

compounds $\text{Cl}_2\text{AlN}(\text{C}_2\text{H}_5)\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2$ and $(\text{C}_6\text{H}_5)_2\text{AlN}(\text{C}_2\text{H}_5)\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2$ are also essentially monomeric in benzene. They also have a relatively low sublimation temperature (50 and 90 °C, respectively) and, hence, are probably monomeric in the solid state as well.

Factors Affecting Chelation. Several factors such as steric effects, electronic effects, thermodynamic effects, and the mechanism of formation influence the degree of association of aluminum–nitrogen derivatives. Other factors such as chelate ring size, entropy, and base strengths should also affect chelate formation and stability. Several of these combined factors have been investigated in this study. Steric effects, the interplay between enthalpy and entropy, the relative base strengths of the two ligand base sites, chelate ring size, and, possibly, the mechanism of formation have been shown to play important roles in chelate formation. Our understanding of these factors and their effects on chelation and association should enable future workers to prepare other chelates.

Steric factors play the most important role in determining whether the monomeric chelate or the dimer is observed (Table V). It is apparent that the nature of both the groups bound to the aluminum and the bridging nitrogen are significant. For example, when methyl groups are bound to aluminum, it is necessary to have an ethyl group on the bridging nitrogen to have a monomeric chelate. If hydrogens are bound to aluminum, an $\text{N}-\text{C}_2\text{H}_5$ bridging group is insufficient to lead to the chelate. A dimer is observed instead. Furthermore, if ethyl groups are bound to aluminum, a methyl group on the bridging nitrogen does not produce sufficient steric hindrance to prevent the dimer from forming. Thus, the steric effects of the group bound to the bridging nitrogen might be more important than those on aluminum. By considering molecular weight data for other compounds in Table IV, it can be seen that the steric effect of the groups on the chelating nitrogen, the $-\text{NR}_2$ groups, is relatively unimportant.

The chelate ring size also has an effect on the stability of the chelated monomer. As the ring size increases from a five- to a six-membered ring, the chelate becomes less stable. This effect may be related to the increased entropy for the unbound longer chains in the dimers over those with shorter chains, resulting in a smaller decrease in entropy when dimers are formed.

The relative base strengths of the two bases of the chelating ligand also can have a significant role. In general, the base strengths of Lewis bases are affected by the steric and electronic properties of groups bound to the basic atom. The compound $(\text{CH}_3)_2\text{AlSC}_2\text{H}_4\text{N}(\text{CH}_3)_2$ is a monomeric chelate.

The $-\text{N}(\text{CH}_3)_2$ group is apparently a stronger base than the bridging sulfur. Hence, chelation is observed. In the case of $(\text{CH}_3)_2\text{AlOC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, chelation might also be expected as amines are usually stronger bases than ethers.¹⁷ However, only a dimer is observed. The polarization of the aluminum–oxygen bond due to the difference in electronegativity could account for the increased basicity of the bridging oxygen.⁷ In addition, the steric effects of the methyl groups would help to decrease the basicity of the $-\text{N}(\text{CH}_3)_2$ group.¹⁵

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Registry No. $\text{H}_2\text{Al}(\text{CH}_3)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 59738-49-7; $\text{H}_2\text{-Al}(\text{C}_2\text{H}_5)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 59738-50-0; $(\text{CH}_3)_2\text{Al}(\text{CH}_3)\text{NC}_2\text{H}_4\text{-N}(\text{CH}_3)_2$, 59738-37-3; $(\text{CH}_3)_2\text{Al}(\text{C}_2\text{H}_5)\text{NC}_2\text{H}_4\text{N}(\text{C}_2\text{H}_5)_2$, 59738-38-4; $(\text{CH}_3)_2\text{Al}(\text{CH}_3)\text{NC}_3\text{H}_6\text{N}(\text{CH}_3)_2$, 59738-39-5; $(\text{C}_2\text{H}_5)_2\text{-Al}(\text{CH}_3)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 59738-40-8; $(\text{C}_2\text{H}_5)_2\text{Al}(\text{CH}_3)\text{NC}_3\text{H}_6\text{-N}(\text{CH}_3)_2$, 59738-41-9; $(\text{CH}_3)_2\text{AlOC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 59738-42-0; $(\text{CH}_3)_2\text{AlSC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 59738-43-1; $(\text{C}_6\text{H}_5)_2\text{Al}(\text{C}_2\text{H}_5)\text{NC}_2\text{H}_4\text{-N}(\text{CH}_3)_2$, 59738-44-2; $\text{Cl}_2\text{Al}(\text{C}_2\text{H}_5)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 59738-07-7; $\text{Cl}_2\text{Al}(\text{CH}_3)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 59738-08-8; $(\text{CH}_3)_2\text{Al}(\text{C}_2\text{H}_5)\text{NC}_2\text{-H}_4\text{N}(\text{CH}_3)_2$, 55975-87-6; $\text{H}(\text{CH}_3)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 142-25-6; $\text{H}(\text{C}_2\text{H}_5)\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 123-83-1; $\text{H}(\text{CH}_3)\text{NC}_3\text{H}_6\text{N}(\text{CH}_3)_2$, 4543-96-8; $\text{H}(\text{C}_2\text{H}_5)\text{NC}_2\text{H}_4\text{N}(\text{C}_2\text{H}_5)_2$, 105-04-4; $\text{HOC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 24721-92-4; $\text{HSC}_2\text{H}_4\text{N}(\text{CH}_3)_2$, 108-02-1; $(\text{C}_2\text{H}_5)_3\text{Al}$, 97-93-8; $\text{H}_3\text{Al-N}(\text{CH}_3)_3$, 17013-07-9; triphenylalane, 841-76-9; Al_2Me_6 , 15632-54-9.

References and Notes

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Dithiocarbamates of Cu(I), Cu(II), and Cu(III). An Electrochemical Study

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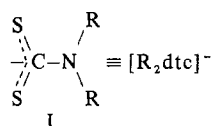
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An electrochemical study of the $\text{Cu}^{n+}/[\text{R}_2\text{dtc}]^-$ system in aprotic solvents defines the electron transfer relationships between bis-chelated complexes of copper in the three oxidation states I, II, and III. $\text{Cu}(\text{R}_2\text{dtc})_2$ undergoes single one-electron oxidation and reduction steps at a platinum electrode: $[\text{Cu}^{\text{III}}(\text{R}_2\text{dtc})_2]^+ + e^- = \text{Cu}^{\text{II}}(\text{R}_2\text{dtc})_2$; $\text{Cu}^{\text{II}}(\text{R}_2\text{dtc})_2 + e^- = [\text{Cu}^{\text{I}}(\text{R}_2\text{dtc})_2]^-$. These redox processes have been characterized for 16 different substituents R by normal pulse voltammetry, ac voltammetry, cyclic voltammetry, spectroelectrolysis, and coulometry. Bis-chelated Cu(I) complexes have been characterized in solution although attempts to isolate the $[\text{Cu}(\text{R}_2\text{dtc})_2]^-$ anion in the solid state failed. The redox potentials vary strongly with the nature of the substituent.

Introduction

During the past decade, it has been established that the dithiocarbamate ligand (I) confers on transition metals many

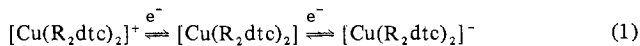
unusual properties such as spin isomerism of the iron(III) complexes¹ and the oligomeric structures of the silver(I) (hexameric),² copper(I) (tetrameric),³ and gold(I) (dimeric)⁴



complexes. Quite recently, the dithiocarbamate ligand has been shown to possess the unsuspected capacity of effectively stabilizing first-row transition metals in unusually high formal oxidation states [e.g., Mn(IV), Ni(IV), and Fe(IV)⁵⁻⁷]. In the case of copper, dithiocarbamate complexes of formally Cu(I), Cu(II), and Cu(III) ions have been isolated. A suspected Cu(IV) species, Cu(R₂dtc)₃ (X = Cl or Br),⁸ has been reformulated as a Cu(II) complex [Cu₂X₆]²⁻[Bitt]²⁺ where [Bitt]²⁺ is the 3,5-bis(*N,N*-dialkylmonium)-1,2,4-trithiolane cation.⁹ Structurally, the copper dithiocarbamates present an interesting series; the copper(I) complexes are generally yellow, tetrameric species in the solid state as well as in solution, whereas in the solid, the copper(II) compounds are often dimeric showing axial interactions.¹⁰ Two types of copper(III) complex have been isolated. Halogen oxidation of Cu(*n*-Bu₂dtc)₂ or [Cu(*n*-Bu₂dtc)]₄ yields diamagnetic Cu(*n*-Bu₂dtc)₂X₂ with X = Cl, Br.¹¹ Alternatively, the oxidants FeCl₃ and Fe(ClO₄)₃·6H₂O (and I₂) yield the diamagnetic, square-planar, monomeric [Cu(R₂dtc)₂]⁺ cation which can be crystallized with the large anions [FeCl₄]⁻, ClO₄⁻, and I₃⁻.¹²⁻¹⁴ Interestingly, more recent studies have implicated copper(III) (aqueous media) in a biochemical role in copper enzyme reactions.¹⁵

Many copper dithiocarbamate complexes have been isolated with nonintegral average oxidation states. Where crystallographic evidence is available, the complexes can be rationalized in terms of the appropriate proportions of Cu(I)/Cu(II), Cu(I)/Cu(III), and Cu(II)/Cu(III) species. Examples are provided by the structures of the compounds Cu₃(Et₂dtc)₂Cl₃,¹⁶ [Cu((pip)(dtc))₂]₂[Cu₂Br₄],¹⁷ and [Cu₃(*n*-Bu₂dtc)₆][Cd₂Br₆].¹⁸

The ability of many first-row transition-metal dithiocarbamate complexes to sustain more than a single one-electron, reversible oxidation and reduction step has been demonstrated¹⁹ and detailed studies have been presented for the manganese,⁵ iron,⁶ and nickel⁷ compounds. This paper examines in detail the redox properties of the copper dithiocarbamates. Some electrochemical measurements have been reported on Cu(Et₂dtc)₂.¹⁹⁻²¹ In the present work the following electron transfer series is established



and the effect of substituents in perturbing the redox potential is defined.

Experimental Section

Compounds. (a) **Bis(disubstituted dithiocarbamate)copper(II), Cu(R₂dtc)₂.** The dithiocarbamate ligands were prepared from the appropriate amine by reaction with CS₂ in aqueous alkali. The copper(II) compounds were prepared from these solutions of ligand, although the ligands were isolated and recrystallized for all other electrochemical studies. A metathetical reaction between stoichiometric quantities of CuCl₂·4H₂O and the dithiocarbamate in aqueous solution resulted in the precipitation of the crude complex. Recrystallization from either CH₂Cl₂-petroleum ether (80-100 °C) or CH₂Cl₂-ethanol mixtures yielded lustrous brown-black crystals of the desired complex. Analytical data (C, H, N) for these known complexes were satisfactory.

(b) **Bis(*N,N*-diisopropylidithiocarbamate)copper(III) perchlorate, [Cu((*i*-Pr)₂dtc)₂]₂ClO₄,** after ref 14. A benzene solution (40 ml) of Cu((*i*-Pr)₂dtc)₂ (2 g) was gently stirred as an ethanolic solution (10 ml) of Fe(ClO₄)₃·6H₂O (1 g) was added dropwise. Stirring was continued for 1 h after completion of addition, at which point the solvent was decanted from the bright green oil. The crude product was dissolved in CH₂Cl₂ and recrystallized by the slow addition of

Et₂O. Anal. Calcd for C₁₄H₂₈ClCuN₂O₄S₄: C, 32.6; H, 5.5; N, 5.4. Found: C, 32.6; H, 5.7; N, 5.3.

(c) **Bis(*N,N*-diisopropylidithiocarbamate)copper(III) Tetrafluoroborate, [Cu((*i*-Pr)₂dtc)₂]₂BF₄.** A rapid stream of air was passed through a benzene solution (40 ml) of Cu((*i*-Pr)₂dtc)₂ to aerate and stir the solution. Et₂O·BF₃ (1.5 ml of 40% solution in Et₂O) was added dropwise over a period of 10 min. Aeration was continued for 1 h after which time the solution was neutralized and dried with Na₂CO₃. The supernatant liquid was decanted and the solid mixture extracted with CH₂Cl₂ (3 × 10 ml). The combined extracts were reduced to half volume and the product crystallized by addition of Et₂O. Anal. Calcd for C₁₄H₂₈BCuF₄N₂S₄: C, 33.4; H, 5.6; N, 5.6. Found: C, 33.5; H, 5.3; N, 5.0.

(d) **Bis(*N,N*-diethylidithiocarbamate)copper(III) Tetrafluoroborate, [Cu(Et₂dtc)₂]₂BF₄.** This complex was prepared similarly to the diisopropyl derivative described above. Anal. Calcd for C₁₀H₂₀BCuF₄N₂S₄: C, 26.9; H, 4.5; N, 6.3. Found: C, 27.6; H, 5.1; N, 6.4.

(e) **(*N,N*-Diethylidithiocarbamate)copper(I), Cu(Et₂dtc)**, after ref 22. A CS₂ solution (20 ml) of Cu(Et₂dtc)₂ (1 g) was shaken with finely divided copper-bronze (ca. 2 g) for 12 h. The resulting translucent red solution was filtered and the bright yellow product was crystallized by careful addition of Et₂O.

(f) **Bis(*N,N*-diisopropylidithiocarbamate)copper(III) Triiodide, Cu((*i*-Pr)₂dtc)₂I₃.** This complex was prepared by iodine oxidation of Cu((*i*-Pr)₂dtc)₂ after ref 13. Anal. Calcd for C₁₄H₂₈CuI₃N₂S₄: C, 21.1; H, 3.5; N, 3.5; Cu, 8.0; S, 16.1; I, 47.8. Found: C, 20.9; H, 3.9; N, 3.2; Cu, 8.1; S, 15.6; I, 48.3.

Electrochemical. All measurements were made with a three-electrode, Princeton Applied Research Model 170 instrument with Pt working and auxiliary electrodes. Unless otherwise noted, measurements were made on ca. 10⁻³ M depolarizer in 0.1 M Et₄NClO₄/acetone solutions with potentials referred to a Ag|AgCl|0.1 M LiCl|acetone electrode.²³ The phase sensitive ac voltammograms were measured in phase with the input alternating potential. An applied ac potential (80 Hz) of 10 mV peak-peak and a scan rate of 10 mV s⁻¹ was used unless noted otherwise. Coulometry, electrolysis, and spectral monitoring of electrolyzed solutions were carried out in vessels of our own design.²⁴

Results and Discussion

The electrochemical oxidation and reduction of a series of 16 Cu(R₂dtc)₂ complexes have been studied using normal pulse, ac, and cyclic voltammetry at a platinum electrode. All the complexes exhibit similar parameters for their oxidation and reduction steps, which implies that the redox processes are closely related (Tables I and II). Cu((*i*-Pr)₂dtc)₂ is representative and has been studied in detail.

Oxidation. The normal pulse voltammogram for the oxidation of Cu((*i*-Pr)₂dtc)₂ has a half-wave potential of +0.602 V. The log (*i*₁ - *i*)/*i* vs. *E* plot confirms this value and has a gradient of 58 mV, being in accord with a reversible one-electron process. Ac voltammetry yields a peak potential of +0.604 V and a wave shape very close to that predicted theoretically for a reversible ac polarogram.²⁵ Cyclic voltammograms (potential scan rates 20-200 mV s⁻¹) are centered at +0.603 V with the ratio of forward and reverse scan peak currents (*i*_f/*i*_r) of 1.0 ± 0.1. The peak-peak separation (Δ*E*_p) at a scan rate of 200 mV s⁻¹ is 62 mV (cf. calculated for *n* = 1, 60 mV). Coulometric oxidation of Cu((*i*-Pr)₂dtc)₂ at +0.70 V affords an *n* value of 1.0. The electronic spectrum of the resultant solution is comparable with that of a chemically prepared solution of [Cu((*i*-Pr)₂dtc)₂]₂BF₄ (Figure 1). Subsequent reductive electrolysis completely regenerated the copper(II) complex (spectral evidence).

Under the same electrochemical conditions [Cu((*i*-Pr)₂dtc)₂]₂BF₄ showed successive reductions at +0.590 and -0.470 V, corresponding closely to the oxidation and reduction potentials of the Cu((*i*-Pr)₂dtc)₂. Coulometric reduction of [Cu((*i*-Pr)₂dtc)₂]₂BF₄ at +0.30 V gave an *n* value of 1.0. The progress of the electrolysis was followed by the change in the absorption spectrum (700-320 nm) from that of [Cu((*i*-Pr)₂dtc)₂]⁺ to Cu((*i*-Pr)₂dtc)₂ with two isosbestic points at

Table I. Parameters for Oxidation Process of Cu(R,R'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_p/concn , mA M ⁻¹	E_p , V	$\Delta E_{1/2}$, mV	i_p/concn , mA M ⁻¹	ΔE_p , mV	i_f/i_r	Av $i_f/\text{Cu}^{1/2}$, mA s ^{1/2} /M mV ^{1/2}
Me	Me	0.698	53	210	0.699	92	62	59	1.0	7.6
Et	Et	0.704	57	215	0.696	95	65	70	1.0	7.8
<i>i</i> -Pr	<i>i</i> -Pr	0.603	56	191	0.604	95	54	64	1.0	7.2
Me	<i>n</i> -Bu	0.692	57	208	0.695	95	47	65	1.0	6.4
<i>n</i> -Bu	<i>n</i> -Bu	0.684	58	212	0.686	93	57	68	1.0	7.7
<i>i</i> -Bu	<i>i</i> -Bu	0.670	55	206	0.673	100	51	64	1.0	7.4
<i>c</i> -Hx	<i>c</i> -Hx	0.574	58	<i>b</i>	0.572	104	<i>b</i>	65	1.1	<i>b</i>
Bz	Bz	0.775	60	187	0.771	93	54	68	1.0	7.7
pyrr		0.727	50	<i>b</i>	0.722	105	<i>b</i>	64	1.0	<i>b</i>
pip		0.676	59	<i>b</i>	0.679	93	<i>b</i>	65	1.1	<i>b</i>
2-Me(pip)		0.654	55	200	0.656	93	59	59	1.0	7.1
4-Me(pip)		0.685	58	187	0.685	94	52	60	1.0	6.2
2,6-Me ₂ (pip)		0.655	61	179	0.656	93	52	59	1.0	7.1
Ph	Ph	0.711	55	198	0.706	93	55	65	1.0	6.8
Ph	Me	0.712	53	197	0.704	93	58	60	1.0	7.7
Ph	Et	0.707	53	195	0.704	94	56	62	1.0	7.6

^a Scan rate, 200 mV s⁻¹. ^b Too insoluble for reliable data.

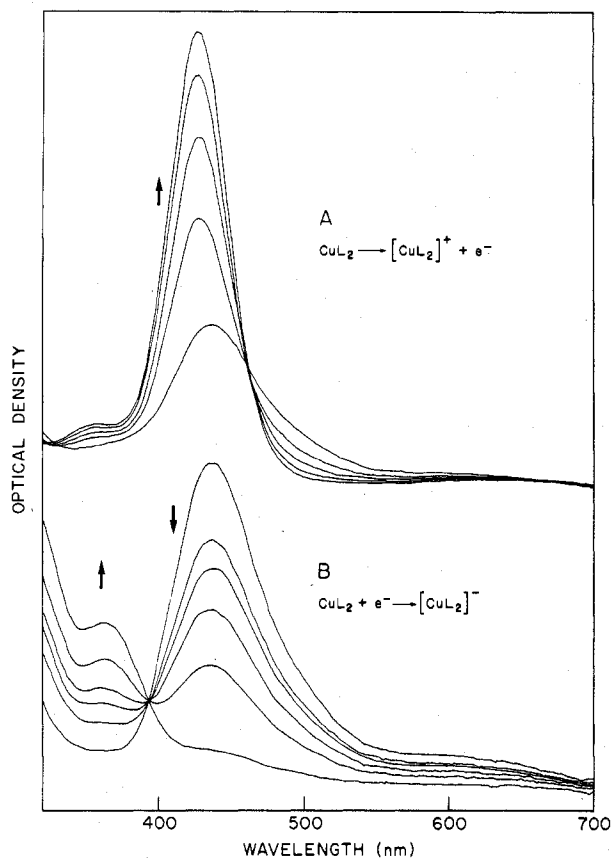
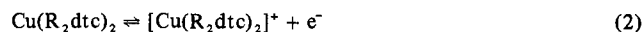


Figure 1. Spectra of a solution of Cu((*i*-Pr)₂dtc)₂ sampled during: (A) oxidative electrolysis, and (B) reductive electrolysis. Arrows indicate direction of spectral changes on oxidation to [Cu((*i*-Pr)₂dtc)₂]⁺ and reduction to [Cu((*i*-Pr)₂dtc)₂]⁻. Both spectra were obtained in acetone containing 0.1 M Et₄NClO₄.

464 and 328 nm. Hence the oxidation process for the series is unambiguously defined as:



Reduction. The voltammetric parameters [($E_{3/4} - E_{1/4}$) and ΔE_p] for the reduction of Cu(R₂dtc)₂ complexes (Table II) suggest that the electrode processes are often only quasi-reversible. Assuming a tetrahedral Cu(I) complex, the quasi-reversibility associated with the reduction probably arises from the relaxation process involved in a stereochemical change

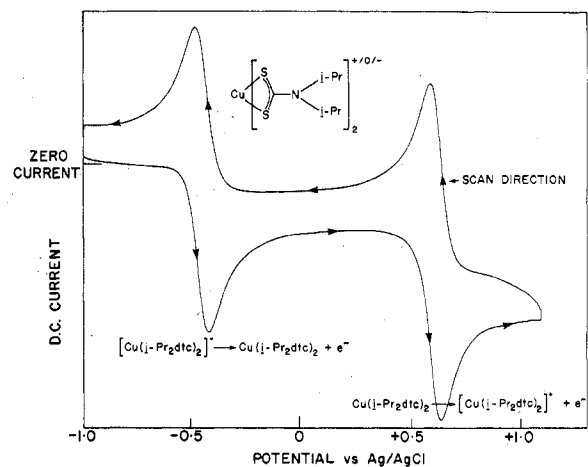


Figure 2. Cyclic voltammogram (acetone-0.1 M Et₄NClO₄) of [Cu((*i*-Pr)₂dtc)₂]⁻ showing the two successive oxidation steps through Cu((*i*-Pr)₂dtc)₂ and [Cu((*i*-Pr)₂dtc)₂]⁺. The [Cu((*i*-Pr)₂dtc)₂]⁻ solution was generated by electrolytic reduction of Cu((*i*-Pr)₂dtc)₂. Scan speed, 200 mV s⁻¹.

from square-planar Cu(II) to tetrahedral Cu(I).

Coulometric reduction of Cu((*i*-Pr)₂dtc)₂ at -0.70 V gave an *n* value of 1.0 and spectral data on the process exhibit one isosbestic point in the range 700–320 nm at 392 nm (Figure 1) consistent with the simple reduction to a Cu(I) species:

$$\text{Cu}((\text{i-Pr})_2\text{dtc})_2 + e^- \rightleftharpoons [\text{Cu}((\text{i-Pr})_2\text{dtc})_2]^- \quad (3)$$

Cyclic voltammetry on the reduced solution shows two oxidations of the Cu(I) complex at the expected potentials (Figure 2).

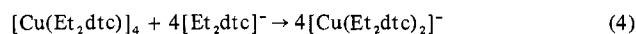
In order to strengthen the evidence for [Cu(R₂dtc)₂]⁻ species, a titrimetric study, monitored by ac voltammetry scanning the potential ranges 0 to -0.5 V and 0 to +1.0 V, was undertaken. A deoxygenated acetone solution (0.1 M Et₄NClO₄) of NaEt₂dtc (8.0 × 10⁻³ M) was titrated into a similar solution of [Cu(Et₂dtc)₄] (2.63 × 10⁻⁵ mol in ca. 20 ml of solution). The broad ac oxidation peak of [Cu(Et₂dtc)₄] at ca. 0.7 V grew, as did a second peak at -0.37 V. Cyclic voltammetry showed both waves to be oxidation steps. At the 1:1 end point, the ac peak currents of both oxidation waves were of approximately the same ratio as the ac peak currents of the respective reduction and oxidation waves of Cu(Et₂dtc)₂. Addition of [Et₂dtc]⁻ beyond this point resulted in the growth of the broad asymmetric ac wave at +0.2 V, characteristic of the irreversible oxidation of the uncoordinated ligand.⁷ These

Table II. Parameters for Reduction Process of Cu(R,R'dtc)₂ Complexes

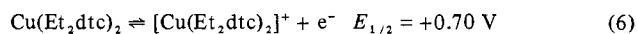
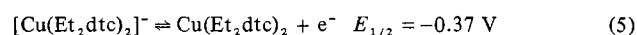
Compd		Normal pulse voltammetry			Ac voltammetry			Cyclic voltammetry ^a		
R	R'	E _{1/2} , V	E _{3/4} - E _{1/4} , mV	i _p /concn, mA M ⁻¹	E _p , V	ΔE _{1/2} , mV	i _p /concn, mA M ⁻¹	ΔE _p , mV	i _f /i _r	Av i _f /Cv ^{1/2} , mA s ^{1/2} /M mV ^{1/2}
Me	Me	-0.334	54	210	-0.334	93	56	59	1.0	7.2
Et	Et	-0.365	78	215	-0.369	102	56	78	1.0	8.3
<i>i</i> -Pr	<i>i</i> -Pr	-0.474	61	200	-0.466	103	36	76	1.0	6.7
Me	<i>n</i> -Bu	-0.367	56	203	-0.366	99	36	71	1.0	6.6
<i>n</i> -Bu	<i>n</i> -Bu	-0.390	57	210	-0.386	99	44	76	1.0	7.2
<i>i</i> -Bu	<i>i</i> -Bu	-0.405	61	206	-0.406	100	41	76	1.0	7.1
<i>c</i> -Hx	<i>c</i> -Hx	-0.493	58	<i>b</i>	-0.484	112	<i>b</i>	80	1.1	<i>b</i>
Bz	Bz	-0.228	58	200	-0.238	109	20	95	1.1	6.8
pyrr		-0.306	56	<i>b</i>	-0.300	94	<i>b</i>	62	1.1	<i>b</i>
pip		-0.367	53	<i>b</i>	-0.365	94	<i>b</i>	61	1.1	<i>b</i>
2-Me(pip)		-0.382	54	200	-0.379	93	54	62	1.0	7.0
4-Me(pip)		-0.367	57	190	-0.367	100	39	75	1.0	6.2
2,6-Me ₂ (pip)		-0.414	80	185	-0.400	106	30	80	1.0	7.2
Ph	Ph	-0.265	46	164	-0.265	94	31	69	1.2	7.4
Ph	Me	-0.288	50	196	-0.293	92	44	66	0.9	7.6
Ph	Et	-0.307	61	200	-0.308	95	44	70	1.1	7.2

^a Scan rate 200 mV s⁻¹. ^b Too insoluble for reliable data.

data imply the existence in solution of [Cu(Et₂dte)₂]⁻



with two successive oxidations corresponding to

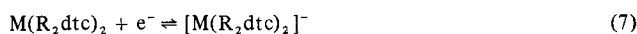


Aerial oxidation of this pale yellow solution of [Cu(Et₂dte)₂]⁻ generated the brown Cu(Et₂dte)₂ which was identified by its electronic spectrum and electrochemical behavior.

Attempts to isolate the anionic Cu(I) complex were unsuccessful. Although the required species can be formed in oxygen-free solutions by metathetical reaction of [Cu(Et₂dte)₄] and [Et₂dte]⁻, we were unable to isolate the complex. Addition of EtOH to CH₂Cl₂ solutions of [*n*-Bu₄N][Cu(Et₂dte)₂] followed by cooling only resulted in the reisolation of [Cu(Et₂dte)₄].

Trends in Redox Potentials. The dependence of E_{1/2} of the Cu(II)/(III) and Cu(II)/(I) couples parallels that described previously for the dithiocarbamates of manganese, iron, and nickel.⁵⁻⁷ A plot of oxidation potential vs. reduction potential (Figure 3) is approximately linear and reinforces the generality of the earlier observations that those substituents which enhance ease of oxidation (e.g., R = cyclohexyl and isopropyl) render reduction more difficult and vice versa.

In addition to the substituent dependence, we have noted elsewhere that the redox potentials for the uncharged metal complexes depend markedly on the nature of the central metal atom.¹⁹ Thus, for the square coordinated complexes, the reduction step,



occurs at potentials more positive by about 1 V for M = Cu compared with M = Ni.

The effect of charge on redox potentials can be discerned from the data summarized in Table III. Redox couples are grouped into pairs which involve the same changes in d-electron configuration. In each case the pairs involve a comparable 0 ⇌ -1 and +1 ⇌ 0 couple and with the exception of the Ni(Et₂dte)₂ and Cu(Et₂dte)₂ pair, all couples refer to the tris chelates. It should be noted that, although the pairs are isoelectronic, the spin states are not always compatible.

The magnitude of the potential difference, ΔE_{1/2}, between the isoelectronic couples which comprise a pair, is a striking feature of the tabulated data. The data in each case conform with the expectation that cationic complexes are reduced at

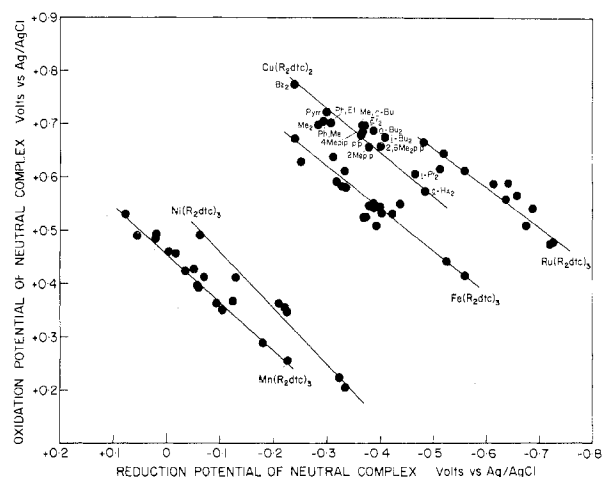


Figure 3. Relationship between the oxidation and reduction potentials of Cu(R,R'dtc)₂ compounds for different substituents R,R'. The metal dependence of this relationship is illustrated by the corresponding curves for Mn(R,R'dtc)₃, Fe(R,R'dtc)₃, Ni(R,R'dtc)₃, and Ru(R,R'dtc)₃. Data for the tris complexes are taken from ref 5-7 and 26.

Table III. Charge Effects on Redox Potentials^a

Complex	Formal oxidation states in couple	Charge on complex	d-electron configuration	Redox potential	Potential diff ΔE _{1/2} , V
Mn(Et ₂ dte) ₃	III ⇌ II	0 ⇌ -1	4 ⇌ 5	-0.07	0.62
Fe(Et ₂ dte) ₃	IV ⇌ III	+1 ⇌ 0	4 ⇌ 5	+0.55	
Fe(Et ₂ dte) ₃	III ⇌ II	0 ⇌ -1	5 ⇌ 6	-0.38	1.44
Co(Et ₂ dte) ₃	IV ⇌ III	+1 ⇌ 0	5 ⇌ 6	+1.06	
Co(Et ₂ dte) ₃	III ⇌ II	0 ⇌ -1	6 ⇌ 7	-0.98	1.35
Ni(Et ₂ dte) ₃	IV ⇌ III	+1 ⇌ 0	6 ⇌ 7	+0.37	
Ni(Et ₂ dte) ₂	II ⇌ I	0 ⇌ -1	8 ⇌ 9	-1.34	2.04
Cu(Et ₂ dte) ₂	III ⇌ II	+1 ⇌ 0	8 ⇌ 9	+0.70	

^a Data taken from ref 5-7 and 24. ^b Potential vs. Ag|AgCl|0.1 M LiCl in acetone.

more positive potentials than their uncharged congeners. The potential difference, ΔE_{1/2}, ranges from 0.62 to 2.04 V and this is ascribed primarily to the influence of charge on the depolarizer. Interestingly, ΔE_{1/2} is largest for pairs which involve the low-spin 3d⁶ (tris complexes) and the low-spin 3d⁸ (bis complexes) configurations. However, the discrimination

between redox potentials due to the charge effect is greatly reduced for the isoelectronic Mn/Fe pair (d^4-d^5) which does not contain a d-electron configuration of special stability. This correlation between $E_{1/2}$ and d-electron configuration for first-row transition-metal complexes has been described elsewhere.¹⁹

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Registry No. Cu(Me₂dte)₂, 137-29-1; Cu(Et₂dte)₂, 13681-87-3; Cu(*i*-Pr)₂dte)₂, 14354-07-5; Cu(Me(*n*-Bu)dte)₂, 59765-84-3; Cu(*n*-Bu)₂dte)₂, 13927-71-4; Cu(*i*-Bu)₂dte)₂, 51205-55-1; Cu(*c*-Hx)₂dte)₂, 51120-55-9; Cu(Bz₂dte)₂, 34409-33-1; Cu((pyrr)dte)₂, 23301-60-2; Cu((pip)dte)₂, 15225-85-1; Cu((2-Me(pip))dte)₂, 59765-85-4; Cu((4-Me(pip))dte)₂, 59765-86-5; Cu((2,6-Me₂(pip))dte)₂, 59765-87-6; Cu(Ph₂dte)₂, 15683-27-9; Cu(PhMedte)₂, 38991-27-4; Cu(PhEtdte)₂, 53020-87-4; [Cu(*i*-Pr)₂dte)₂]ClO₄, 59765-89-8; [Cu(*i*-Pr)₂dte)₂]BF₄, 59790-37-3; [Cu(Et₂dte)₂]BF₄, 59796-00-8; Cu(*i*-Pr)₂dte)₂]₃, 59765-90-1; [Cu(Et₂dte)₂]₄, 52133-93-4.

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Solution Equilibria of Nickel(II) Complexes with Optically Active Tetraamines Containing Pyrrolidinyl Groups

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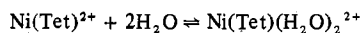
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The temperature dependence of the square planar-octahedral equilibrium of the nickel(II) complexes with optically active tetraamines including two pyrrolidinyl groups has been studied in water, acetonitrile, and nitromethane. The equilibrium parameters were obtained by variable-temperature spectroscopic measurements. The equilibrium constants disclosed the preferential order in the octahedral-type coordination of these tetraamines to nickel(II) ion: 1,2-bis[2(*S*)-2-aminomethyl-1-pyrrolidinyl]ethane (AMPE) \approx 1,2-bis[2(*S*)-2-*N*-methylaminomethyl-1-pyrrolidinyl]ethane (MMPE) > 1,3-bis[2(*S*)-2-aminomethyl-1-pyrrolidinyl]propane (AMPP) \gg *N,N'*-bis[2(*S*)-2-pyrrolidinylmethyl]-1,3-trimethylenediamine (PMTN) > *N,N'*-bis[2(*S*)-2-pyrrolidinylmethyl]ethylenediamine (PMEN) > *N,N'*-bis[2(*S*)-2-pyrrolidinylmethyl]-1-(*S*),2(*S*)-cyclohexanediamine (SS-PMCN) > *N,N'*-bis[2(*S*)-2-pyrrolidinylmethyl]-1(*R*),2(*R*)-cyclohexanediamine (RR-PMCN) (25 °C). This result was compared with the trien and 2,3,2-tet complexes.

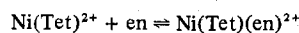
Since the investigation of bis(stilbenediamine)nickel(II) by Lifschitz et al.,¹ the equilibrium between blue (octahedral) and yellow (square planar) species of bis(diamine) or tetraamine complexes of nickel(II) ion has been well investigated.²⁻⁸ For example, the 1:1 complex of nickel(II) ion with triethylenetetramine (trien) consists almost entirely of octahedral species in an aqueous solution at room temperature, and its planar species increases with the addition of an excess of neutral salts, or with a rise in temperature.⁷

In the previous papers,⁹⁻¹¹ we have reported that the optically active tetraamines containing two pyrrolidinyl groups as shown in Figure 1 coordinate to nickel(II) ion with a certain stereoselectivity; the tetraamines which have the two pyrrolidinyl groups at their inner parts form mostly blue species in aqueous solutions at room temperature, whereas other tetraamines having the two pyrrolidinyl groups as the terminal

groups preferentially form yellow species. It was further recognized that the two species of the tetraamine complexes coexist in solution as represented below



where Tet is a tetraamine. Similar equilibria have been observed for the mixed complexes of the tetraamines with ethylenediamine (en)



It was found that these equilibria between the two species depend greatly on the temperature. Then, it appeared of interest to obtain the thermodynamic parameters such as the equilibrium constant by means of the temperature dependence of the absorption spectra, and to further investigate the scope and mechanism of the selective coordination of the tetraamines.