

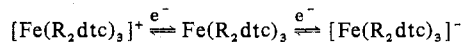
Contribution from the Research School of Chemistry,
Australian National University, Canberra, Australia 2600**Tris(dithiocarbamato) Complexes of Iron(II),
Iron(III), and Iron(IV). An Electrochemical Study**

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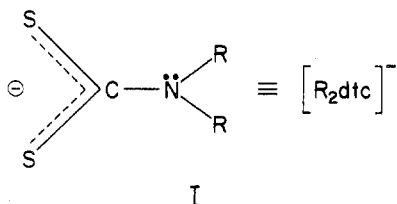
The electron-transfer behavior of 20 iron(III)-dithiocarbamato complexes has been studied in acetone at a platinum electrode. The complexes exhibit relatively facile, metal-based, reversible oxidation and reduction steps corresponding to the series



Some unusual reactions of these complexes have been examined; e.g., $\text{Fe}(\text{R}_2\text{dtc})_3$ reacts with Hg and O_2 to afford $\text{Hg}(\text{R}_2\text{dtc})_2$, and $\text{Fe}(\text{pyrrdtc})_3$ reacts with HClO_4 to afford the Fe(IV) complex $[\text{Fe}(\text{pyrrdtc})_3]\text{ClO}_4$. Substituent effects on the redox potentials of dithiocarbamates and xanthates have been rationalized in terms of the electron-releasing power of the substituents and the RNR angle of the dithiocarbamates. Mixed-ligand species have also been characterized by voltammetry. The contribution of the high-spin \rightleftharpoons low-spin equilibrium of the $\text{Fe}(\text{R}_2\text{dtc})_3$ species to the redox potentials has been examined theoretically and experimentally and found to be remarkably small. Finally, the physicochemical correlations from this and other work are interpreted as requiring the canonical form of the ligand ${}^2\text{-S}_2\text{CN}^+\text{R}_2$ to favor low-spin while ${}^-\text{S}_2\text{CNR}_2$ favors high-spin behavior.

Introduction

Iron(III) dithiocarbamates have excited considerable interest over the past decade on account of their unusual electronic properties.¹ The dithiocarbamate ligand (I) appears to



generate values of the ligand field and Racah parameters, Δ and B , which place $\text{Fe}(\text{RR}'\text{dtc})_3$ complexes at the ${}^6\text{A}_1\text{-}{}^2\text{T}_2$ electronic crossover.² (Cubic notation is used throughout for convenience.) Since the high- and low-spin states in this region possess nearly equal free energies, it is not surprising that the magnetic and spectroscopic properties are exceptionally responsive to changes of temperature and pressure.^{2,3} Furthermore, subtle changes of the ligand substituents R and R' are sufficient to change the position of the spin-state equilibrium through differences in their inductive, mesomeric, and steric effects.⁴ These effects have been described in a review¹ and subsequent publications.

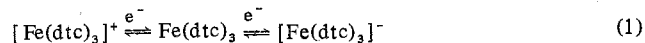
The dynamics of the spin-state interconversion are also important, not only for the basic understanding of intersystem crossing processes but also for the study of electron-transfer reactions, including those in biochemical systems.^{5,6} The observation of average Mössbauer⁷⁻¹³ and PMR¹⁴⁻¹⁶ spectra for iron(III) dithiocarbamates implies a rapid relaxation rate for the spin equilibrium of $>10^7 \text{ sec}^{-1}$ with an upper limit of about 10^{13} sec^{-1} being inferred¹ from the observation of separate absorption bands in their electronic spectra.

For these reasons, the iron(III) dithiocarbamates provide an unusual opportunity to study the redox properties of a system in spin equilibrium. Such a study also has direct relevance to electron-transfer processes in certain biochemical systems. For example, there have been recent proposals that the spin-state changes of the cytochromes are intimately connected with the mechanism of oxidative phosphorylation coupled with the suggestion that energy might be conserved via a spin-state-dependent redox potential of the cytochrome.¹⁷

In marked contrast to the extensive studies of redox behavior of the 1,2-dithiolene complexes,¹⁸ few systematic and unambiguous electrochemical data are available for 1,1-dithio

chelates. As an extension of our earlier work on 1,3-dithiochelates¹⁹ and for the reasons noted above, we have initiated systematic studies of the redox properties of the first-row transition metal dithiocarbamates. A preliminary electrochemical survey of these complexes in nonaqueous media reveals that the Cr(III), Mn(III), Fe(III), Co(III), Ni(II), and Cu(II) compounds are electroactive with the measured redox potentials displaying a marked dependence on both the metal ion and the substituent on the dithiocarbamate ligand.²⁰ Detailed studies with manganese complexes demonstrated the existence of and interrelationships between the complexes $\text{Mn}(\text{dtc})_2$, $[\text{Mn}(\text{dtc})_3]^-$, $\text{Mn}(\text{dtc})_3$, and $[\text{Mn}(\text{dtc})_3]^+$.²¹

In this paper, the detailed chemical and electrochemical characterization is described for the redox series



with an emphasis on the effect of substituents on redox potentials. Although the earlier literature contains only fragmentary and sometimes contradictory electrochemical data for iron dithiocarbamates,^{22,23} the recent isolation and characterization of iron(IV)²⁴ and iron(II)²⁵ complexes substantiate our interpretation of the redox processes.

Experimental Section

Compounds. $\text{Fe}(\text{dtc})_3$ complexes were prepared as previously described⁴ and analyzed (C, H, N) satisfactorily. $[\text{Fe}(\text{dtc})_3]^+$ salts were prepared in an analogous manner to that used to prepare the corresponding Mn(IV) complexes.²¹ The complexes were recrystallized and analyzed prior to use. Anal. Calcd for $\text{Fe}((i\text{-Pr})_2\text{dtc})_3\text{BF}_4$: C, 37.6; H, 6.3; N, 6.3; S, 28.7. Found: C, 37.2; H, 6.7; N, 6.1; S, 28.9. Calcd for $\text{Fe}(\text{pyrrdtc})_3\text{BF}_4$: C, 31.0; H, 4.2; N, 7.2; S, 33.1. Found: C, 31.0; H, 4.2; N, 7.1; S, 32.3. Calcd for $\text{Fe}(\text{pipdtc})_3\text{BF}_4$: C, 34.7; H, 4.9; N, 6.7; S, 30.9. Found: C, 34.6; H, 4.9; N, 6.6; S, 31.3.

Instrumentation. Experimental procedures and instrumentation were those employed previously.²¹ Electrochemical work was carried out in acetone-0.1 M Et_4NClO_4 and potentials are recorded vs. a Ag-AgCl-0.1 M LiCl-acetone reference electrode.

Results and Discussion

(a) General Data. At a platinum electrode, the tris(dithiocarbamato)iron(III) complexes undergo relatively facile oxidation and reduction steps which involve reversible one-electron-transfer steps. For example, $\text{Fe}(\text{Et}_2\text{dtc})_3$ displays reversible redox behavior in acetone at a platinum electrode (see later) with $E(\text{Ox}) = 0.545 \text{ V}$ and $E(\text{Red}) = -0.378 \text{ V}$. At a hanging mercury drop electrode (HMDE), however, the

Table I. Parameters for Oxidation Processes of $\text{Fe}(\text{RR}'\text{dtc})_3$ Complexes^a

Compd		Normal-pulse voltammetry			Ac voltammetry			Cyclic voltammetry			
R	R'	$E_{1/2}$, V	$E_{3/4} - E_{1/4}$, mV	i_p/C , mA M^{-1}	E_p , V	$\Delta E_{1/2}$, mV	i_p/C , mA M^{-1}	i_{pa}/i_{pb}^c	ΔE_p^c , mV	$i_{pa}/Cv^{1/2}$ (av), mA $\text{sec}^{1/2} M^{-1}$	$i_{pa}/Cv^{1/2}$ mV ^{-1/2}
Me	Me	0.58 ₄	52	200	0.58 ₂	91	64	1.0	61	8.4	
Et	Et	0.54 ₃	52	184	0.54 ₅	95	52	1.1	62	6.5	
<i>n</i> -Pr	<i>n</i> -Pr	0.53 ₃	64	195	0.53 ₂	97	58	1.0	75	6.0	
<i>i</i> -Pr	<i>i</i> -Pr	0.44 ₁	53	197	0.44 ₂	94	61	1.0	65	7.5	
Me	<i>n</i> -Bu	0.54 ₃	51	188	0.54 ₁	91	66	1.0	65	8.6	
<i>n</i> -Bu	<i>n</i> -Bu	0.55 ₂	53	172	0.55 ₀	98	50	1.0	67	6.6	
<i>i</i> -Bu	<i>i</i> -Bu	0.52 ₃	52	176	0.53 ₀	93	50	1.0	60	5.5	
<i>i</i> -Pnt	<i>i</i> -Pnt	0.54 ₂	55	177	0.54 ₂	96	39	1.0	70	6.0	
<i>n</i> -Hx	<i>n</i> -Hx	0.54 ₁	53	166	0.54 ₂	95	36	1.0	65	6.0	
<i>c</i> -Hx	<i>c</i> -Hx	0.41 ₆	48	<i>b</i>	0.41 ₅	90	<i>b</i>	1.0	64	<i>b</i>	
Benzyl	Benzyl	0.66 ₇	52	157	0.67 ₁	93	45	1.1	66	5.8	
Pyrrolidyl		0.61 ₁	63	172	0.61 ₂	93	51	1.1	63	7.8	
Piperidyl		0.52 ₄	52	169	0.52 ₄	93	57	1.0	67	6.7	
2,6-Dimethylpiperidyl		0.50 ₀	50	<i>b</i>	0.49 ₉	90	<i>b</i>	~0.9	60	<i>b</i>	
2-Methyl piperidyl		0.51 ₀	60	<i>b</i>	0.50 ₈	92	<i>b</i>	1.0	62	<i>b</i>	
4-Methylpiperidyl		0.52 ₂	57	160	0.52 ₄	95	38	1.0	64	4.7	
Morpholyl		0.62 ₉	53	172	0.62 ₉	92	50	1.0	61	6.0	
Ph	Ph	0.63 ₇	53	161	0.63 ₇	94	55	1.0	61	6.5	
Ph	Me	0.58 ₉	53	>156	0.59 ₁	94	>38	1.1	66	>5.4	
Ph	Et	0.58 ₁	53	118	0.58 ₀	92	42	1.1	60	5.4	

^a Potentials vs. Ag-AgCl. ^b Too unstable or insoluble for reliable data. ^c Scan rate 200 mV/sec.

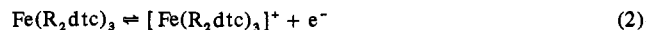
Table II. Coulometric *n* Values for Selected Redox Processes

Compd	Process	<i>n</i> value
$\text{Fe}(\text{pyrrdtc})_3$	$\text{Fe(III)} \rightarrow \text{Fe(IV)}$ oxidn	0.9
$\text{Fe}(\text{pipdtc})_3$	$\text{Fe(III)} \rightarrow \text{Fe(IV)}$ oxidn	1.0
$\text{Fe}((i\text{-Pr})_2\text{dtc})_3$	$\text{Fe(III)} \rightarrow \text{Fe(IV)}$ oxidn	1.0
$\text{Fe}((i\text{-Pr})_2\text{dtc})_3\text{BF}_4$	$\text{Fe(IV)} \rightarrow \text{Fe(III)}$ redn	0.8
$\text{Fe}(\text{pipdtc})_3\text{BF}_4$	$\text{Fe(IV)} \rightarrow \text{Fe(III)}$ redn	1.0
$\text{Fe}(\text{pyrrdtc})_3\text{BF}_4$	$\text{Fe(IV)} \rightarrow \text{Fe(III)}$ redn	0.9
$\text{Fe}(\text{pyrrdtc})_3$	$\text{Fe(III)} \rightarrow \text{Fe(II)}$ redn	1.2
$\text{Fe}((n\text{-Bu})_2\text{dtc})_3$	$\text{Fe(III)} \rightarrow \text{Fe(II)}$ redn	1.2
$\text{Fe}((i\text{-Pr})_2\text{dtc})_3$	$\text{Fe(III)} \rightarrow \text{Fe(II)}$ redn	1.5

redox behavior is quite complex and has not been characterized. A facile reaction between mercury and ferric dithiocarbamates (in the presence of oxygen) has been established and is discussed later. In view of these complications, the ensuing discussion is restricted to the simple redox reactions observed at platinum electrodes.

(b) **Iron(IV)-Dithiocarbamato Complexes.** Iron(IV) dithiocarbamates were initially reported by Pasek and Straub²⁴ and by others.²⁶ The available physicochemical data on these compounds, including magnetism, establish a triplet ($S = 1$) ground state consistent with a t_2^4 electron configuration for iron(IV).

The detailed electrochemical data for the oxidation of $\text{Fe}(\text{dtc})_3$ compounds (Table I) confirm that the complexes undergo a single, reversible, one-electron oxidation consistent with the equation



Coulometric *n* values for selected compounds are included in Table II. The redox potentials of the $\text{Fe(III)}-\text{Fe(IV)}$ couples are independent of whether the data are measured on $\text{Fe}(\text{R}_2\text{dtc})_3$ or $[\text{Fe}(\text{R}_2\text{dtc})_3]^+$ solutions. Oxidative electrolysis of $\text{Fe}((i\text{-Pr})_2\text{dtc})_3$ in acetone-0.1 *M* Et_4NClO_4 has been followed spectrophotometrically with the final spectrum corresponding to that of $[\text{Fe}((i\text{-Pr})_2\text{dtc})_3]^+$ prepared by chemical procedures (Figure 1). This oxidized solution, on reduction, affords $\text{Fe}((i\text{-Pr})_2\text{dtc})_3$. Finally, a complete single-crystal X-ray structure²⁷ of the 1-pyrrolidinedicarbodithioate (pyrrdtc) complex of iron(IV) confirms that the ligands possess the usual geometry and bond lengths found for chelating dithiocarbamato ligands. The contraction of the Fe-S

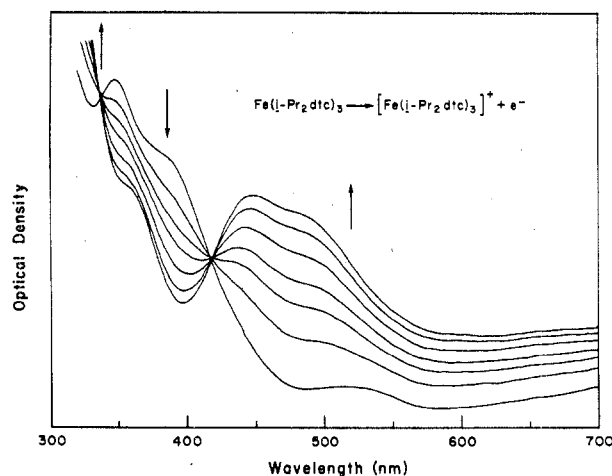
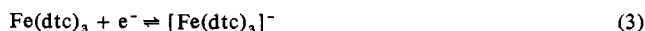


Figure 1. Spectra of a solution of $\text{Fe}((i\text{-Pr})_2\text{dtc})_3$ sampled after partial oxidative electrolysis. Arrows indicate direction of spectral change on oxidation of $\text{Fe}((i\text{-Pr})_2\text{dtc})_3$ to $[\text{Fe}((i\text{-Pr})_2\text{dtc})_3]^+$.

bond length from 2.41 Å for the high-spin iron(III)-pyrrolidyl complex to 2.30 Å for the low-spin iron(IV) compound^{27,28} is consistent with the removal of antibonding e electrons ($t_2^3e^2 \rightarrow t_2^4$) and a higher positive charge on the central iron atom. Accordingly, the redox reactions are effectively centered on the metal ion.

(c) **Iron(II) Dithiocarbamates.** All the ferric complexes studied are relatively easy to reduce with reduction potentials spanning the region -0.24 to -0.55 V depending on the substituents. Coulometry by exhaustive electrolysis yields *n* values of 1.2, 1.2, and 1.5 electrons for the reductions of $\text{Fe}((n\text{-Bu})_2\text{dtc})_3$, $\text{Fe}(\text{pyrrdtc})_3$, and $\text{Fe}((i\text{-Pr})_2\text{dtc})_3$, respectively. Examination of the data in Table III suggests that the reduction step probably has a slower rate of heterogeneous electron transfer than the $\text{Fe(III)} \rightleftharpoons \text{Fe(IV)}$ step. For the present case, it will be shown the redox couple involves the anionic complex $[\text{Fe}(\text{dtc})_3]^-$



Ferrous complexes of this type have been isolated only very recently.²⁵

Electrochemical methods can be very effective for following

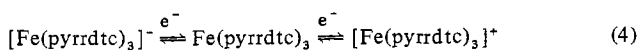
Table III. Parameters for Reduction Processes of Fe(RR'dtc)₃ Complexes^a

Compd		Normal-pulse voltammetry			Ac voltammetry			Cyclic voltammetry		
		<i>E</i> _{1/2} , V	<i>E</i> _{1/4} - <i>E</i> _{3/4} , mV	<i>i</i> _p / <i>C</i> , mA M ⁻¹	<i>E</i> _p , V	Δ <i>E</i> _{1/2} , mV	<i>i</i> _p / <i>C</i> , mA M ⁻¹	<i>i</i> _p / <i>i</i> _p ^b <i>c</i>	Δ <i>E</i> _p ^c , mV	<i>i</i> _p ^f / <i>C</i> _v ^{1/2} , (av), mA sec ^{1/2} M ⁻¹
Me	Me	-0.32 ₉	54	214	-0.32 ₇	93	64	1.0	61	8.5
Et	Et	-0.38 ₁	52	189	-0.37 ₈	96	46	1.0	62	6.9
<i>n</i> -Pr	<i>n</i> -Pr	-0.40 ₇	62	177	-0.40 ₂	92	50	1.0	60	5.0
<i>i</i> -Pr	<i>i</i> -Pr	-0.52 ₈	51	203	-0.52 ₅	96	57	1.0	69	7.8
Me	<i>n</i> -Bu	-0.39 ₂	53	195	-0.38 ₆	90	68	1.0	75	8.4
<i>n</i> -Bu	<i>n</i> -Bu	-0.39 ₁	52	185	-0.38 ₆	98	46	1.1	71	6.9
<i>i</i> -Bu	<i>i</i> -Bu	-0.42 ₄	53	178	-0.42 ₁	95	34	1.0	78	6.6
<i>i</i> -Pnt	<i>i</i> -Pnt	-0.39 ₉	60	190	-0.39 ₈	94	39	1.0	75	6.0
<i>n</i> -Hx	<i>n</i> -Hx	-0.39 ₈	60	177	-0.39 ₅	105	39	1.0	65	6.0
<i>c</i> -Hx	<i>c</i> -Hx	-0.55 ₂	56	<i>b</i>	-0.55 ₉	104	<i>b</i>	1.1	78	<i>b</i>
Benzyl	Benzyl	-0.24 ₄	50	161	-0.24 ₀	95	40	1.0	72	6.3
Pyrrolidyl		-0.33 ₅	56	195	-0.33 ₂	93	46	1.0	70	7.9
Piperidyl		-0.37 ₃	54	181	-0.37 ₁	95	44	1.1	79	6.9
2,6-Dimethylpiperidyl		-0.43 ₈	53	<i>b</i>	-0.43 ₆	~95	<i>b</i>	~0.9	75	<i>b</i>
2-Methylpiperidyl		-0.39 ₄	65	<i>b</i>	-0.39 ₃	95	<i>b</i>	1.1	65	<i>b</i>
4-Methylpiperidyl		-0.36 ₆	66	190	-0.36 ₉	95	45	1.0	70	4.5
Morpholyl		-0.25 ₅	50	180	-0.25 ₁	94	47	1.0	72	6.5
Ph	Ph	-0.31 ₁	53	175	-0.31 ₁	92	51	1.1	61	6.6
Ph	Me	-0.32 ₁	59	>163	-0.31 ₆	96	>32	1.2	76	>5.3
Ph	Et	-0.33 ₃	57	175	-0.33 ₅	91	40	1.1	65	5.1

^a Potentials vs. Ag-AgCl. ^b Too unstable or insoluble for reliable data. ^c Scan rate 200 mV/sec.

the course of the reaction between a metal ion and ligands under conditions of controlled concentration. In particular, titration of metal ions into solutions of the ligand enables the nature and concentration of the species formed to be monitored. Unfortunately, with the present species, the redox activity of the uncomplexed ferrous and ferric ions in the potential range of interest limits accurate experiments of this type to those involving the addition of each of these metal ions to a solution of dithiocarbamate ligand, i.e., to conditions of very low free metal ion concentration.

Consider first the addition of Fe²⁺ (from the [Fe-(H₂O)₆](ClO₄)₂ salt in acetone-Et₄NClO₄ solution) to Na(pyrrdtc)·2H₂O solution. The results are very similar to those observed previously with Mn²⁺ and pyrrdtc⁻.²¹ The first species formed is [Fe(pyrrdtc)₃]⁻, at the 1:3 end point, being characterized by two oxidation steps at *E*_p = -0.32 V and +0.62 V which correspond to successive one-electron oxidations to the Fe(IV) species



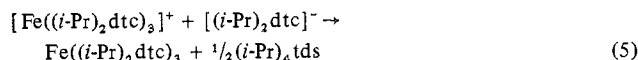
The formation of [Fe(pyrrdtc)₃]⁻ by titrimetry with an electrochemical behavior identical with that of the species generated by electrolytic reduction of the iron(III) complex establishes the identity of this complex as the tris(dithiocarbamato)ferrous species [Fe(pyrrdtc)₃]⁻.

Further addition of Fe²⁺ results in the disappearance at the 1:2 end point of the [Fe(pyrrdtc)₃]⁻ species and the formation of Fe(pyrrdtc)₂ although extra additions of Fe²⁺ at this stage result in poorly defined voltammograms. Although the data obtained are less accurate, titration of pyrrdtc⁻ into Fe²⁺ solutions qualitatively yields the same products as the titration in the opposite sense.

With Fe³⁺, when these titrations are performed, the first end point (on addition of Fe³⁺ to pyrrdtc⁻) is the 1:3 species Fe(pyrrdtc)₃. Further additions of Fe³⁺ yield complex and unresolved electrochemical behavior.

(d) Redox Reactions of the Iron Dithiocarbamate System. The following qualitative observations have been recorded in acetone-0.1 M Et₄NClO₄ solution. Consider first the iron(IV) complexes. These compounds are capable of oxidizing unchelated dithiocarbamate ligands to the tetraalkylthiuram

disulfide (R₄tds). For example, the reduction of [Fe((*i*-Pr)₂dtc)₃]⁺ by [(*i*-Pr)₂dtc]⁻ in acetone is readily followed by electrochemical means and results in the formation of Fe((*i*-Pr)₂dtc)₃, i.e.



The reaction is expected to be general for the iron(IV) compounds. Similar reactions of free dithiocarbamate ligands have been observed for the corresponding Mn(IV) complexes.²¹

Using spectrophotometric methods, the addition of HClO₄ solution (70% solution) to [Fe((*i*-Pr)₂dtc)₃]BF₄ in acetone-0.1 M Et₄NClO₄ results in only a 3% decrease in the concentration of the Fe(IV) species over 30 min after the initial drop in concentration due to dilution effects. Hence the complex may be regarded as stable to this noncoordinating acid. However, if HClO₄ is replaced by HCl, the same procedure results in the rapid destruction of the iron(IV) complex. In nonacidic media, chloride ion from Et₄NCl also destroys this complex.

Iron(III) dithiocarbamates in the presence of HCl (or FeCl₃) are known to give five-coordinate species Fe(dtc)₂X (X = Cl, Br, I) which have been isolated and characterized by Martin and coworkers.^{29,30} This process can be followed spectrophotometrically by addition of HCl solution to both Fe(pyrrdtc)₃ and Fe(Et₂dtc)₃ in acetone-0.1 M Et₄NClO₄ yielding spectra characteristic of the five-coordinate species. For example, with HCl and Fe(Et₂dtc)₃ peaks are observed at 610, 475 (sh), and 436 nm; literature values for the isolated complex Fe(Et₂dtc)₂Cl in chloroform solution are 617, 500 (sh?), and 450 nm.²⁹ With HCl and Fe(pyrrdtc)₃, peaks are observed at 600, 478, and 438 nm. Addition of further HCl solution results in destruction of these species, and a compound with a spectral peak at 362 nm results, in both instances consistent with formation of the FeX₄⁻ species.²⁹ Fe(pyrrdtc)₃ is stable to attack by chloride ion in the form of Et₄NCl.

In their reaction with "noncoordinating" acids the ferric complexes exhibit a substituent dependence. Fe((*i*-Pr)₂dtc)₃ in the acetone-perchlorate media yields with HClO₄ a complex with peaks at 580, 438, and 341 nm. Interestingly, this spectrum is the same as that obtained by titrating Fe((*i*-Pr)₂dtc)₃ with ferric ions (as the ClO₄⁻) to the end point corresponding to [Fe((*i*-Pr)₂dtc)₂]⁺. It appears that this

compound is a bis-chelated iron(III) cation which is also formed by the perchlorate acid hydrolysis of $\text{Fe}((i\text{-Pr})_2\text{dtc})_3$, perhaps in a solvated form.

With $\text{Fe}(\text{pyrrdtc})_3$ (in the presence or absence of air) reaction with HClO_4 solution yields the iron(IV) complex which crystallizes from the acetone-0.1 M Et_4NClO_4 medium as the perchlorate salt $\text{Fe}(\text{pyrrdtc})_3\text{ClO}_4$. Anal. Calcd: C, 30.3; H, 4.1; N, 7.1. Found: C, 30.6; H, 4.4; N, 6.9. The complex dissolves in CH_2Cl_2 to give the characteristic spectrum of the $[\text{Fe}(\text{pyrrdtc})_3]^+$ cation (490, 449, 353, and 307 nm). The complex may be conveniently and cleanly prepared by this simple reaction.

$\text{Fe}(\text{Et}_2\text{dtc})_3$ in acetone- Et_4NClO_4 is effectively inert to oxygen. Addition of HClO_4 to these solutions (or under anaerobic conditions) results in the formation of some $[\text{Fe}(\text{Et}_2\text{dtc})_3]^+$ (electronic spectrum: 488, 448, and 353 nm). On addition of HClO_4 to $\text{Fe}(\text{Et}_2\text{dtc})_3$, cyclic voltammetry shows that the oxidation process of $\text{Fe}(\text{Et}_2\text{dtc})_3$ (eq 2) turns to the reduction of $[\text{Fe}(\text{Et}_2\text{dtc})_3]^+$ (eq 3) at the same potential. Peak current (I_p) values suggest that only 50% of $\text{Fe}(\text{III})$ is converted to the $\text{Fe}(\text{IV})$ compound.

In the perchlorate medium, other "noncoordinating" acids give $\text{Fe}(\text{IV})$ compounds; e.g., $\text{HBF}_4\text{-Fe}(\text{pyrrdtc})_3$ and $\text{H}_2\text{SO}_4\text{-Fe}(\text{Et}_2\text{dtc})_3$.

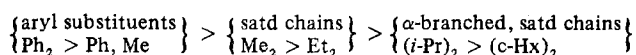
In view of the complicated behavior of ferric dithiocarbamates at a mercury electrode, the interaction of Hg and $\text{Fe}(\text{dtc})_3$ was examined. A concentrated solution of $\text{Fe}(\text{Et}_2\text{dtc})_3$ in acetone saturated with O_2 is decolorized in 2 min when shaken with elemental mercury. The mercury fragments into small spheres which show no tendency to recombine, suggesting that a surface-active coating has been formed during reaction with the ferric dithiocarbamate. Isolation of the soluble decomposition product from the acetone solution provides an off-white material which analyzes for $\text{Hg}(\text{Et}_2\text{dtc})_2$. Anal. Calcd: C, 24.2; H, 4.1; N, 5.6. Found: C, 24.3; H, 4.0; N, 6.2. No attempt has been made to ascertain the fate of the iron.

The same experiment conducted under anaerobic conditions shows neither fragmentation of the mercury pool nor decolorization of the solution, even after standing over a mercury pool for 2 months.

Interaction of the dithiocarbamate ligands with the mercury electrode after electron transfer may also contribute to the complicated redox behavior. Such processes have been noted for other dithiocarbamate complexes at the dropping mercury electrode.³¹

In view of the rapidity with which mercury decomposes quite concentrated solutions of $\text{Fe}(\text{Et}_2\text{dtc})_3$ (and also $\text{Fe}((i\text{-Pr})_2\text{dtc})_3$, $\text{Fe}(\text{Me}_2\text{dtc})_3$, and presumably others), it would seem that polarographic analysis of ferric dithiocarbamates at a dropping mercury electrode (or simply in the presence of mercury and any O_2) could be quite unreliable (cf. ref 32). Such complications are expected to be most important at the lower concentrations where the ratio of mercury surface area to concentration is a maximum.

(e) **Substituent Effects.** The general effects of substituents on redox potentials, noted earlier,^{20,21} may be rationalized in terms of the electron-releasing or -withdrawing characteristics of the R group at nitrogen. The following order for ease of reduction of the complexes is observed experimentally (cf. Figure 2)



In addition to this electronic effect, there appears to be a steric effect depending on the expected RNR angle at the nitrogen atom. These trends also emerge from the high-spin and/or low-spin magnetic properties of iron(III) dithiocarbamate complexes,³ as shown.

Ease of redn	azeti- dine	>	pyrrol- idine	>	piper- idine	~ Et ₂	>	(c-Hx) ₂
No. of atoms in ring	4		5		6		open	open
Magnetism	high spin		high spin		intermediate spin		low spin	low spin

The ability of substituents to increase the ease of reduction of the ferric complex is always paralleled by a similar shift to more positive oxidation potentials, making oxidation of the ferric complex more difficult.^{20,21} The relationship between the oxidation and reduction potentials of the ferric complexes is close to linear (Figure 3). This correlation reflects the relative abilities of various substituents to stabilize $\text{Fe}(\text{II})$ or $\text{Fe}(\text{IV})$ with respect to $\text{Fe}(\text{III})$. Those substituents which stabilize $\text{Fe}(\text{IV})$ destabilize $\text{Fe}(\text{II})$ and vice versa.

The general trend of redox potentials with substituents applies to all dithiocarbamate systems so far examined.^{20,21} Figure 2 illustrates that each substituent exerts the same relative effect on oxidation potentials for both the tervalent

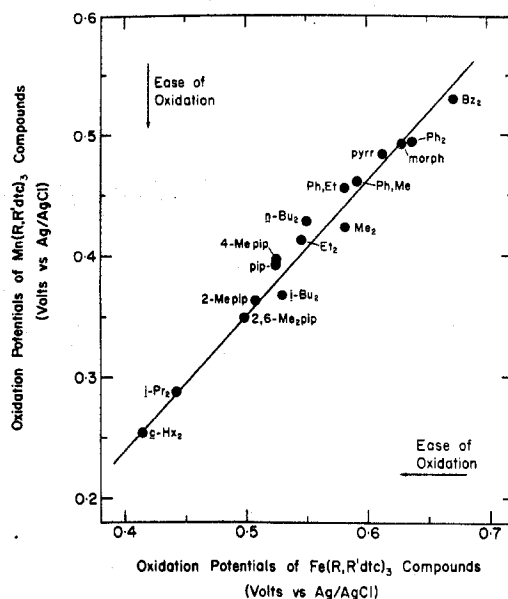


Figure 2. Graphical illustration of the relationship between the oxidation potentials of the complexes $\text{Fe}(\text{RR}'\text{dtc})_3$ and $\text{Mn}(\text{RR}'\text{dtc})_3$.

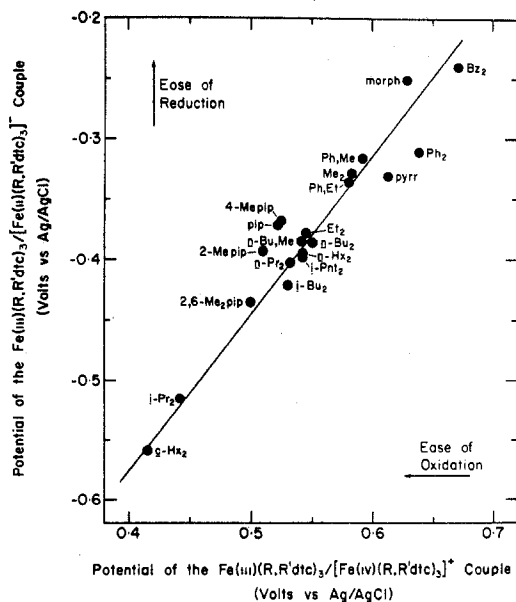
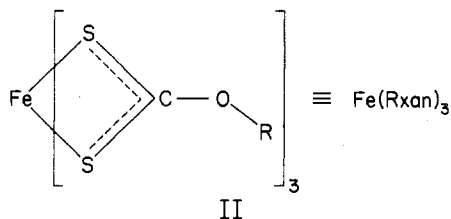


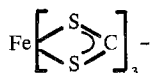
Figure 3. Relation between the oxidation and reduction potentials of the ferric complexes, $\text{Fe}(\text{RR}'\text{dtc})_3$.

manganese and the tervalent iron dithiocarbamates. A parallel correlation exists for reduction potentials and for the other transition metal dithiocarbamates.

The closely related iron alkyl xanthates (II) minimize the



above difficulty of discriminating between steric and electronic effects. With only a single substituent on the oxygen atom, the possibility of steric factors modifying the geometry at the atom attached to the



system is eliminated. As the compositions of the inner $\text{Fe}(\text{S}_2\text{C}-)_3$ cores are identical for xanthates and dithiocarbamates, inductive substituent trends are expected to be clear-cut. Indeed, this is verified by voltammetric experiments (reductions at ca. +0.1 V and oxidation at ca. +1.2 V) and by the ease of reduction decreasing as expected for the following series of low-spin $\text{Fe}(\text{Rxn})_3$ complexes:³³ R = benzyl > Me > Et > *i*-Pr. Cyclic voltammetry indicates the reduction processes involve only one electron and are reversible. The reduction product is expected to be the iron(II) complex $[\text{Fe}(\text{Rxn})_3]^-$ by analogy with the dithiocarbamates. Complexes of this stoichiometry have been isolated.³⁴ The oxidation of ferric xanthate is not strictly reversible by cyclic voltammetry and the order of benzyl and methyl substituents is interchanged in the trend of oxidation potentials. In view of the complementary behavior and nature of the xanthates and dithiocarbamates, the inductive trend, as evidenced with the xanthate reductions, is expected to be appropriate for the dithiocarbamates. However, the substituent ring size, presumably by virtue of its effect on the electronic structure at the nitrogen atom, also contributes to the electronic and hence redox properties of the dithiocarbamates.

Data on the redox behavior of mixed-ligand species of Fe(III) enhance the arguments presented above. Mixed dithiocarbamate species with the ligands *N,N*-dibenzylthiocarbamate and *N,N*-dicyclohexylthiocarbamate are prepared in situ by simply mixing solutions of pure $\text{Fe}((\text{c-Hx})_2\text{dtc})_3$ and $\text{Fe}(\text{Bz}_2\text{dtc})_3$ in the voltammetric vessel at room temperature. Ligand-exchange equilibrium is established rapidly and ac voltammetry shows both the reduction and oxidation steps expected for the four compounds (see Figure 4), viz., $\text{Fe}((\text{c-Hx})_2\text{dtc})_3$, $\text{Fe}((\text{c-Hx})_2\text{dtc})_2(\text{Bz}_2\text{dtc})$, $\text{Fe}((\text{c-Hx})_2\text{dtc})(\text{Bz}_2\text{dtc})_2$, and $\text{Fe}(\text{Bz}_2\text{dtc})_3$.

Assignment of redox potentials for the mixed-ligand species is based on the above substituent argument, with the expectation that successive replacement of $[\text{Bz}_2\text{dtc}]^-$ by $[(\text{c-Hx})_2\text{dtc}]^-$ should afford complexes which are easier to oxidize. Although the redox potentials embody potential shifts due to the complex set of preceding and following equilibria (ligand exchange) which may be coupled with the electron transfer, the observed oxidation potential increases linearly with successive replacement of $[\text{Bz}_2\text{dtc}]^-$ by $[(\text{c-Hx})_2\text{dtc}]^-$. Attempts to isolate the mixed-ligand iron(III) complexes by chromatography were unsuccessful since the equilibrium is so rapidly established that only the separation of $\text{Fe}((\text{c-Hx})_2\text{dtc})_3$ and $\text{Fe}(\text{Bz}_2\text{dtc})_3$ results.

The corresponding cobalt(III) dithiocarbamates are effectively nonlabile and $\text{Co}((\text{c-Hx})_2\text{dtc})_3$ and $\text{Co}(\text{Bz}_2\text{dtc})_3$ show

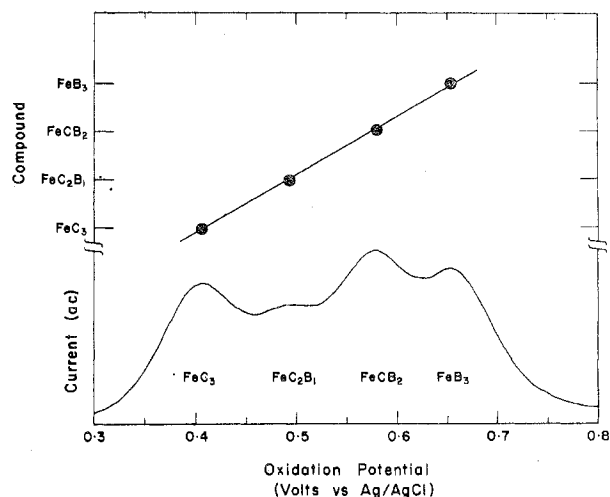
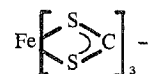


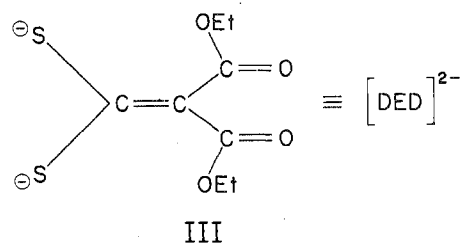
Figure 4. Bottom curve: ac voltammetry (oxidation) on a solution containing a mixture of mixed-ligand species FeC_3 , FeC_2B , FeCB_2 , and FeB_3 where C \equiv dicyclohexylthiocarbamate and B \equiv dibenzylthiocarbamate. Top curve: relationship between complex composition and ac peak potential.

no voltammetric evidence of ligand exchange after 5 hr in acetone solution at room temperature. However, mixed-ligand complexes of Co(III) are readily prepared by other routes and have been isolated and characterized. The redox behavior of these nonlabile species parallels the above findings both with regard to assignment of redox potentials and their linear dependence on successive ligand replacement.³³

Further evidence for the generality of the substituent effect, which entails a more drastic change in ligand while still retaining the



core, is provided by comparing the redox data for the ferric xanthates and dithiocarbamates. The xanthates are much easier to reduce (and harder to oxidize) than the dithiocarbamate complexes as expected on the basis of the greater electron-releasing power of $-\text{NR}_2$ compared with the $-\text{OR}$ substituent. An exceptionally dramatic shift in the redox potential of the Fe(III)–Fe(IV) couple is apparent with ligand III. In accord with the relatively large electron density at



the sulfur donors, the redox couple of $[\text{Fe}(\text{DED})_3]^{3-}$ – $[\text{Fe}(\text{DED})_3]^{2-}$ is -1.20 V vs. Ag–AgI.³⁵ Hence, for a series of 1,1-dithio ligands, the ease of reduction of the iron(IV) complexes decreases dramatically: $[\text{Rxn}]^- > [\text{R}_2\text{dtc}]^- > [\text{DED}]^{2-}$.

The difference between the reduction potentials of the ferric xanthates and dithiocarbamates of ~ 600 mV allows ready identification of mixed ferric species containing both xanthate and dithiocarbamate ligands. Solution mixtures of $\text{Fe}(\text{Bzxn})_3$ and $\text{Fe}((\text{i-Pr})_2\text{dtc})_3$ undergo ligand exchange and afford voltammograms which confirm the presence of all the expected mixed-ligand complexes. Equilibria between the mixed-ligand complexes is rapidly established, suggesting that pre- and perhaps post-electron-transfer reactions may affect the ap-

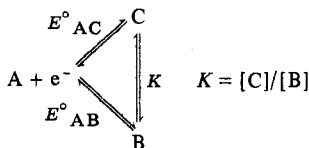
parent redox potential. Employing cyclic voltammetry and bidirectional scanning ac voltammetry, peak heights of the electroactive species are dependent on scan direction due to these shifts in equilibria which arise from preferential electrolysis of the different species as the potential range is scanned.

Using ac voltammetry, the reduction potentials for the mixed-ligand species, obtained at a scan rate of 50 mV/sec, are as follows: Fe(Bzxn)₃, +0.22 V; Fe(Bzxn)₂((i-Pr)₂dtc) 0.00 V; Fe(Bzxn)((i-Pr)₂dtc)₂, -0.19 V; Fe((i-Pr)₂dtc)₃, -0.52 V. The redox potentials of the mixed-ligand complexes have been assigned on the basis of the trend in redox potential expected for the substituents. The dependence of potential on the ligands deviates from linearity since the E_p values for reduction of the mixed-ligand species are less negative than expected.

(f) Redox Properties of a System in Spin Equilibrium.

Electrochemical measurements²⁰ have established that the oxidation and reduction potentials for dithiocarbamates of Cr(III), Mn(III), Fe(III), and Co(III) display an almost identical dependence upon the R₁ and R₂ substituents²⁰ (cf. Figure 2). This indicates that the substituent dependence of the redox potentials of the iron complexes is dominated by electron density at the metal center rather than by differences in electronic configuration of the metal ion. This view is reinforced by the absence of detectable trends in the redox potentials of iron(III) dithiocarbamates which contain different proportions of low-spin and high-spin isomers. For example, the oxidation potentials of the low-spin complexes Fe((i-Pr)₂dtc)₃ and Fe(Ph₂dtc)₃ differ by ca. 300 mV but with the latter compound being oxidized at about the same potential as the high-spin complex Fe(pyrrdtc)₃. This insensitivity of redox potential to spin state is at first sight surprising, but can be rationalized providing the time scale of the spin interconversion is extremely fast. Indeed, Mössbauer and NMR spectra of iron(III) dithiocarbamates demonstrate¹ that the relaxation times are certainly very much shorter than 10⁻⁷ sec.

Consider the reversible reduction of a compound A to give two electroactive products, B and C, which differ in spin but exhibit a very rapid interconversion with an equilibrium constant K .



From the Nernst equation, the redox potential for the reduction can be expressed in terms of the concentration of either C or B, i.e.

$$E_{AC} = E^\circ_{AC} - \frac{RT}{nF} \ln \frac{[C]}{[A]} \quad (I)$$

$$E_{AB} = E^\circ_{AB} - \frac{RT}{nF} \ln \frac{[B]}{[A]} \quad (II)$$

where E_{AC} and E_{AB} are the measured potentials. If the degree of reduction of A is represented by α , the equilibrium concentrations of the reduced species are $[B] = \alpha/(1+K)$ and $[C] = [K/(1+K)]\alpha$. Accordingly, the measured potential can be expressed as

$$E_{1/2}(\text{measd}) = E^\circ_{AC} - \frac{RT}{nF} \ln \left(\frac{K}{1+K} \right) \quad (III)$$

$$= E^\circ_{AB} - \frac{RT}{nF} \ln \left(\frac{1}{1+K} \right) \quad (IV)$$

where the logarithmic term in α vanishes when $\alpha = 1/2$ to give

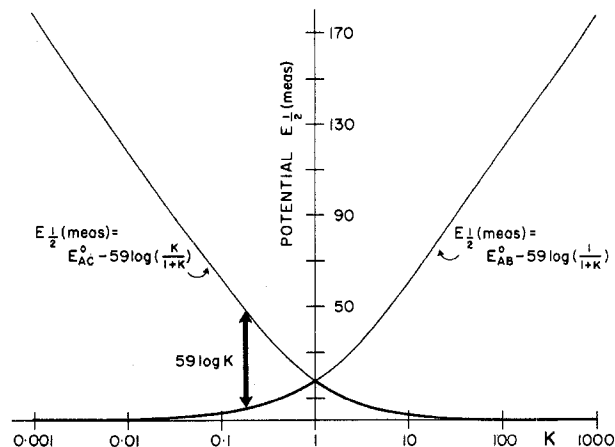


Figure 5. Graphical plots of the relationships (in mV) $E_{1/2}(\text{measd}) = E^\circ_{AC} - 59 \log [K/(1+K)]$ and $E_{1/2}(\text{measd}) = E^\circ_{AB} - 59 \log [1/(1+K)]$. It should be noted that each curve refers to a different reference potential, viz., E°_{AC} and E°_{AB} , respectively.

$E_{1/2}(\text{measd})$ and the standard reduction potentials are correlated by the equation

$$E^\circ_{AB} = E^\circ_{AC} - \frac{RT}{nF} \ln K \quad (V)$$

In the specific case of the ${}^6A_1-{}^2T_2$ spin equilibrium of iron(III) dithiocarbamates, we can write $A \equiv t_2^4\text{-Fe(IV)}$, $B \equiv t_2^5\text{-Fe(III)}$, and $C \equiv t_2^3e^2\text{-Fe(III)}$. Since the kinetics of establishing the spin equilibrium are very fast, they do not perturb the measured potential and

$$E_{1/2}(\text{measd}) = E^\circ(\text{Fe}^{\text{IV}} - \text{Fe}^{\text{III}}_{\text{hs}}) - \frac{RT}{F} \ln \frac{K}{1+K} \quad (VI)$$

The variation of $E_{1/2}(\text{measd})$ with K is illustrated in Figure 5 and can be considered in the two regions $K > 1$ and $K < 1$ which correspond to high-spin and low-spin ground states, respectively. The measured potential $E_{1/2}(\text{measd})$ asymptotes to E°_{AC} as $K \rightarrow \infty$ or to E°_{AB} as $K \rightarrow 0$, but at intermediate values of K , the reduction potential is displaced to more positive values by the spin equilibrium. The maximum deviation of the measured potential from the standard [$E_{1/2}(\text{measd}) - E^\circ_{AC}$] or [$E_{1/2}(\text{measd}) - E^\circ_{AB}$] is $(RT/F) \ln 2$ or 17.8 mV (cf. Figure 5).

Since the Fe(IV)–Fe(III) redox potentials measured in this work fall in the range $+0.67 \geq E_{1/2}(\text{measd}) \geq +0.41$ V, it is not surprising that the small perturbations (i.e., ≤ 18 mV) arising from different proportions of low-spin and high-spin isomers do not emerge. Hence it can be concluded that the measured potential should not vary significantly from the redox potential of the ground-state spin form of the ferric complexes.

As noted earlier, the definitive relationship between substituent and redox potential observed for other metal dithiocarbamates holds equally well for iron.²⁰ With the exception of pyrrolidyl, all of the derivatives studied in the present work possess the low-spin ground state; i.e., $E_{1/2}(\text{measd})$ refers to the region $0 \leq K \leq 1$, so that it is not surprising that this relationship is preserved. However, it is significant that $E_{1/2}(\text{measd})$ for high-spin Fe(pyrrdtc)₃, where $K \gg 1$, also conforms to the simple expectations of Figures 2 and 5 establishing unambiguously that the reduction and oxidation potentials of iron(III) dithiocarbamates do not reflect the intrinsic low-spin \rightleftharpoons high-spin equilibrium but display the same substituent dependence as is found for other trivalent transition metals from the first row.

These conclusions should be general and suggest that proposals for biological pathways involving spin-state-dependent redox potentials^{6,17,36-38} would need to involve relaxation rates for the spin interconversion which are considerably slower than

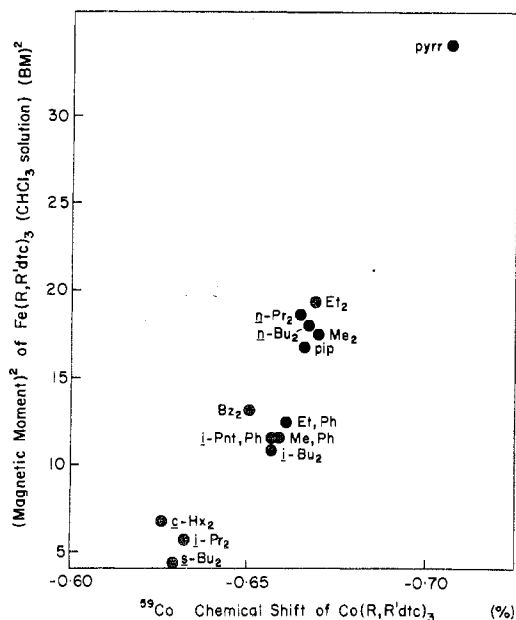


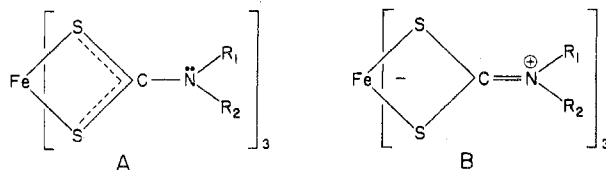
Figure 6. Correlation between μ_{eff}^2 of $\text{Fe}(\text{RR}'\text{dte})_3$ and the ^{59}Co resonance of $\text{Co}(\text{RR}'\text{dte})_3$.

the rate of electron transfer in order to affect a potential shift of any appreciable magnitude.

(g) **Physicochemical Correlations with Redox Behavior.** It is informative to compare the substituent effects which emerge from electrochemical studies with those which have been reported previously from measurements of paramagnetic susceptibility¹⁻⁴ and cobalt-59 spectra.³⁹ For a six-coordinate cobalt(III) compound with O_h symmetry, the chemical shift of the ^{59}Co resonance, σ , is given by

$$\sigma = 32k_{\sigma\pi}^2 / \Delta \langle r_{3d} \rangle^3$$

where $k_{\sigma\pi}$ is an orbital reduction factor and Δ is the ligand field splitting parameter. If the assumption is made that $k_{\sigma\pi}^2 / \langle r_{3d} \rangle^3$ remains constant for a series of cobalt(III) dithiocarbamates, then the chemical shift should reflect the trend in Δ for the different substituents. For the corresponding iron(III) dithiocarbamates, a parallel trend should be reproduced in the magnetic susceptibility and, indeed, the plot of μ_{eff}^2 vs. σ is found to show such a correlation (cf. Figure 6). It has been suggested previously³ that the R_1NR_2 angle in $\text{Fe}(\text{S}_2\text{CNR}_1\text{R}_2)_3$ might be expected to increase toward 120° with the bulkier R groups, the concomitant increase in C-N bond order thereby modifying Δ , μ_{eff} , and σ . In particular, it was concluded that, as the electron density at the sulfur atoms is enhanced (canonical form B), stronger $\text{S} \rightarrow \text{M}$ σ



bonding should generate larger values of Δ favoring the low-spin $\text{Fe}(\text{R}_2\text{dte})_3$ isomer and less negative ^{59}Co NMR shifts for $\text{Co}(\text{R}_2\text{dte})_3$.

Attention has been drawn in section e to the fact that the stronger electron-releasing substituents (i.e., favoring the B form) are associated with those complexes which are easier to oxidize and harder to reduce. From the above arguments, such complexes should exhibit magnetic moments displaying a predominance of the low-spin state and, indeed, such a correlation can be discerned in a plot of magnetic moment squared vs. oxidation potential (cf. Figure 7). The aryl

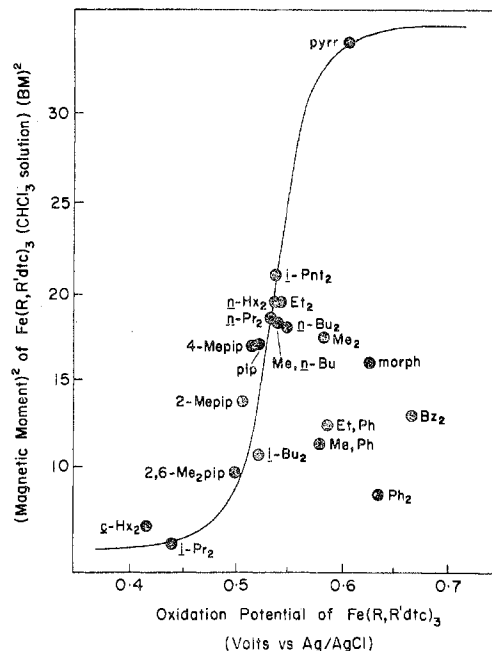
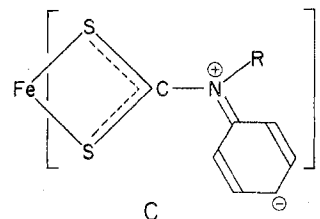


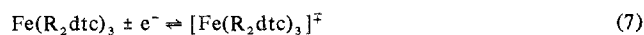
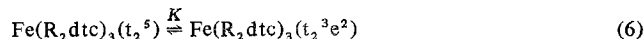
Figure 7. Oxidation potentials of $\text{Fe}(\text{RR}'\text{dte})_3$ vs. μ_{eff}^2 for the same complexes.

substituent introduces anomalies as illustrated by the (Me)(Ph), (Et)(Ph), Ph_2 , and Bz_2 derivatives which are displaced from the correlation curve to more positive potentials. The morpholyl derivative is also displaced. It appears that the withdrawal of π electrons by the aryl group, represented by canonical form C, reduces the electron density at the metal



center, destabilizes the $\text{Fe}(\text{IV})$ species, and raises the oxidation potential. At the same time, the additional stabilization of metal t_2 orbitals increases Δ sufficiently to favor the low-spin state.

It is gratifying that a correlation between μ_{eff}^2 (which is related² to the spin equilibrium constant K) and the redox potential can be discerned in view of the fact that this is a comparison of the energy separation between two $\text{Fe}(\text{III})$ spin isomers with that between the redox-related couple $\text{Fe}(\text{III})$ - $\text{Fe}(\text{IV})$, i.e., a comparison of the effects of substituents on the position of the spin equilibrium 6, with its effect on a redox process in which an electron is transferred (eq 7).



Furthermore, it must be recalled that μ_{eff}^2 is an imperfect measure of the spin equilibrium constant K . This approximation arises because the sixfold degeneracy of the low-spin 2T_2 state is lifted both by spin-orbit coupling and distortions of the ligand field to give three Kramers doublets whose separations are of a similar energy to that of the 6A_1 - 2T_2 interval. Although the magnetic moment measured in solution reflects the distribution of molecules between these levels, the estimated value of K is only approximate because the energies of the Kramers doublets are not known with certainty.²

Interpretations of the substituent effect which are in conflict with that proposed here have been presented by other workers

Table IV. Structural Data for $\text{Fe}(\text{Et}_2\text{dtc})_3$

	Magnetic moment, BM	
	4.3	2.2
Temp, K	297	79
Predominant ligand form	A	B
Fe-S, Å	2.357	2.306
S-C, Å	1.708	1.721
C-N, Å	1.337	1.323
N-C(Et), Å	1.496	1.480

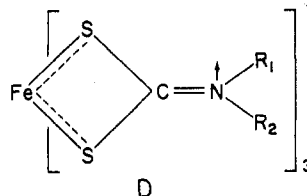
and require comment. Eley, Myers, and Duffy⁴⁰ have employed the aqueous pK_a value, uncorrected, of the parent secondary amine, HNR_1R_2 , as a measure of the inductive effects of R_1 and R_2 on the parent amine. They have argued that the greater the pK_a , the more favored is limiting form B, but they have preferred to associate this form with diminished covalency of the Fe-S bond and high-spin behavior. While the pK_a of HNR_1R_2 in water is a measure of the σ basicity of a tetrahedral nitrogen atom toward the proton, it reproduces neither the planar stereochemistry of the nitrogen nor the π symmetry of the FeS_2CNC_2 skeleton which is characteristic of the structures of metal dithiocarbamates. Although it is claimed by these workers that the magnetic moments in aprotic solvents, "with notable exceptions", vary linearly with pK_a in the range $0.79 < pK_a < 11.25$, the data are also subject to the opposite interpretation that the actual correlation line should be drawn almost at right angles through the 23 amines which lie in the confined region $9.29 < pK_a < 11.25$. In this interpretation, the "notable exceptions" become morpholyl ($pK_a = 8.49$) and the 13 amines which contain an aryl group ($0.79 < pK_a < 9.68$). The incorporation of an aryl group displaces the pK_a of the free amine to lower values and reinforces our view above that such dithiocarbamates are subject to exceptional π -mesomeric effects (cf. form C).

Eley, Myers, and Duffy's interpretation of the substituent effect is seriously at variance with recent accurate crystal structure determinations⁴¹ of $\text{Fe}(\text{Et}_2\text{dtc})_3$ performed at 297 K ($\mu_{\text{eff}} = 4.3$ BM) and 79 K ($\mu_{\text{eff}} = 2.2$ BM). The two determinations reveal trends in geometry which associate the limiting form A with high spin and form B with low spin as proposed originally by Ewald, Martin, Sinn, and White³ (cf., Table IV).

In a recent paper, Golding and Lehtonen have proposed⁴² that the reversible reduction^{20,43} of $\text{Fe}(\text{R}_2\text{dtc})_3$ occurs through the ligand nitrogen atom rather than at the iron center. They have argued that, since the nitrogen atom in form B has a partial positive charge, it is the logical point of attack in a reduction process (cf. structure 3 of their paper). As the accumulated structural,²⁷ spectral,²⁴ and electrochemical²⁰ evidence favors the assignment of the redox processes of $\text{Fe}(\text{R}_2\text{dtc})_3$ complexes as metal based, form B must be associated with difficulty rather than ease of reduction. Furthermore, the redox potentials possess thermodynamic rather than kinetic significance and must reflect the stabilities of the oxidized (or reduced) forms relative to iron(III). Stabilization of iron(IV) in $[\text{Fe}(\text{R}_2\text{dtc})_3]^+$ should be favored by delocalization of the high positive charge associated with form B whereas the converse is likely to be true for the reduced species $[\text{Fe}(\text{R}_2\text{dtc})_3]^-$. The mechanism of reduction may involve the nitrogen atom, but as the redox processes are reversible, the potentials provide no information on the mechanistic pathway of the reduction process.

The small linear decrease of the Mössbauer isomer shift with diminishing magnetic moment of iron(III) dithiocarbamates^{12,44} has been interpreted¹² as evidence for back-donation of iron 3d electrons into empty ligand π orbitals. The effective s-electron density at the iron nucleus is increased due to deshielding of the nuclear charge consequent on the decrease of d-electron density. The limiting canonical form

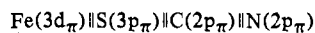
which enhances this delocalization of metal d electrons is the B form modified to include Fe-S double bonding (see D), in



agreement with the X-ray data summarized in Table IV. The limiting resonance form employed by Eley, Duffy, and Uhrich to represent back-donation of metal electrons to the ligand is incorrect and a combination of the two limiting canonical forms A and D is required to describe delocalization of the Fe 3d electrons.

The simple relationship proposed⁴² between reduction potentials and the $-\text{NCH}_2-$ proton hyperfine interaction constant in the ${}^6\text{A}_1$ state is also consistent with our association of the D form with the low-spin ${}^2\text{T}_2$ state. Thus the spin density of nitrogen in the ${}^6\text{A}_1$ state is found to increase rapidly in passing from the high- to the low-spin complexes consistent with an enhanced delocalization of d electrons in the D form.

In conclusion, we suggest that the redox behavior of iron dithiocarbamates can be correlated satisfactorily with X-ray data and the available physicochemical data. Our interpretation is diametrically opposed to that proposed by Eley et al. and followed by Golding and Lehtonen. While the use of limiting canonical forms is convenient for highlighting certain features, it must be remembered that the "vertical" π system is fully delocalized over the planar metal-chelate grouping (the symbol \parallel is used to denote overlap).



Registry No. $\text{Fe}(\text{Me}_2\text{dtc})_3$, 14484-64-1; $\text{Fe}(\text{Et}_2\text{dtc})_3$, 13963-59-2; $\text{Fe}((n\text{-Pr})_2\text{dtc})_3$, 15407-44-0; $\text{Fe}((i\text{-Pr})_2\text{dtc})_3$, 15280-39-4; $\text{Fe}((\text{Me})(\text{Bu})\text{dtc})_3$, 36763-17-4; $\text{Fe}((n\text{-Bu})_2\text{dtc})_3$, 14526-32-0; $\text{Fe}((i\text{-Bu})_2\text{dtc})_3$, 19543-96-5; $\text{Fe}((i\text{-Pnt})_2\text{dtc})_3$, 21350-68-5; $\text{Fe}((n\text{-Hx})_2\text{dtc})_3$, 23674-38-6; $\text{Fe}((c\text{-Hx})_2\text{dtc})_3$, 21288-88-0; $\text{Fe}(\text{Bz}_2\text{dtc})_3$, 23451-11-8; $\text{Fe}(\text{pyrrdtc})_3$, 21288-86-8; $\text{Fe}(\text{pipdtc})_3$, 20487-62-1; $\text{Fe}(2,6\text{-Me}_2\text{pipdtc})_3$, 36763-01-6; $\text{Fe}(2\text{-Mepipdtc})_3$, 32248-54-7; $\text{Fe}(4\text{-Mepipdtc})_3$, 55333-51-2; $\text{Fe}(\text{morpdtc})_3$, 14285-01-9; $\text{Fe}(\text{Ph}_2\text{dtc})_3$, 23683-89-8; $\text{Fe}((\text{Ph})(\text{Me})\text{dtc})_3$, 15635-69-5; $\text{Fe}((\text{Ph})(\text{Et})\text{dtc})_3$, 15635-70-8; $\text{Fe}(\text{pyrrdtc})_3\text{ClO}_4$, 39838-28-3; $\text{Hg}(\text{Et}_2\text{dtc})_2$, 14239-51-1; $\text{Fe}((i\text{-Pr})_2\text{dtc})_3\text{BF}_4$, 35270-35-0; $\text{Fe}(\text{pyrrdtc})_3\text{BF}_4$, 35270-36-1; $\text{Fe}(\text{pipdtc})_3\text{BF}_4$, 55333-52-3.

References and Notes

- R. L. Martin and A. H. White, *Transition Met. Chem.*, **4**, 113 (1968).
- A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. R. Soc. London, Ser. A*, **280**, 235 (1964).
- A. H. Ewald, R. L. Martin, E. Sinn, and A. H. White, *Inorg. Chem.*, **8**, 1837 (1969).
- A. H. White, E. Kokot, R. Roper, H. Waterman, and R. L. Martin, *Aust. J. Chem.*, **17**, 294 (1964).
- J. K. Beattie, N. Sutin, D. H. Turner, and G. W. Flynn, *J. Am. Chem. Soc.*, **95**, 2052 (1973).
- J. K. Beattie and R. J. West, *J. Am. Chem. Soc.*, **96**, 1933 (1974).
- E. Frank and C. R. Abeledo, *Inorg. Chem.*, **5**, 1453 (1966).
- R. M. Golding and H. J. Whitfield, *Trans. Faraday Soc.*, **62**, 1713 (1966).
- R. M. Golding, *Mol. Phys.*, **12**, 13 (1967).
- R. Richards, C. E. Johnson, and H. A. O. Hill, *J. Chem. Phys.*, **48**, 5231 (1968).
- P. B. Merrithew and P. G. Rasmussen, *Inorg. Chem.*, **11**, 325 (1972).
- R. R. Eley, N. V. Duffy, and D. L. Uhrich, *J. Inorg. Nucl. Chem.*, **34**, 3681 (1972).
- L. M. Epstein and D. K. Straub, *Inorg. Chem.*, **8**, 784 (1969).
- R. M. Golding, W. C. Tennant, C. R. Kanekar, R. L. Martin, and A. H. White, *J. Chem. Phys.*, **45**, 2688 (1966).
- R. M. Golding, W. C. Tennant, J. P. M. Bailey, and A. Hudson, *J. Chem. Phys.*, **48**, 764 (1968).
- R. M. Golding, B. D. Lukeman, and E. Sinn, *J. Chem. Phys.*, **56**, 4147 (1972).
- D. F. Wilson, P. L. Dutton, M. Erecinska, J. G. Lindsay, and N. Sato, *Acc. Chem. Res.*, **5**, 234 (1972).
- J. A. McCleverty in "Reactions of Molecules at Electrodes", N. S. Hush,

- Ed., Wiley-Interscience, New York, N.Y., 1971.
- (19) A. M. Bond, A. R. Hendrickson, and R. L. Martin, *J. Am. Chem. Soc.*, **95**, 1449 (1973), and references therein.
- (20) R. Chant, A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Aust. J. Chem.*, **26**, 2533 (1973).
- (21) A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Inorg. Chem.*, **13**, 1933 (1974).
- (22) J. A. McCleverty, D. G. Orchard, and K. Smith, *J. Chem. Soc. A.*, 707 (1971).
- (23) G. Cauquis and D. Lachenal, *Inorg. Nucl. Chem. Lett.*, **9**, 1095 (1973).
- (24) E. A. Pasek and D. K. Straub, *Inorg. Chem.*, **11**, 259 (1972).
- (25) J. L. K. F. de Vries, J. M. Trooster, and E. de Boer, *Inorg. Chem.*, **12**, 2730 (1973).
- (26) R. M. Golding, C. M. Harris, K. J. Jessop, and W. C. Tennant, *Aust. J. Chem.*, **25**, 2567 (1972), and references therein.
- (27) R. L. Martin, N. M. Rohde, G. B. Robertson, and D. Taylor, *J. Am. Chem. Soc.*, **96**, 3647 (1974).
- (28) P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1163 (1972).
- (29) R. L. Martin and A. H. White, *Inorg. Chem.*, **6**, 712 (1967).
- (30) B. F. Hoskins, R. L. Martin, and A. H. White, *Nature (London)*, **211**, 627 (1966).
- (31) A. M. Bond, A. T. Casey, and J. R. Thackeray, *Inorg. Chem.*, **12**, 887 (1973).
- (32) R. Engst, W. Schnaak, and H. Woggon, *Z. Anal. Chem.*, **222**, 388 (1966).
- (33) A. R. Hendrickson and R. L. Martin, unpublished results.
- (34) D. G. Holah and C. N. Murphy, *Can. J. Chem.*, **49**, 2726 (1971).
- (35) F. J. Hollander, R. Pedelty, and D. Coucouvanis, *J. Am. Chem. Soc.*, **96**, 4032 (1974).
- (36) R. J. P. Williams, *Cold Spring Harbor Symp. Quant. Biol.*, **36**, 53 (1971).
- (37) M. F. Perutz, *Nature (London)*, **228**, 726 (1970).
- (38) J. L. Hoard, *Science*, **174**, 1295 (1971).
- (39) R. L. Martin and A. H. White, *Nature (London)*, **223**, 394 (1969).
- (40) R. R. Eley, R. R. Myers, and N. V. Duffy, *Inorg. Chem.*, **11**, 1128 (1972).
- (41) J. G. Leopoldt and P. Coppens, *Inorg. Chem.*, **12**, 2269 (1973).
- (42) R. M. Golding and K. Lehtonen, *Aust. J. Chem.*, **27**, 2083 (1974).
- (43) R. M. Golding, K. Lehtonen, and B. J. Ralph, *J. Inorg. Nucl. Chem.*, **36**, 2047 (1974).
- (44) P. B. Merrithew and P. G. Rasmussen, *Inorg. Chem.*, **11**, 325 (1972).

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Synthesis and Spectroelectrochemical Properties of Pentaammineruthenium(II) Complexes of Quinone Diimines

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Reported are the syntheses and spectral characterizations of a series of ruthenium(II) complexes of the type $(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{L}^{\text{r+}}$, where the ligand L represents the *p*-quinone diimine of *p*-phenylenediamine, 1-amino-4-dimethylaminobenzene, 1,4-diaminonaphthalene, and *p*-aminophenol. The stabilization of the various benzoquinone diimines by complexation to pentaammineruthenium(II) is accompanied by a greatly enhanced basicity of the ligand. For *p*-benzoquinone diimine, the $\text{p}K_a$ of the free ligand is 5.75, whereas a value of 10.6 is determined for the corresponding ruthenium complex. The electronic spectra of all of the complexes are characterized by an intense ($\log \epsilon \approx 4.5$) band at about 18 kK. Deprotonation causes a shift of this band toward smaller energies. This absorption band is assigned to a ligand-to-metal charge transfer, the excited state of the complex having a smaller basicity than the ground state. The results of spectroelectrochemical measurements of a number of these complexes are reported. Potential cycling between -500 and $+150$ mV vs. SCE corresponds to the two-electron process ruthenium(II) diimine \rightleftharpoons ruthenium(II) diamine.

The syntheses and electronic properties of a variety of mono- and binuclear complexes of ruthenium(II) pentaammine with heterocyclic nitrogen donors have been reported.¹⁻⁴ Primary amines, i.e., molecules lacking π -accepting properties, however, have not been used systematically as ligands. Only a few transition metal complexes containing the chelating ligand *o*-phenylenediamine have been described.⁵ In particular, a thorough study of the five-membered series of one-electron oxidation-reduction reactions of bis(*o*-phenylenediamine)metal complexes has been reported. The terminal oxidized product of this series represents the bis(*o*-benzoquinone)metal complex.⁶ A recent single-crystal X-ray study demonstrated the presence of the bidentate ligand *o*-benzoquinone diimine in the complex ion $[\text{Fe}(\text{CN})_4\text{C}_6\text{H}_4(\text{NH})_2]^{2-}$.⁷ On the other hand the ligand behavior of *p*-phenylenediamine has been studied only very rarely. A dark blue product was described as the result of the reaction of pentacyanoammineferrate(III) with *p*-phenylenediamine.⁸ This product was formulated as the binuclear complex $[(\text{CN})_5\text{FeHNC}_6\text{H}_4\text{NHFe}(\text{CN})_5]^{6-}$ without specifying the electronic structure of the bridging ligand. In particular it has not been clarified whether the ligand has to be described as the partially deprotonated diamine, as the *p*-benzoquinone diimine, or as a radical ion. The coordinating properties of the corresponding oxygen compounds, hydroquinone and *p*-benzoquinone, have been studied in the case of the reaction of pentacyanocobaltate(II) with *p*-benzoquinone. In the binuclear species $[(\text{CN})_5\text{CoOCC}_6\text{H}_4\text{OCO}(\text{CN})_5]^{6-}$ the bridging ligand is represented by the dianion of hydroquinone. An unstable decomposition product contains *p*-quinone as a ligand.⁹ The redox properties of *p*-phenylenediamine and related compounds have been inves-

tigated by studying their reactions with the hexacyanoferrate(II)-hexacyanoferrate(III) couple.¹⁰

In the course of our studies of mixed-valence complexes¹¹ we became interested in *p*-phenylenediamine as a possible bridging ligand in binuclear ruthenium-ammine complexes. As a first step suitable mononuclear complexes have to be synthesized. The electronic spectra of these compounds should provide information concerning the electronic structure of the ligand molecule. Preliminary experiments led to the conclusion that the extremely reactive *p*-benzoquinone diimine is stabilized by coordination to pentaammineruthenium(II). A spectroelectrochemical study has been carried out in order to correlate the optical and redox properties of the pentaammineruthenium-*p*-phenylenediamine system.

Experimental Section

Reagents. Chloropentaammineruthenium(III) chloride¹² was prepared from hexaammineruthenium(III) chloride (Johnson Matthey). Silver(I) trifluoroacetate was obtained by dissolving silver(I) oxide in the stoichiometric amount of trifluoroacetic acid and evaporating to dryness. *p*-Phenylenediamine (Fluka, Puriss) was further purified by vacuum sublimation at 140°. 1-Amino-4-dimethylaminobenzene (*N,N*-dimethyl-4-aniline) and *p*-aminophenol were purchased from Fluka and used without further purification. 1,4-Diaminonaphthalene was obtained from Sandoz AG, Basel, Switzerland.

Analyses. Ruthenium was determined colorimetrically.¹³ C, H, and N microanalyses were carried out by the Microanalytical Laboratory of ETH, Zürich, Switzerland.

Syntheses. (*p*-Benzoquinone diimine)pentaammineruthenium(II) hexafluorophosphate (I). A 0.100-g amount of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (0.342 mmol) and 0.151 g of AgCF_3COO (0.684 mmol) were covered with 3 ml of water. This mixture was kept at 50° until AgCl had