Lett.*, **12**, 255 (1976).

(28) B. M. Mattson, J. R. Heiman, and L. H. Pignolet, *Inorg. Chem.*, **15**, 564 (1976).

(29) R. Chant, A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Inorg. Chem.*, **14**, 1894 (1975).

step, so it is a one-electron oxidation at the electrode surface, presumably involving ligand exchange with mercury in addition to oxidation, but mechanistic details are not known.

(vii) Conclusion on the Electrochemical Oxidation of Co(R_2dtc)$_3$. As is the case for the reduction step, oxidation of Co(R_2dtc)$_3$ is very solvent and electrode-material dependent. Electrochemical data imply that the elusive cobalt(IV) species can be obtained, e.g. [Co(c-Hx$_2$dtc)$_3$]$^+$, under synthetic conditions and more readily on the short time scale electrochemical experiments in inert solvents such as CH_2Cl_2 for many dithiocarbamate complexes. Figure 10 shows a plot of $E°$ for the Co(RR′dtc)$_3$/[Co(RR′dtc)$_3$]$^+$ couple and $E°$ for the known Fe(III)/Fe(IV), Fe(RR′dtc)$_3$/[Fe(RR′dtc)$_3$]$^+$, couple in acetone. The excellent correlation provides further evidence that the cobalt(IV) species does exist. However, the very positive potential at which it is generated means that an internal redox reaction to produce cobalt(III) plus oxidized ligand is thermodynamically favorable. Such process(es) lead to formation of the cobalt(III) dimer [Co$_2$(R_2dtc)$_5$]$^+$ in the noncoordinating CH_2Cl_2 solvent. In other solvents this species may or may not be stable depending on the R group. The cobalt(IV) complex is therefore inherently unstable, and we have failed to isolate this species in the solid state. Dimer formation is well established in both solid state and solution chemistry for many dithiocarbamate complexes.[5,6] It is of course possible that [Co(R_2dtc)$_3$]$^+$ is in equilibrium with [Co$_2$(R_2dtc)$_6$]$^{2+}$ as is the case with the complex Os(R_2dtc)$_3$ where the reaction

$$2[\mathrm{Os(R_2dtc)_3}]^+ \rightleftharpoons [\mathrm{Os_2(R_2dtc)_6}]^{2+} \tag{14}$$

has been well characterized.[30] Alternatively, since a seven-coordinate complex of Co(IV) would be unexpected, the equilibrium reaction

$$2[\mathrm{Co(R_2dtc)_3}]^+ \rightleftharpoons [\mathrm{Co_2(R_2dtc)_5}]^{2+} + {}^1/_2(\text{thiuram disulfide}) \tag{15}$$

could be consistent with the observed data. However, in all cases a cobalt(IV) species is implicated in the reaction pathway.

Our data partially explain the inconsistencies in the literature on the chemical oxidation of Co(R_2dtc)$_3$. The diamagnetic oligomeric complexes reported by Gahan and O'Connor would certainly appear to be [Co$_2$(R_2dtc)$_5$]$^+$ and not Co(IV) compounds as claimed. While we were unable to isolate the cyclohexyl derivative of cobalt(IV) claimed to have been prepared by Saleh and Straub, we find that this or a related species can exist in CH_2Cl_2. However, their claimed [Co(Et$_2$dtc)$_3$]BF$_4$ species, for which very little data are provided, seems most unlikely. In our hands, controlled-potential electrolysis leads directly to formation of [Co$_2$(Et$_2$dtc)$_5$]$^+$ and the Co(IV) complex of the diethyldithiocarbamate derivative appears to have only a transient existence, even on the electrochemical time scale.

Appendix of Symbols and Abbreviations

E	potential
i	current
$E°$	standard redox potential
$E_{1/2}$	half-wave potential—defined by $i = (1/2)i_d$
$E_{3/4} - E_{1/4}$	difference in potential between $i = (3/4)i_d$ and $i = (1/4)i_d$
i_d	limiting diffusion-controlled current
E_p	peak position
i_p	peak current
dc	direct current
ac	alternating current
ΔE_p	separation in forward- and reverse-scan potentials in cyclic voltammetry
$(i_p)_f/(i_p)_r$	ratio of forward- and reverse-scan peak heights in cyclic voltammetry
k_s	rate constant for heterogeneous charge transfer
α	charge-transfer coefficient
dtc	dithiocarbamate
Me	methyl
Et	ethyl
i-Pr	isopropyl
n-Bu	*n*-butyl
i-Bu	isobutyl
Pe	pentyl
Hx	hexyl
Oc	octyl
Ph	phenyl
Bz	benzyl
c-Hx	cyclohexyl
m-tol	*m*-tolyl
pipdtc	piperidine-*N*-carbodithioate
2-Mepipdtc	2-methylpiperidine-*N*-carbodithioate
3-Mepipdtc	3-methylpiperidine-*N*-carbodithioate
4-Mepipdtc	4-methylpiperidine-*N*-carbodithioate
2,6-Me$_2$-pipdtc	2,6-dimethylpiperidine-*N*-carbodithioate
pyrrdtc	pyrrolidine-*N*-carbodithioate
morphdtc	morpholine-*N*-carbodithioate

Registry No. Co(Me$_2$dtc)$_3$, 23677-76-1; Co(Et$_2$dtc)$_3$, 13963-60-5; Co(*i*-Pr$_2$dtc)$_3$, 59220-40-5; Co(*n*-Bu$_2$dtc)$_3$, 28090-32-6; Co(*i*-Bu$_2$dtc)$_3$, 28090-33-7; Co(*n*-Pe$_2$dtc)$_3$, 28090-34-8; Co(*n*-Hx$_2$dtc)$_3$, 86527-75-5; Co(*n*-Oc$_2$dtc)$_3$, 86527-76-6; Co(Me,*n*-Budtc)$_3$, 55059-62-6; Co(Et,*n*-Budtc)$_3$, 86527-77-7; Co(*n*-Bu,*t*-Budtc)$_3$, 86527-78-8; Co(MePhdtc)$_3$, 86527-79-9; Co(EtPhdtc)$_3$, 36015-82-4; Co(*i*-PrPhdtc)$_3$, 86527-80-2; Co(*n*-BuPhdtc)$_3$, 86527-81-3; Co(MeBzdtc)$_3$, 86527-82-4; Co(EtBzdtc)$_3$, 86527-83-5; Co(Bz$_2$dtc)$_3$, 33539-56-9; Co(c-Hx$_2$dtc)$_3$, 51205-54-0; Co(*i*-Pr,c-Hxdtc)$_3$, 86527-84-6; Co(Et,*m*-toldtc)$_3$, 35924-68-6; Co(pipdtc)$_3$, 20487-61-0; Co(2-Mepipdtc)$_3$, 86527-85-7; Co(3-Mepipdtc)$_3$, 86527-86-8; Co(4-Mepipdtc)$_3$, 86527-87-9; Co(2,6-Me$_2$pipdtc)$_3$, 86527-88-0; Co(pyrrdtc)$_3$, 24412-38-2; Co(morphdtc)$_3$, 27796-33-4; Co(Ph$_2$dtc)$_3$, 86561-41-3; Co(PhMedtc)$_3$, 86527-79-9; Hg, 7439-97-6; Pt, 7440-06-4.

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