with the lower values applying to exchanges that are formally spin forbidden (e.g. Co(II)/Co(III) couples) and the upper values associated with the adiabatic exchanges in couples such as $Ru(bpy)_3^{2+/3+}$. A value of $\kappa_{el} = 0.04$ for the $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ exchange is therefore not unreasonable as this couple is intermediate between Ru(II)/(III) and Co(II)/Co(III) systems in several respects, including reorganization barriers and the orbital origin of the exchanged electron.

In the $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ couple the electron to be exchanged is believed to reside in either a $\delta^*$ or $\pi^*$ orbital.[6a,40-42] The bond distance changes accompanying this $\delta^*$ or $\pi^*$ electron exchange are consistent with a change in the population of a weakly antibonding orbital and are intermediate between those observed for couples in which a nonbonding $\pi$ electron is exchanged and those in which an antibonding $\sigma^*$ electron is exchanged. This trend may be illustrated by the consideration of several metal complex couples in which one partner has a $d^7$ configuration, as set out in Table II. It can be seen from the first three entries that the exchange of a $\sigma^*$ electron in either a $d^6/d^7$ or a $d^7/d^8$ couple proceeds at a moderate rate, $10^3$–$10^4$ $M^{-1}$ $s^{-1}$, and involves considerable change in metal–ligand bond distances. In the case of $Co(bpy)_3^{+/2+}$, on the other hand, a high-spin Co(II) electronic configuration results in the exchange of a nonbonding $\pi$ electron. A negligible inner-sphere reorganization barrier allows for an exchange rate constant of $\geq 10^9$ $M^{-1}$ $s^{-1}$. Similar structural and exchange parameters are found for the low-spin $d^5/d^6$ tris(polypyridine) complexes of iron, ruthenium, and osmium.[30] The only other rhodium couple for which self-exchange data have been measured is $Rh(bpy)_3^{2+/3+}$ (Table II). Although this $d^6/d^7$ couple should be analagous to $Co(terpy)_2^{2+/3+}$, the electron exchange, at $\geq 10^9$ $M^{-1}$ $s^{-1}$, is much more rapid. It has been suggested that the metal $\sigma^*$ and ligand $\pi^*$ orbitals are very close in energy such that $Rh^{II}(bpy)_3^{2+}$ may exist as or be in equilibrium with $[Rh^{III}(bpy)_2(bpy^-)]^{2+}$, allowing for a low-energy electron exchange via L $\pi^*$ orbitals.

The replacement of $H_2O$ by other ligands in the axial positions in $Rh_2(O_2CR)_4L_2$ has a much larger effect on the Rh–Rh bond length than does a change in the nature of the bridging carboxylate group.[2] Variations in the $\sigma$-donor ability of L are also predicted to affect the differences in Rh–Rh and Rh–L bond distances upon oxidation to the corresponding cations. It is suggested that the oxidation of a rhodium dimer with axial triphenylphosphine ligands (which involves the removal of a $\sigma$ electron[6,41]) will yield a cation with shorter Rh–P bonds but a longer Rh–Rh bond, in contrast to rhodium dimers with O-donor ligands.[41] Electron-transfer reactions involving a series of rhodium carboxylate dimers with P-donor ligands are currently under investigation to determine how changes in L affect the electron exchange parameters.

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**Supplementary Material Available:** Tables of kinetic data (4 pages). Ordering information is given on any current masthead page.

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# Characterization of Pentakis(dithiocarbamato)dicobalt(III) Complexes, $[Co_2(RR'dtc)_5]^+$, and Related Complexes in Dichloromethane Using Electrochemical and Cobalt-59 NMR Techniques

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Controversy has arisen as to whether $[Co(RR'dtc)_3]^+$ or $[Co_2(RR'dtc)_5]^+$ is the product of oxidation of $Co(RR'dtc)_3$. In this work electrochemical and $^{59}Co$ NMR techniques have been used to examine the chemistry and redox properties of cobalt dithiocarbamate complexes in dichloromethane solution in an endeavor to rationalize literature data. Electrochemical measurements at platinum electrodes show that the species $Co(RR'dtc)_3$, $[Co(RR'dtc)_3]^+$, $[Co_2(RR'dtc)_5]^+$, and also $[Co_2(RR'dtc)_5]^{2+}$ may exist under appropriate conditions. On oxidation of $Co(RR'dtc)_3$, $[Co(RR'dtc)_3]^+$ is formed as either a stable intermediate (RR'dtc = c-$Hx_2$dtc) or a transient intermediate (RR'dtc = pyrrdtc). $[Co_2(RR'dtc)_5]^+$ is produced from this species via an internal redox reaction at a rate that is extremely sensitive to substituent effects. The rate of transformation of $[Co(RR'dtc)_3]^+$ to $[Co_2(RR'dtc)_5]^+$ is concentration-dependent, implying the formation of a dimeric intermediate such as $[Co_2(RR'dtc)_6]^{2+}$. Reaction of $[CoL_3]^+$ and $[CoL'_3]^+$ (L and L' are different dithiocarbamate ligands) produces a mixture of $[Co_2L_5]^+$, $[Co_2L_3L'_2]^+$, $[Co_2L_2L'_3]^+$, and $[Co_2L'_5]^+$, which is again consistent with the formation of dimeric intermediates. $[Co_2(RR'dtc)_5]^{2+}$ can be identified by electrochemical oxidation of $[Co_2(RR'dtc)_5]^+$ at low temperature, but it is unstable – generating $[Co(RR'dtc)_3]^+$ (R = R' = c-Hx) at ambient temperature under conditions of cyclic voltammetry. $Co_2(RR'dtc)_5$ produced by reduction of $[Co_2(RR'dtc)_5]^+$ has no inherent stability and very rapidly converts to $Co(RR'dtc)_3$ and $Co(RR'dtc)_2$. $[Co_2(RR'dtc)_5]^+$ itself decomposes slowly in dichloromethane to $Co(RR'dtc)_3$ as demonstrated by $^{59}Co$ NMR and electrochemical measurements. Cobalt-59 NMR demonstrates that in solution $[Co_2(RR'dtc)_5]^+$ has two nonequivalent cobalt centers, in accordance with a previously published crystal structure. The formally cobalt(IV) complexes are generated at very positive potentials and are far more reactive than similar high-oxidation-state dithiocarbamates of other metals. Electrochemical data in acetone are qualitatively similar to those in dichloromethane.

## Introduction

Tris(dithiocarbamato)cobalt(III) complexes, $Co(RR'dtc)_3$, have been extensively studied.[3-6] A related and also formally cobalt(III) compound, pentakis(diethyldithiocarbamato)dicobalt(III) tetrafluoroborate, $[Co_2(Et_2dtc)_5]BF_4$, has been made from Co-

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**Table I.** Analytical Data for $[Co_2(RR'dtc)_5]^+$ Complexes

| | % calcd | | | | | % found | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C | H | N | F | S | C | H | N | F | S |
| $[Co_2(Et_2dtc)_5]BF_4$ | 31.7 | 5.3 | 7.4 | 8.0 | 33.9 | 31.3 | 5.5 | | | 33.2 |
| $[Co_2(c\text{-}Hx_2dtc)_5]BF_4$ | 52.5 | 7.5 | 4.7 | 5.1 | 21.6 | 51.2 | 7.3 | | 4.9 | |
| $[Co_2(Bz_2dtc)_5]BF_4$ | 57.5 | 4.5 | 4.5 | 4.9 | 20.5 | 57.2 | 4.2 | | 5.4 | |
| $[Co_2(morphdtc)_5]BF_4$ | 29.6 | 4.0 | 6.9 | 7.5 | 31.6 | 29.1 | 3.8 | 6.5 | 7.8 | 31.1 |

$(Et_2dtc)_3$ by reaction with boron trifluoride diethyl etherate. Available evidence indicates this reaction occurs via a redox process.[7,8] The analogous reaction with $Fe(RR'dtc)_3$ produces the formally Fe(IV) complex $[Fe(RR'dtc)_3]^+$,[9-11] but evidence for the corresponding $[Co(RR'dtc)_3]^+$ as an intermediate in the formation of $[Co_2(RR'dtc)_5]^+$ has been contradictory.

Using the $BF_3$ reaction, Saleh and Straub[12] claimed to have prepared paramagnetic $[Co(RR'dtc)_3]^+$ (R = R' = Et or c-Hx) whereas Gahan and O'Connor[13] claimed a diamagnetic oligomeric $[Co(RR'dtc)_3]BF_4$ complex. The same reaction in the hands of Hendrickson and Martin produced only the well-characterized $[Co_2(RR'dtc)_5]^+$ complex.[8] Chemical reactions of $[Co_2(RR'dtc)_5]^+$ with a range of ligands have been studied and they frequently produce $Co(RR'dtc)_3$ as a product. Claimed chemical reactions of $[Co(IV)(RR'dtc)_3]^+$ may therefore be uncertain and may proceed via the dimer.[14]

Work from these laboratories demonstrated that dimers are formed in dichloromethane on the synthetic time scale by electrochemical means with the exception of R = R' = c-Hx where controlled-potential electrolysis produced a species[5] that had a visible spectrum different from that of an authentic sample of the dimer $[Co_2(c\text{-}Hx_2dtc)_5]^+$. This species may have been the elusive Co(IV) complex.

The chemistry of the various cobalt compounds is still not clear, and in this work we have attempted to seek definitive methods of distinguishing between $Co(RR'dtc)_3$, $[Co(RR'dtc)_3]^+$, and $[Co_2(RR'dtc)_5]^+$ so that their respective chemistries can be properly understood. Since their relationships are believed to be redox based, voltammetric studies at platinum electrodes have been extensively used in this investigation. Cobalt-59 NMR should also offer a clear method of distinguishing the different species[9] and also has therefore been used extensively in this work. New synthetic routes to the formation of the oxidized $Co(RR'dtc)_3$ complexes have also been explored. The mechanism of the much used $BF_3$ reaction is not well understood. Electrochemical oxidation and the use of other well-recognized oxidants should provide a more definitive study of these processes, if they are indeed redox based.

## Experimental Section

**Nomenclature.** An appendix of symbols and abbreviations used follows at the end of the text.

**Preparations.** $Co(RR'dtc)_3$ complexes were prepared by using standard literature methods.[3,5,15] These compounds are generally obtained as dark green solids.

$[Co_2(RR'dtc)_5]^+$ complexes were prepared by reaction of $Co(RR'dtc)_3$ with either $BF_3{\cdot}OEt_2$ or a nitrosyl salt such as $NOPF_6$ or $NOSbF_6$. An excess of the oxidant was very slowly added, with stirring, to $Co(RR'dtc)_3$ in benzene (usually a saturated solution or a slurry). The reaction mixture was stirred thoroughly and was left open to the air and set aside to evaporate to dryness (usually overnight). A dark brown/green crude product (a powdery solid, a sticky solid or an oil, depending mainly on the R and R' groups) was obtained. The crude product was extracted with dichloromethane and filtered. A cream/fawn-colored insoluble fraction was isolated, which is believed to be an oxidized form of the ligand, although it has not yet been fully characterized. The filtrate was set aside and again allowed to evaporate to dryness. The resulting solid ($[Co_2(RR'dtc)_5]^+$ and usually a $Co(RR'dtc)_3$ impurity) was purified by dissolving in the minimum quantity of dichloromethane, slowly adding diethyl ether until precipitation commenced, and then cooling to 0 °C in an ice/water bath. The brown solid ($[Co_2(RR'dtc)_5]^+$) was collected by vacuum filtration. The recrystallization procedure was repeated a number of times.

For R = R' = c-Hx, for R = R' = *i*-Pr, and for R = c-Hx, R' = *i*-Pr the above procedure at 0 °C or lower temperatures leads to the formation of $[Co(RR'dtc)_3]^+$ initially, but on standing, the dimer is formed. The stability of $[Co(RR'dtc)_3]^+$ is a function of concentration as well as temperature. At concentrations less than about $10^{-4}$ $M[Co(c\text{-}Hx_2dtc)_3]^+$ has considerable stability in solution even at 20 °C. See the Results and Discussion for further details.

Microanalyses were carried out by AMDEL Australian Microanalytical Service.

**Electrochemical Instrumentation.** Electrochemical studies employing voltammetric methods were carried out on a Princeton Applied Research (PAR) (Princeton, NJ) Model 174A polarographic analyzer. A platinum-wire or a rotating platinum-disk working electrode (Metrohm) and a platinum-wire auxiliary electrode were used for all measurements. All potentials were measured against a Ag/AgCl (saturated LiCl; $CH_2Cl_2$) reference electrode. This electrode was frequently calibrated against the $Fe(C_5H_5)_2{}^+/Fe(C_5H_5)_2$ redox couple via oxidation of $10^{-3}$ M $Fe(C_5H_5)_2$ in $CH_2Cl_2$ (0.1 M $Bu_4NClO_4$).

Controlled-potential-electrolysis experiments were performed at a platinum-gauze working electrode by using a PAR Model 173 potentiostat/galvanostat in conjunction with a Model 179 digital coulometer. In these experiments the auxiliary electrode was made from platinum gauze and was separated from the test solution by a salt bridge with a porous Vycor frit. The reference electrode was identical with that used for voltammetric measurements.

Unless stated otherwise, electrochemical measurements were made at (20 ± 1) °C in dichloromethane (0.1 M $Bu_4NClO_4$). Solutions were degassed with solvent-saturated nitrogen, and a continuous stream of nitrogen was passed over the solutions while measurements were being undertaken. All solvents and chemicals were AR grade.

**NMR Spectroscopy.** Cobalt-59 NMR spectra were recorded on a JEOL FX 100 spectrometer at 23.77–23.81 MHz at 25 °C using an external $^7Li$ lock. Chemical shifts were referenced against external saturated aqueous $K_3[Co(CN)_6]$; the high frequency positive convention was used.

## Results and Discussion

The reaction of $Co(RR'dtc)_3$ (saturated solution) with $BF_3{\cdot}OEt_2$ in our hands invariable produces either $[Co_2(RR'dtc)_5]^+$ or a mixture of $[Co_2(RR'dtc)_5]^+$ and unreacted $Co(RR'dtc)_3$. After a large number of recrystallizations, analytical data for the products are consistent with the formulation of pure $[Co_2(RR'dtc)_5]BF_4$ (see Table I). During the synthesis another product, not containing cobalt, is also formed. This material has not been fully characterized but definitely appears to be derived from an oxidized form of the ligand. Mattson et al.[16] suggested that, in the analogous preparation of $[Ru_2(RR'dtc)_5]BF_4$, the byproduct is the 3,5-bis(*N*,*N*-diethyliminio)-1,2,4-trithiolane dication, $[Et_4bitt]^{2+}$. Reaction of $Co(RR'dtc)_3$ (saturated solution) with $NOPF_6$ or $NOSbF_6$ produced $[Co_2(RR'dtc)_5]PF_6$ or $[Co_2(RR'dtc)_5]SbF_6$. Nitrosyl salts are known to be strong one-electron oxidants, which suggests that the formation of the cobalt dimers

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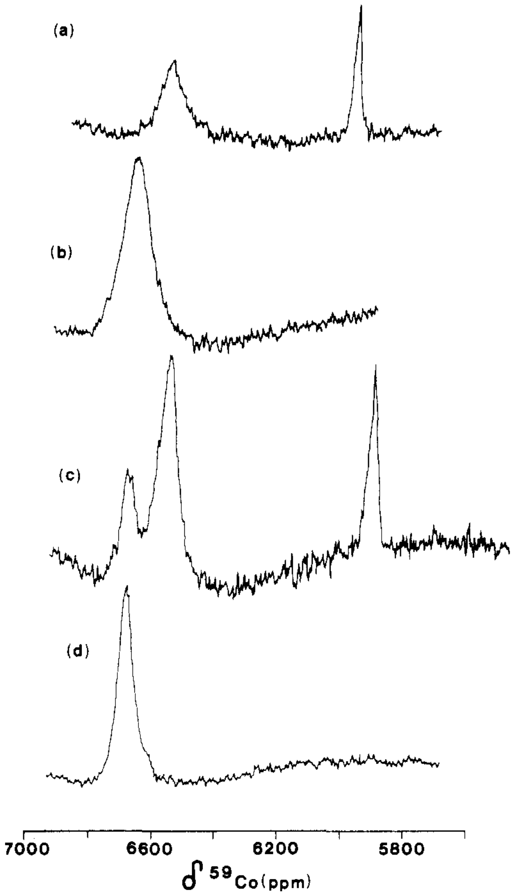

**Figure 1.** Cobalt-59 NMR spectra in dichloromethane at 25 °C for (a) the cobalt dimer $[Co_2(Bz_2dtc)_5]^+$, (b) $Co(Bz_2dtc)_3$, (c) the impure cobalt dimer $[Co_2(2\text{-}Mepipdtc)_5]^+$, and (d) $Co(2\text{-}Mepipdtc)_3$.

**Table II.** Cobalt-59 Chemical Shifts for $Co(RR'dtc)_3$ and $[Co_2(RR'dtc)_5]^+$ Complexes in Dichloromethane at 20 °C

| | | $^{59}$Co chem shift,[a] ppm | | |
|---|---|---|---|---|
| R | R' | $Co(RR'dtc)_3$ | $[Co_2(RR'dtc)_5]^+$ | |
| Me | Me | 6830 | 6710 | 6050 |
| Et | Et | 6790 | 6660 | 5980 |
| *n*-Pr | *n*-Pr | 6740 | 6630 | 5970 |
| Bz | Bz | 6650 | 6540 | 5960 |
| c-Hx | c-Hx | 6330 | 6200 | 5570 |
| N-heterocyclic derivatives | | | | |
| pip | | 6760 | 6620 | 5960 |
| 2-Mepip | | 6680 | 6550 | 5890 |
| 4-Mepip | | 6760 | 6640 | 5970 |
| 2,6-Me$_2$pip | | 6540 | 6400 | 5790 |
| pyrr | | 7200 | 7030 | 6260 |
| morph | | 6800 | 6680 | 5990 |

[a] Chemical shifts referenced against 1 M $K_3[Co(CN)_6]$ in water.

is indeed via a redox process. Chemical oxidation of dilute solutions of $Co(RR'dtc)_3$ (R = R' = c-Hx; R = R' = *i*-Pr; R = c-Hx, R' = *i*-Pr) leads to the identification of $[Co(RR'dtc)_3]^+$ as a relatively stable intermediate (see later).

**Cobalt-59 NMR Studies.** Room-temperature $^{59}$Co NMR spectra of $[Co_2(RR'dtc)_5]^+$ compounds in dichloromethane typically show two or three cobalt signals (Figure 1); the third signal is due to $Co(RR'dtc)_3$ formed by decomposition of $[Co_2(RR'dtc)_5]^+$ (see later). Table II summarizes $^{59}$Co NMR chemical shifts for $[Co_2(RR'dtc)_5]^+$ and $Co(RR'dtc)_3$ complexes. Cobalt-59 NMR provides a convenient method for distinguishing between $Co(RR'dtc)_3$ and $[Co_2(RR'dtc)_5]^+$. The fact that the dimer shows two signals shows the presence of two nonequivalent cobalt atoms, which is consistent with the known structure of $[Co_2(Et_2dtc)_5]^+$ in the solid state.[8] The structure may be regarded as consisting of a $[Co(Et_2dtc)_2]^+$ fragment coordinated in the cis position by sulfur atoms from an octahedral $Co(Et_2dtc)_3$ molecule of opposite chirality. On this basis, the cobalt signal for each $[Co_2(RR'dtc)_5]^+$ closest to that of the corresponding $Co(RR'dtc)_3$ itself is assigned to the octahedral fragment of the dimer. In general, this signal for the dimer is approximately 120 ppm to lower frequency relative to the signal for $Co(RR'dtc)_3$ and the separation between the two signals for the dimer is usually about 670 ppm, these relative shifts being fairly independent of the nature of R and R'. The observation of two signals for the dimer also indicates that any possible exchange between various isomers, some of which would render the cobalt atoms equivalent,[17] is slow on the NMR time scale.

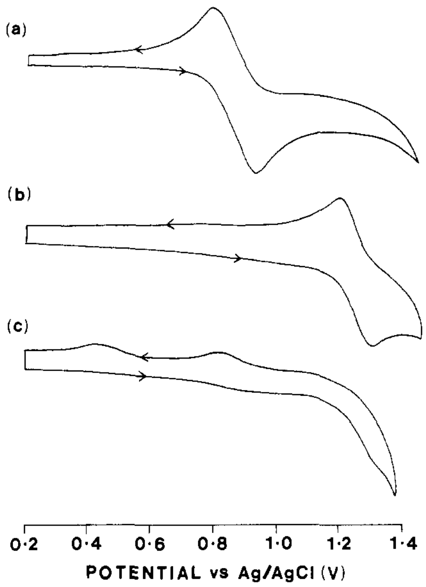

**Figure 2.** Cyclic voltammograms (scan rate 200 mV s$^{-1}$) at a platinum electrode in dichloromethane (0.1 M $Bu_4NClO_4$) for oxidation of approximately 5 × 10$^{-4}$ M (a) $Co(Et_2dtc)_3$ at 20 °C, (b) $[Co_2(Et_2dtc)_5]^+$ at −70 °C and (c) $[Co_2(Et_2dtc)_5]^+$ at 20 °C.

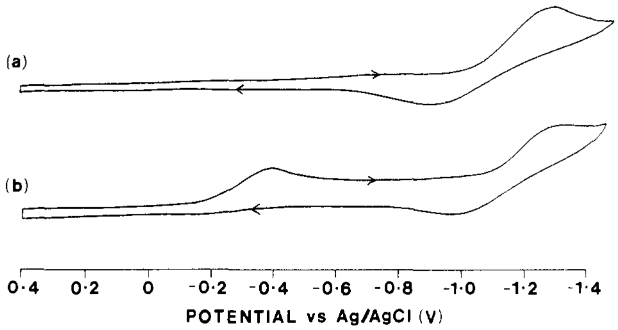

**Figure 3.** Cyclic voltammograms (scan rate 200 mV s$^{-1}$) at a platinum electrode in dichloromethane (0.1 M $Bu_4NClO_4$) at 20 °C for reduction of approximately 5 × 10$^{-4}$ M (a) $Co(Me_2dtc)_3$ and (b) $[Co_2(Me_2dtc)_5]^+$.

**Electrochemical Studies.** Low-temperature electrochemistry of the dimer $[Co_2(RR'dtc)_5]^+$ is very well defined and very different from that of $Co(RR'dtc)_3$. A reversible one-electron oxidation is observed at very positive potentials close to the solvent limit and approximately 400 mV more positive than for the oxidation of $Co(RR'dtc)_3$ (see Figure 2). Electrochemical data are summarized in Table III. On reduction, an irreversible process is observed at much less negative potentials than for $Co(RR'dtc)_3$, but in addition the reduction processes associated with $Co(RR'dtc)_3$ are also observed (Figure 3). When the reaction mixture is allowed to stand with periodic monitoring by recording voltammograms at low temperature, the electrochemical response shows considerable time dependence (Figure 4). With time, an oxidation grows at potentials where $Co(RR'dtc)_3$ is oxidized and

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**Table III.** Electrochemical Data for Oxidation and Reduction of ~5 × $10^{-4}$ M Co(RR′dtc)$_3$ and [Co$_2$(RR′dtc)$_5$]$^+$ Complexes at a Platinum Electrode in Dichloromethane (0.1 M Bu$_4$NClO$_4$) at a Scan Rate of 200 mV s$^{-1}$ [a]

| | oxidation process[f] | | | | reduction process[f] | | |
|---|---|---|---|---|---|---|---|
| | (CoL$_3$/[CoL$_3$]$^+$)[b] | | ([Co$_2$L$_5$]$^+$/[Co$_2$L$_5$]$^{2+}$)[c] | | (CoL$_3$/[CoL$_3$]$^-$)[d] | | ([Co$_2$L$_5$]$^+$/(CoL$_3$))[e] |
| L | $E_p^{ox}$ | $E_p^{red}$ | $E_p^{ox}$ | $E_p^{red}$ | $E_p^{red}$ | $E_p^{ox}$ | $E_p^{red}$ |
| Me$_2$dtc | 0.98 | 0.85 | 1.37 | 1.24 | −1.30 | −0.97 | −0.38 |
| Et$_2$dtc | 0.92 | 0.79 | 1.31 | 1.19 | −1.47 | −0.90 | −0.50 |
| *i*-Pr$_2$dtc | 0.78 | 0.66 | 1.24[g] | 1.12 | −1.96[h] | | −0.79 |
| Bz$_2$dtc | 1.05 | 0.91 | 1.56 | 1.41 | −1.40 | −0.78 | −0.48 |
| c-Hx$_2$dtc | 0.75 | 0.64 | 1.24[g] | 1.14 | −2.04[h] | | −0.84 |
| *i*-Pr-c-Hxdtc | 0.77 | 0.65 | 1.26[g] | 1.06 | −2.00[h] | | −0.82 |
| morphdtc | 1.05 | 0.95 | 1.53 | 1.39 | −1.30 | −0.72 | −0.32 |
| pyrrdtc | 0.94 | 0.82 | 1.38 | 1.25 | −1.32 | −0.70 | −0.44 |
| 4-Mepipdtc | 0.92 | 0.80 | 1.38 | 1.25 | −1.44 | −0.86 | −0.55 |

[a] Oxidation of ferrocene at a platinum electrode in dichloromethane (0.1 M Bu$_4$NClO$_4$) at 20 °C gave an $E_{1/2}^r$ ($E°$) value of 0.48 (0.02) V vs. Ag/AgCl. L = RR′dtc. [b] Data obtained in ref 5 are about 50 mV less positive due to use of a different reference electrode. [c] [Co$_2$L$_5$]$^{2+}$ decomposes at 20 °C. Peak potentials obtained at −78 °C. [d] Data obtained at 20 °C. [CoL$_3$]$^-$ is unstable for some complexes, and the process [CoL$_3$]$^-$ → CoL$_2$ + [L]$^-$ may contribute to the response.[5] [e] Data obtained at 20 °C. The process is completely irreversible. [f] All peak pootentials in volts. [g] Controlled-potential electrolysis produces [CoL$_3$]$^+$, which decomposes with time to generate [Co$_2$L$_5$]$^+$. [h] The processes Co(III) + e$^-$ → Co(II) and Co(II) + 2e$^-$ → Co(0) are not resolved. See ref 5 for further details.

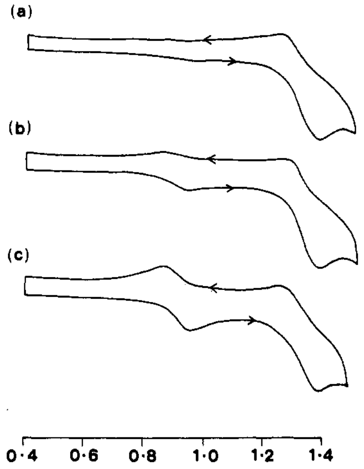

**Figure 4.** Cyclic voltammograms (scan rate 200 mV s$^{-1}$) at a platinum electrode in dichloromethane (0.1 M Bu$_4$NClO$_4$) at −70 °C showing the time dependence of the electrochemical response of approximately 5 × $10^{-4}$ M [Co$_2$(Me$_2$dtc)$_5$]$^+$: (a) $t$ = 0; (b) $t \simeq$ 2 h; (c) $t \simeq$ 24 h.

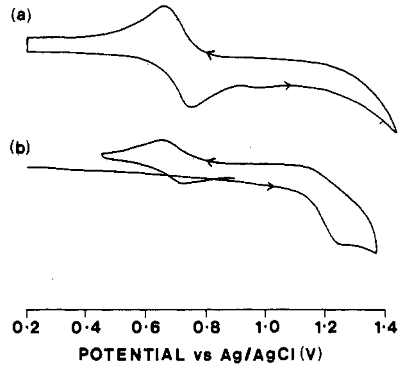

**Figure 5.** Cyclic voltammograms (scan rate 200 mV s$^{-1}$) at a platinum electrode in dichloromethane (0.1 M Bu$_4$NClO$_4$) at 20 °C for oxidation of approximately 5 × $10^{-4}$ M (a) Co(c-Hx$_2$dtc)$_3$ and (b) [Co$_2$(c-Hx$_2$dtc)$_5$]$^+$.

the reduction wave for the dimer at less negative potential diminishes with time. Thus, [Co$_2$(RR′dtc)$_5$]$^+$ seems to be unstable in CH$_2$Cl$_2$ solution and decomposes to form Co(RR′dtc)$_3$. Deliberate addition of water did not appear to alter the rate of decomposition, nor is the rate of decomposition light-sensitive. However, chloride significantly increases the rate of formation of Co(RR′dtc)$_3$, and this represents a likely route for decomposition in dichloromethane.

At room temperature the oxidation of [Co(RR′dtc)$_5$]$^+$ in dichloromethane occurs near the solvent limit and is chemically irreversible. However, in the case of [Co$_2$(c-Hx$_2$dtc)$_5$]$^+$ a new peak appeared on the reverse and subsequent scans which is chemically reversible and occurs at a potential identical with that of the reversible oxidation of Co(c-Hx$_2$dtc)$_3$ (Figure 5), indicating that [Co(c-Hx$_2$dtc)$_3$]$^+$ is a product of the irreversible oxidation of [Co$_2$(c-Hx$_2$dtc)$_5$]$^+$. The same pattern of behavior is also observed with [Co$_2$(*i*-Pr-c-Hxdtc)$_5$]$^+$ and [Co$_2$(*i*-Pr$_2$dtc)$_5$]$^+$.

Controlled-potential electrolysis (reduction) at −0.7 V of [Co$_2$(Me$_2$dtc)$_5$]BF$_4$ at room temperature is a one-electron process. The initially brown solution turns green and then produces electrochemical behavior identical with that of an authentic sample of Co(Me$_2$dtc)$_3$. At a rotating platinum-disk electrode the limiting current per unit concentration is the same as for the oxidation of Co(RR′dtc)$_3$, thus defining the reduction as a one-electron step. All data are consistent with the reduction process being

$$[\mathrm{Co_2(RR'dtc)_5}]^+ + e^- \rightarrow \mathrm{Co(RR'dtc)_3} + \mathrm{Co(RR'dtc)_2} \quad (1)$$

with Co(RR′dtc)$_2$ being electroinactive over the potential range examined,[5] but on the time scale of controlled-potential electrolysis it is converted to Co(RR′dtc)$_3$ and other cobalt-containing species via aerial oxidation or other pathways. Under no conditions was the reduction step for [Co$_2$(RR′dtc)$_5$]$^+$ chemically reversible, implying that Co$_2$(RR′dtc)$_5$ has no inherent stability.

In contrast to the instability of Co$_2$(RR′dtc)$_5$, [Co$_2$(RR′dtc)$_5$]$^{2+}$ can be observed on the electrochemical time scale at low temperatures (Figure 2b), but it is clear that the cobalt dimer redox series [Co$_2$(RR′dtc)$_5$]$^{0/+/2+}$ does not have the stability of the corresponding ruthenium series.[18,19] Decomposition to Co(RR′dtc)$_3$ or [Co(RR′dtc)$_3$]$^+$ occurs in all cases.

Electrochemical techniques allow ready distinction between [Co(RR′dtc)$_3$]$^-$, Co(RR′dtc)$_3$, [Co(RR′dtc)$_3$]$^+$, [Co$_2$(RR′dtc)$_5$]$^+$, and [Co$_2$(RR′dtc)$_5$]$^{2+}$. Consequently electrochemistry can be used to monitor the interconversions among the different species.

Controlled-potential electrolysis for oxidation of Co(c-Hx$_2$dtc)$_3$ (approximately 5 × $10^{-4}$ M) unambiguously shows the formation of [Co(c-Hx$_2$dtc)$_3$]$^+$. As the course of the electrolysis is monitored at 0 °C by using a rotating platinum electrode, the reversible one-electron oxidation changes to a one-electron reduction process (Figure 6). Similar results were obtained with NOPF$_6$ as the oxidant. Room-temperature oxidation of Co(c-Hx$_2$dtc)$_3$ (approximately 5 × $10^{-4}$ M) gives mixture of [Co(*c*-Hx$_2$dtc)$_3$]$^+$ and [Co$_2$(*c*-Hx$_2$dtc)$_5$]$^+$, and on standing, [Co(c-Hx$_2$dtc)$_3$]$^+$ is clearly converted to [Co$_2$(c-Hx$_2$dtc)$_5$)]$^+$ even at 0 °C. As the concentration of Co(c-Hx$_2$dtc)$_3$ is lowered, increased stability is observed

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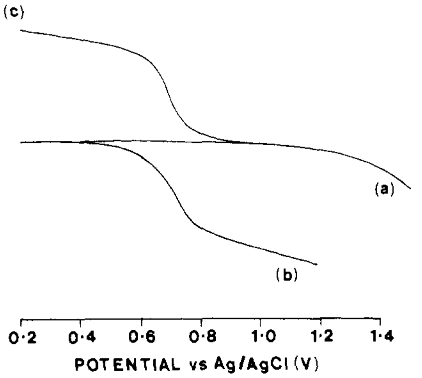

**Figure 6.** Voltammograms at a rotating platinum-disk electrode (500 rpm; scan rate 20 mV $s^{-1}$) in dichloromethane (0.1 M $Bu_4NClO_4$) for (a) blank (0.1 M $Bu_4NClO_4$) in dichloromethane), (b) oxidation of approximately 5 × $10^{-4}$ M $Co(c\text{-}Hx_2dtc)_3$, and (c) reduction of $[Co(c\text{-}Hx_2dtc)_3]^+$ ($[Co(c\text{-}Hx_2dtc)_3]^+$ having been formed by controlled-potential electrolysis of $Co(c\text{-}Hx_2dtc)_3$ at + 0.9 V on a platinum electrode at 0 °C).

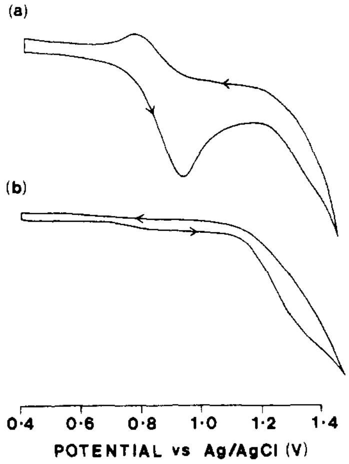

**Figure 7.** Cyclic voltammograms (scan rate 200 mV $s^{-1}$) at a platinum electrode in dichloromethane (0.1 M $Bu_4NClO_4$) at 20 °C for oxidation of approximately 5 × $10^{-4}$ M (a) $Co(pyrrdtc)_3$ and (b) $[Co_2(pyrrdtc)_5]^+$.

for the oxidized product $[Co(c\text{-}Hx_2dtc)_3]^+$. Conversion of $[Co(c\text{-}Hx_2dtc)_3]^+$ to $[Co_2(c\text{-}Hx_2dtc)_5]^+$ occurs via a second-order process, and the stability of $[Co(c\text{-}Hx_2dtc)_3]^+$ in dilute solution is consistent with non-unity-order kinetics. The magnetic moment of $[Co(c\text{-}Hx_2dtc)_3]^+$ in dichloromethane solution at −20 °C as determined by the Evans' method[20] (using the dichloromethane resonance) is close to 1.7 $\mu_B$, thus indicating low-spin cobalt(IV), at least at low temperatures. At higher temperatures Saleh and Straub[12] indicate that this may be a mixed-spin complex.

The electrochemical oxidation of approximately 5 × $10^{-4}$ M $Co(pyrrdtc)_3$, unlike the majority of the other complexes, is only partially reversible in the chemical sense (scan rate = 200 mV $s^{-1}$) at room temperature.[5] With access to an authentic sample of the dimer it can be shown that this oxidation process generates $[Co_2(pyrrdtc)_5]^+$ as a product even on the short time scale of electrochemistry (Figure 7). At low temperatures the $Co(pyrrdtc)_3 \rightleftharpoons [Co(pyrrdtc)_3]^+ + e^-$ process is chemically reversible. The degree of chemical reversibility is extremely concentration-dependent. Figure 8 shows data for a scan rate of 200 mV $s^{-1}$ as a function of concentration. At concentrations greater than $10^{-3}$ M the process is almost chemically irreversible, whereas at the $10^{-4}$ M level the ratio of oxidation to reduction current is almost unity. Scan rate and concentration dependence are consistent with a second-order chemical reaction coupled to electron transfer. Controlled-potential electrolysis (oxidation) on $Co(pyrrdtc)_3$ at +1.1 V produces the dimer $[Co_2(pyrrdtc)_5]^+$ without any evidence for the formation of $[Co(pyrrdtc)_3]^+$. This example represents the other extreme in the rate of conversion of $[Co(RR'dtc)_3]^+$ to $[Co_2(RR'dtc)_5]^+$; other compounds show behavior intermediate between these extremes.

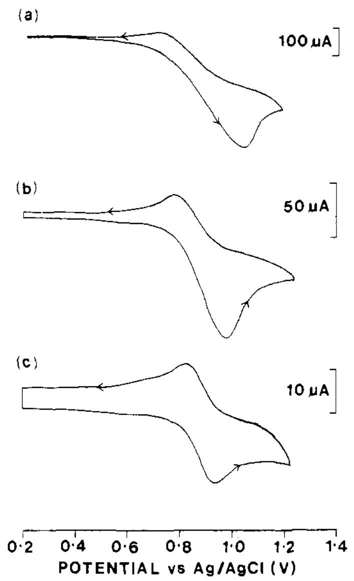

**Figure 8.** Cyclic voltammograms at a platinum electrode in dichloromethane (0.1 M $Bu_4NClO_4$) at 20 °C for oxidation of $Co(pyrrdtc)_3$ at 200 mV $s^{-1}$ at concentrations of approximately (a) 3.5 × $10^{-3}$ M, (b) $10^{-3}$ M, and (c) 1.5 × $10^{-4}$ M.

The above data demonstrate that in particular cases both $[Co(RR'dtc)_3]^+$ and $[Co_2(RR'dtc)_5]^+$ exist but that $[Co(RR'dtc)_3]^+$ is extremely reactive. The data in this work enables some conclusions to be reached on the formation of the dimer from $[Co(RR'dtc)_3]^+$. It must involve some kind of internal redox mechanism and not a reaction between $[Co(RR'dtc)_3]^+$ and $Co(RR'dtc)_3$. Furthermore it occurs via a non-unity-order process as evidenced by the increased stability of $[Co(RR'dtc)_3]^+$ in dilute solutions. $Co(RR'dtc)_3$ and $[Co_2(RR'dtc)_5]^+$ are oxidized at very positive potentials so that both $[Co(RR'dtc)_3]^+$ and $[Co_2(RR'dtc)_5]^{2+}$ are extremely reactive. Oxidation of $[RR'dtc]^-$ to thiuram disulfide occurs at approximately 0 V in $CH_2Cl_2$, and this itself is further oxidized to produce $[bitt]^{2+}$ + S at approximately 1 V. Our data in $CH_2Cl_2$ is essentially the same as reported in other solvents.[21,22] Neither $[RR'dtc]^-$ or thiuram disulfide, $(RR'dtc)_2$, are seen as products of the chemical or electrochemical oxidation of $Co(pyrrdtc)_3$ in $CH_2Cl_2$. The synthetic method (R = R' = c-Hx) also produces a white material that is probably an amine derived from the decomposition of $[bitt]^{2+}$, which is known to be unstable.[21,22]

A reasonable mechanism appears to be the following:

$$Co(RR'dtc)_3 \rightleftharpoons [Co(RR'dtc)_3]^+ + e^- \tag{2}$$

$$2[Co(RR'dtc)_3]^+ \rightarrow [Co_2(RR'dtc)_6]^{2+} \tag{3}$$

$$[Co_2(RR'dtc)_6]^{2+} \rightarrow [Co_2(RR'dtc)_5]^+ + {}^1/_2[R_2R'_2bitt]^{2+} + S \tag{4}$$

(where $[R_2R'_2bitt]^{2+}$ = 3,5-bis(*N*,*N*-dialkyliminio)-1,2,4-trithiolane dication if R = R' = alkyl). The dication $[R_2R'_2bitt]^{2+}$ is unstable in dichloromethane, and further decomposition occurs.

Evidence for an intermediate $[Co_2(RR'dtc)_6]^{2+}$ is also provided by the enhanced stability of $[Co(RR'dtc)_3]^+$ (R = R' = c-Hx) at low concentrations and by the second-order kinetics for decomposition of $[Co(RR'dtc)_3]^+$. Further evidence is provided by the oxidation of a mixture of $Co(Et_2dtc)_3$ and $Co(i\text{-}Pr_2dtc)_3$. Figure 9 shows the cobalt-59 NMR spectra before and after oxidation; the products of the oxidation are identified as $[Co_2(Et_2dtc)_5]^+$, $[Co_2(Et_2dtc)_3(i\text{-}Pr_2dtc)_2]^+$, $[Co_2(Et_2dtc)_2(i\text{-}Pr_2dtc)_3]^+$, and $[Co_2(i\text{-}Pr_2dtc)_5]^+$. These are the logical decomposition

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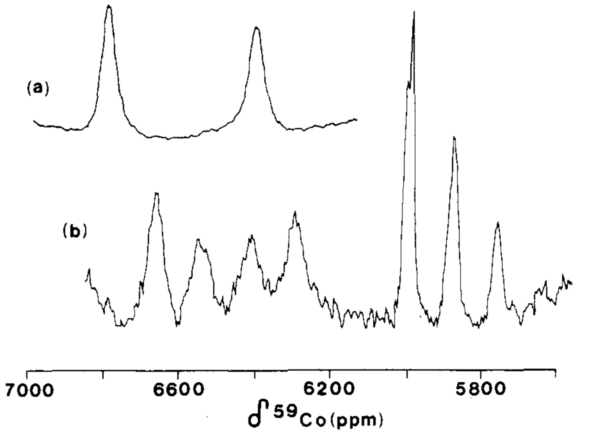

**Figure 9.** Cobalt-59 NMR spectra in dichloromethane at 25 °C for a mixture of $Co(Et_2dtc)_3$ and $Co(i\text{-}Pr_2dtc)_3$ (a) before and (b) after chemical oxidation with $NOPF_6$.

products of $[Co_2(Et_2dtc)_6]^{2+}$, $[Co_2(Et_2dtc)_3(i\text{-}Pr_2dtc)_3]^{2+}$, and $[Co_2(i\text{-}Pr_2dtc)_6]^{2+}$. $[Co_2(RR'dtc)_5]^{2+}$ could also be a very reactive intermediate. Other mechanisms have previously been postulated for ruthenium.[19,23] In the case of cobalt this work has demonstrated that direct conversion of $[Co(RR'dtc)_3]^+$ to $[Co_2(RR'dtc)_5]^+$ can occur without initial presence of $Co(RR'dtc)_3$.

Voltammetric data in acetone show that the dimer $[Co_2(Me_2dtc)_5]^+$ is oxidized at more positive potentials than the monomer $Co(Me_2dtc)_3$, as is also the case in dichloromethane. In accordance with the published cyclic voltamograms of Barbier et al.,[24] electrochemical oxidation of $Co(Me_2dtc)_3$ is chemically irreversible, generating $[Co_2(Me_2dtc)_5]^+$. The dimer, like the monomer, is more reactive in acetone than in dichloromethane. The claimed stability of Co(IV) dithiocarbamates in acetone[24] and the voltammetry of the dimer in acetone, as published,[24] cannot be substantiated. Further work is required to fully understand the chemistry and electrochemistry of $Co(RR'dtc)_3$ and $[Co_2(RR'dtc)_5]^+$ in acetone.

## Conclusions

The present investigations have shown unequivocally that $[Co(RR'dtc)_3]^+$ does exist as a formally low-spin cobalt(IV) complex. However, it is extremely reactive and can only be identified at ambient temperatures for R = c-Hx or *i*-Pr and R′ = *c*-Hx or *i*-Pr in the noncoordinating solvent $CH_2Cl_2$. The cobalt(IV) cation undergoes an internal redox reaction to produce the cobalt(III) dimer $[Co_2(RR'dtc)_5]^+$. The rate of formation of the dimer very much depends on the R and R′ groups and the concentration. With the ligand $[pyrrdtc]^-$ the transformation occurs even on the time scale of cyclic voltammetry, scan rate 200 mV $s^{-1}$, for concentrations in the millimolar range.

$[Co_2(RR'dtc)_5]^+$ itself is unstable and slowly decomposes to $Co(RR'dtc)_3$. Electrochemical data demonstrate that $[Co_2(RR'dtc)_5]^{2+}$ has a finite existence at low temperatures, but $[Co_2(RR'dtc)_5]^-$ decomposes very rapidly to generate $Co(RR'dtc)_3$. NMR data show that the structural form of the dimer in solution is similar to that in the solid state with nonequivalent cobalt centers. The cobalt dimers are far more reactive than their ruthenium analogues.[19]

## Appendix of Symbols and Abbreviations

| | |
|---|---|
| $E$ | potential |
| $i$ | current |
| $E_p$ | peak potential |
| $\delta$ | NMR chemical shift |
| dtc | dithiocarbamate |
| Bz | benzyl |
| c-Hx | cyclohexyl |
| pipdtc | piperidine-*N*-carbodithioate |
| 2-Mepipdtc | 2-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.** $[Co_2(Me_2dtc)_5]BF_4$, 55744-52-0; $[Co_2(c\text{-}Hx_2dtc)_5]BF_4$, 59733-07-2; $[Co_2(Bz_2dtc)_5]BF_4$, 55744-65-5; $[Co_2(morphdtc)_5]BF_4$, 98612-98-7; $Co(Me_2dtc)_3$, 23677-76-1; $Co(Et_2dtc)_3$, 13963-60-5; $Co(i\text{-}Pr_2dtc)_3$, 24412-36-0; $Co(Bz_2dtc)_3$, 33539-56-9; $Co(c\text{-}Hx_2dtc)_3$, 51205-54-0; $Co(pipdtc)_3$, 20487-61-0; $Co(2\text{-}Mepipdtc)_3$, 86527-85-7; $Co(4\text{-}Mepipdtc)_3$, 86527-87-9; $Co(2,6\text{-}Me_2pipdtc)_3$, 86527-88-0; $Co(pyrrdtc)_3$, 24412-38-2; $Co(morphdtc)_3$, 27796-33-4; $[Co_2(Me_2dtc)_5]^+$, 55744-55-3; $[Co_2(pipdtc)_5]^+$, 98612-99-8; $[Co_2(2\text{-}Mepipdtc)_5]^+$, 98613-00-4; $[Co_2(4\text{-}Mepipdtc)_5]^+$, 98613-01-5; $[Co_2(2,6\text{-}Me_2pipdtc)_5]^+$, 98613-02-6; $[Co_2(pyrrdtc)_5]^+$, 55744-53-1; $Co(i\text{-}Pr\text{-}c\text{-}Hxdtc)_3$, 86527-84-6; $[Co(Me_2dtc)_3]^+$, 52690-17-2; $[Co(Et_2dtc)_3]^+$, 52637-77-1; $[Co(i\text{-}Pr_2dtc)_3]^+$, 52637-79-3; $[Co(Bz_2dtc)_3]^+$, 91670-38-1; $[Co(c\text{-}Hx_2dtc)_3]^+$, 52637-81-7; $[Co(i\text{-}Pr\text{-}c\text{-}Hxdtc)_3]^+$, 98613-03-7; $[Co(morphdtc)_3]^+$, 89183-77-7; $[Co(pyrrdtc)_3]^+$, 97161-79-0; $[Co(4\text{-}Mepipdtc)_3]^+$, 98634-08-3; $[Co_2(Me_2dtc)_5]^{2+}$, 98613-04-8; $[Co_2(Et_2dtc)_5]^{2+}$, 98613-05-9; $[Co_2(i\text{-}Prdtc)_5]^{2+}$, 98613-06-0; $[Co_2(Bz_2dtc)_5]^{2+}$, 98613-07-1; $[Co_2(c\text{-}Hx_2dtc)_5]^{2+}$, 98613-08-2; $[Co_2(i\text{-}Pr\text{-}c\text{-}Hxdtc)_5]^{2+}$, 98634-09-4; $[Co_2(morphdtc)_5]^{2+}$, 98613-09-3; $[Co_2(pyrrdtc)_5]^{2+}$, 98634-10-7; $[Co_2(4\text{-}Mepipdtc)_5]^{2+}$, 98613-10-6; $[Co(Me_2dtc)_3]^-$, 98613-11-7; $[Co(Et_2dtc)_3]^-$, 18042-20-1; $[Co(i\text{-}Pr_2dtc)_3]^-$, 98613-12-8; $[Co(Bz_2dtc)_3]^-$, 98613-13-9; $[Co(c\text{-}Hxdtc)_3]^-$, 98613-14-0; $[Co(i\text{-}Pr\text{-}c\text{-}Hxdtc)_3]^-$, 98613-15-1; $[Co(morphdtc)_3]^-$, 98613-16-2; $[Co(pyrrdtc)_3]^-$, 98613-17-3; $[Co(4\text{-}Mepipdtc)_3]^-$, 98613-18-4; $[Co_2(Et_2dtc)_3(i\text{-}Pr_2dtc)_2]^+$, 98613-19-5; $[Co_2(Et_2dic)_2(i\text{-}Pr_2dtc)_3]^+$, 98613-20-8.

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