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Tris(dithiocarbamato) Complexes of Manganese(II), Manganese(III), and Manganese(IV). An Electrochemical Study

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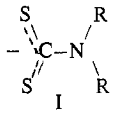
An electrochemical study of the $Mn^{n+} + R_2dtc^-$ system in aprotic solvents establishes that the dithiocarbamate ligand forms tris-chelated complexes of manganese in the three oxidation states II, III, and IV. Thus, $Mn(R_2dtc)_3$ undergoes single one-electron oxidation and reduction steps at a platinum electrode: $[Mn^{IV}(R_2dtc)_3]^+ + e^- \rightleftharpoons Mn^{III}(R_2dtc)_3$; $Mn^{III}(R_2dtc)_3 + e^- \rightleftharpoons [Mn^{II}(R_2dtc)_3]^-$. These redox processes have been examined for 16 different substituents R by normal pulse voltammetry, ac voltammetry, cyclic voltammetry, coulometry, and exhaustive electrolysis. Several Mn(IV) complexes have been isolated and characterized. Tris-chelated Mn(II) complexes have been characterized in solution. Titrations of Mn^{2+} into pyrrolidyldithiocarbamate solutions and *vice versa* have been monitored by electrochemical means. These experiments show the existence of 1:2 and 1:3 compounds of Mn(II), *i.e.*, $Mn(Pyrr(dtc))_2$ and $[Mn(Pyrr(dtc))_3]^-$. A plot of E(red) *vs.* E(oxid) for the 16 substituents yields a linear relation with a slope of 1.1 over a potential range of approximately 300 mV confirming that the substituent effect of R imposes similar shifts on the oxidation and reduction potentials. The complex with benzyl substituents is hardest to oxidize and easiest to reduce; the dicyclohexyl-substituted complex is easiest to oxidize and hardest to reduce.

Introduction

With complexes of thio chelates, electrochemical methods have proved particularly valuable for firmly establishing the electron transfer relation of members of the unsaturated 1,2-dithio complexes (dithiolenes)[1,2] with the redox potentials of these species providing a firm basis for synthetic studies of these complexes.[3]

Although Schrauzer predicted that 1,3- and 1,1-dithio complexes would not possess the unusually high electron affinity of the 1,2-dithio chelates,[4] it has been shown that many 1,3-dithio chelates do display polarographically reversible reduction steps.[5-7] The $E_{1/2}$ values of the reduction steps correlate well with the known chemistry of these complexes.[8]

These electrochemical studies have now been extended to the 1,1-dithio chelates, namely dithiocarbamates (I)



$\equiv [R_2dtc]^-$

I

for which a preliminary electrochemical survey has revealed that many of their transition metal complexes are also capable of sustaining redox reactions.[9] The potentials are sensitive to the nature of the substituents on the nitrogen of the dithiocarbamate ligand and a correlation with the $3d^n$ electron configuration is found for the metals Cr, Mn, Fe, Co, Ni, and Cu. Characterization of many new dithiocarbamate species, mainly by Cras, Willemse, and others,[10-12] confirms that the complexes contain metal ions in unusual oxidation states. In spite of the sustained and detailed investigations of the chemistry of metal dithiocarbamates, those of manganese have been relatively neglected. Their existence was recognized first by Cambi and Cagnasso[13] who isolated the yellow divalent species $Mn(R_2dtc)_2$ and commented on their ready oxidation to the dark-violet trivalent complexes $Mn(R_2dtc)_3$. Subsequent investigations[14-16] have confirmed these early observations and established that $Mn(R_2dtc)_3$ complexes are monomeric in solution and are relatively unstable to light and moisture. Manganese(IV) species have been mentioned in three reports although the complexes have not been characterized[17-19]. Nonaqueous electrochemical studies of manganese complexes have been restricted to a few 1,2-dithiochelated[20,21] and porphyrin compounds.[22] Unfortunately, the possibility of the redox reactions being centered on the 1,2-dithio ligands leads to ambiguities in assigning metal ion oxidation states and reduces the value of these results in the comparative electrochemistry of manganese.

In this paper, we describe the electrochemical characterization of the $Mn^{n+} + [R_2dtc]^-$ system in nonaqueous media (acetone and dichloromethane). Under these experimental conditions the interrelation (by electron transfer) between complexes of the type

$$[Mn(R_2dtc)_3]^+ \rightleftharpoons [Mn(R_2dtc)_3]^0 \rightleftharpoons [Mn(R_2dtc)_3]^-$$

can be defined in detail.

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Experimental Section

Electrochemical. Electrochemical measurements were performed in acetone|0.1 *M* $[Et_4N]ClO_4$ or CH_2Cl_2|0.1 *M* $[n\text{-}Bu_4N]BF_4$ *vs.* a Ag|AgCl|0.1 *M* LiCl reference electrode as previously described.[23] A three-electrode, *iR* compensated system with a platinum auxiliary electrode was used throughout. Some conventional polarography was undertaken at a dropping mercury electrode (dme) although normal pulse voltammetry, ac voltammetry, and cyclic voltammetry were performed at a platinum disk electrode with a geometric area of ~0.27 cm^2. PAR Model 170 instrumentation was used throughout. Phase sensitive ac measurements were made at a scan rate of 5 mV/sec at 80 Hz with a phase angle of 90° with respect to the input alternating potential and with an ac perturbation of 5 mV peak–peak. Normal pulse voltammograms were obtained at a scan rate of 5 mV/sec from an initial position of zero current through the redox wave with a pulse frequency of 2.0 pulses/sec. All solutions were degassed with Ar or N_2 saturated with the appropriate solvent and the polarographic measurements were made at ambient temperature (~22°) under a blanket of the inert gas. Electrolysis studies were carried out at potentials up to 200 mV beyond the $E_{1/2}$ value of the redox couple of interest.

Instrumentation. Electronic spectra were obtained on a Cary 14 spectrophotometer. Ir spectra were obtained on Perkin-Elmer 225 and 457 instruments.

Compounds. (a) **Tris(dithiocarbamato)manganese(III), $Mn(R_2\text{-}dtc)_3$.** The dithiocarbamate ligands were prepared from the appropriate amine by reaction with CS_2 in aqueous alkali. The manganese(III) complexes were prepared from these solutions although the ligands were isolated and recrystallized for all other synthetic and electrochemical studies. Oxidation of stoichiometric quantities of $MnCl_2 \cdot 4H_2O$ and the dithiocarbamate in aqueous solution was accomplished aerially or in some instances by the careful addition of H_2O_2. The neutral trivalent complexes were recrystallized from either CH_2Cl_2–petroleum ether (80–100°) or CH_2Cl_2–ethanol mixtures and dried under vacuum over silica gel. All analytical data are collected in Table I.

(b) **Tris(*N,N*-dicyclohexyldithiocarbamato)manganese(IV) Tetrafluoroborate, $[Mn(c\text{-}Hx_2dtc)_3][BF_4]$.** Boron trifluoride etherate (2 ml of approximately 40% solution) was added dropwise to a stirred benzene solution (120 ml) of $Mn(c\text{-}Hx_2dtc)_3$ (2 g) in the presence of a vigorous stream of air. After addition of the $Et_2O \cdot BF_3$ was completed, bubbling was continued for 3 hr. The resulting suspension was dried, neutralized with anhydrous Na_2CO_3, and filtered. The desired product was obtained from the remaining solid mass by repeated extraction with CH_2Cl_2. Careful addition of benzene or diethyl ether to the combined extracts affords the complex in the form of dark crystals, yield approximately 75%.

(c) **Tris(pyrrolidyldithiocarbamato)manganese(IV) tetrafluoroborate, $[Mn(Pyrr(dtc))_3][BF_4]$, and (d) tris(diisopropyldithiocarbamato)manganese(IV) tetrafluoroborate, $[Mn(i\text{-}Pr_2dtc)_3][BF_4]$** were prepared and purified by the general procedure described for the dicyclohexyl derivative in approximately 45 and 60% yields, respectively.

(e) **Tris(pyrrolidyldithiocarbamato)manganese(IV) Perchlorate, $[Mn(Pyrr(dtc))_3][ClO_4]$.** $Mn(ClO_4)_2 \cdot 6H_2O$ (0.2 g), dissolved in a minimal volume of ethanol, was added dropwise over a period of 20 min to a vigorously stirred benzene solution of (0.5 g) $Mn(pyrr(dtc))_3$. Although the reaction appeared to be very fast, stirring was continued for 1 hr after which time the finely divided solid was collected and recrystallized from either nitromethane or CH_2Cl_2 by slow addition of benzene or ether, yield approximately 60%.

(f) **Bis(pyrrolidyldithiocarbamato)manganese(II), $Mn(Pyrr(dtc))_2$.** $Mn(ClO_4)_2 \cdot 6H_2O$ (1 g), was added to a Schlenck tube and the system flushed with dry argon. An argon-saturated 3:1 mixture of acetone: 2,2-dimethoxypropane (20 ml) was forced into the tube under a positive argon pressure. To the resulting solution was added an argon-saturated solution of $Na[Pyrr(dtc)] \cdot 2H_2O$ (0.5 g), using the same technique. When precipitation was complete, the crystalline, yellow solid was filtered under positive pressure, washed with the oxygen-free solvent mixture (20 ml), and pumped dry. The air-sensitive solid was manipulated under argon in a glove bag.

Results and Discussion

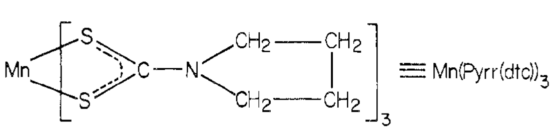
Conventional dc polarography at a dropping mercury electrode for most of the Mn(III) compounds showed complex behavior, particularly the reduction waves which exhibited at least two steps centered near −0.5 V. This behavior may reflect the oxidation of the mercury electrode in the presence of dithiocarbamate ligands originating from the reduced manganese species. Although such complex behavior is capable of furnishing some very intricate electrochemistry, this aspect is not the concern of the present work. Accordingly, the redox properties of these complexes have only been characterized at a platinum electrode where they exhibit well-defined electrochemical behavior yielding parameters of thermodynamic significance.

Table I. Analytical Data for Dithiocarbamato Complexes of Manganese (Found in Parentheses)

R	R′	C	H	N
		$Mn(RR'\text{-}dtc)_3$		
Me	Me	26.0 (26.1)	4.4 (4.5)	10.1 (10.2)
Et	Et	36.1 (36.0)	6.1 (5.9)	8.4 (8.1)
i-Pr	*i*-Pr	43.2 (43.1)	7.3 (7.4)	7.2 (7.4)
i-Bu	*i*-Bu	48.5 (48.2)	8.2 (7.6)	6.3 (6.1)
c-Hx	*c*-Hx	56.8 (56.8)	8.1 (8.1)	5.1 (4.9)
Benzyl	Benzyl	62.0 (62.3)	4.9 (4.6)	4.8 (4.8)
Pyrr		36.5 (36.6)	4.9 (5.1)	8.5 (8.5)
Pip		40.4 (40.8)	5.7 (5.7)	7.9 (7.6)
$2,6\text{-}Me_2Pip$		46.5 (46.5)	6.8 (6.5)	6.8 (6.7)
2MePip		43.7 (43.4)	6.3 (6.1)	7.3 (7.1)
4MePip		43.7 (44.7)	6.3 (6.4)	7.3 (6.8)
Morpholyl[a]		30.7 (30.1)	4.2 (4.1)	6.7 (6.6)
Ph	Ph	59.6 (58.2)	3.8 (3.6)	5.3 (5.2)
Ph	Me	47.9 (47.6)	4.0 (4.2)	7.0 (7.0)
Ph	Et	50.4 (50.0)	4.7 (4.5)	6.5 (6.3)
		$[Mn(RR'\text{-}dtc)_3][BF_4]$		
c-Hx	*c*-Hx	51.4 (51.5)	7.3 (7.3)	4.6 (4.6)
i-Pr	*i*-Pr[b]	40.6 (40.1)	6.4 (6.3)	5.9 (5.9)
Pyrr[c]		31.0 (31.1)	4.2 (4.6)	7.2 (6.9)
		$Mn(RR'\text{-}dtc)_2$		
Pyrr[d]		34.6 (34.8)	4.6 (5.0)	8.1 (8.1)

[a] $^1/_2CHCl_3$. [b] $^1/_2C_6H_6$, Mn 7.7 (7.5). [c] Mn 9.5 (9.7); B 1.9 (1.8); F 13.1 (12.8); S 33.1 (33.0). [d] Mn 15.8 (15.7); S, 36.9 (36.9).

A. **Manganese(IV) Complexes.** All the manganese(III) compounds display a relatively facile oxidation step with $E_{1/2}$ values spanning the potential range +0.25 to +0.53 V relative to Ag|AgCl (Table II). As all the evidence suggests that the oxidation processes are the same for the 16 dithiocarbamates examined, only one representative example shall be discussed in detail, *viz.*, tris(pyrrolidyldithiocarbamato)manganese(III).



II

The oxidation process for this compound at a platinum electrode was found to have a half-wave potential ($E_{1/2}$) of +0.487 V, obtained from normal pulse voltammetry, and an ac peak potential (E_p) of +0.484 V. The experimentally determined ac wave shape closely fits the theoretical shape for a one-electron polarographic oxidation,[24] *cf.* $\Delta E_p/2$ calcd for $n = 1$, 90 mV (found, 95 mV). The plot of $\log((i_l - i)/i)$ *vs.* E obtained from the pulse voltammogram yields a straight line with zero intercept at +0.482 V and a slope of 57 mV. The cyclic voltammetry parameters were derived from potential scan rates of 20 to 200 mV/sec. All voltammograms were centered at 0.487 V; the ratio of currents for the cathodic and anodic sweep, *i.e.*, $i_p{}^f/i_p{}^b$, was constant at 1.0 indicating

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Table II. Parameters for Oxidation Process of Mn(RR′-dtc)$_3$ Complexes

Compd		Normal pulse voltammetry			Ac voltammetry			Cyclic voltammetry		
R	R′	$E_{1/2}$, V	$E_{3/4} - E_{1/4}$, mV	i_l/C, mA M^{-1}	E_p, V	$\Delta E_{1/2}$, mV	i_p/C, mA M^{-1}	i_p^f/i_p^b [a]	ΔE_p,[a] mV	$i_p^f/Cv_{1/2}$ (av), mA sec$^{1/2}$ M^{-1} mV$^{-1/2}$
Me	Me	0.425	54	164	0.424	94	42	0.93	64	5.1
Et	Et	0.409	59	170	0.413	94	42	1.03	59	5.1
i-Pr	*i*-Pr	0.288	55	150	0.289	98	32	1.03	69	4.9
n-Bu	*n*-Bu	0.429	56	152	0.429	103	23	1.02	75	5.0
i-Bu	*i*-Bu	0.366	59	142	0.367	106	20	0.99	80	5.0
c-Hx	*c*-Hx	0.251	53	132	0.255	100	30	1.02	67	5.2
Benzyl	Benzyl	0.530	56	135	0.530	100	30	1.02	65	4.9
Pyrr		0.487	53	169	0.484	95	46	1.00	64	5.8
Pip		0.395	55	125	0.394	97	34	1.02	65	4.3
2-MePip		0.367	50	127	0.364	95	32	1.02	66	5.1
4-MePip		0.395	56	145	0.397	100	22	1.01	65	4.4
2,6-diMePip		0.350	60	*b*	0.351	100	*b*	1.03	65	*b*
Morpholyl		0.487	56	159	0.492	95	39	0.96	67	5.6
Ph	Ph		*b*		0.495	130	*b*		*b*	
Ph	Me	0.461	56	150	0.461	97	34	1.02	70	5.2
Ph	Et	0.457	55	138	0.457	97	33	0.97	67	4.7

[a] Scan rate 200 mV/sec. [b] Too insoluble for reliable data.

Table III. Electronic Spectra (Data Obtained in CH_2Cl_2; λ in nm; ε × 1000 mol^{-1} cm^2)

	λ (log ε)	λ	λ (log ε)
Mn(Pyrr(dtc))$_3$	500 (3.50)		355 (3.97)
[Mn(Pyrr(dtc))$_3$]BF$_4$	485 (4.07)	425 (sh)	407 (4.12)
[Mn(Pyrr(dtc))$_3$]ClO$_4$	485 (4.07)	428 (sh)	407 (4.12)
[Mn(*i*-Pr$_2$dtc)$_3$]BF$_4$	479 (4.03)	422 (sh)	409 (4.06)
[Mn(*c*-Hx$_2$dtc)$_3$]BF$_4$	480 (4.03)	424 (sh)	411 (4.09)

the oxidized product is reasonably stable in solution. ΔE_p values of 64 mV at scan rates up to 200 mV/sec suggest a relatively fast electron transfer step.

A coulometric value for the number of electrons transferred per molecule (*n*) of 0.9, (CH_2Cl_2, *vide infra*) taken together with the evidence of reversibility presented above, confirms that the electrode reaction involves a simple single-electron transfer.

$$\mathrm{Mn(Pyrr(dtc))_3} \rightleftharpoons [\mathrm{Mn(Pyrr(dtc))_3}]^+ + e^- \qquad (1)$$

It was observed that the Mn(R_2dtc)$_3$ complexes are relatively unstable in solution and even light sensitive, a fact which inevitably detracts from the accuracy of data which incorporate limiting currents. Nevertheless, taken in conjuction with the coulometric *n* value for the oxidation of Mn(Pyrr(dtc))$_3$ the values of i_l (concentration)$^{-1}$ definitely establish that the first oxidation process of all the manganese(III) dithiocarbamates examined involves a one-electron transfer step.

In order to compare the products of chemical oxidation with those resulting from the electrochemical one-electron oxidation we have synthesized and characterized representative examples of [Mn(R_2dtc)$_3$]$^+$ complexes. Two recent publications[18,19] suggest [Mn(Et_2dtc)$_3$]$^+$ can be isolated with BF_4^- and ClO_4^- as counterions, although no analytical or physicochemical data have been published for these compounds.

An adaption of the method originated by Pasek and Straub[18] for the oxidation of Fe(R_2dtc)$_3$, *viz.*, oxidation of Mn(R_2dtc)$_3$ in benzene in the presence of $Et_2O \cdot BF_3$, yields the BF_4^- salts of [Mn(R_2dtc)$_3$]$^+$.

Alternatively, oxidation of Mn(R_2dtc)$_3$ in the presence of manganese(II) perchlorate affords [Mn(R_2dtc)$_3$]ClO$_4$. These oxidized compounds appear to be stable, and for those not containing the explosive ClO_4^- entity, the analytical data agree well with expected values (Table I).

Further physicochemical data substantiate the formulation of the complexes as formally Mn(IV) salts. Conductance measurements in nitromethane solution at 0.903 × 10^{-3} *M* confirm that [Mn(Pyrr(dtc))$_3$]BF$_4$ is 1:1 electrolyte with a molar conductance of 84.2 ohm^{-1}cm^2 mol^{-1} (*cf.* [*n*-Bu$_4$N]I; 84 ohm^{-1}cm^{2}mol^{-1}). The infrared spectrum shows the characteristic bands of the dithiocarbamate entity and bands typical[25] of an ionic BF_4^- species at approximately 1050 (br), 515, and 522 cm^{-1}. The room temperature magnetic moment of 3.8 BM (Gouy method) is consistent with a 3d^3 ion, *i.e.*, Mn(IV). The electronic spectra for all the Mn(IV) compounds contain two strong charge transfer bands at approximately 480 and 410 nm (Table III). As expected, the spectra of the BF_4^- and ClO_4^- salts of [Mn(Pyrr(dtc))$_3$]$^+$ are identical. The presence of the perchlorate ion is confirmed by characteristic infrared absorption[26] at approximately 1090 cm^{-1} (Nujol mull).

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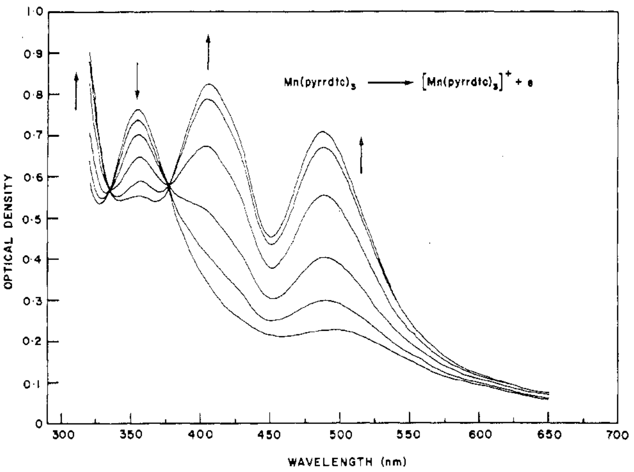

Figure 1. Oxidative electrolysis of $Mn(Pyrr(dtc))_3$ in CH_2Cl_2–0.1 *M* $[n\text{-}Bu_4N]BF_4$ followed spectrophotometrically. Arrows indicate the progress of the electrolysis with the initial and final spectra corresponding to $Mn(Pyrr(dtc))_3$ and $[Mn(Pyrr(dtc))_3]^+$, respectively. *Cf.* Table III for spectral data of chemically prepared $[Mn(Pyrr(dtc))_3]^+$ salts.

The X-ray crystal structure of $[Mn(Pip(dtc))_3]ClO_4$ confirms the above formulation with the manganese atom being surrounded by three dithiocarbamate ligands.[27]

Unfortunately $[Mn(Pyrr(dtc))_3]BF_4$ is not sufficiently soluble or stable in acetone to permit its spectral characterization when generated in an electrochemical experiment. However, in dichloromethane this decomposition is sufficiently arrested to enable reliable and reproducible data to be obtained. Accordingly, the electrochemical data for these species have been reexamined voltammetrically in dichloromethane with 0.1 *M* $[n\text{-}Bu_4N]BF_4$ as supporting electrolyte, against the Ag|AgCl, 0.1 *M* LiCl reference electrode in acetone, isolated *via* a buffer bridge of dichloromethane–$[n\text{-}Bu_4N]BF_4$.

As Table IV shows, the voltammetric data for $Mn(Pyrr(dtc))_3$ are almost identical in the two solvents and the electrochemical reaction appears to be a simple electron transfer, identical with that postulated for acetone solutions (eq 1).

Exhaustive oxidative electrolysis of $Mn(Pyrr(dtc))_3$ at a platinum gauze anode in dichloromethane solution yielded a coulometric *n* value of 0.9 which further corroborates the process defined by eq 1. The course of the electrolysis has been followed by monitoring the changes in the electronic spectrum of the solution as electrolysis proceeds. Sampling of the solution throughout the electrolytic oxidation of $Mn(Pyrr(dtc))_3$ affords the spectra illustrated in Figure 1 with the first and final spectra being identical with the spectra of analytically pure $Mn(Pyrr(dtc))_3$ and $[Mn(Pyrr(dtc))_3]BF_4$.

$[Mn(Pyrr(dtc))_3]BF_4$ undergoes two one-electron reduction steps (Table IV). The coincidence of the first reduction potential of this compound with the oxidation potential of $Mn(Pyrr(dtc))_3$ confirms that the two compounds are interrelated as described in eq 2 and provides extra evidence

$$[Mn(Pyrr(dtc))_3]^+ + e^- \rightleftharpoons Mn(Pyrr(dtc))_3 \qquad (2)$$

that the redox potentials have thermodynamic significance. Exhaustive electrolysis of the Mn(IV) complex, commencing with the BF_4^- salt, yields a coulometric *n* value of 1.1 and a final electronic spectrum compatible with that of $Mn(Pyrr(dtc))_3$.

It has been suggested that $Mn(R_2dtc)_4$ is formed from solutions of $Mn(R_2dtc)_3$.[17] One possible check on the existence of a tetrakis compound is to react a dithiocarbamate $[R_2dtc]^-$

Table IV. Voltammetric Data in Acetone and CH_2Cl_2[a]

		Normal pulse voltammetry			Ac voltammetry			Cyclic voltammetry		
Complex	Solvent	$E_{1/2}$, V	$E_{3/4} - E_{1/4}$, mV	i_l/C, mA M^{-1}	E_p, V	$\Delta E_{1/2}$, mV	i_p/C, mA M^{-1}	i_p^f/i_p^b	ΔE_p, mV	$i_p^f/Cv^{1/2}$ (av), mA sec$^{1/2}$ M^{-1} mV$^{-1/2}$
			Mn(III)/Mn(IV) Couple							
$Mn(Pyrr(dtc))_3$	Acetone– 0.1 *M* $[Et_4N]ClO_4$	0.487	53	169	0.484	95	46	1.00	64	5.8
$Mn(Pyrr(dtc))_3$	Dichloromethane– 0.1 *M* $[n\text{-}Bu_4N]BF_4$	0.510	67	131	0.510	130	21	1.02	75	3.1
$[Mn(Pyrr(dtc))_3]BF_4$	Dichloromethane– 0.1 *M* $[n\text{-}Bu_4N]BF_4$	0.520	67	132	0.524	106	20	1.01	71	3.0
			Mn(III)/Mn(II) Couple							
$Mn(Pyrr(dtc))_3$	Acetone– 0.1 *M* $[Et_4N]ClO_4$	0.017	54	135	0.021	95	48	1.02	64	5.7
$Mn(Pyrr(dtc))_3$	Dichloromethane– 0.1 *M* $[n\text{-}Bu_4N]BF_4$	0.09_2	70	128	0.09_2	115	22	1.00	75	3.1
$[Mn(Pyrr(dtc))_3]BF_4$	Dichloromethane– 0.1 *M* $[n\text{-}Bu_4N]BF_4$	0.10_0	65	136	0.10_5	106	23	1.00	70	2.8

[a] Reference electrode, Ag|AgCl|0.1 *M* LiCl in acetone. Electrode buffered from CH_2Cl_2 solution *via* CH_2Cl_2|0.1 *M* $[n\text{-}Bu_4N]BF_4$ and acetone|0.1 *M* $[Et_4N]ClO_4$ bridges.

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(27) K. L. Brown, unpublished results.

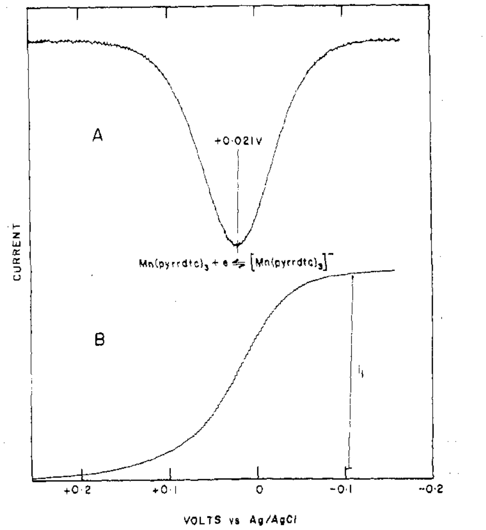

Figure 2. Reduction of $Mn(Pyrr(dtc))_3$ (10^{-3} M) in acetone-0.1 M $[Et_4N]ClO_4$, illustrating polarograms typical of those obtained for the complexes examined in this work: (A) ac polarogram, 80 Hz; (B) normal pulse polarogram, 2 pulses sec^{-1}.

with $[Mn(Pyrr(dtc))_3]^+$ in the hope of obtaining $[Mn(Pyrr(dtc))_3(R_2dtc)]$. In fact, when $[Et_2dtc]^-$ and $[Mn(Pyrr(dtc))_3]BF_4$ are mixed in acetone and the reaction followed electrochemically insoluble $[Mn(Pyrr(dtc))_3]^+$ readily dissolves and forms $Mn(Pyrr(dtc))_3$ and presumably tetraethylthiuram disulfide, (Et_4tds).

$$[Mn(Pyrr(dtc))_3]^+ + [Et_2dtc]^- \rightarrow Mn(Pyrr(dtc))_3 + {}^1/_2Et_4tds \quad (3)$$

This reaction is not unexpected under the experimental conditions employed and the result does not exclude the possibility that $Mn(R_2dtc)_4$ may be isolated *via* an alternative synthetic procedure.

B. Manganese(II) Complexes. Manganese(II) complexes with the stoichiometry $[Mn(R_2dtc)_3]^-$ have not been isolated although unsuccessful attempts to prepare them have been reported.[28] The following work discusses the electrochemical characterization in solution of this species. A detailed discussion will be restricted to the behavior of the representative pyrrolidyldithiocarbamato derivative $[Mn(Pyrr(dtc))_3]^-$, although an examination of Table V reveals that the other substituted dithiocarbamato complexes exhibit very similar behavior.

Reduction of $Mn(Pyrr(dtc))_3$ at a platinum electrode is very facile at $E_{1/2}$ = +0.017 V and E_p = +0.021 V. Typical voltammograms are illustrated in Figure 2. Cyclic voltammetry data (Table V) are in accord with the process being a one-electron redox process with the reduced species having reasonable stability in acetone solution

$$Mn(Pyrr(dtc))_3 + e^- \rightleftharpoons [Mn(Pyrr(dtc))_3]^- \quad (4)$$

The controlled potential electrolytic reduction in acetone affords an n value of 1.0 and a virtually colorless solution of $[Mn(Pyrr(dtc))_3]^-$. The two, single-electron oxidations of this species (Figure 3) are in accord with eq 5.

$$[Mn(Pyrr(dtc))_3]^- \xrightleftharpoons{-e^-} Mn(Pyrr(dtc))_3 \xrightleftharpoons{-e^-} [Mn(Pyrr(dtc))_3]^+ \quad (5)$$

As published work suggests $[Mn(R_2dtc)_3]^-$ cannot be isolated, we have attempted to confirm the electrochemical indications for the existence of this species in solution by

Table V. Parameters for Reduction Process of $Mn(RR'\text{-}dtc)_3$ Complexes

Compd		Normal pulse voltammetry			Ac voltammetry			Cyclic voltammetry		
R	R'	$E_{1/2}$, V	$E_{3/4}-E_{1/4}$, mV	i_l/C, mA M^{-1}	E_p, V	$\Delta E_{1/2}$, mV	i_p/C, mA M^{-1}	i_p^f/i_p^b [a]	ΔE_p,[a] mV	$i_p^f/Cv_{1/2}$ (av), mA $sec^{1/2}$ M^{-1} $mV^{-1/2}$
Me	Me	−0.035	55	159	−0.034	95	46	1.01	62	5.5
Et	Et	−0.074	59	163	−0.070	98	40	1.03	61	5.4
i-Pr	*i*-Pr	−0.186	61	148	−0.180	104	27	1.03	78	4.9
n-Bu	*n*-Bu	−0.056	62	160	−0.051	113	18	1.01	75	5.2
i-Bu	*i*-Bu	−0.130	61	156	−0.125	109	22	1.02	88	5.2
c-Hx	*c*-Hx	−0.230	84	154	−0.226	97	20	0.98	62	4.5
Benzyl	Benzyl	+0.074	54	135	+0.077	95	33	1.01	62	4.8
Pyrr		+0.017	55	154	+0.021	95	48	1.02	64	5.7
Pip		−0.062	56	125	−0.058	98	51	1.03	68	4.3
2-MePip		−0.098	57	148	−0.093	91	36	1.01	63	4.8
4-MePip		−0.056	63	132	−0.056	98	29	1.02	61	4.8
2,6-diMePip		−0.114	64	*b*	−0.110	90	*b*	1.03	62	*b*
Morpholyl		+0.055	60	150	+0.055	93	42	0.98	61	4.8
Ph	Ph		*b*		+0.020	135	*b*		*b*	
Ph	Me	−0.007	58	153	−0.004	95	36	1.01	64	5.2
Ph	Et	−0.022	56	144	−0.017	97	36	1.00	65	4.7

[a] Scan rate 200 mV/sec. [b] Too insoluble for reliable data.

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(28) D. G. Holah and C. N. Murphy, *Can. J. Chem.*, 49, 2726 (1971).

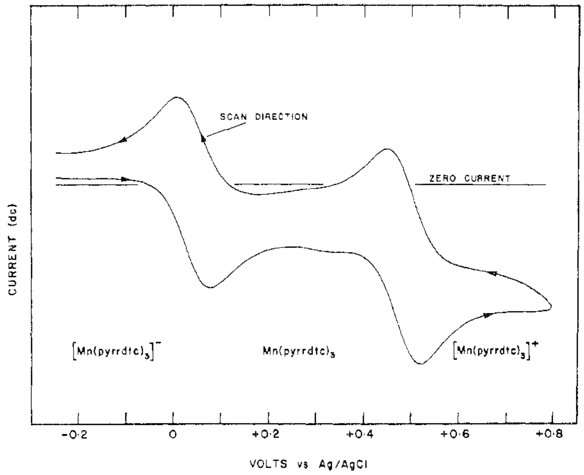

Figure 3. Cyclic voltammogram (acetone–0.1 *M* [Et_4N]ClO_4) of [Mn(Pyrr(dtc))$_3$]$^-$ showing the two single electron oxidation steps through Mn(Pyrr(dtc))$_3$ to [Mn(Pyrr(dtc))$_3$]$^+$. The [Mn(Pyrr(dtc))$_3$]$^-$ solution was electrolytically generated by reduction of Mn(Pyrr(dtc))$_3$.

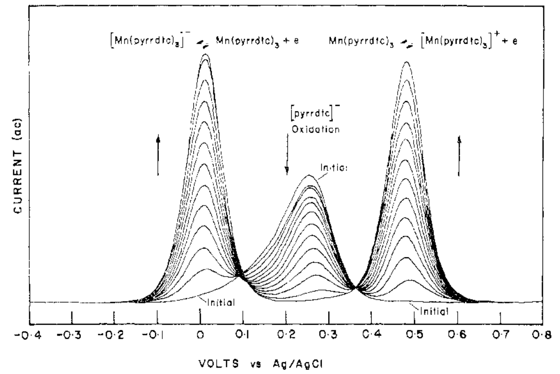

Figure 4. Ac polarographic scans of the titration of Mn^{2+} into [Pyrr(dtc)]$^-$ solution up to the 1:3 end point [Mn(Pyrr(dtc))$_3$]$^-$ illustrating the disappearance of [Pyrr(dtc)]$^-$ and finally the complete ac polarogram of [Mn(Pyrr(dtc))$_3$]$^-$.

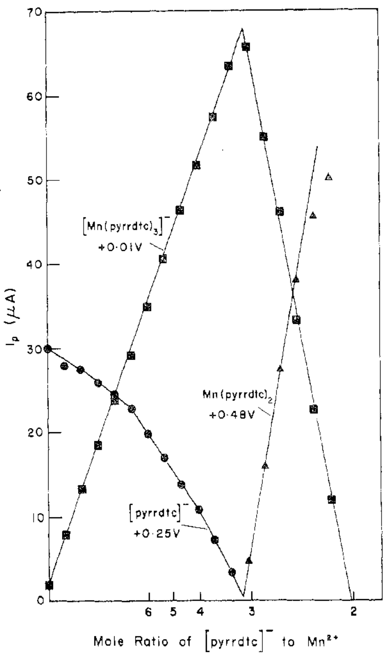

Figure 5. Ac peak currents for the titration of Mn^{2+} (1.05 × 10^{-2} *M*) into [Pyrr(dtc)]$^-$ (3.83 × 10^{-3} *M*) both in acetone–0.1 *M* [Et_4N]ClO_4. All currents have been corrected for dilution effects. Mn(Pyrr(dtc))$_2$ points have been obtained by subtracting the current contribution of the +0.48-V peak due to residual [Mn(Pyrr(dtc))$_3$]$^-$. This contribution has been obtained from the interrelation of the +0.01- and +0.48-V peaks for [Mn(Pyrr(dtc))$_3$]$^-$.

electrochemically monitoring both the titrations of Mn^{2+} into [Pyrr(dtc)]$^-$ and of [Pyrr(dtc)]$^-$ into Mn^{2+} solutions. From the nature of the redox processes examined, [Mn(Pyrr(dtc))$_3$]$^-$ when formed in these solutions would be expected to show oxidation waves at +0.021 and +0.484 V.

The titrations were performed under strictly anaerobic conditions using solutions of [$Mn(H_2O)_6$][ClO_4]$_2$ and Na[Pyrr(dtc)]·$2H_2O$ in acetone-[Et_4N]ClO_4. All titrations were monitored by ac voltammetry at 80 Hz and at the end points the solutions were also subjected to cyclic voltammetry, scanning the range −0.4 to +0.8 V.

(i) Titration. Mn^{2+} into [Pyrr(dtc)]$^-$ Solution. The initial ac scan shows a peak at +0.25 V due to the irreversible oxidation of [Pyrr(dtc)]$^-$, presumably to thiuram disulfide. Mn^{2+} is not electroactive in this potential region −0.4 to +0.8 V. Addition of Mn^{2+} results in the progressive disappearance of this peak and its replacement by the expected two peaks (Figure 4) (reversible consecutive oxidations established by cyclic voltammetry) at E_p = +0.01 and +0.48 V (*cf.* eq 5). The observed ratio of Mn^{2+}:[Pyrr(dtc)]$^-$ of 1:3 at the end point confirms that the complex formed is [Mn(Pyrr(dtc))$_3$]$^-$ (Figure 5). Continued additions of Mn^{2+} beyond the [Mn(Pyrr(dtc))$_3$]$^-$ end point sees the peak at +0.01 V decrease, but the peak at +0.48 V remains relatively constant. The +0.01-V peak disappears at the 1:2 end point which corresponds to the formation of Mn(Pyrr(dtc))$_2$. This suggests that the peak at +0.48 V is due to the oxidation of Mn(Pyrr(dtc))$_2$

$$\text{Mn(Pyrr(dtc))}_2 \rightleftharpoons [\text{Mn(Pyrr(dtc))}_2]^+ + e^- \rightarrow \text{coupled chemical reaction (see later)} \quad (6)$$

Cyclic voltammetry confirms the process is an oxidation.

Just prior to the 1:2 end point, and without further titration, precipitation of a very pale product causes the +0.48-V peak to rapidly fall to <20% of its value near the 1:2 end point over 5 min reflecting the relatively low solubility of the presumably polymeric complex, Mn(Pyrr(dtc))$_2$. No precipitation of Mn(Pyrr(dtc))$_2$ occurs before the 1:3 end point. The titration data are summarized by the following processes

$$Mn^{2+} + 3[\text{Pyrr(dtc)}]^- \rightarrow [\text{Mn(Pyrr(dtc))}_3]^- \quad (7)$$

$$2[\text{Mn(Pyrr(dtc))}_3]^- + Mn^{2+} \rightarrow 3\text{Mn(Pyrr(dtc))}_2 \quad (8)$$

There is no evidence for further degradation of Mn(Pyrr(dtc))$_2$ to a 1:1 species although this could be masked by solubility and kinetic considerations.

(ii) Titration. [Pyrr(dtc)]$^-$ into a Mn^{2+} Solution (Figure 6). The conclusion, necessary for a rational interpretation of the preceding titration results, that Mn(Pyrr(dtc))$_2$ exhibits an oxidation wave at the same potential as the oxidation of Mn(Pyrr(dtc))$_3$ (eq 1), is substantiated by titration in the opposite sense, *i.e.*, [Pyrr(dtc)]$^-$ into a Mn^{2+} solution. This titration effectively confirms the earlier results with the initial growth of the +0.48-V peak (oxidation) maximizing at the 1:2 end point followed by the growth and leveling of the +0.01-V peak at the 1:3 end point. At this point continued titration only causes the growth of the peak due to the [Pyrr(dtc)]$^-$ oxidation process. The stepwise titration is summarized by the following equations

$$Mn^{2+} + 2[\text{Pyrr(dtc)}]^- \rightarrow \text{Mn(Pyrr(dtc))}_2 \quad (9)$$

$$\text{Mn(Pyrr(dtc))}_2 + [\text{Pyrr(dtc)}]^- \rightarrow [\text{Mn(Pyrr(dtc))}_3]^- \quad (10)$$

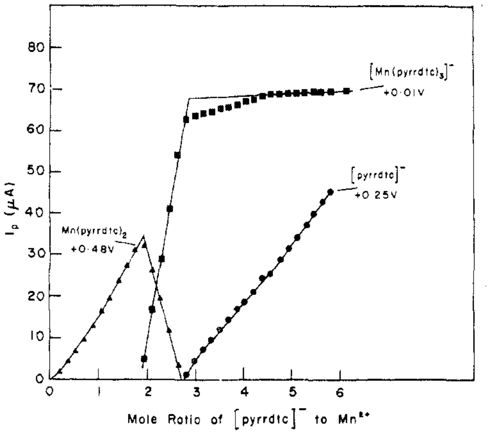

Figure 6. Ac peak currents for the titration of [Pyrr(dtc)]$^-$ (2.49×10^{-2} *M*) into Mn^{2+} (1.45×10^{-3} *M*) both in acetone–0.1 *M* [Et_4N]-ClO_4. As in Figure 5 the peak at +0.48 V has been corrected for the contribution of [Mn(Pyrr(dtc))$_3$]$^-$. All peaks are corrected for dilution effects.

It is worth noting that the nonlinearity of the titration curves is due to the commencement of precipitation of Mn(Pyrr(dtc))$_2$ early in the titration and its subsequent dissolution as [Mn(Pyrr(dtc))$_3$]$^-$ on addition of excess ligand.

Although Mn(Pyrr(dtc))$_2$ is not a tris-chelated complex of manganese, the assignment of the single oxidation wave at +0.48 V to this species requires positive verification. Pure Mn(Pyrr(dtc))$_2$ was prepared from Mn^{2+} and [Pyrr(dtc)]$^-$ in acetone under strictly anaerobic conditions as pale yellow crystals (Table I). The complex was pelletized in an oxygen-free atmosphere and quickly added to a deoxygenated solution of acetone-[Et_4N]ClO_4 in the polarographic apparatus. The earlier noted relative insolubility of the complex was confirmed. The small amount which dissolved yielded an ac peak at +0.48 V confirming the origin of the peak in the titration work. The presence of a small quantity of the much more soluble [Mn(Pyrr(dtc))$_3$]$^-$ species is readily quenched by addition of a very small quantity of Mn^{2+}. Cyclic voltammetry indicates the oxidation of Mn(Pyrr(dtc))$_2$ is not reversible. Addition of [Pyrr(dtc)]$^-$ to the solution of Mn(Pyrr(dtc))$_2$ generates (after eq 10) a voltammogram identical with that already associated with [Mn(Pyrr(dtc))$_3$]$^-$.

Although we have not attempted to isolate [Mn(dtc)$_3$]$^-$ species, the coulometric and both titration procedures confirm its existence and it has been electrochemically characterized. The failure of Holah and Murphy[28] to isolate the complex may be due to the relatively low solubility of Mn(R_2dtc)$_2$. The present evidence suggests there is little dissociation of [Mn(Pyrr(dtc))$_3$]$^-$ in acetone although it readily reacts with excess Mn^{2+} to yield Mn(Pyrr(dtc))$_2$.

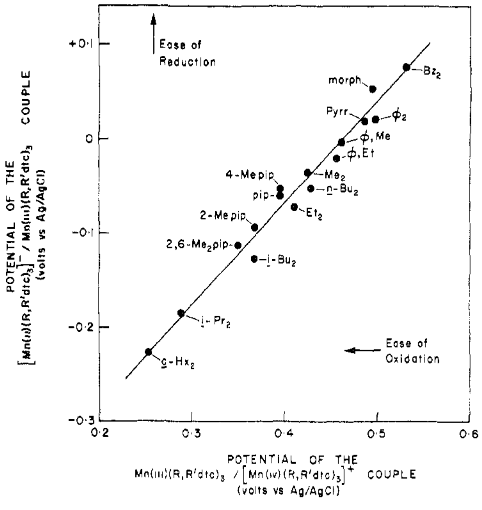

Figure 7. Relationship between the oxidation and reduction potentials of Mn(RR′dtc)$_3$ compounds. Gradient of full line is 1·1.

C. Substituent Effects. Figure 7 illustrates the effect of substituents at the nitrogen atom of the ligand on both the oxidation and reduction potentials of manganese(III) complexes. The straight line plot (slope: ΔE(red)/ΔE(ox) = 1.1) indicates the remarkable consistency of this effect on both redox processes. Although the relative importance of steric factors, suspected to be operative at the nitrogen atom,[29] is unknown, there does appear to be a definite correlation of redox potentials with substituent inductive effects. An increase in chain length and branching affords easier oxidation and more difficult reduction while, as expected, the introduction of phenyl groups produces the reverse trend. Comparison of the present data with those of the iron(III) dithiocarbamates[9] illustrates the parallelism of substituent effects between different metal ions.

Acknowledgment. The authors thank K. L. Brown for communicating his results on the structure of [Mn^{IV}(Pip(dtc))$_3$]-ClO_4 prior to publication.

Registry No. Mn(Me_2dtc)$_3$, 33291-09-7; Mn(Et_2dtc)$_3$, 15740-71-3; Mn(*i*-Pr_2dtc)$_3$, 25753-58-6; Mn(*i*-Bu_2dtc)$_3$, 25753-60-0; Mn(*c*-Hx_2dtc)$_3$, 27796-39-0; Mn($Benzyl_2$dtc)$_3$, 33291-11-1; Mn(Pyrr(dtc))$_3$, 51540-47-7; Mn(Pip(dtc))$_3$, 15169-83-2; Mn(2,6-Me_2Pip(dtc))$_3$, 51540-48-8; Mn(2MePip(dtc))$_3$, 51540-49-9; Mn(4MePip(dtc))$_3$, 51540-50-2; Mn(Morpholyl(dtc))$_3$, 27796-38-9; Mn(Ph_2dtc)$_3$, 51540-51-3; Mn(PhMe(dtc))$_3$, 36869-11-1; Mn(PhEt(dtc))$_3$, 33291-12-2; [Mn(*c*-Hx_2dtc)$_3$][BF_4], 51540-52-4; [Mn(*i*-Pr_2dtc)$_3$][BF_4], 51607-36-4; [Mn(Pyrr(dtc))$_3$][BF_4], 51540-53-5; Mn(Pyrr(dtc))$_2$, 51540-55-7; Mn(Pyrr(dtc))$_3$][ClO_4], 51540-54-6.

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(29) A. H. Ewald, R. L. Martin, E. Sinn, and A. H. White, *Inorg. Chem.*, 8, 1837 (1969).