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# Dithiocarbamates of Nickel in the Formal Oxidation States I–IV. Electrochemical Study

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The electron-transfer properties of 16 nickel(II) dithiocarbamate complexes have been studied in acetone at a platinum electrode. Their oxidation (+0.8 to +1.0 V) is difficult and irreversible with the overall process conforming to the stoichiometry $3Ni(R_2dtc)_2 \rightarrow 2[Ni(R_2dtc)_3]^+ + Ni^{2+} + 4e^-$. The nickel(IV) cation exhibits two successive, relatively facile, reversible reduction steps corresponding to the one-electron-transfer series $[Ni(R_2dtc)_3]^+ \overset{e^-}{\rightleftharpoons} Ni(R_2dtc)_3 \overset{e^-}{\rightleftharpoons} [Ni(R_2dtc)_3]^-$. Both reduction products are unstable according to the equilibria $Ni(R_2dtc)_3 \rightleftharpoons Ni(R_2dtc)_2 + {}^1/_2(R_2tds)$; $[Ni(R_2dtc)_3]^- \rightleftharpoons Ni(R_2dtc)_2 + R_2dtc^-$. Although the formally nickel(III) species could not be prepared and isolated chemically, they are readily formed from $Ni(R_2dtc)_2$ and the electrochemically generated $R_2NCSS\cdot$ radical. The $Ni(R_2dtc)_2$ complexes undergo a one-electron reduction at quite negative potentials (−1.2 to −1.5 V): $Ni(R_2dtc)_2 + e^- \rightleftharpoons [Ni(R_2dtc)_2]^-$. Substituent effects on the redox potentials of nickel dithiocarbamates parallel closely those measured for the oxidation of the free ligand: $[R_2dtc]^- \rightarrow R_2NCSS\cdot + e^-$. Mixed-ligand species have been characterized by voltammetry and unusual reactions of some of the complexes are reported.

## Introduction

Electrochemical methods are proving to be invaluable for establishing the electron-transfer relationships between members of the 1,1-dithio chelates of first-row transition metals.[2] In particular, it has been established that both manganese[3] and iron[4] with the dithiocarbamate ligand will support the three-membered electron-transfer series

$$[M(R_2dtc)_3]^+ \overset{e^-}{\rightleftharpoons} M(R_2dtc)_3 \overset{e^-}{\rightleftharpoons} [M(R_2dtc)_3]^- \qquad (1)$$

with the metal ions in formal oxidation states of IV–II. The chemical and electrochemical redox relationships have been analyzed for a variety of substituents (R) using electrochemical techniques such as normal pulse, ac and cyclic voltammetry, coulometry, and spectroelectrolysis, the potentials being found to be dependent upon the electronic properties of R.

The corresponding dithiocarbamate complexes of nickel introduce several new features. The common oxidation state is +2 rather than +3 and $Ni(R_2dtc)_2$ compounds are monomeric, are square planar, and are of a low-spin $3d^8$ electron configuration. Unlike manganese and iron, the corresponding tris-chelated species $Ni(R_2dtc)_3$ and $[Ni(R_2dtc)_3]^-$ have not been isolated. However, oxidation of $Ni(R_2dtc)_2$ with a variety of reagents[5-11] affords the $[Ni(R_2dtc)_3]^+$ cation which has been shown to possess a distorted octahedral geometry in the case of the di-*n*-butyl derivative.[12,13] The isolation of mixed-halo complexes of Ni(III) and Ni(IV)—$Ni((n\text{-}Bu)_2dtc)_2I$ and $Ni(Et_2dtc)_2Br_2$—has also been described,[6,14] although their characterization is incomplete. Oxidation of $Ni(R_2dtc)_2$ with thiuram disulfide ($R_2tds$) yields ESR spectra consistent with the formation of a low-spin ($S = {}^1/_2$) Ni(III) species.[15]

Spectrophotometric studies have revealed that the dark brown color of the $[Ni((n\text{-}Bu)_2dtc)_3]^+$ cation is photochemically and thermally bleached in $CH_3CN$ and related solvents in a reversible manner.[13] Treatment of $[Ni(R_2dtc)_3]^+$ solutions with isocyanides and phosphines leads to the isolation[16] of a variety of mixed-ligand complexes of nickel(II), $[Ni(R_2dtc)(CNR)_2]^+$, $[Ni(R_2dtc)(PPh_3)_2]^+$, and $[Ni(R_2dtc)(diphos)]^+$, where diphos is the chelating phosphine $Ph_2PCH_2CH_2PPh_2$.

Electrochemical oxidation of $Ni(R_2dtc)_2$ is difficult and irreversible.[2,8,9,17,18] In the present paper, detailed results are presented[18] which establish that nickel dithiocarbamates display a rich and extensive electrochemical behavior which spans the four formal oxidation states Ni(IV), Ni(III), Ni(II), and Ni(I). The two common stereochemistries displayed by nickel (square planar and octahedral) enable two distinct electron-transfer series to be characterized, viz.

$$NiL_3^+ \leftarrow NiL_2 \overset{e^-}{\rightleftharpoons} NiL_2^- \qquad (2)$$

$$NiL_3^+ \overset{e^-}{\rightleftharpoons} NiL_3 \overset{e^-}{\rightleftharpoons} NiL_3^- \qquad (3)$$

The redox interrelationships and coupled chemical reactions are developed fully below. Some substantiating studies with nickel xanthates and mixed-ligand dithiocarbamates are also described.

## Experimental Section

**Syntheses. General Preparative Method for $Ni(R_2dtc)_2$.** An aqueous solution of the sodium or potassium salt of the appropriate dithiocarbamate, prepared by the usual method (KOH, $CS_2$, $HNR_2$), was added to a vigorously stirred solution of $NiCl_2{\cdot}6H_2O$. The crude green product was filtered, washed with water and ice-cold methanol and

**Table I.** Parameters for Reduction Process of $Ni(RR'dtc)_2$ Complexes

| Compd | | Normal-pulse voltammetry | | | Ac voltammetry | | | Cyclic voltammetry[a] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| R | R' | $E_{1/2}$, V | $E_{3/4} - E_{1/4}$, mV | $i_l$/concn, mA $M^{-1}$ | $E_p$, V | $\Delta E_{1/2}$,[b] mV | $i_p$/concn, mA $M^{-1}$ | $\Delta E_p$, mV | $i_f/i_r$ | $i_f/Cv^{1/2}$,[c] mA sec$^{1/2}$ mV$^{-1}$ |
| Me | Me | $-1.35_3$ | 53 | *d* | $-1.35_3$ | 82 | *d* | 55 | 1.2 | *d* |
| Et | Et | $-1.34_5$ | 62 | 163 | $-1.34_4$ | 97 | 59 | 61 | 1.1 | 6.0 |
| *i*-Pr | *i*-Pr | $-1.48_0$ | 55 | 195 | $-1.47_5$ | 94 | 48 | 62 | 1.0 | 6.3 |
| Me | *n*-Bu | $-1.37_6$ | 53 | 194 | $-1.37_0$ | 103 | 52 | 61 | 1.1 | 6.9 |
| *n*-Bu | *n*-Bu | $-1.39_4$ | 60 | 199 | $-1.38_9$ | 97 | 39 | 72 | 1.0 | 6.8 |
| *i*-Bu | *i*-Bu | $-1.41_0$ | 62 | 199 | $-1.40_5$ | 97 | 36 | 69 | 1.0 | 6.8 |
| c-Hx | c-Hx | | | *d* | $-1.49_0$ | | *d* | | | *d* |
| Bz | Bz | $-1.24_8$ | 56 | 178 | $-1.24_3$ | 86 | 52 | 65 | 1.2 | 8.6 |
| pyr | | $-1.34_0$ | 55 | *d* | $-1.32_5$ | 87 | *d* | 72 | 1.1 | *d* |
| pip | | $-1.37_2$ | 50 | *d* | $-1.37_2$ | 87 | *d* | 63 | 1.1 | *d* |
| 2-Mepip | | $-1.37_5$ | 58 | 211 | $-1.37_3$ | 90 | 56 | 61 | 1.0 | 7.8 |
| 4-Mepip | | $-1.34_5$ | 60 | 186 | $-1.34_3$ | 91 | 53 | 60 | 1.1 | 6.7 |
| 2,6-$Me_2$pip | | $-1.38_4$ | 65 | *d* | $-1.38_6$ | 95 | *d* | 61 | 1.5 | *d* |
| Ph | Ph | $-1.22_5$ | 53 | 165 | $-1.21_9$ | 84 | 34 | | | *e* |
| Ph | Me | $-1.30_0$ | 46 | 164 | $-1.28_1$ | 80 | 37 | | | *e* |
| Ph | Et | $-1.32_2$ | 53 | 164 | $-1.31_3$ | 82 | 37 | | | *e* |

[a] Scan rate 200 mV sec$^{-1}$. [b] Width at half peak height. [c] Average value. [d] Too insoluble for reliable data. [e] Irreversible process.

was dried by suction. Recrystallization from hot $CHCl_3$ by addition of petroleum ether (80–100°C) or EtOH yielded crystals of the required nickel dithiocarbamate. These compounds analyzed satisfactorily (C, H, N) and yielded the expected NMR spectra.

**(a) Tris(*N*,*N*-di-*n*-butyldithiocarbamato)nickel(IV) Tetrafluoroborate, $[Ni(S_2CN(C_4H_9)_2)_3]BF_4$.** $Ni((n\text{-}Bu)_2dtc)_2$ (1.5 g) was dissolved in benzene (30 ml) and stirred by a constant stream of air. Boron trifluoride etherate (2 ml of 40% solution) was added dropwise to this solution over a period of 10 min. The solution was aerated for a further 1 hr after which it was neutralized with anhydrous sodium carbonate. The solid was filtered from the solution containing the crude product which was obtained by addition of ether. Recrystallization from dichloromethane or nitromethane solution by addition of diethyl ether afforded dark brown, well-formed crystals of the desired product. Anal. Calcd for $C_{27}H_{54}BF_4N_3NiS_6$: C, 25.4; H, 7.1; N, 5.5; Ni, 7.7; S, 25.4. Found: C, 25.3; H, 6.9; N, 5.2; Ni, 7.6; S, 25.3.

**(b) Tris(*N*,*N*-diethyldithiocarbamato)nickel(IV) Tetrafluoraborate, $[Ni(S_2CN(C_2H_5)_2)_3]BF_4$.** (i) This compound was prepared by the above method. Anal. Calcd for $C_{15}H_{30}BF_4N_3NiS_6$: C, 30.5; H, 5.1; N, 7.1. Found: C, 30.4; H, 5.5; N, 6.9.

(ii) $Ni(Et_2dtc)_2$ (0.16 g), $Ni(H_2O)_6(BF_4)_2$ (0.15 g), and tetraethylthiuram disulfide (0.25 g) were refluxed in acetone (5 min). The solution was reduced to dryness and the solid dissolved in $CH_2Cl_2$. On the addition of $Et_2O$ and cooling, the complex separated as crystals (0.3 g). Anal. Calcd for $C_{15}H_{30}BF_4N_3NiS_6$: C, 30.5; H, 5.1; N, 7.1. Found: C, 30.6; H, 5.2; N, 6.8.

**Instrumental Work.** Electrochemical measurements were performed in acetone–0.1 *M* $Et_4NClO_4$ using PAR170 three-electrode instrumentation with *iR* compensation. The reference electrode Ag–AgCl–(0.1 *M* LiCl–acetone) was separated from the voltammetric vessel by an acetone–0.1 *M* $Et_4NClO_4$ bridge as described previously.[19] All ac voltammetry data were obtained at a frequency of 80 Hz. Coulometry and spectroelectrochemical studies utilized apparatus of our own design.[20] Electronic spectra were obtained with a Cary 14 instrument and NMR spectra were run on a Minimar 100-MHz spectrometer.

## Results and Discussion

The redox chemistry of the nickel dithiocarbamates is particularly rich in the range of formal oxidation states displayed by nickel, viz., I–IV. As the redox interrelations between these species are quite complex, the paper will deal with the electron-transfer processes that are observed for the stable and isolable complexes $Ni(R_2dtc)_2$ and $[Ni(R_2dtc)_3]^+$ and their interaction with $[R_2dtc]^-$ and $R_2NCSS\cdot$ to form less stable and transient species such as $[Ni(R_2dtc)_3]^-$ and $Ni(R_2dtc)_3$.

At a mercury electrode the redox processes are more complex than at platinum, especially for the higher oxidation state complexes. Similar observations were noted previously for the iron and manganese dithiocarbamate complexes.[3,4] In view of these added complications at mercury, all results reported here refer to a platinum electrode. Qualitative observations (at Pt) suggest the redox behavior in $CH_3CN$ and $CH_2Cl_2$ is similar to that observed in acetone.

**(a) Reduction of $Ni(R_2dtc)_2$.** The nickel(II) complexes undergo a quasireversible one-electron reduction although the potentials are quite negative (−1.24 to −1.49 V), Table I. From the cyclic voltammetric data, increasing the scan rate, 20 → 200 mV sec$^{-1}$, increases the cathodic and anodic peak separation and improves the ratio of the peak currents of the forward ($i_f$) and reverse ($i_r$) scans. Lowering the temperature to −70°C improves the $i_f/i_r$ value to 1.0 but increases the cathodic and anodic peak separation ($\Delta E_p$) to 110 mV at 20 mV sec$^{-1}$ and to 252 mV at 200 mV sec$^{-1}$ for the complex $Ni((n\text{-}Bu)_2dtc)_2$. Hence it may be concluded that the one-electron reduction step

$$Ni(R_2dtc)_2 + e^- \rightleftharpoons [Ni(R_2dtc)_2]^- \tag{4}$$

involves a relatively slow rate of electron transfer ($k_s$) and affords a reduced complex which is only moderately stable in acetone solution. Cyclic voltammograms (100 mV/sec) show virtually no evidence for loss of $[R_2dtc]^-$ from the reduced species of $Ni((n\text{-}Bu)_2dtc)_2$.

The substituent dependence of this formally Ni(I)–Ni(II) redox couple closely parallels that reported previously[3,4] for the Fe(II), Fe(III), Fe(IV), Mn(II), Mn(III), and Mn(IV) couples (see Figure 1). However, this information does not enable a differentiation to be made as to whether the reduction is metal or ligand based. ESR studies are in progress to resolve this question.

**(b) Reduction of $[Ni(R_2dtc)_3]^+$.** These cationic compounds exhibit two relatively facile reduction steps; i.e., both couples are more positive than −0.35 V vs. Ag–AgCl (Table II). The $[Ni((n\text{-}Bu)_2dtc)_3]^+$ derivative has been selected for the most detailed examination because of the available X-ray crystal structure data[13] and good solubility of this species.

The first reduction at +0.35 V is shown by cyclic voltammetry to be quasireversible in all except the most carefully dried and purified solutions where, by cyclic voltammetry, $i_f/i_r$ = 1.1 and $\Delta E_p$ = 60 mV at 200 mV sec$^{-1}$ and, by ac voltammetry (80 Hz), $\Delta E_{p/2}$ = 93 mV. The reduction of $[Ni(Et_2dtc)_3]^+$ provides comparable results. The one-electron-transfer step appears to involve the formally Ni(III) species $Ni((n\text{-}Bu)_2dtc)_3$, viz.

$$[Ni((n\text{-}Bu)_2dtc)_3]^+ + e^- \rightleftharpoons Ni((n\text{-}Bu)_2dtc)_3 \tag{5}$$

Coulometric reduction of the Ni(IV) species at +0.30 V

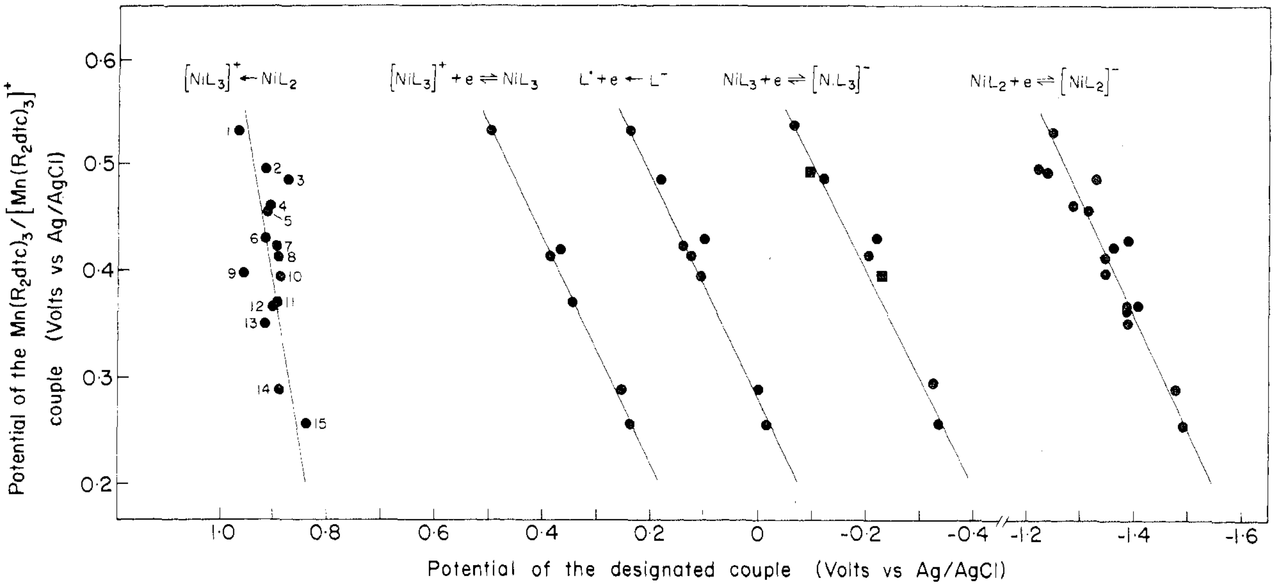

Figure 1. Substituent effect on the designated couples compared with that of the corresponding substituent for the reversible $Mn(R_2dtc)_3$-$[Mn(R_2dtc)_3]^+$ couple. $R_2$: 1, $Bz_2$; 2, $Ph_2$; 3, pyr; 4, Ph, Me; 5, Ph, Et; 6, $(n\text{-}Bu)_2$; 7, $Me_2$; 8, $Et_2$; 9, 4-Mepip; 10, pip; 11, $(i\text{-}Bu)_2$; 12, 2-Mepip; 13, 2,6-$Me_2$pip; 14, $(i\text{-}Pr)_2$; 15, $(c\text{-}Hx)_2$. See tables for origin of data; ■ indicates data obtained from scan direction opposite to that of the remainder of Ni(II)–Ni(III) data.

Table II. Redox Potentials of Selected Couples

| Complex | | $[R_2dtc]^-$ oxidn[b] | Redox potential, V *vs.* Ag–AgCl[a] | | | | |
|---|---|---|---|---|---|---|---|
| | | | $NiL_3 + e^- \rightleftharpoons [NiL_3]^-$ | | $[NiL_3]^+ + e^- \rightleftharpoons NiL_3$ | | |
| R | R′ | | *c* | *d* | *e* | *f* | *g* |
| Me | Me | 0.14 | | | 0.389 | | |
| Et | Et | 0.13 | −0.201 | −0.209 | 0.364 | 0.385 | 0.350 |
| Et | Et | | | −0.200[h] | 0.355[h] | | |
| *i*-Pr | *i*-Pr | 0.00 | | −0.322 | 0.223 | 0.251 | 0.215 |
| *n*-Bu | *n*-Bu | | | −0.225[h] | 0.345[h] | | |
| *n*-Bu | *n*-Bu | 0.10 | | −0.220 | 0.355 | 0.369 | 0.337 |
| *n*-Pr | *n*-Pr | | | | | 0.369 | 0.350 |
| *i*-Bu | *i*-Bu | | | | | 0.348 | 0.324 |
| c-Hx | c-Hx | −0.01 | | −0.335 | 0.205 | 0.238 | 0.208 |
| Bz | Bz | 0.24 | −0.067 | −0.062 | 0.492 | 0.495 | 0.480 |
| pyr | | 0.18 | −0.120 | −0.130 | 0.411 | | |
| pip | | 0.11 | | −0.225 | 0.349 | | |

[a] Data obtained by ac voltammetry; frequency 80 Hz; scan rate 10 mV/sec. [b] Anodic scan. Data exhibit marked scan rate and concentration dependence. [c] Sufficient $NiL_3^-$ in solution to observe $NiL_3^- \rightarrow NiL_3 + e^-$ couple on anodic scan. [d] $NiL_3$ generated by reaction of L· and $NiL_2$ (see text). Potential obtained from cathodic scan. [e] $NiL_3$ generated by reaction of L· and $NiL_2$ (see text). Potential obtained from anodic scan. [f] $[NiL_3]^+$ generated by oxidation of $NiL_2$ cathodic scan. [g] As for *f*; anodic scan. [h] Cathodic scan on analytically pure $[Ni(R_2dtc)_3]BF_4$.

reproducibly afforded an *n* value of 1.0. However, product characterization (by visible spectroscopy) shows that $Ni((n\text{-}Bu)_2dtc)_2$ and not $Ni((n\text{-}Bu)_2dtc)_3$ is the end product on a longer time scale experiment. Monitoring the reduction process (0.0 V) spectrophotometrically in the range 700–330 nm establishes, on the basis of two isosbestic points (397 and 378 nm) and ε values (Figure 2), that 1 mol of $[Ni((n\text{-}Bu)_2dtc)_3]^+$ is reduced to 1 mol of $Ni((n\text{-}Bu)_2dtc)_2$ and presumably the thiuram disulfide, $(n\text{-}Bu)_2NCS_2S_2CN(n\text{-}Bu)_2$, viz.

$$[Ni((n\text{-}Bu)_2dtc)_3]^+ + e^- \rightleftharpoons Ni((n\text{-}Bu)_2dtc)_3 \rightleftharpoons Ni((n\text{-}Bu)_2dtc)_2 + {}^1/_2(n\text{-}Bu)_4tds \qquad (6)$$

The reverse reaction ($R_4tds + Ni(R_2dtc)_2$) to give $Ni(R_2dtc)_3$ does occur although only to a minor extent. Addition of $Et_4tds$ to $Ni(Et_2dtc)_2$ results in the appearance of the formal Ni(III)–Ni(IV) couple with an ac peak potential of $0.35_5$ V. Addition of $Ni(Et_2dtc)_3BF_4$ to this solution simply increases the ac current at this potential.

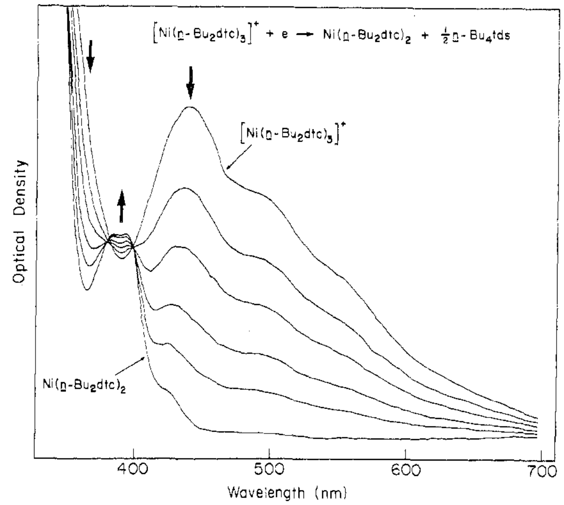

Figure 2. Electrolytic reduction (0.0 V) of $[Ni((n\text{-}Bu)_2dtc)_3]BF_4$ at room temperature followed spectrophotometrically.

The second reduction step of $[Ni((n\text{-}Bu)_2dtc)_3]^+$ (−0.22 V) corresponds to the couple involving the formal oxidation states Ni(III) and Ni(II)

$$Ni((n\text{-}Bu)_2dtc)_3 + e^- \rightleftharpoons [Ni((n\text{-}Bu)_2dtc)_3]^- \qquad (7)$$

As it happens, both species are unstable with regard to spontaneous decomposition. As noted above $Ni((n\text{-}Bu)_2dtc)_3$ decomposes to $Ni((n\text{-}Bu)_2dtc)_2$ and $(n\text{-}Bu)_4tds$. This fact is reflected in the relative current ratios of the first and second reduction waves of $[Ni((n\text{-}Bu)_2dtc)_3]^+$. At a rotating Pt electrode (RPE) (100 Hz) the limiting current ratio improves to the 1:1 limit on lowering the temperature of the solution, i.e.

$$\frac{i_l(\mathrm{III} \rightarrow \mathrm{II})}{i_l(\mathrm{IV} \rightarrow \mathrm{III})} = 0.68 \text{ (at } 18^\circ\text{C)}$$

$$\frac{i_l(\mathrm{III} \rightarrow \mathrm{II})}{i_l(\mathrm{IV} \rightarrow \mathrm{III})} = 1.0 \text{ (at } -70^\circ\text{C)}$$

**Table III.** Parameters for Oxidation Process of $Ni(RR'dtc)_2$ Complexes[a]

| Compd | | Normal-pulse voltammetry | | | Ac voltammetry | | |
|---|---|---|---|---|---|---|---|
| R | R' | $E_{1/2}$, V | $E_{3/4} - E_{1/4}$, mV | $i_1$/concn, mA $M^{-1}$ | $E_p$, V | $\Delta E_{1/2}$,[b] mV | $i_p$/concn, mA $M^{-1}$ |
| Me | Me | $0.89_8$ | 56 | *c* | $0.89_5$ | 93 | *c* |
| Et | Et | $0.89_4$ | 50 | 123 | $0.89_1$ | 97 | 8 |
| *i*-Pr | *i*-Pr | $0.88_9$ | 72 | 112 | $0.89_0$ | 130 | 4 |
| Me | *n*-Bu | $0.90_0$ | 67 | 126 | $0.89_0$ | 120 | 9 |
| *n*-Bu | *n*-Bu | $0.91_2$ | 70 | 116 | $0.91_7$ | 142 | 3 |
| *i*-Bu | *i*-Bu | $0.90_2$ | 60 | 139 | $0.90_4$ | 121 | 4 |
| *c*-Hx | *c*-Hx | | | *c* | $0.84_0$ | | *c* |
| Bz | Bz | $0.97_1$ | 62 | 162 | $0.96_7$ | 120 | 13 |
| pyr | | $0.88_0$ | 44 | *c* | $0.87_6$ | 92 | *c* |
| pip | | $0.88_5$ | 63 | *c* | $0.88_4$ | 98 | *c* |
| 2-Mepip | | $0.90_1$ | 68 | 132 | $0.89_6$ | 107 | 15 |
| 4-Mepip | | $0.96_8$ | 70 | 146 | $0.96_3$ | 123 | 11 |
| 2,6-$Me_2$pip | | $0.91_9$ | 86 | *c* | $0.91_5$ | 120 | *c* |
| Ph | Ph | $0.91_3$ | 77 | 136 | $0.91_5$ | | *c* |
| Ph | Me | $0.90_3$ | 65 | 159 | $0.90_4$ | 110 | 16 |
| Ph | Et | $0.91_0$ | 55 | 140 | $0.90_6$ | 110 | 14 |

[a] By cyclic voltammetry processes were irreversible (see Figure 4). [b] Width at half peak height. [c] Too insoluble for reliable data.

This behavior is also reflected in the cyclic voltammetric studies at 18°C with the ratios of the peak currents for the first and second reductions approaching 1.0 at increasing scan speeds, viz., $v$ (mV $sec^{-1}$) ($i_p(1)/i_p(2)$) = 20 (3.9), 50 (3.4), 100 (2.5), 200 (2.1), 500 (1.9), and 10,000 (1.8). These ratios are also very dependent on the purity of the solvent. A similar trend is observed for $[Ni(Et_2dtc)_3]^+$.

The product of the reduction $[Ni((n\text{-}Bu)_2dtc)_3]^-$ is also unstable via loss of a ligand (vide infra)

$$[Ni((n\text{-}Bu)_2dtc)_3]^- \rightleftharpoons Ni((n\text{-}Bu)_2dtc)_2 + [(n\text{-}Bu)_2dtc]^- \quad (8)$$

Furthermore, the liberated ligand reacts with the Ni(IV) complex via

$$[Ni(R_2dtc)_3]^+ + [R_2dtc]^- \rightarrow Ni(R_2dtc)_2 + R_4tds \quad (9)$$

This reaction has been followed spectrophotometrically in acetone solutions by the successive additions of solid ligand and shows the decay of 1 mol of $[Ni(R_2dtc)_3]^+$ to 1 mol of $Ni(R_2dtc)_2$ ($\epsilon$ values) with isosbestic points at 397 and 378 nm (scanned range 400–340 nm). The spectral chart is virtually identical with that presented in Figure 2.

With this information the coulometric and spectrophotometric results from the second reduction of $[Ni((n\text{-}Bu)_2dtc)_3]^+$ may be understood. Reduction at –0.50 V affords an $n$ value of 1.0 and spectrophotometric monitoring of the reduction proves 1 mol of $[Ni((n\text{-}Bu)_2dtc)_3]^+$ affords 1 mol of $Ni((n\text{-}Bu)_2dtc)_2$ and presumably 0.5 mol of $(n\text{-}Bu)_4tds$—an identical answer with that obtained from the electrolytic reduction at 0.0 V (cf. Figure 2), i.e., at less negative potential than the second reduction. In a recent note,[17] Lachenal has attributed this result to the rapid decomposition of $Ni(R_2dtc)_3$, whereas we suggest that two electrons are actually transferred to the majority of $[Ni(R_2dtc)_3]^+$ species at the electrode but subsequent reactions prematurely deplete the concentration of Ni(IV) in the bulk of solution, viz.

$$[Ni(R_2dtc)_3]^+ + 2e^- \rightarrow [Ni(R_2dtc)_3]^- \quad (10)$$

$$[Ni(R_2dtc)_3]^- \rightleftharpoons Ni(R_2dtc)_2 + [R_2dtc]^- \quad (11)$$

$$[Ni(R_2dtc)_3]^+ + [R_2dtc]^- \rightarrow Ni(R_2dtc)_2 + R_4tds \quad (12)$$

Hence the overall reaction is

$$2[Ni(R_2dtc)_3]^+ + 2e^- \rightarrow 2Ni(R_2dtc)_2 + R_4tds \quad (13)$$

which satisfies all of the data presented. The reaction of Ni(IV) with the liberated ligand is so rapid that no $[R_2dtc]^-$ oxidation wave is observed on examining the resultant solution by cyclic voltammetry.

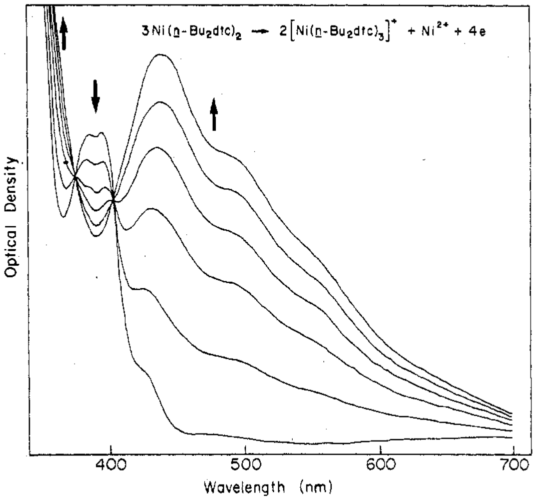

**Figure 3.** Electrolytic oxidation (+1.2 V) of $Ni((n\text{-}Bu)_2dtc)_2$ followed spectrophotometrically.

In an attempt to slow up the dissociation of $[Ni(R_2dtc)_3]^-$ and so minimize reaction of $[R_2dtc]^-$ with the Ni(IV) species, the electrolysis was repeated at –70°C. The spectral results (on solutions returned to room temperature) were essentially identical with those obtained from the room-temperature electrolysis. However, a small quantity of $[R_2dtc]^-$ could be detected voltammetrically at the completion of electrolysis at –70°C. Although no direct evidence is available, reaction 14

$$[Ni(R_2dtc)_3]^+ + [Ni(R_2dtc)_3]^- \rightarrow 2Ni(R_2dtc)_2 + R_4tds \quad (14)$$

may also be operative.

Finally, the third reduction of $[Ni((n\text{-}Bu)_2dtc)_3]^+$ at –1.4 V simply corresponds to the $Ni((n\text{-}Bu)_2dtc)_2$–$[Ni((n\text{-}Bu)_2dtc)_2]^-$ couple described above for pure $Ni((n\text{-}Bu)_2dtc)_2$.

**Oxidation of $Ni(R_2dtc)_2$.** The electrochemical oxidation of $Ni(R_2dtc)_2$ is relatively difficult (+0.9 V) (Table III) and irreversible with a complex electrode process. Fortunately, the products from oxidation are readily characterized and the overall process has been shown to be

$$3Ni(R_2dtc)_2 \rightarrow 2[Ni(R_2dtc)_3]^+ + Ni^{2+} + 4e^- \quad (15)$$

The following experimental facts on the di-*n*-butyl derivative establish the stoichiometry and products of the oxidation. Coulometry at +1.20 V affords the nonintegral $n$ value of 1.4 ± 0.1 electrons/mol of $Ni((n\text{-}Bu)_2dtc)_2$. Spectrophotometric monitoring of the electrolysis (Figure 3) shows the progressive

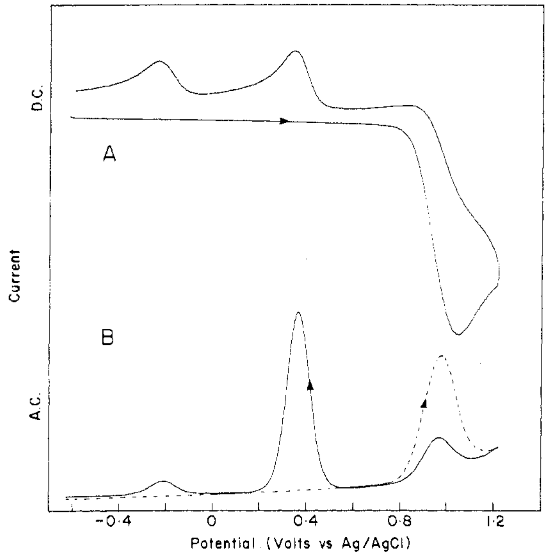

**Figure 4.** Irreversible oxidation of $Ni((n\text{-}Bu)_2dtc)_2$: (A) cyclic voltammogram, 500 mV $sec^{-1}$; (B) cyclic ac voltammogram, 80 Hz, 100 mV $sec^{-1}$. Scan directions are arrowed showing the appearance of $[Ni((n\text{-}Bu)_2dtc)_3]^+$ and its successive reductions on the cathodic scan.

development of the Ni(IV) species $[Ni((n\text{-}Bu)_2dtc)_3]^+$ at the expense of the parent Ni(II) species $Ni((n\text{-}Bu)_2dtc)_2$. Molar extinction coefficients and the two well-defined isosbestic points (372 and 401 nm) confirm the simple 3 → 2 stoichiometry of the oxidation. The NMR spectrum of solid isolated from the electrolyzed solution agrees with that of $[Ni((n\text{-}Bu)_2dtc)_3]BF_4$. In addition, cyclic voltammograms of $Ni((n\text{-}Bu)_2dtc)_2$ develop the same reduction waves of $[Ni((n\text{-}Bu)_2dtc)_3]^+$ as observed for a pure sample of this cationic species (Figure 4).

At -70°C the voltammetric oxidation (200 mV/sec) of $Ni((n\text{-}Bu)_2dtc)_2$ shows a more complex wave with three apparent oxidation peaks ($E_p \approx +0.9, +1.17$, and $+1.45$ V). On the cathodic scan no evidence is seen for $[Ni((n\text{-}Bu)_2dtc)_3]^+$ although a new peak ($E_p \approx 0.43$ V) probably represents reduction of an intermediate in the formation of $[Ni((n\text{-}Bu)_2dtc)_3]^+$. This intermediate has not been identified.

**Oxidation of $[R_2dtc]^-$.** The oxidation of $[R_2dtc]^-$ at a Pt electrode in acetonitrile has been studied recently by Cauquis and Lachenal, who showed that the initial radical product of oxidation $R_2dtc\cdot$ rapidly ($k_f = 2 \times 10^5\ M^{-1}$ l. $sec^{-1}$) dimerizes to the thiuram disulfide.[21] However, if the oxidation is performed in the presence of $Ni(R_2dtc)_2$, it appears the Ni(II) complex competitively scavenges the ligand radical $R_2NCSS\cdot$ to the detriment of the usual dimerization reaction (cf. Figure 5). The resulting complex is the formally Ni(III) complex $Ni(R_2dtc)_3$ which exhibits the Ni(III)-Ni(IV) and Ni(III)-Ni(II) couples at the same potentials as those observed when starting with chemically prepared $[Ni(R_2dtc)_3]^+BF_4^-$. Hence the oxidation and coupled chemical reaction are

$$[R_2dtc]^- \rightleftharpoons R_2dtc\cdot + e^- \qquad (16)$$

$$Ni(R_2dtc)_2 + R_2dtc\cdot \rightarrow Ni(R_2dtc)_3 \qquad (17)$$

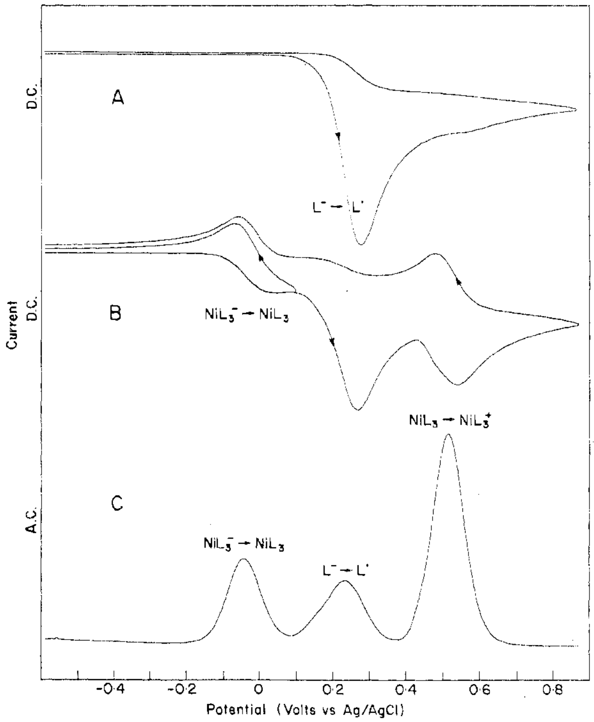

**Figure 5.** (A) Cyclic voltammogram of $[Bz_2dtc]^-$. (B) Cyclic voltammogram of solution A with $Ni(Bz_2dtc)_2$ added, illustrating the newly formed, formally Ni(II)-Ni(III) and Ni(III)-Ni(IV) couples. (C) Ac voltammogram of solution B, 80 Hz, 20 mV $sec^{-1}$.

The possibility that the oxidation of $Ni(R_2dtc)_2$ in the presence of $[R_2dtc]^-$ corresponds to the concerted process, such as (18) appears an unlikely alternative as the ac potential of

$$\begin{array}{l} Ni(R_2dtc)_2 \rightarrow [Ni(R_2dtc)_2]^+ + e^- \\ \quad \big\downarrow [R_2dtc]^- \\ Ni(R_2dtc)_3 \rightarrow [Ni(R_2dtc)_3]^+ + e^- \end{array} \qquad (18)$$

the observed couple is virtually independent of the concentration of $[R_2dtc]^-$. Although $Ni(R_2dtc)_3$ could not be prepared chemically as a stable compound, the radical reaction provides a ready source of the relatively unstable entity $Ni(R_2dtc)_3$ in the electrochemical vessel and has been exploited (with ac voltammetry) to furnish the potentials for the Ni(III)-Ni(IV) couples for a range of substituents (Table II).

The remarkably facile reaction of electrochemically generated $R_2dtc\cdot$ with $Ni(R_2dtc)_2$ to yield $Ni(R_2dtc)_3$ suggests other applications of this principle in the generation of unusual compounds, although in practice the wider application to complexes with other than dithiocarbamate ligands is often hindered by ligand scrambling. For example, consider first the Ni(II) dithiocarbamate of $[(c\text{-}Hx)_2dtc]^-$ and $[Bz_2dtc]^-$ and the tris, mixed-ligand species. The formally Ni(IV)-Ni(III) couples for these four compounds were obtained directly by oxidizing (+1.3 V) mixtures of varying mole ratios of $Ni(Bz_2dtc)_2$ and $Ni((c\text{-}Hx)_2dtc)_2$. The cathodic ac scan showed the expected peaks of the four Ni(IV)-Ni(III) couples. Similar results have been presented earlier for mixed-ligand complexes of iron.[4] The couples showed the following potentials: $Ni(Bz_2dtc)_3$, 0.461 V; $Ni(Bz_2dtc)_2((c\text{-}Hx)_2dtc)$, 0.391 V; $Ni(Bz_2dtc)((c\text{-}Hx)_2dtc)_2$, 0.289 V; $Ni((c\text{-}Hx)_2dtc)_3$, 0.188 V. Each successive couple differs by approximately 90 mV. It should be noted that these data have been obtained at a scan rate of 200 mV/sec and hence are displaced with respect to the data in Table II. These data enable the identification of the species formed in reactions such as that between $Ni((c\text{-}Hx)_2dtc)_2$ and the $Bz_2dtc\cdot$ radical. Although $Ni((c\text{-}Hx)_2dtc)_2(Bz_2dtc)$ is the main product, ligand exchange presumably accounts for the formation of some $Ni((c\text{-}Hx)_2dtc)(Bz_2dtc)_2$. Addition of $[(c\text{-}Hx)_2dtc]^-$ to solutions of $Ni(Bz_2dtc)_2$ results in ligand exchange and affords no extra information. Similarly, addition of $[Et_2dtc]^-$ to $Ni(Etxan)_2$ affords a reversible oxidation process at +0.265 V and no evidence of the oxidation of $[Et_2dtc]^-$. This observation suggests ligand-exchange reaction 19 is operative. The ob-

$$3Ni(Etxan)_2 + 2[Et_2dtc]^- \rightarrow 2[Ni(Etxan)_3]^- + Ni(Et_2dtc)_2 \qquad (19)$$

served oxidation is that of $[\mathrm{Ni(Etxan)_3}]^-$ (vide infra).

**Oxidation of $[\mathrm{Ni(R_2dtc)_3}]^-$ and $[\mathrm{Ni(Etxan)_3}]^-$.** Addition of excess $[\mathrm{R_2dtc}]^-$ to solutions of $\mathrm{Ni(R_2dtc)_2}$ should afford $[\mathrm{Ni(R_2dtc)_3}]^-$ in relatively low concentrations. Although spectral studies of these solutions (1200–700 nm) show no evidence of octahedral Ni(II) species, voltammetric examination detects a small current due to the Ni(II)–Ni(III) couple at the same potential as that obtained from the second reduction of $[\mathrm{Ni(R_2dtc)_3}]^+$ (Figure 5). Generally the Ni(II)–Ni(III) couple falls relatively close to the ligand oxidation wave but it is well resolved by ac voltammetry. Cooling a solution of the dibenzyl derivative (−70°C) causes a dramatic shift (to more positive potentials) of the ligand oxidation wave and leaves the Ni(II)–Ni(III) couple in a clear region of the voltammogram. It is suspected that fast chemical reactions probably play an important role in the observation of the Ni(II)–Ni(III) couple under these experimental conditions. This useful reaction has also been employed to obtain the potentials of the Ni(II)–Ni(III) couple for a range of substituent groups (Table II).

In view of the fact that the corresponding xanthate complex $[\mathrm{Ni(Etxan)_3}]^-$ is sufficiently stable for isolation and characterization[22] and in view of its close relation to the proposed $[\mathrm{Ni(R_2dtc)_3}]^-$ species, its electrochemistry has been examined. $\mathrm{Ni(Etxan)_2}$ exhibits irreversible oxidation ($E_\mathrm{p}$ = 0.92 V) and reduction ($E_\mathrm{p}$ = −0.74 V) waves. However, on addition of $[\mathrm{Etxan}]^-$ (potassium salt) a new reversible couple is established at +0.265 V. $[\mathrm{Etxan}]^-$ is oxidized irreversibly with $E_\mathrm{p}$ = 0.27 V. On the basis of the dithiocarbamate work and the known chemistry of the xanthate species, the new oxidation is suggested to be

$$[\mathrm{Ni(Etxan)_3}]^- \rightleftharpoons \mathrm{Ni(Etxan)_3} + e^- \qquad (20)$$

That this oxidation is more difficult than that observed for the dithiocarbamate is in accord with the lower electron-releasing ability of the $-\mathrm{OR}$ group compared with that of the $-\mathrm{NR_2}$ group.[4]

**Effect of the Dithiocarbamate Substituents on the Redox Couples.** The effects of substituents on the redox couples $\mathrm{Ni(R_2dtc)_2}$–$[\mathrm{Ni(R_2dtc)_2}]^-$, $[\mathrm{Ni(R_2dtc)_3}]^+$–$\mathrm{Ni(R_2dtc)_3}$, and $\mathrm{Ni(R_2dtc)_3}$–$[\mathrm{Ni(R_2dtc)_3}]^-$ and the two irreversible processes $[\mathrm{R_2dtc}]^-$–$[\mathrm{R_2dtc}]^-$ and $\mathrm{Ni(R_2dtc)_2}$–$[\mathrm{Ni(R_2dtc)_3}]^+$ are illustrated in Figure 1 where the data are presented vs. the reversible $\mathrm{Mn(R_2dtc)_3}$–$[\mathrm{Mn(R_2dtc)_3}]^+$ couple. The data for the $[\mathrm{R_2dtc}]^-$–$\mathrm{R_2dtc}^\cdot$ process have been obtained from oxidative ac voltammetry on solutions containing $[\mathrm{R_2dtc}]^-$ and $\mathrm{Ni(R_2dtc)_2}$.

As noted in previous papers[2-4] the substituent effect on the redox potential is related to the inductive and mesomeric effects, i.e., the electron donor–acceptor properties of the substituents. For the oxidation of $\mathrm{Ni(R_2dtc)_2}$ the correlation is rather poor although the general trend is consistent with previous results. This departure is undoubtedly due to the extremely complex and irreversible nature of the oxidation process. Interestingly, the irreversible ligand oxidation shows a good substituent correlation and closely *parallels* the dependence observed for the redox steps of the metal complexes.

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**Registry No.** $\mathrm{Ni(Me_2dtc)_2}$, 15521-65-0; $\mathrm{Ni(Et_2dtc)_2}$, 14267-17-5; Ni((*i*-Pr)$_2$dtc)$_2$, 15694-55-0; Ni(Me(*n*-Bu)dtc)$_2$, 56377-18-5; Ni((*n*-Bu)$_2$dtc)$_2$, 13927-77-0; Ni((*i*-Bu)$_2$dtc)$_2$, 28371-07-5; Ni((c-Hx)$_2$dtc)$_2$, 14592-16-6; $\mathrm{Ni(Bz_2dtc)_2}$, 38542-61-9; $\mathrm{Ni(pyrdtc)_2}$, 30117-29-4; $\mathrm{Ni(pipdtc)_2}$, 41476-75-9; Ni(2-Mepipdtc)$_2$, 56377-19-6; Ni(4-Mepipdtc)$_2$, 56377-20-9; Ni(2,6-Me$_2$pipdtc)$_2$, 56377-21-0; $\mathrm{Ni(Ph_2dtc)_2}$, 15683-31-5; $\mathrm{Ni(PhMedtc)_2}$, 38991-26-3; $\mathrm{Ni(PhEtdtc)_2}$, 30145-37-0; $\mathrm{Ni(Bz_2dtc)_3}$, 56377-15-2; $[\mathrm{Ni(Bz_2dtc)_3}]^+$, 56377-22-1; Ni(Bz$_2$dtc)$_2$(c-Hx)$_2$dtc, 56377-23-2; [Ni(Bz$_2$dtc)$_2$(c-Hx)$_2$dtc]$^+$, 56377-27-6; Ni(Bz$_2$dtc)((c-Hx)$_2$dtc)$_2$, 56377-24-3; [Ni(Bz$_2$dtc)((c-Hx)$_2$dtc)$_2$]$^+$, 56377-25-4; Ni((c-Hx)$_2$dtc)$_3$, 56377-14-1; [Ni((c-Hx)$_2$dtc)$_3$]$^+$, 56377-26-5; $\mathrm{Ni(Etxan)_2}$, 21375-69-9; $[\mathrm{Ni(Etxan)_3}]^-$, 19587-55-4; $\mathrm{Ni(Etxan)_3}$, 56377-07-2; $[\mathrm{Ni(S_2CN(C_4H_9)_2)_3}]\mathrm{BF_4}$, 56377-08-3; $[\mathrm{Ni(S_2CN(C_2H_5)_2)_3}]\mathrm{BF_4}$, 54721-62-9; $\mathrm{Ni(Me_2dtc)_3}$, 56377-09-4; $\mathrm{Ni(Et_2dtc)_3}$, 25370-86-9; Ni((*i*-Pr)$_2$dtc)$_3$, 56377-10-7; Ni((*n*-Bu)$_2$dtc)$_3$, 56377-11-8; Ni((*n*-Pr)$_2$dtc)$_3$, 56377-12-9; Ni((*i*-Bu)$_2$dtc)$_3$, 56377-13-0; Ni((c-Hx)$_2$dtc)$_3$, 56377-14-1; $\mathrm{Ni(Bz_2dtc)_3}$, 56377-15-2; $\mathrm{Ni(pyrdtc)_3}$, 56377-16-3; $\mathrm{Ni(pipdtc)_3}$, 56377-17-4.

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