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Investigations of Mixed-Ligand Cobalt Dithiocarbamate Complexes by Cobalt-59 Nuclear Magnetic Resonance Spectroscopy, Mass Spectrometry, and Electrochemistry

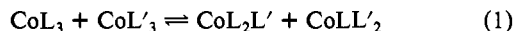
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Tris(dithiocarbamate) complexes of cobalt(III), CoL_3 and CoL'_3 (where L and L' are different dithiocarbamate ligands), undergo ligand exchange at elevated temperatures both in an inert organic solvent and in the solid state to give $\text{CoL}_2\text{L}'$ and CoLL'_2 . The mixed-ligand complexes may also be prepared by methods based on controlled-potential electrochemical oxidation or reduction of cobalt(III) dithiocarbamate complexes. In contrast to these preparative-scale electrolyses, short-time-scale voltammetric and polarographic data for oxidation and reduction exhibit independent responses for the mixed-ligand complexes, implying that the formally cobalt(IV) and cobalt(II) mixed-ligand species undergo slow rather than rapid ligand exchange. Cobalt-59 NMR spectroscopy and electrochemistry in CH_2Cl_2 solution and mass spectrometry are useful techniques to illustrate ligand exchange. Cobalt-59 chemical shifts of the dithiocarbamate complexes cover a wide range and allow identification of the mixed-ligand species in many reaction mixtures as the ligand exchange for the oxidation state III complexes is slow on the NMR (and synthetic) time scales at ambient temperatures. Generally, ^{59}Co NMR chemical shifts do not correlate in a simple linear fashion with electrochemical E° data (or with ^{13}C NMR data), implying that steric effects influence the two techniques in different ways. However, for the mixed-ligand series CoL_3 , $\text{CoL}_2\text{L}'$, CoLL'_2 , and CoL'_3 , the E° and ^{59}Co chemical shifts do correlate exceedingly well. Positive and negative ion mass spectra of CoL_3 species generally show the molecular ions $[\text{CoL}_3]^+$ and $[\text{CoL}_3]^-$, respectively, but the most abundant ions are $[\text{CoL}_2]^+$ and $[\text{CoL}_2]^-$. Mass spectrometric examination of mixtures of CoL_3 and CoL'_3 show evidence of ligand exchange. Mass spectrometry in the gas phase and electrochemical data show interesting correlations.

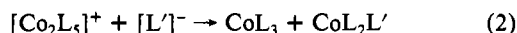
Introduction

The chemistry of transition-metal dithiocarbamate complexes has been studied extensively.³⁻⁵ Iron(III), nickel(II), and mercury(II) complexes all undergo rapid ligand-exchange reactions in solution to form mixed-ligand complexes.⁶⁻⁹ However, in the case of cobalt(III) complexes CoL_3 (L = RR'dtc), a number of workers^{3,10-12} have commented on their extreme stability with respect to substitution and exchange reactions. For example, Pignolet et al.¹² have noted that the exchange reaction



where L and L' are different dithiocarbamate ligands) could not be detected by ^1H NMR after reaction for several hours in refluxing nitrobenzene (195 °C). Similarly, Martin et al.¹¹ could find no voltammetric evidence for ligand exchange on mixing CoL_3 and CoL'_3 in acetone at ambient temperatures.

While no direct reaction between CoL_3 and CoL'_3 to produce mixed-ligand complexes has yet been reported, mixed-ligand complexes of the type $\text{CoL}_2\text{L}'$ have been prepared¹³ by interaction of the dimeric $[\text{Co}_2\text{L}_5]^+$ cation¹⁴ with $[\text{L}']^-$ as shown in eq 2. The



mixed-ligand complex can be separated from CoL_3 by chroma-

tographic techniques and isolated as an extremely stable compound.

In studies of the electrochemistry of CoL_3 complexes¹⁵ it has been noted that CoL_2 , $[\text{CoL}_3]^-$, CoL_3 , $[\text{Co}_2\text{L}_5]^+$, and $[\text{CoL}_3]^+$ can be associated with the redox chemistry of Co(II), Co(III), and Co(IV). Consequently, a number of reaction pathways leading to mixed-ligand complexes may be available via oxidation or reduction processes if the formal oxidation state II and IV complexes are kinetically more labile than their oxidation state III counterparts, as would be expected.

In this work, we describe investigations aimed at further synthesizing and characterizing mixed-ligand complexes of Co(III). Reactions were examined in both solution and solid phases using ^{59}Co NMR, electrochemistry, and mass spectrometry.

Experimental Section

Nomenclature. An appendix of symbols and abbreviations used follows at the end of the text. Undefined symbols have their conventional electrochemical or spectroscopic meaning.

Preparations. The Co(III) dithiocarbamate complexes were synthesized by standard literature methods.^{3,16} Mixed Co(III) dithiocarbamate complexes $\text{CoL}_2\text{L}'$ and CoLL'_2 were prepared as for CoL_3 by using equimolar amounts of two different amines during the preparation, followed by chromatographic separation, or alternatively, they were produced by the method described in ref 13. Other methods of preparation of the mixed-ligand complexes are described later in the text.

Instrumentation. NMR spectra were recorded on a JEOL FX 100 spectrometer: ^{59}Co at 23.77–23.8 MHz with a 20-kHz spectral window and ^{13}C at 25 MHz with an 8-kHz spectral window with wide-band proton decoupling. $\text{Cr}(\text{acac})_3$ was added as a paramagnetic relaxant for the ^{13}C spectra. Cobalt-59 chemical shifts were referenced against $\text{K}_3[\text{Co}(\text{CN})_6]$. Measurements were at 25 °C, and an external ^7Li lock was used. High-frequency positive convention is used for chemical shifts.

Electrochemical studies employing voltammetric methods were carried out with a Princeton Applied Research (PAR, Princeton, NJ) Model 174A polarographic analyzer or a PAR Model 170 electrochemistry system. Both platinum and conventional dropping mercury working electrodes were used with a platinum auxiliary electrode. All potentials were measured against a Ag/AgCl (saturated LiCl in CH_2Cl_2) reference electrode. Controlled-potential electrolysis experiments were performed with a PAR Model 173 potentiostat/galvanostat employing mercury-pool or platinum-gauze working electrodes. Platinum-wire auxiliary electrodes were separated from the test solution via a salt bridge, and the Ag/AgCl reference electrode described above was used. All electrochemical

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Table I. Cobalt-59 and Carbon-13 NMR Data for Co(RR'dtc)₃ Complexes

RR'dtc Complexes				
Co(RR'dtc) ₃		cobalt-59		carbon-13
R	R'	δ ^a	w, Hz ^b	δ ^c
Me	Me	6830	570	204.4
Et	Et	6790	850	203.6
<i>i</i> -Pr	<i>i</i> -Pr	6390	1030	204.1
<i>n</i> -Pr	<i>n</i> -Pr	6740	1200	204.7
<i>i</i> -Bu	<i>i</i> -Bu	6640	1630	205.2
<i>n</i> -Bu	<i>n</i> -Bu	6760	1700	204.2
<i>s</i> -Bu	<i>s</i> -Bu	6350	1500	204.9
<i>n</i> -Pe	<i>n</i> -Pe	6760	1940	204.2
<i>n</i> -Hx	<i>n</i> -Hx	6750	2120	204.2
<i>n</i> -Oc	<i>n</i> -Oc	6760	2740	204.2
Me	<i>i</i> -Pr	6700	400	203.9
Me	<i>i</i> -Bu	6700	820	204.8
Me	<i>n</i> -Bu	6800	1540	204.0
Me	<i>n</i> -Oc	6790	1500	205.0
Et	<i>n</i> -Bu	6780	1430	203.4
Et	<i>t</i> -Bu	6800	1500	206.6
<i>n</i> -Bu	<i>t</i> -Bu	5990	1510	206.5
Me	Ph	6660	1150	206.7
Et	Ph	6680	1250	206.9
<i>n</i> -Pr	Ph	6650	2000	<i>d</i>
<i>n</i> -Bu	Ph	6660	1830	207.2
Me	Bz	6760	1430	205.7
Et	Bz	6725	1770	205.3
Bz	Bz	6650	2400	206.8
<i>c</i> -Hx	<i>c</i> -Hx	6330	1890	203.8
<i>i</i> -Pr	<i>c</i> -Hx	6360	1700	203.4
Et	2-OHEt	6750	850	<i>d</i>
Et	3-OHPh	6670	2800	<i>d</i>
Et	4-Mepy	6710	1250	207.0
Et	<i>m</i> -tol	6690	1700	206.6

N-Heterocyclic Derivatives			
ligand	cobalt-59		carbon-13
	δ ^a	w, Hz ^b	δ ^c
pip	6760	1030	202.5
2-Mepip	6680	1370	202.9
3-Mepip	6750	1250	202.4
4-Mepip	6760	1800	202.8
2,6-Me ₂ pip	6540	1300	203.9
pyrr	7200	1150	199.9
morph	6800	1150	203.5

^a Chemical shifts relative to 1 M K₃[Co(CN)₆] in water.

^b Full width at half-height. ^c Chemical shifts relative to Me₄Si.

^d Insufficiently soluble for carbon-13 NMR spectrum to be observed.

measurements were made at 20 ± 1 °C in dichloromethane (0.1 M Bu₄NClO₄) at concentrations in the range 5 × 10⁻³ – 1 × 10⁻⁴ M. Solutions were degassed with solvent-saturated nitrogen, and a continuous stream of nitrogen was passed over the solutions while measurements were being undertaken.

Electron-impact positive ion mass spectra were obtained on a Finnigan 3200 series low-resolution quadrupole mass spectrometer system, coupled to a Finnigan 6000 series interactive data system. The spectra were measured under the following conditions: electron energy 30–70 eV, filament emission current 0.5 mA, collector voltage 34.8 V, and electron multiplier voltage 1600 V. Samples were introduced via a solids insertion probe and lock at a temperature generally in the range 200–350 °C. Ionization chamber pressures of (3 – 5) × 10⁻⁶ torr were employed. Negative ion chemical ionization mass spectra were recorded on a Finnigan 4000 series mass spectrometer using methane as the reagent gas.

Thermogravimetric analyses were carried out on a Stern Redcroft thermobalance (HT model). Approximately 90 mg of the solid sample was placed in a Pt crucible and left in the oven for a 2-h run, during which time the temperature rose from 25 to 900 °C.

Results and Discussion

Physical methods of measurement on CoL₃ complexes will first be discussed to show which techniques are most suitable for examining the ligand-exchange reactions.

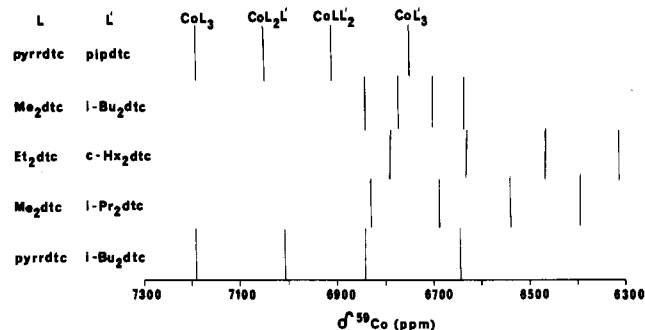


Figure 1. Cobalt-59 NMR chemical shifts in CH₂Cl₂ at 30 °C for the cobalt dithiocarbamates CoL₃, CoL₂L', CoLL'₂, and CoL'₃.

(i) **NMR Spectra.** Cobalt-59^{17–21} and carbon-13²² NMR studies have been reported previously for a few CoL₃ complexes, but no data for these nuclei appear to be available on mixed-ligand complexes.

Table I lists the ⁵⁹Co chemical shifts for a large number of CoL₃ complexes and covers a range of over 1000 ppm. Peak widths at half-height vary markedly and are a reflection of the moderately large electric quadrupole moment of the ⁵⁹Co nucleus (*I* = 7/2), which makes the peak width extremely sensitive to the symmetry about the cobalt atom. Table I also includes ¹³C chemical shifts for the CS₂ portion of the ligand in CoL₃ complexes, and although the signals are much sharper than for cobalt, the chemical shift range is much smaller and it will emerge that ⁵⁹Co NMR is the preferred technique to investigate mixed-ligand complexes on the grounds of both superior dispersion and vastly superior sensitivity.

To confirm that ⁵⁹Co NMR would provide adequate resolution to identify mixed-ligand complexes, several series of CoL₃, CoL₂L', CoLL'₂, and CoL'₃ complexes were prepared by the published method¹³ and the results are shown in Figure 1. In all cases the chemical shifts of CoL₃ and CoL'₃ in the mixtures were the same as for the pure compounds (indicating no detectable exchange at room temperature in CH₂Cl₂) and the chemical shifts of CoL₂L' and CoLL'₂ fall between those of the parent complexes as expected.

In order to determine the suitability of ⁵⁹Co NMR for monitoring pathways of electrochemical redox reactions undertaken at 10⁻¹–10⁻³ M concentration in subsequent work, the concentration dependence of the ⁵⁹Co chemical shift for Co(*i*-Pr₂dte)₃ was examined in the presence and absence of 0.1 M Bu₄NClO₄. Over the concentration range 1 × 10⁻³–0.15 M the chemical shift in dichloromethane was invariant at 6395 ± 5 ppm and independent of the presence or absence of the supporting electrolyte. The concentration independence is consistent with the monomeric formulation of this complex. Importantly, CoL₃ complexes can be detected by ⁵⁹Co NMR at concentrations used in electrochemical measurements (millimolar range).

(ii) **Electrochemical Measurements.** Figure 2a shows alternating-current voltammograms at Pt electrodes for oxidation of CoL₃, CoL₂L', CoLL'₂, and CoL'₃ where L = Bz₂dte and L' = *c*-Hx₂dte. The mixed-ligand complexes CoL₂L' and CoLL'₂ show reversible one-electron oxidations as is the case for pure CoL₃ and CoL'₃. Oxidations on the electrochemical time scale are believed to be the simple processes¹⁵



(where X = L₃, L₂L', LL'₂, L'₃). In this work the assumption that the peak potential, *E*^p, is equal to the standard redox potential,

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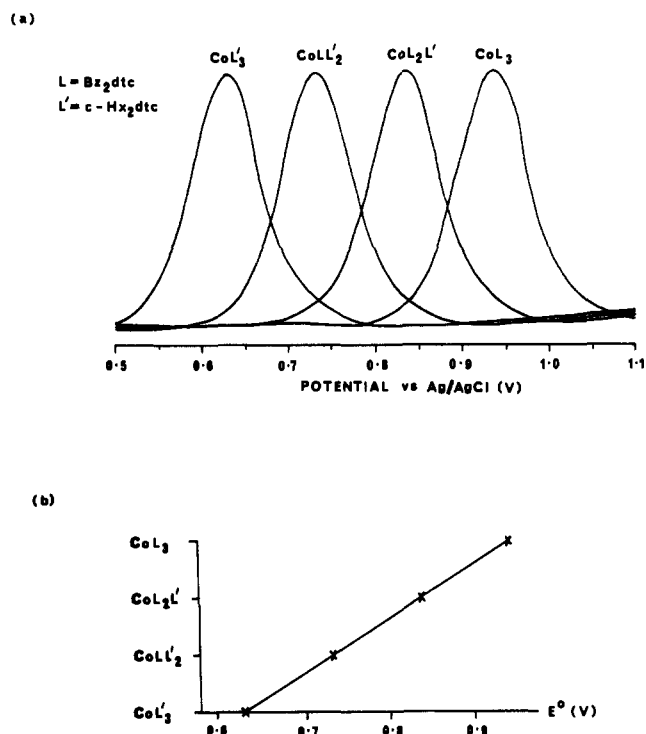


Figure 2. (a) Alternating-current voltammogram at a platinum electrode in CH_2Cl_2 (0.1 M Bu_4NClO_4) for the cobalt dithiocarbamates CoL_3 , $\text{CoL}_2\text{L}'$, CoLL'_2 , and CoL'_3 where $\text{L} = \text{Bz}_2\text{dte}$ and $\text{L}' = \text{c-Hx}_2\text{dte}$ (applied signal 10 mV peak to peak at 200 Hz). (b) Plot showing the linear additive relationships of E° values for the compounds in (a).

E° , was made. A linear progression of E° values for the CoL_3 , $\text{CoL}_2\text{L}'$, CoLL'_2 , and CoL'_3 complexes was observed (see Figure 2b).

Under cyclic conditions with repetitive scanning of the mixed-ligand complexes, no evidence for ligand exchange to generate $[\text{CoL}_3]^+$ or $[\text{CoL}'_3]^+$ was observed. Similar experiments on the reduction of Co(III) at a dropping mercury electrode using differential pulse polarography showed no evidence for ligand exchange between $[\text{CoL}_3]^+$ and $[\text{CoL}'_3]^+$ on the polarographic time scale. Interestingly, neither ^{59}Co or ^{13}C chemical shift data correlate in any linear fashion with electrochemical E° data when the whole range of complexes is considered. However, for the very closely related subset CoL_3 , $\text{CoL}_2\text{L}'$, CoLL'_2 , and CoL'_3 an excellent linear correlation does exist. Substituent effects for the mixed-ligand series are very systematic in both electrochemical and NMR measurements. E° values reflect the thermodynamic influence of substituent effects whereas cobalt-59 and carbon-13 NMR chemical shifts include a number of nonthermodynamic terms. A general lack of correlation between the two sets of physical data presumably reflects a different mode of influence of steric terms.²³

(iii) Mass Spectra. The positive ion mass spectrometry of CoL_3 complexes has been investigated in detail to determine its usefulness in studies of mixed-ligand complexes. Figure 3 (supplementary material) shows the mass spectrum for $\text{Co}(\text{Me}_2\text{dte})_3$; numerical data of mass to charge ratio, m/e , and intensities, I , for all the CoL_3 complexes are given in Table S1 (supplementary material). Several important observations can be made; the molecular ions $[\text{CoL}_3]^+$ are normally observed although intensities vary considerably. Interestingly, the only compounds that showed no molecular ions were $\text{Co}(i\text{-PrPhdte})_3$ and $\text{Co}(n\text{-BuPhdte})_3$ and these are also the only two compounds for which no direct electrochemical evidence for the formation of $[\text{CoL}_3]^+$ could be found in CH_2Cl_2 solution.¹⁵ Mass spectrometry is a form of gas-phase electrochemistry, and the instability of $[\text{CoL}_3]^+$ for these two ligands appears to occur in both the gas phase and in solution.

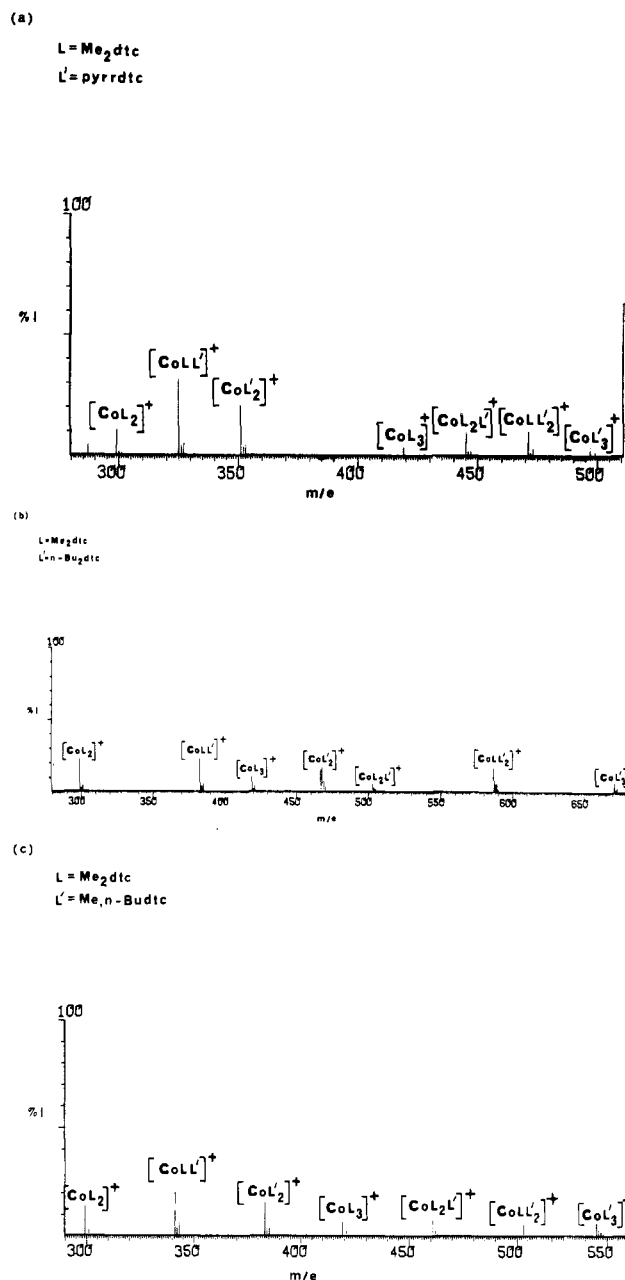


Figure 4. Positive ion mass spectra of mixtures of CoL_3 and CoL'_3 : (a) $\text{L} = \text{Me}_2\text{dte}$, $\text{L}' = \text{pyrddtc}$; (b) $\text{L} = \text{Me}_2\text{dte}$, $\text{L}' = n\text{-Bu}_2\text{dte}$; (c) $\text{L} = \text{Me}_2\text{dte}$, $\text{L}' = \text{Me},n\text{-Budtc}$.

The fragmentation scheme for $[\text{CoL}_3]^+$ is fairly simple, generally only involving loss of ligand, CS_2 , S_2 , CS , or R in most breakdown steps, and is similar to that found in other studies²⁴⁻²⁶ of metal dithiocarbamate complexes. $[\text{CoL}_2]^+$ is usually the ion with greatest intensity. Mass spectra of $\text{CoL}_2\text{L}'$ complexes showed the parent ion $[\text{CoL}_2\text{L}']^+$ as well as low-intensity peaks due to $[\text{CoL}_3]^+$, $[\text{CoL}'_3]^+$, and $[\text{CoLL}'_2]^+$. Intense peaks due to $[\text{CoL}_2]^+$, $[\text{CoL}'_2]^+$, and $[\text{CoLL}'_2]^+$ were also observed. These observations suggest that ligand exchange may occur under conditions of mass spectrometry, and this was confirmed as follows. Figure 4 shows the high-molecular-weight region of the mass spectra of some mixtures of CoL_3 and CoL'_3 . Clearly, m/e values corresponding to mixed-ligand complexes $[\text{CoL}_2\text{L}']^+$ and $[\text{CoLL}'_2]^+$ are seen as well as $[\text{CoLL}'_2]^+$. In Figure 4a an almost statistical distribution (i.e. 1:3:3:1) of intensities is seen for

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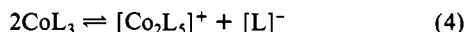
$[\text{CoL}_3]^+$, $[\text{CoL}_2\text{L}']^+$, $[\text{CoLL}'_2]^+$, and $[\text{CoL}'_3]^+$ and 1:2:1 for $[\text{CoL}_2]^+$, $[\text{CoLL}']^+$, and $[\text{CoL}'_2]^+$ although this is not always the case as shown in Figure 4b, c. This confirms that cobalt(III) dithiocarbamate complexes are labile under conditions of positive ion mass spectrometry and thus this technique is not suitable to study the products of possible ligand-exchange reactions between CoL_3 and CoL'_3 carried out under other conditions.

Negative ion mass spectra of metal dithiocarbamate complexes have not been widely reported.²⁷⁻³⁰ The parent ion in negative ion mass spectrometry is normally expected to be present as a peak of relatively high intensity. However, with CoL_3 complexes, relatively weak $[\text{CoL}_3]^-$ peaks but intense $[\text{CoL}_2]^-$ fragments were found (Figure 5, supplementary material), indicating substantial instability of $[\text{CoL}_3]^-$ in the gas phase. Similarly, instability of $[\text{CoL}_3]^-$ was also indicated by electrochemical studies in inert solvents,¹⁵ once again providing a good correlation between mass spectrometry and electrochemistry.

(iv) Exchange Reactions. (a) Exchange Reactions in Oxidation State III. The mass spectral results presented above imply that under the conditions of elevated temperature used in this technique exchange reactions could be occurring. Mixtures of $\text{Co}(\text{Et}_2\text{dtc})_3$ and $\text{Co}(i\text{-Pr}_2\text{dtc})_3$ were heated in the solid state over a range of temperatures from 160 to 220 °C, for a range of pressures from 1 to 760 mmHg, in the presence of both air and nitrogen, and for durations ranging from 2 to 4 days. Prior to heating of the solid mixtures thermogravimetric measurements were made on the complexes to ensure that the reaction temperatures were below the decomposition temperatures of the complexes. After reaction, the solids were dissolved in dichloromethane and ^{59}Co NMR readily showed the presence of the mixed-ligand complexes $\text{CoL}_2\text{L}'$ and CoLL'_2 , confirming that solid-state ligand exchange does indeed occur.

Despite the report¹² that ligand-exchange reactions of cobalt dithiocarbamate complexes do not occur after refluxing in nitrobenzene solution at 195 °C, we have observed exchange reactions in chloronaphthalene. Refluxing of $\text{Co}(\text{Et}_2\text{dtc})_3$ and $\text{Co}(i\text{-Pr}_2\text{dtc})_3$ at 155 °C in chloronaphthalene for 4–5 h, followed by chromatographic separation of the cobalt dithiocarbamate complexes and subsequent ^{59}Co NMR examination in CH_2Cl_2 , provides convincing evidence for the formation of $\text{CoL}_2\text{L}'$ and CoLL'_2 . Perhaps surprisingly, Brinkhoff^{31a} has observed that mixing $\text{Co}(\text{Et}_2\text{dtc})_3$ and $\text{Co}(\text{Et}_2\text{txan})_3$ in chloroform and refluxing produces $\text{Co}(\text{Et}_2\text{txan})(\text{Et}_2\text{dtc})_2$. Similarly, ready exchange of cobalt dithiophosphate complexes has been reported.^{31b} Specific effects may be operative in some systems to cause exchange under milder conditions than in refluxing nitrobenzene.

Interconversion of compounds at elevated temperatures in the solid state has been observed in other areas of chemistry.³² The mechanism of exchange may be postulated to involve the enhanced formation of the dimer cation $[\text{Co}_2\text{L}_5]^+$ at higher temperature:



The mass spectrum of $[\text{Co}_2\text{L}_5]^+$, apart from detection of fragments from the anion, is not surprisingly indistinguishable

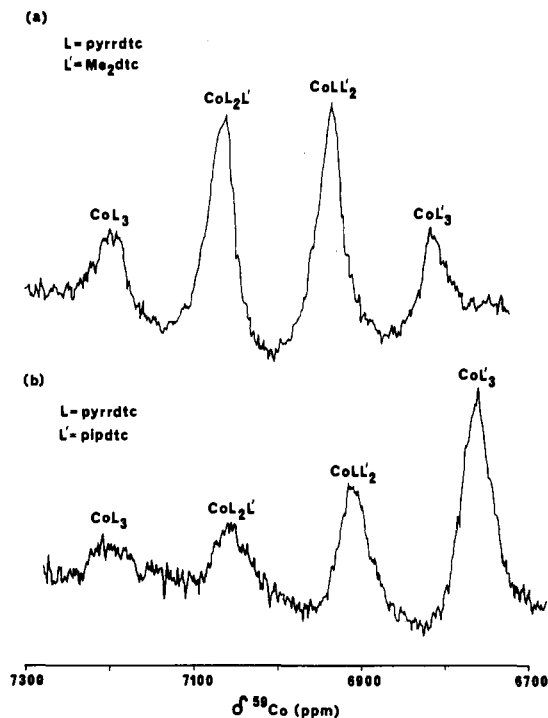
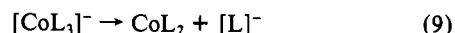
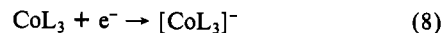


Figure 6. Cobalt-59 NMR spectra in CH_2Cl_2 at 30 °C for the cobalt dithiocarbamates CoL_3 , $\text{CoL}_2\text{L}'$, CoLL'_2 , and CoL'_3 : (a) $\text{L} = \text{pyrddtc}$, $\text{L}' = \text{Me}_2\text{dtc}$; (b) $\text{L} = \text{pyrddtc}$, $\text{L}' = \text{pipdtc}$.

from that of CoL_3 . With the instrumentation available to us, we were unable to examine molecular weights above 800, although with single-ion counting on CoL_3 complexes evidence for $[\text{Co}_2\text{L}_4]^+$ could be found. In the particular case of the relatively low molecular weight complex $\text{Co}(\text{Me}_2\text{dtc})_3$, single-ion-counting mass spectrometric evidence for $[\text{Co}_2(\text{Me}_2\text{dtc})_5]^+$ could also be found.

MacDonald and Shannon³³ have demonstrated via mass spectrometry that many acetylacetonates exist in the gas phase as dimeric species. Similarly, the formation of dimers is known for many dithiocarbamates,³⁻⁵ and although NMR data in this work and other data all indicate that CoL_3 exists predominantly as the monomer in both solution and in the solid state^{3-5,34-36} at ambient temperatures, it is not unreasonable to propose that formation of $[\text{Co}_2\text{L}_5]^+$ may be enhanced at elevated temperature. We have shown using ^{59}Co NMR that $[\text{Co}_2\text{L}_5]^+$ reacts readily with $[\text{L}']^-$ in CH_2Cl_2 at ambient temperatures to produce $\text{CoL}_2\text{L}'$ and CoL_3 , in agreement with the literature.¹³ Equations 4–7 would therefore seem to provide a favorable route to the enhanced rate of exchange noted at high temperatures. The reactions must occur in the solid phase followed by vaporization of the products.

(b) Exchange Reactions in Oxidation State II. In oxidation state II cobalt is known to be chemically labile. Electrochemical reduction of CoL_3 to $[\text{CoL}_3]^-$ may occur with subsequent loss of ligand in inert solvents (see eq 9). More recent studies show that loss of ligand is catalyzed by traces of oxygen.³⁷



In dichloromethane no exchange reactions were observed with short-time-scale polarographic experiments in the absence of oxygen as described above. In long-time-scale electrolysis experiments ligand-exchange reactions are readily performed at 20 °C by simultaneous electrochemical reduction of CoL_3 and CoL'_3

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Table II. Cobalt-59 NMR Chemical Shifts for Mixed-Ligand Complexes

ligands		$\delta(^{59}\text{Co})^a$			
L	L'	CoL ₃	CoL ₂ L'	CoLL' ₂	CoL' ₃
pyrrdtc	<i>i</i> -Bu ₂ dtc	7190	7010	6840	6640
pyrrdtc	pipdtc	7190	7060	6910	6760
pyrrdtc	Me ₂ dtc	7200	7070	6950	6820
pyrrdtc	<i>i</i> -Pr ₂ dtc	7200	6920	6650	6390
Me ₂ dtc	<i>i</i> -Pr ₂ dtc	6830	6690	6540	6400
Me ₂ dtc	<i>i</i> -Bu ₂ dtc	6840	6770	6700	6640
pyrrdtc	<i>c</i> -Hx ₂ dtc	7200	6960	6590	6320
morphdtc	<i>c</i> -Hx ₂ dtc	6790	6660	6550	6310
Et ₂ dtc	<i>c</i> -Hx ₂ dtc	6790	6630	6470	6320
morphdtc	<i>i</i> -Pr ₂ dtc	6800	6660	6530	6400
Et ₂ dtc	<i>i</i> -Pr ₂ dtc	6800	6670	6530	6400
<i>n</i> -Bu ₂ dtc	<i>i</i> -Pr ₂ dtc	6760	6630	6520	6410
pipdtc	<i>c</i> -Hx ₂ dtc	6770	6610	6440	6310
<i>n</i> -Bu ₂ dtc	<i>c</i> -Hx ₂ dtc	6750	6610	6450	6310
<i>n</i> -Hx ₂ dtc	<i>i</i> -Pr ₂ dtc	6770	6660	6530	6410
<i>n</i> -Oc ₂ dtc	<i>i</i> -Pr ₂ dtc	6820	6670	6530	6390
<i>n</i> -Hx ₂ dtc	<i>c</i> -Hx ₂ dtc	6780	6600	6420	
pyrrdtc	EtPhdtc	7200	7020	6830	
Me ₂ dtc	<i>c</i> -Hx ₂ dtc	6830	6680	6570	6320

^a Chemical shifts relative to 1 M K₃[Co(CN)₆] in water.

or reduction of CoL₃ in the presence of [L']⁻ at a mercury-pool electrode. Subsequent aerial oxidation of the cobalt(II) species to cobalt(III) leads to ⁵⁹Co NMR identification of CoL₃, CoL₂L', CoLL'₂, and CoL'₃. Essentially the same results were obtained by mixing cobalt(II) nitrate and equimolar quantities of [L]⁻ and [L']⁻ in water in the presence of oxygen and filtering off the solid followed by purifying and dissolving in dichloromethane. Figure 6a shows that for some ligand combinations the formation of complexes is close to the statistical distribution, whereas for others this is not the case, as shown in Figure 6b. This method of synthesis offers a more convenient preparation of mixed-ligand complexes than the reaction of [L']⁻ with [Co₂L₅]⁺. Table II summarizes mixed-ligand ⁵⁹Co NMR data obtained from these experiments, and it can be noted that, except for two combinations of L and L', all four cobalt(III) complexes could be observed.

(c) Exchange Reactions in Oxidation State IV. It was shown previously that under short-time-scale electrochemical conditions no exchange of formally Co(IV) complexes occurs. Longer time scale experiments, such as oxidative controlled-potential electrolysis of CoL₃ at Pt electrodes followed by addition of [L']⁻ and isolation of solid material, does lead to the identification of mixed-ligand complexes by ⁵⁹Co NMR measurements. However, since it is known that [Co₂L₅]⁺ is isolated as a product of electrolysis of CoL₃,¹⁵ the interpretations of these experiments or related ones are open to doubt as they are likely to reflect the chemistry of [Co₂L₅]⁺ rather than that of [CoL₃]⁺. However, on the basis of data from short-time-scale voltammetric measurements, exchange reactions of [CoL₃]⁺ are not extraordinarily fast.

Conclusion. In summary, mixed-ligand complexes can be formed directly by heating a mixture of CoL₃ and CoL'₃ in the solid state and in solution or by reducing or oxidizing CoL₃ in the presence of a source of [L']⁻. In oxidation state II the exchange

reactions presumably occur via the lability of the d⁷ configuration. In oxidation states III and IV the chemistry associated with the dimer [Co₂L₅]⁺ is believed to be an important intermediate in the steps leading to the formation of mixed-ligand complexes.

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Appendix: Symbols and Abbreviations³⁸

L or L'	RR'dtc ligand
2-OHEt	2-hydroxyethyl
3-OHPh	3-hydroxyphenyl
4-Mepy	4-methylpyridine

Registry No. Co(Me₂dtc)₃, 23677-76-1; Co(Et₂dtc)₃, 13963-60-5; Co(*i*-Pr₂dtc)₃, 24412-36-0; Co(*n*-Pr₂dtc)₃, 28459-60-1; Co(*i*-Bu₂dtc)₃, 28090-33-7; Co(*n*-Bu₂dtc)₃, 28090-32-6; Co(*s*-Bu₂dtc)₃, 95313-05-6; Co(*n*-Pe₂dtc)₃, 28090-34-8; Co(*n*-Hx₂dtc)₃, 86527-75-5; Co(*n*-Oc₂dtc)₃, 86527-76-6; Co(*i*-PrMedtc)₃, 74994-08-4; Co(*i*-BuMedtc)₃, 95313-06-7; Co(*n*-BuMedtc)₃, 55059-62-6; Co(*n*-OcMedtc)₃, 95313-07-8; Co(*n*-BuEtdtc)₃, 86527-77-7; Co(*i*-BuEtdtc)₃, 95313-08-9; Co(*n*-Bu-*i*-Budtc)₃, 86527-78-8; Co(MePhdtc)₃, 86527-79-9; Co(EtPhdtc)₃, 36015-82-4; Co(*n*-PrPhdtc)₃, 95313-09-0; Co(*n*-BuPhdtc)₃, 86527-81-3; Co(MeBzdtc)₃, 86527-82-4; Co(EtBzdtc)₃, 86527-83-5; Co(Bzdtc)₃, 33539-56-9; Co(*c*-Hx₂dtc)₃, 51205-54-0; Co(*i*-Pr-*c*-Hxdtc)₃, 86527-84-6; Co(2-OHEtEtdtc)₃, 95313-10-3; Co(3-OHPhEtdtc)₃, 95313-11-4; Co(4-MepyEtdtc)₃, 95313-12-5; Co(*m*-tolEtdtc)₃, 35924-68-6; Co(pipdtc)₃, 20487-61-0; Co(2-Me-pipdtc)₃, 86527-85-7; Co(3-Me-pipdtc)₃, 86527-86-8; Co(4-Me-pipdtc)₃, 86527-87-9; Co(2,6-Me₂pipdtc)₃, 86527-88-0; Co(pyrrdtc)₃, 24412-38-2; Co(morphdtc)₃, 27796-33-4; Co(pyrrdtc)₂(*i*-Bu₂dtc), 95313-13-6; Co(pyrrdtc)₂(*i*-Bu₂dtc)₂, 95313-14-7; Co(pyrrdtc)₂(pipdtc), 95313-15-8; Co(pyrrdtc)(pipdtc)₂, 95313-16-9; Co(pyrrdtc)₂(Me₂dtc), 95313-17-0; Co(pyrrdtc)(Me₂dtc)₂, 95313-18-1; Co(pyrrdtc)₂(*i*-Pr₂dtc), 95313-19-2; Co(pyrrdtc)(*i*-Pr₂dtc)₂, 95313-20-5; Co(Me₂dtc)₂(*i*-Pr₂dtc), 95313-21-6; Co(Me₂dtc)(*i*-Pr₂dtc)₂, 95313-22-7; Co(Me₂dtc)₂(*i*-Bu₂dtc), 95313-23-8; Co(Me₂dtc)(*i*-Bu₂dtc)₂, 95313-24-9; Co(pyrrdtc)₂(*c*-Hxdtc), 95313-25-0; Co(pyrrdtc)(*c*-Hxdtc)₂, 95313-26-1; Co(morphdtc)₂(*c*-Hxdtc), 95313-27-2; Co(morphdtc)(*c*-Hxdtc)₂, 95313-28-3; Co(Et₂dtc)₂(*c*-Hxdtc), 95313-29-4; Co(Et₂dtc)(*c*-Hxdtc)₂, 95344-19-7; Co(morphdtc)₂(*i*-Pr₂dtc), 95313-30-7; Co(morphdtc)(*i*-Pr₂dtc)₂, 95313-31-8; Co(Et₂dtc)₂(*i*-Pr₂dtc), 95313-32-9; Co(Et₂dtc)(*i*-Pr₂dtc)₂, 95344-10-8; Co(*n*-Bu₂dtc)₂(*i*-Pr₂dtc), 95344-11-9; Co(*n*-Bu₂dtc)(*i*-Pr₂dtc)₂, 95313-33-0; Co(pipdtc)(*c*-Hx₂dtc), 95313-34-1; Co(pipdtc)(*c*-Hx₂dtc)₂, 95313-35-2; Co(*n*-Bu₂dtc)₂(*c*-Hx₂dtc), 95313-36-3; Co(*n*-Bu₂dtc)(*c*-Hx₂dtc)₂, 95313-37-4; Co(*n*-Hx₂dtc)₂(*i*-Pr₂dtc), 95313-38-5; Co(*n*-Hx₂dtc)(*i*-Pr₂dtc)₂, 95313-39-6; Co(*n*-Oc₂dtc)₂(*i*-Pr₂dtc), 95313-40-9; Co(*n*-Oc₂dtc)(*i*-Pr₂dtc)₂, 95313-41-0; Co(*n*-Hx₂dtc)₂(*c*-Hxdtc), 95313-42-1; Co(*n*-Hx₂dtc)(*c*-Hxdtc)₂, 95313-43-2; Co(pyrrdtc)₂(EtPhdtc), 95313-44-3; Co(pyrrdtc)(EtPhdtc)₂, 95313-45-4; Co(Me₂dtc)₂(*c*-Hx₂dtc), 58601-83-5; Co(Me₂dtc)(*c*-Hx₂dtc)₂, 95313-46-5; Co(Bzdtc)₂(*c*-Hx₂dtc), 95313-47-6; Co(Bzdtc)(*c*-Hx₂dtc)₂, 95313-48-7; Co, 7440-48-4.

Supplementary Material Available: Table S1, listing the relative intensities of fragmentation products obtained from the positive ion mass spectra of a range of Co(RR'dtc)₃ complexes, and Figures 3 and 5, showing positive and negative ion spectra (6 pages). Ordering information is given on any current masthead page.

(38) Other symbols and abbreviations are as defined in ref 15.