

Electrospray Mass Spectrometric Study of the Nature and Lability of Cationic Complexes Generated by the Reaction of Solutions of Neutral Iron(III), Cobalt(III), Nickel(II) and Copper(II) Dithiocarbamates with Nitrosonium Tetrafluoroborate

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Cationic products formed by reaction of $\text{Fe}(\text{R}_2\text{dtc})_3$, $\text{Co}(\text{R}_2\text{dtc})_3$, $\text{Ni}(\text{R}_2\text{dtc})_2$, and $\text{Cu}(\text{R}_2\text{dtc})_2$ ($\text{R}_2\text{dtc} = \text{S}_2\text{CNR}_2$, dithiocarbamate) with NOBF_4 in dichloromethane are readily identified directly from the solutions by electrospray mass spectrometry (ESMS). Previously characterized species such as $[\text{Fe}(\text{R}_2\text{dtc})_3]^+$, $[\text{Co}_2(\text{R}_2\text{dtc})_5]^+$, $[\text{Ni}(\text{R}_2\text{dtc})_3]^+$, and $[\text{Cu}(\text{R}_2\text{dtc})_2]^+$ are major products resulting from NO^+ acting as a one-electron oxidant, and intact ions corresponding to these formulations are observed in the electrospray mass spectra at low ion source energies. At higher ion source energies, fragment ions such as $[\text{Fe}(\text{R}_2\text{dtc})_2]^+$, $[\text{Ni}(\text{R}_2\text{dtc})_2]^+$ etc are observed. The paramagnetic Fe(IV), Ni(IV), and Cu(III) complexes are all shown to be kinetically labile, since complete ligand exchange occurs on mixing different cations. In contrast, mixing different dicobalt(III) cations shows exchange of the $[\text{Co}(\text{R}_2\text{dtc})_2]^+$ units rather than global ligand exchange. The previously unreported sulfur-rich cations $[\text{Co}_2(\text{R}_2\text{dtc})_5\text{S}]^+$ are identified as products of the reaction between $\text{Co}(\text{R}_2\text{dtc})_3$ and NOBF_4 , and $[\text{Co}_2(\text{R}_2\text{dtc})_5\text{S}_2]^+$ is observed to be a product of the reaction of $[\text{Co}_2(\text{R}_2\text{dtc})_5\text{S}]^+$ with elemental sulfur. Other products identified by reaction of neutral dithiocarbamates with NOBF_4 include $[\text{Fe}(\text{R}_2\text{dtc})_2\text{NO}]^+$, $[\{\text{Fe}(\text{R}_2\text{dtc})_3\}_2(\text{R}_4\text{bitt})]^{2+}$ ($[\text{R}_4\text{bitt}]^{2+} = 3,5\text{-bis}(N,N\text{-dialkyliminium } 1,2,4\text{-trithiolane})$) and $[\text{Cu}(\text{R}_2\text{dtc})_2\text{S}]^+$. The studies undertaken in this work confirm the relative ease of identifying cationic species in solution by ESMS irrespective of whether they are diamagnetic or paramagnetic and whether they are kinetically labile or inert in the ligand exchange sense.

Introduction

The redox chemistry of neutral $\text{M}(\text{R}_2\text{dtc})_3$ and $\text{M}(\text{R}_2\text{dtc})_2$ transition metal dithiocarbamate complexes has been extensively reviewed.³⁻⁷ A particular feature of note when oxidation takes place is the formation of unusually stable high oxidation state $[\text{M}(\text{R}_2\text{dtc})_3]^+$ and $[\text{M}(\text{R}_2\text{dtc})_2]^+$ complexes as well as a range of $[\text{M}_2(\text{R}_2\text{dtc})_5]^+$ and other cationic moieties. The exact nature of the products formed depends on the metal. The formation of cationic, higher oxidation state dithiocarbamates in these reactions suggests that the new technique of electrospray mass spectrometry (ESMS) should facilitate the identification of products formed when reactions involving oxidation are of interest.

ESMS, unlike other forms of mass spectrometry, allows preexisting ions in solution to be very gently transferred to the gas phase with minimal fragmentation. The ES technique has been developed mainly by Fenn and his co-workers,⁸⁻¹⁰ and its most common applications have been in the area of mass spectrometric studies of large biomolecules.¹¹⁻¹³ However, recent work in our laboratories has shown that ESMS may advantageously be applied to a wide variety of inorganic and organometallic ionic species.¹⁴⁻²⁰ In the cases of nonlabile cations and

anions, such as $[(\text{P-P})\text{Pt}(\text{R}_2\text{dtc})]^+$ ($\text{P-P} = \text{diphosphine}$; $\text{R}_2\text{dtc} = \text{dithiocarbamate } \text{S}_2\text{CNR}_2$) and $[\text{Cr}(\text{CO})_5\text{I}]^-$ the intact ions are usually observed without difficulty.¹⁴⁻¹⁷ For labile complexes, fragment ions formed by loss of one or more ligands may be observed together with the intact ions. Interestingly, in cationic or anionic systems where ligands are exchanging rapidly on the NMR time scale at room temperature, the ESMS technique allows observation of the individual species at room temperature and provides a viable alternative to low-temperature NMR studies for their characterization. Examples of labile systems to which this technique has already been applied include Cu(I) mixed ligand cations,¹⁸ phosphine complexes of Hg(II),¹⁹ and mixed tris-(dithiophosphato)zinc(II) anions.²⁰

Oxidation studies of $\text{M}(\text{R}_2\text{dtc})_3$ and $\text{M}(\text{R}_2\text{dtc})_2$ complexes have usually been undertaken by standard chemical reactions or electrochemically.³⁻⁷ In this paper we report studies on the reactions of $\text{Fe}(\text{R}_2\text{dtc})_3$, $\text{Co}(\text{R}_2\text{dtc})_3$, $\text{Ni}(\text{R}_2\text{dtc})_2$, and $\text{Cu}(\text{R}_2\text{dtc})_2$ with NOBF_4 . In a few areas of chemistry, NO^+ has been shown to act as a powerful, innocent one-electron oxidant to produce NO gas, in oxidative addition reactions to generate nitrosyl compounds, and in other ways.^{21,22} If NOBF_4 acts solely as an innocent one-electron oxidant, the products formed with the dithiocarbamate compounds noted above are predicted to be $[\text{Fe}(\text{R}_2\text{dtc})_3]^+$, $[\text{Co}_2(\text{R}_2\text{dtc})_5]^+$, $[\text{Ni}(\text{R}_2\text{dtc})_3]^+$, and $[\text{Cu}(\text{R}_2\text{dtc})_2]^+$.

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dtc)₂]⁺, respectively. However, a range of reaction mechanisms must occur in order to achieve the relevant oxidation state and coordination number, and simple electron transfer reactions cannot always be the only reaction pathway.

In this paper therefore we wish to evaluate by ESMS the composition of species formed by reaction of metal dithiocarbamates with NOBF₄ and to determine the kinetic lability of paramagnetic high oxidation state metal dithiocarbamates by examining the ligand exchange reactions of mixtures of different cations.

Experimental Section

Preparations and Instrumentation. Fe(R₂dtc)₃,²³ Co(R₂dtc)₃,²⁴ [Co₂(R₂dtc)₅]⁺,²⁵ Ni(R₂dtc)₂,²⁶ and Cu(R₂dtc)₂²⁷ were prepared by literature methods.³ [Co₂(R₂dtc)₅S₂]⁺ was prepared by adding elemental sulfur to a solution containing [Co₂(R₂dtc)₅]⁺ and [Co₂(R₂dtc)₅S]⁺ as described in the text. NOBF₄ (Aldrich) was used as received, and all solvents were AR grade or better.

Electrospray mass spectra were recorded by using a VG Bio-Q triple quadrupole mass spectrometer²⁸ with a water/methanol/acetic acid (50:50:1%) mobile phase. The compounds were dissolved in dichloromethane (2 mM) at room temperature, and a small amount of solid NOBF₄ was added. After a few minutes reaction (color change), a portion of this solution was diluted 1:10 with methanol. The diluted solution was injected directly into the spectrometer via a Rheodyne injector equipped with a 10-μL loop using a Phoenix 20 micro LC syringe pump to deliver the solution to the vaporization nozzle of the electrospray ion source at a flow rate of 3 μL min⁻¹. Voltages at the first skimmer electrode (B1) were varied between 100 V and the minimum possible consistent with retaining a stable ion jet. This varies from time to time but is usually in the range 25–30 V. Increasing the B1 voltage enhances the formation of daughter ions following intermolecular collisions within the ion source which operates at atmospheric pressure. In addition, ions of a particular *m/z* value (e.g. the peak maximum in an isotopic mass distribution) can be selected and passed through a collision cell into a second mass analyzer. At low ion energies and with no added collision gas the stabilities of the selected ions can be investigated. Collisionally activated decomposition (CAD) mass spectra of these selected ions were obtained by admitting argon to the collision cell to a pressure that gave an approximately 50% reduction in the parent ion abundance, usually with an accelerating voltage of 200 V.

Results and Discussion

All peaks in the ES mass spectra are identified by the most intense *m/z* value within the isotopic mass distribution. In all cases the agreement between experimental and calculated isotopic mass distribution was excellent.

Iron Dithiocarbamates. The chemistry of iron dithiocarbamates has been widely studied, and compounds in oxidation states II, III, and IV have been isolated. Fe(R₂dtc)₂ is air sensitive and is rapidly oxidized to stable Fe(R₂dtc)₃.^{3–5} Pasek and Straub²⁹ first generated the Fe(IV) compounds [Fe(R₂dtc)₃]⁺ from the Fe(III) compound in benzene solution by air oxidation in the presence of BF₃. Subsequently other mild oxidants such as FeCl₃³⁰ and reaction with oxygen in the presence of perchloric acid,³¹ as well as electrochemical oxidation,³² have been employed to prepare the Fe(IV) cations.

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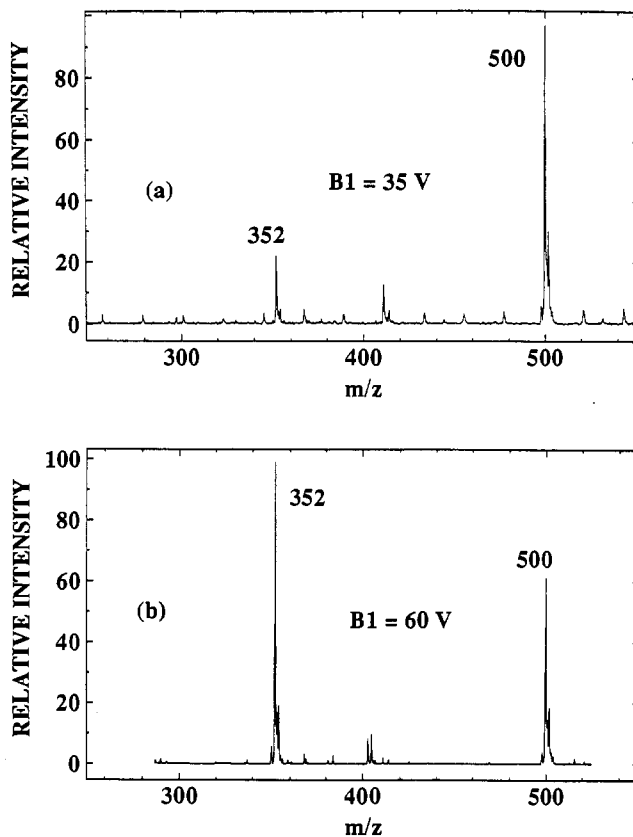
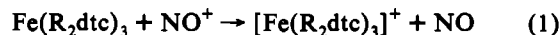
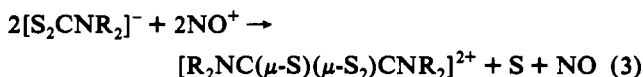


Figure 1. Positive ion ES mass spectra obtained when a solution of Fe(Et₂dtc)₃ is reacted with NOBF₄: (a) B1 = 35 V (b) B1 = 60 V.

Oxidation of Fe(R₂dtc)₃ in dichloromethane (2.0 mM) with nitrosonium tetrafluoroborate resulted in a change from dark red brown to colorless. Figure 1a shows the ES mass spectrum at a low ion source energy of 35 V of an oxidized solution of Fe(Et₂dtc)₃ diluted 1:10 with methanol before injection into the ES mass spectrometer. The peak at *m/z* 500 is due to the intact ion [Fe(Et₂dtc)₃]⁺ and that at *m/z* 352 is assigned to [Fe(Et₂dtc)₂]⁺. As the ion source energy is increased to 60 V (Figure 1b) the relative intensity of the peak at *m/z* 352 increases, which suggests it is formed from the intact ion (*m/z* 500) by collisional activation within the ion source. Generally similar results were obtained after the oxidation of a number of other iron(III) tris(dithiocarbamates). Data for strong peaks observed at low ion source energies (that is, with minimal fragmentation) are given in Table I. In the case of Fe(R₂dtc)₃ compounds, ESMS data suggests that NO⁺ acts predominantly as a one-electron oxidant according to eq 1.



In addition to the species identified so far, weak peaks were frequently observed at higher *m/z* values. These can be assigned to the formation of small amounts of cations such as [Fe(R₂dtc)₃]₂(R₄bitt)²⁺ ([R₄bitt]²⁺ = 3,5-bis(*N,N*-diethyliminium 1,2,4-trithiolane dication⁷) of unknown structure which contain coordinated and oxidized ligand. NO⁺ is strong enough to oxidize [dtc]⁻ to thiuram disulfide (tds) and [R₄bitt]²⁺ as in eqs 2 and 3. Presumably small amounts of [R₄bitt]²⁺ are



generated from [dtc]⁻ released during the course of the oxidation

Table I. Cations Identified by ESMS from the Reaction between $\text{Fe}(\text{R}_2\text{dtc})_3$ and NOBF_4

reaction	ions in ES mass spectrum (m/z) ^a
$\text{Fe}(\text{Et}_2\text{dtc})_3 + \text{NOBF}_4$	$[\text{Fe}(\text{Et}_2\text{dtc})_3]^+$ (500), $[\text{Fe}(\text{Et}_2\text{dtc})_2]^+$ (352)
$\text{Fe}(\text{Pr}_2\text{dtc})_3 + \text{NOBF}_4$	$[\text{Fe}(\text{Pr}_2\text{dtc})_3]^+$ (584), $[\text{Fe}(\text{Pr}_2\text{dtc})_2]^+$ (408)
$\text{Fe}(\text{Bu}_2\text{dtc})_3 + \text{NOBF}_4$	$[\text{Fe}(\text{Bu}_2\text{dtc})_3]^+$ (668), $[\text{Fe}(\text{Bu}_2\text{dtc})_2\text{NO}]^+$ (494), $[\text{Fe}(\text{Bu}_2\text{dtc})_2]^+$ (464)
$\text{Fe}(\text{Bz}_2\text{dtc})_3 + \text{NOBF}_4$	$[\text{Fe}(\text{Bz}_2\text{dtc})_3]^+$ (872), $[\text{Fe}(\text{Bz}_2\text{dtc})_2\text{NO}]^+$ (630), $[\text{Fe}(\text{Bz}_2\text{dtc})_2]^+$ (600)
$\text{Fe}(\text{morphdtc})_3 + \text{NOBF}_4$	$[\text{Fe}(\text{morphdtc})_3]^+$ (542), $[\text{Fe}(\text{morphdtc})_2]^+$ (380)
$\text{Fe}(\text{pipdtc})_3 + \text{NOBF}_4$	$[\text{Fe}(\text{pipdtc})_3]^+$ (536), $[\text{Fe}(\text{pipdtc})_2\text{NO}]^+$ (406), $[\text{Fe}(\text{pipdtc})_2]^+$ (376)
$[\text{Fe}(\text{Pr}_2\text{dtc})_3]^+ + [\text{Fe}(\text{Bu}_2\text{dtc})_3]^+$	$[\text{Fe}(\text{Bu}_2\text{dtc})_3]^+$ (668), $[\text{Fe}(\text{Pr}_2\text{dtc})(\text{Bu}_2\text{dtc})_2]^+$ (640), $[\text{Fe}(\text{Pr}_2\text{dtc})_2(\text{Bu}_2\text{dtc})]^+$ (612), $[\text{Fe}(\text{Pr}_2\text{dtc})_3]^+$ (584), $[\text{Fe}(\text{Bu}_2\text{dtc})_2]^+$ (464), $[\text{Fe}(\text{Pr}_2\text{dtc})(\text{Bu}_2\text{dtc})]^+$ (436), $[\text{Fe}(\text{Pr}_2\text{dtc})_2]^+$ (408)
$[\text{Fe}(\text{Pr}_2\text{dtc})_3]^+ + [\text{Fe}(\text{pipdtc})_3]^+$	$[\text{Fe}(\text{Pr}_2\text{dtc})_3]^+$ (584), $[\text{Fe}(\text{Pr}_2\text{dtc})_2(\text{pipdtc})]^+$ (568), $[\text{Fe}(\text{Pr}_2\text{dtc})(\text{pipdtc})_2]^+$ (552), $[\text{Fe}(\text{pipdtc})_3]^+$ (536), $[\text{Fe}(\text{Pr}_2\text{dtc})_2]^+$ (408), $[\text{Fe}(\text{Pr}_2\text{dtc})(\text{pipdtc})]^+$ (392), $[\text{Fe}(\text{pipdtc})_2]^+$ (376)

^a Most intense ions observed at low ion source energies. ^b morphdtc = morpholine-*N*-carbodithioate; pipdtc = piperidine-*N*-carbodithioate.

process. In some cases the ions $[\text{Fe}(\text{R}_2\text{dtc})_2\text{NO}]^+$ were also observed. The six coordinate nitrosyl compounds $[\text{Fe}(\text{R}_2\text{dtc})_2\text{NO}(\text{CH}_3\text{CN})]^+$ have previously been prepared in acetonitrile solution.³³ Presumably the reaction



occurs which as well as forming the nitrosyl derivative, provides a source of free dithiocarbamate which on oxidation with NO^+ (eq 3) leads to the formation of $[\text{R}_4\text{bitt}]^{2+}$.

It has been shown³¹ by NMR and electrochemical methods that the oxidation state III $\text{Fe}(\text{R}_2\text{dtc})_3$ compounds are labile and readily exchange ligands. For example, a mixture of $\text{Fe}(\text{cHx}_2\text{dtc})_3$ ($\text{cHx}_2\text{dtc} = (\text{c-C}_6\text{H}_{11})_2\text{NCS}_2$) and $\text{Fe}(\text{Bz}_2\text{dtc})_3$ ($\text{Bz}_2\text{dtc} = (\text{C}_6\text{H}_5\text{CH}_2)_2\text{NCS}_2$) gave four oxidation responses corresponding to all the possible stoichiometric combinations. The corresponding ligand exchange reactions for the oxidation state Fe(IV) compounds can be investigated by ESMS by mixing solutions of two different cations, $[\text{Fe}(\text{R}_2\text{dtc})_3]^+$ and $[\text{Fe}(\text{R}'_2\text{dtc})_3]^+$. In all cases the ES mass spectra for the mixtures show that complete ligand exchange readily occurs with peaks being observed for the original cations and for $[\text{Fe}(\text{R}_2\text{dtc})_2(\text{R}'_2\text{dtc})]^+$ and $[\text{Fe}(\text{R}_2\text{dtc})(\text{R}'_2\text{dtc})_2]^+$. ESMS data for some representative systems are given in Table I. It is now evident that iron dithiocarbamate lability occurs in both the Fe(III) and Fe(IV) oxidation states on the synthetic time scale. The formation of small amounts of high m/z cations such as $[\{\text{Fe}(\text{R}_2\text{dtc})_3\}_2(\text{R}_4\text{bitt})]^{2+}$ and the nitrosyl compounds presumably reflects the general lability of the $[\text{Fe}(\text{R}_2\text{dtc})_3]^{+0}$ system in both oxidation states.

Cobalt Dithiocarbamates. The tris(dithiocarbamates) of cobalt(III), $\text{Co}(\text{R}_2\text{dtc})_3$, have also been widely studied. There has been controversy concerning some aspects of their oxidation chemistry when some workers³⁴ claimed to have isolated paramagnetic $[\text{Co}(\text{R}_2\text{dtc})_3]^+$ by the oxidation of $\text{Co}(\text{R}_2\text{dtc})_3$, although Gahan and O'Connor³⁵ said the product was a diamagnetic oligomeric compound. From the same reaction, Martin and co-workers³⁶ could only isolate the dimeric Co(III) species $[\text{Co}_2(\text{R}_2\text{dtc})_5]^+$, which was characterized by X-ray crystallography. In a series of papers describing chemical, electrochemical, and cobalt-59 NMR studies we have confirmed that $[\text{Co}_2(\text{R}_2\text{dtc})_5]^+$ is always the final oxidation product of $\text{Co}(\text{R}_2\text{dtc})_3$, although in many cases $[\text{Co}(\text{R}_2\text{dtc})_3]^+$ can be detected (electrochemically) as a relatively short-lived intermediate.^{25,37}

Addition of NOBF_4 to a 2 mM solution of $\text{Co}(\text{Et}_2\text{dtc})_3$ in dichloromethane caused an immediate color change from deep green to a less intense reddish brown. After dilution (1:10) with methanol, the solution was injected into the ES mass spectrometer,

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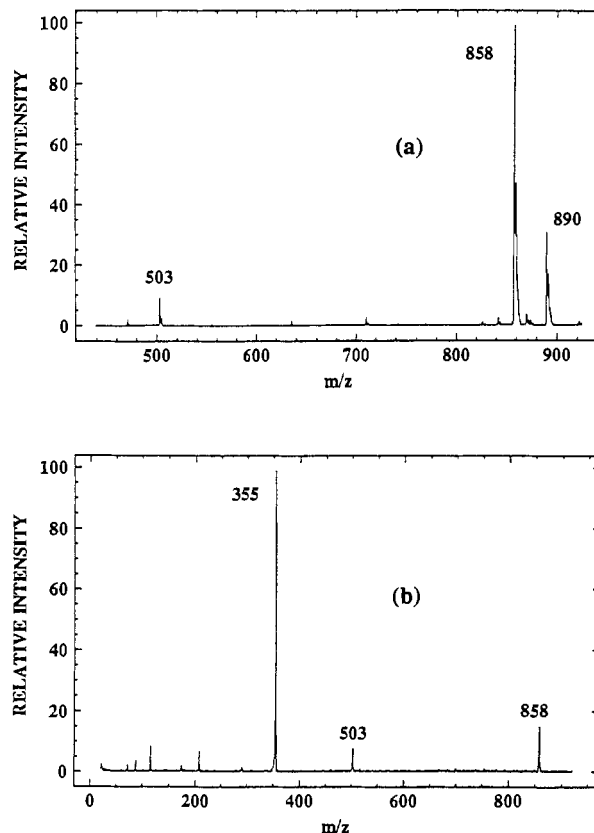
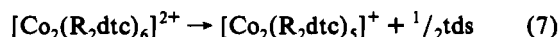
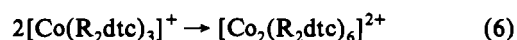


Figure 2. (a) Positive ion ES mass spectrum obtained when a solution of $\text{Co}(\text{Et}_2\text{dtc})_3$ is reacted with NOBF_4 . (b) CADMS for the peak at m/z 858, at 200 V in argon.

and Figure 2a shows the mass spectrum observed. The peak at m/z 858 is due to $[\text{Co}_2(\text{Et}_2\text{dtc})_5]^+$ and the smaller peak at m/z 890 is assigned to $[\text{Co}_2(\text{Et}_2\text{dtc})_5\text{S}]^+$. A very weak peak at m/z 503 is assigned to $[\text{Co}(\text{Et}_2\text{dtc})_3]^+$. Essentially identical results are obtained when an isolated sample of $[\text{Co}_2(\text{Et}_2\text{dtc})_5](\text{BF}_4)$ is examined. Analogous results were obtained for a number of other $[\text{Co}_2(\text{R}_2\text{dtc})_5]^+$ cations as shown in Table II. The mechanism of the formation of $[\text{Co}_2(\text{R}_2\text{dtc})_5]^+$ by the oxidation of $\text{Co}(\text{R}_2\text{dtc})_3$ has been established^{25,37} by electrochemical studies and is assumed to follow the same pathway upon oxidation with NO^+ .



tds = thiuram disulfide

However, as noted above, tds will be oxidized by NO^+ to $[\text{R}_5\text{-bitt}]^{2+}$ and elemental sulfur.

The presence of the species $[\text{Co}_2(\text{R}_2\text{dtc})_5\text{S}]^+$ is unexpected since neither electrochemical measurements nor cobalt-59 NMR

Table II. Cations Identified by ESMS from the Reaction between Co(R₂dtc)₃ and NOBF₄

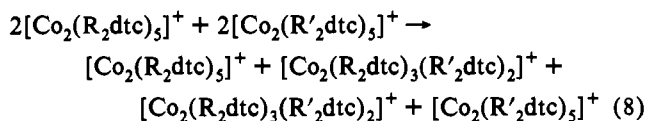
reaction	ions in ES mass spectrum (<i>m/z</i>) ^a
Co(Et ₂ dtc) ₃ + NOBF ₄	[Co ₂ (Et ₂ dtc) ₅ S] ⁺ (890), [Co ₂ (Et ₂ dtc) ₅] ⁺ (858), [Co(Et ₂ dtc) ₃] ⁺ (503)
[Co ₂ (Et ₂ dtc) ₅] ⁺	[Co ₂ (Et ₂ dtc) ₅ S] ⁺ (890), [Co ₂ (Et ₂ dtc) ₅] ⁺ (858), [Co(Et ₂ dtc) ₃] ⁺ (503)
[Co ₂ (Et ₂ dtc) ₅] ⁺ + S ₈	[Co ₂ (Et ₂ dtc) ₅ S ₂] ⁺ (922), [Co ₂ (Et ₂ dtc) ₅ S] ⁺ (890), [Co ₂ (Et ₂ dtc) ₅] ⁺ (858), [Co(Et ₂ dtc) ₃] ⁺ (503)
Co(c-Hx ₂ dtc) ₃ + NOBF ₄	[Co ₂ (c-Hx ₂ dtc) ₅ S ₂] ⁺ (1462), [Co ₂ (c-Hx ₂ dtc) ₅ S] ⁺ (1430), [Co ₂ (c-Hx ₂ dtc) ₅] ⁺ (1398)
[Co ₂ (c-Hx ₂ dtc) ₅] ⁺	[Co ₂ (c-Hx ₂ dtc) ₅ S] ⁺ (1398)
[Co ₂ (Me ₂ dtc) ₅] ⁺	[Co ₂ (Me ₂ dtc) ₅ S] ⁺ (750), [Co ₂ (Me ₂ dtc) ₅] ⁺ (718)
[Co ₂ (pyrrdtc) ₅] ⁺ ^b	[Co ₂ (pyrrdtc) ₅ S] ⁺ (880), [Co ₂ (pyrrdtc) ₅] ⁺ (848)
[Co ₂ (4-Mepipdtc) ₅] ⁺ ^b	[Co ₂ (4-Mepipdtc) ₅ S] ⁺ (1020), [Co ₂ (4-Mepipdtc) ₅] ⁺ (988)
[Co ₂ (Bz ₂ dtc) ₅] ⁺	[Co ₂ (Bz ₂ dtc) ₅ S] ⁺ (1511), [Co ₂ (Bz ₂ dtc) ₅] ⁺ (1479)
[Co ₂ (Me ₂ dtc) ₅] ⁺ + [Co ₂ (c-Hx ₂ dtc) ₅] ⁺	[Co ₂ (c-Hx ₂ dtc) ₅] ⁺ (1399), [Co ₂ (Me ₂ dtc) ₂ (c-Hx ₂ dtc) ₃] ⁺ (1127), [Co ₂ (Me ₂ dtc) ₃ (c-Hx ₂ dtc) ₂] ⁺ (986), [Co ₂ (Me ₂ dtc) ₅] ⁺ (718)

^a Most intense ions observed at low ion source energies. ^b pyrrdtc = pyrrolidine-*N*-carbodithioate; 4-Mepipdtc = 4-methylpiperidine-*N*-carbodithioate.

spectroscopy detected any impurities in the [Co₂(R₂dtc)₅]⁺ compounds,^{25,37} although in the case of the NMR studies this is perhaps not surprising as the ⁵⁹Co signals are broad. Addition of solid S₈ to the solution of [Co₂(Et₂dtc)₅]⁺ resulted in an additional weak peak in the ES mass spectrum at *m/z* 922, which is assigned to [Co₂(Et₂dtc)₅S₂]⁺. Maheu and Pignolet³⁸ have isolated [Os₂(Et₂dtc)₃(Et₂dtcS)₂]⁺ (where Et₂dtcS represents diethyltrithiocarbamate) as a side product in the formation³⁹ of [Os₂(Et₂dtc)₅]⁺ and its structure was determined by X-ray crystallography. Although the structures of [Co₂(Et₂dtc)₅S]⁺ and [Co₂(Et₂dtc)₅S₂]⁺ are presently unknown, the analogies with the osmium compound are obvious. Presumably, elemental S generated by oxidation of tds by NO⁺ is the mechanism by which [Co₂(Et₂dtc)₅S]⁺ is formed in the oxidation of Co(Et₂dtc)₃.

Tandem mass spectrometry on the precursor ion [Co₂(Et₂dtc)₅]⁺, *m/z* 858 (that is, only this peak and not the entire isotopic distribution), showed that in the absence of gas in the collision cell the ion is stable on the time scale of the experiment (~100 μs). When argon was present in the collision cell, using an accelerating voltage of 200 V, fragmentation of the dimer occurred to give predominantly [Co(Et₂dtc)₂]⁺ (*m/z* 355) and a much smaller proportion of [Co(Et₂dtc)₃]⁺ (*m/z* 503) as shown in Figure 2b. This fragmentation pattern is consistent with the view that [Co₂(Et₂dtc)₅]⁺ may be regarded as Co(Et₂dtc)₃ + [Co(Et₂dtc)₂]⁺. The weak peaks at lower *m/z* values in Figure 2b are assigned to species formed by fragmentation of the dithiocarbamate ligands and these have been observed previously³⁷ in the electron impact mass spectrum of Co(Et₂dtc)₃. Similar results were obtained for all the other [Co₂(R₂dtc)₅]⁺ species.

Martin and co-workers³⁶ showed that [Co₂(R₂dtc)₅]⁺ cations are easily cleaved by bidentate anionic ligands (eg acac, acetylacetonate) to give Co(Et₂dtc)₃ and Co(Et₂dtc)₂(acac). The ES mass spectrum of a mixture of [Co₂(Me₂dtc)₅]⁺ (*m/z* 718) and [Co₂(cHx₂dtc)₅]⁺ (*m/z* 1399) gives, in addition to those two peaks, others assigned to [Co₂(Me₂dtc)₃(cHx₂dtc)₂]⁺ (*m/z* 986) and [Co₂(Me₂dtc)₂(cHx₂dtc)₃]⁺ (*m/z* 1127), which demonstrates that the dimeric units cleave and exchange [Co(R₂dtc)₂]⁺ units as shown in eq 8 but that global exchange of dithiocarbamate



ligands does not occur on the timescale of about an hour, ie the [Co₂(R₂dtc)₅]⁺ cations are relatively inert in the kinetic sense, which presumably reflects that they are Co(III) and not Co(IV). This type of exchange was previously demonstrated by using cobalt-59 NMR spectroscopy.²⁵

Nickel Dithiocarbamates. At platinum electrodes Ni(R₂dtc)₂ compounds undergo chemically irreversible oxidation and the

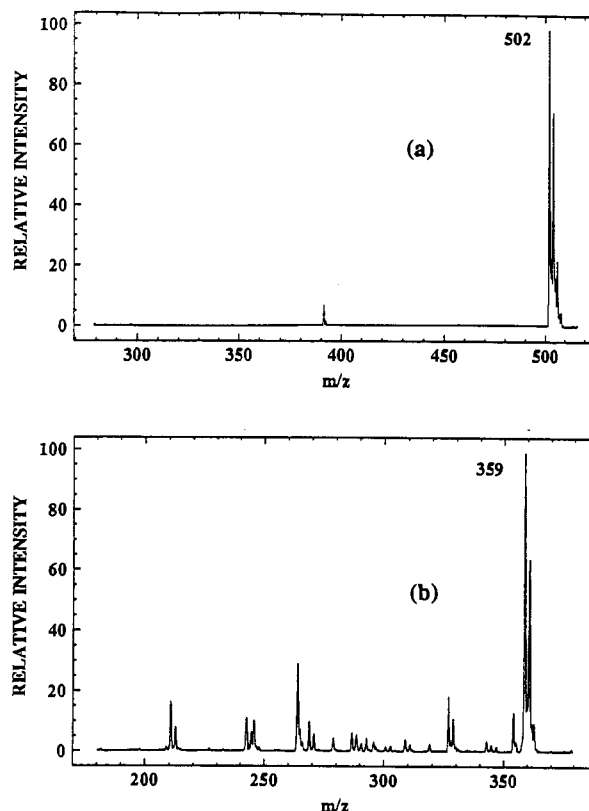


Figure 3. Positive ion ES mass spectra obtained when a solution of (a) Ni(Et₂dtc)₂ is reacted with NOBF₄ or (b) Cu(Et₂dtc)₂ is reacted with NOBF₄.

overall process has been shown^{40,41} to be



ie., yet again, a different overall stoichiometry is observed relative to the iron and cobalt complexes.

Figure 3a shows the ES mass spectrum (B1 = 40 V) of a solution of Ni(Et₂dtc)₂ which had been oxidized with NOBF₄. The peak at *m/z* 502 is due to the intact ion [Ni(Et₂dtc)₃]⁺ and the very weak peak at *m/z* 354 is assigned to [Ni(Et₂dtc)₂]⁺. At higher ion source energies (B1 = 60 V) the relative intensity of the peak due to [Ni(Et₂dtc)₂]⁺ increases, confirming that it is formed from the intact ion by CAD within the ion source, rather than being present as a Ni(III) compound in solution. Analogous ES mass spectra were observed for Ni(Bz₂dtc)₂ and data are summarized in Table III. The aquo cation [Ni(H₂O)₆]²⁺ expected on the basis of eq 9 was not observed, and indeed we have not succeeded in observing any metal aquo cations by ESMS.

When a mixture of Ni(Et₂dtc)₂ and Ni(Bz₂dtc)₂ was oxidized with NOBF₄, then all the possible mixed tris(dithiocarbamate)

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Table III. Cations Identified by ESMS from the Reaction between Ni(R₂dtc)₂ and NOBF₄

reaction	ions in ES mass spectrum (<i>m/z</i>) ^a
Ni(Et ₂ dtc) ₂ + NOBF ₄	[Ni(Et ₂ dtc) ₃] ⁺ (502), [Ni(Et ₂ dtc) ₂] ⁺ (354)
Ni(Bz ₂ dtc) ₂ + NOBF ₄	[Ni(Bz ₂ dtc) ₃] ⁺ (874), [Ni(Bz ₂ dtc) ₂] ⁺ (602)
Ni(Et ₂ dtc) ₂ + Ni(Bz ₂ dtc) ₂ + NOBF ₄	[Ni(Bz ₂ dtc) ₃] ⁺ (874), [Ni(Bz ₂ dtc) ₂ (Et ₂ dtc)] ⁺ (750), [Ni(Bz ₂ dtc)(Et ₂ dtc) ₂] ⁺ (626), [Ni(Et ₂ dtc) ₃] ⁺ (502)

^a Most intense ions observed at low ion source energies.

Table IV. Cations Identified by ESMS from the Reaction between Cu(R₂dtc)₂ and NOBF₄

reaction	ions in ES mass spectrum (<i>m/z</i>) ^a
Cu(Me ₂ dtc) ₂ + NOBF ₄	[Cu(Me ₂ dtc) ₂] ⁺ (303), [Cu(Me ₂ dtc)] ⁺ (183)
Cu(Et ₂ dtc) ₂ + NOBF ₄	[Cu(Et ₂ dtc) ₂] ⁺ (359), [Cu(Et ₂ dtc)] ⁺ (211)
Cu(Pr ₂ dtc) ₂ + NOBF ₄	[Cu(Pr ₂ dtc) ₂] ⁺ (415), [Cu(Pr ₂ dtc)] ⁺ (239)
Cu(Pipdtc) ₂ + NOBF ₄	[Cu(Pipdtc) ₂ S] ⁺ (415), [Cu(Pipdtc) ₂] ⁺ (383), [Cu(Pipdtc)S] ⁺ (255)
[Cu(Me ₂ dtc) ₂] ⁺ + [Cu(Bu ₂ dtc) ₂] ⁺	[Cu(Bu ₂ dtc) ₂] ⁺ (471), [Cu(Bu ₂ dtc)(Me ₂ dtc)] ⁺ (387), [Cu(Me ₂ dtc) ₂] ⁺ (303), [Cu(Bu ₂ dtc)] ⁺ (267), [Cu(Me ₂ dtc)] ⁺ (183)
[Cu(Pipdtc) ₂] ⁺ + [Cu(Bu ₂ dtc) ₂] ⁺	[Cu(Bu ₂ dtc) ₂] ⁺ (471), [Cu(Bu ₂ dtc)(Pipdtc)] ⁺ (427), [Cu(Pipdtc) ₂] ⁺ (383), [Cu(Bu ₂ dtc)S] ⁺ (299), [Cu(Bu ₂ dtc)] ⁺ (267), [Cu(Pipdtc)S] ⁺ (255), [Cu(Pipdtc)] ⁺ (223)

^a Most intense ions observed at low ion source energies.

cations were observed (Table III) showing that ligand exchange is rapid on the synthetic time scale in the oxidation state IV nickel complexes.

Copper Dithiocarbamates. At platinum electrodes copper dithiocarbamate complexes, Cu(R₂dtc)₂, show a well defined reversible one-electron oxidation step,^{42,43} and stable Cu(III) bis-(dithiocarbamate) cations have been isolated.^{44,45} Oxidation of a dichloromethane solution of Cu(Et₂dtc)₂ with NOBF₄ resulted in a color change from dark yellow to pale green and the ES mass spectrum (B1 = 35 V) showed a base peak due to the intact ion [Cu(Et₂dtc)₂]⁺ (*m/z* 359), and a weak peak was observed at *m/z* 211 which corresponds to [Cu(Et₂dtc)]⁺ (Figure 3b) whose intensity increased at higher ion source energies (B1 = 60 V). Similar results were obtained for other copper(II) dithiocarbamates and in some cases sulfur-rich cations such as [Cu(pipdtc)₂S]⁺ and [Cu(pipdtc)S]⁺ were observed, presumably formed in a manner similar to that described for the dicobalt sulfur-rich cations. ESMS data for the cationic copper dithiocarbamates are summarized in Table IV.

Mixing of different copper(III) dithiocarbamate cations, prepared separately in solution by NO⁺ oxidation, leads to global exchange of the ligands, and ESMS data for some mixtures are summarized in Table IV.

General Conclusions

The majority of reactions of metal dithiocarbamates with NOBF₄ studied here correspond to NO⁺ acting as an innocent

one-electron oxidant. That is, [Fe(R₂dtc)₃]⁺, [Co₂(R₂dtc)₅]⁺, [Ni(R₂dtc)₃]⁺, and [Cu(R₂dtc)₂]⁺ are the dominant species formed, as is the case with electrochemical oxidation. However, [Fe(R₂dtc)₂NO]⁺, [[Fe(R₂dtc)₃]₂(R₄bitt)]²⁺, [Co₂(R₂dtc)₅S]⁺, and [Cu(R₂dtc)₂S]⁺ are also observed as minor products. The formation of these compounds is explained in the case of [Fe(R₂dtc)₂NO]⁺ by interaction of NO gas with Fe(R₂dtc)₃ and in the case of the other compounds by generation of [R₄bitt]²⁺ and elemental sulfur by NO⁺ oxidation of [R₂dtc]⁻.

The use of ESMS in inorganic chemistry is still in its infancy. The present study further demonstrates its value in different situations, and importantly, even in these well-studied metal dithiocarbamate systems, ESMS has provided new information such as the discovery of the sulfur-rich dicobalt and copper dithiocarbamate cations. Additionally, the ESMS method enables ligand exchange reactions of the cations to be studied. Ligand exchange reactions are most frequently studied by NMR methods, and when a number of species may be present, as in the mixed ligand [M(R₂dtc)₃]⁺ series, metal NMR spectroscopy is often more convenient than NMR methods based on ligand nuclei. However, with the exception of the dicobalt cations, all of the other cationic species considered here are paramagnetic and therefore cannot be studied by NMR spectroscopy. [Fe(R₂dtc)₃]⁺, [Ni(R₂dtc)₃]⁺, and [Cu(R₂dtc)₂]⁺ in fact represent the first paramagnetic ligand exchange systems to be examined by ESMS.

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