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Reactions of Coordinated Molecules.
XXVIII. Cyclic Voltammetry of Several Transition Metal Metalla-acetylacetonate Complexes

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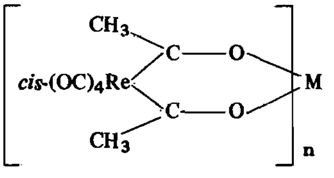
The rhena-acetylacetonate complexes, [cis-$(OC)_4Re(CH_3CO)_2]_nM$, where M is Fe and Cr when n is 3 and Cu when n is 2, and the corresponding acetylacetonate (acac) complexes are examined by cyclic voltammetry as methylene chloride solutions using tetrabutylammonium perchlorate as the supporting electrolyte. Redox potentials of the central coordinating metal ions for the metalla- and the analogous non-metalla-acetylacetonate complexes are determined. The iron complexes exhibit quasi-reversible redox reactions at the iron atom, and the reduction potential for the rhena-acetylacetonate iron complex is 0.63 volts more positive than that of Fe(acac)$_3$. A similar trend is observed for the Cr and Cu complexes, although these complexes exhibit considerable irreversibility. The more positive reduction potentials for the heteronuclear complexes reflects the higher electronegativity of the rhena-acetylacetonate ligands. The redox reactions and the assignments of unexpected anodic peaks are discussed, also.

Introduction

We recently reported the preparation and characterization of several transition metal complexes containing metalla-β-diketonate ligands [2, 3]. The rhena-acetylacetonate complexes of Fe(III), **1**, Cr(III), **2**, and Cu(II), **3**, are particularly interesting because of the unusual colors of these complexes in comparison to the analogous acetylacetonate (acac) complexes. Also, the EPR spectrum of **3** in the vitreous state revealed a copper–rhenium (I = 5/2) superhyperfine interaction, A_f^{Re}, of 22.1 × 10^{-4} cm^{-1}, which might indicate an electronic interaction between the three metal atoms of this complex. Subsequently, the X-ray structure of **3** showed an unexpected molecular geometry. Although the bond distances within the rhena-acetylacetonate ligands of **3** are essentially identical to those of the nearly planar chelate ring in the rhena-acetylacetone molecule [4], the chelate rings of **3** are not planar, and the overall geometry of **3** resembles a 'chaise-longue' chair structure [5]. Infrared data suggest that this structure may be maintained in solution, also.



M	*n*	*cmpd*
Fe(III)	3	1
Cr(III)	3	2
Cu(II)	2	3

An electrochemical study of the complexes **1**–**3** was initiated primarily to determine the redox potentials of the central coordinating metal ions and to compare these potentials to those of the analogous M(acac)$_n$ complexes. Such data should afford a direct comparison of the relative Lewis basicity of the metalla- and non-metalla-acetylacetonate ligands and may reveal any unusual electronic interactions within the rhena-acetylacetonate complexes. We wish to report the results of a cyclic voltammetric study of **1**–**3**, and the analogous M(acac)$_n$ complexes, under identical experimental conditions. The iron complexes exhibit quasi-reversible redox behavior and provide an excellent comparison between these two classes of complexes.

Experimental

The complexes **1**–**3**, Fe(acac)$_3$, Cr(acac)$_3$ and Cu(acac)$_2$ were obtained commercially or were prepared using published procedures [2, 6]. The solvent, methylene chloride, was purified by distillation from phosphorus pentoxide under a nitrogen atmosphere before use. The supporting electrolyte was tetrabutylammonium perchlorate, made by the addition of 4.0 ml of 70% perchloric acid to 50 ml of 1 *M* tetrabutylammonium hydroxide in 250 ml deionized water. The resulting precipitate was filtered, washed, and dried overnight at 100 °C.

The voltammetric unit used was a Bioanalytical Systems, Inc. Model #CV-1A. The i–V curves were recorded using a Hewlett-Packard X–Y recorder 7044A. The cell system was carefully selected to

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avoid contamination by water and oxygen. A 10 ml electrochemical cell was connected to a Ag/AgCl reference electrode by means of a porous Vicor rod to prevent water contamination. The cell contained a glassy carbon working electrode and a platinum wire auxillary electrode. This three-electrode system permitted compensation for cell resistance. A nitrogen atmosphere was maintained with pre-purified nitrogen which was pre-saturated with solvent vapor.

All solutions for which data are given were 5 X 10^{-3} *M* with respect to the electroactive species and 0.1 *M* with respect to tetrabutylammonium perchlorate. The studies were done at the ambient temperature of 24 °C. All potentials are given versus the Ag/AgCl electrode (0.222 V *vs.* SHE, the standard hydrogen electrode) unless stated otherwise.

Results and Discussion

The 300 mV/sec cyclic voltammograms of **1**–**3** and the analogous acetylacetonate (acac) complexes, $Fe(acac)_3$, $Cr(acac)_3$ and $Cu(acac)_2$, respectively, are shown in Fig. 1. Table I summarizes the cyclic voltammetric data. The cyclic voltammogram of the supporting electrolyte shows a very small cathodic wave at *ca.* –0.90 V and a slightly larger anodic wave at *ca.* +1.40 V. The anodic waves of $Cr(acac)_3$, $Cr(Re\text{-}acac)_3$, and $Cu(acac)_2$ at +1.24 V, +1.40 V and +1.34 V, respectively, are assigned to the oxidation of the supporting electrolyte.

The reduction of $Fe(acac)_3$ occurs at –0.83 V as a one-electron, quasi-reversible process. Reoxidation of the reduction product occurs at –0.50 V. This reduction potential is more negative than the reduction potential of –0.667 V (*vs.* SCE) observed for $Fe(acac)_3$ in acetonitrile solution using polarography and cyclic voltammetry [7]. The lower dielectric constant of methylene chloride accounts for most of this negative shift [8]. Other electrochemical studies of $Fe(acac)_3$ and related compounds indicate that the presence of coordinating cations, such as lithium ion, or protons will shift the reduction potentials to more positive values [9–11]; however, these species are not present in the solutions studied here. The reduction of $Fe(acac)_3$ in acetonitrile [7] appears to be more reversible than in methylene chloride which may indicate that other solvent effects are important, also.

The cause of the slight irreversibility of the redox reactions of $Fe(acac)_3$ under our conditions is not known. Using a slow scan rate, the cyclic voltammograms reveal a quasi-reversible redox process as shown in Fig. 1. However, as the scan rate is increased, the intensity of the anodic wave at –0.50 V decreases with the concomitant appearance of a new anodic wave at +0.40 V. This anodic wave also appears in the cyclic voltammograms of $Cr(acac)_3$ and $Cu(acac)_2$, and its assignment is discussed below.

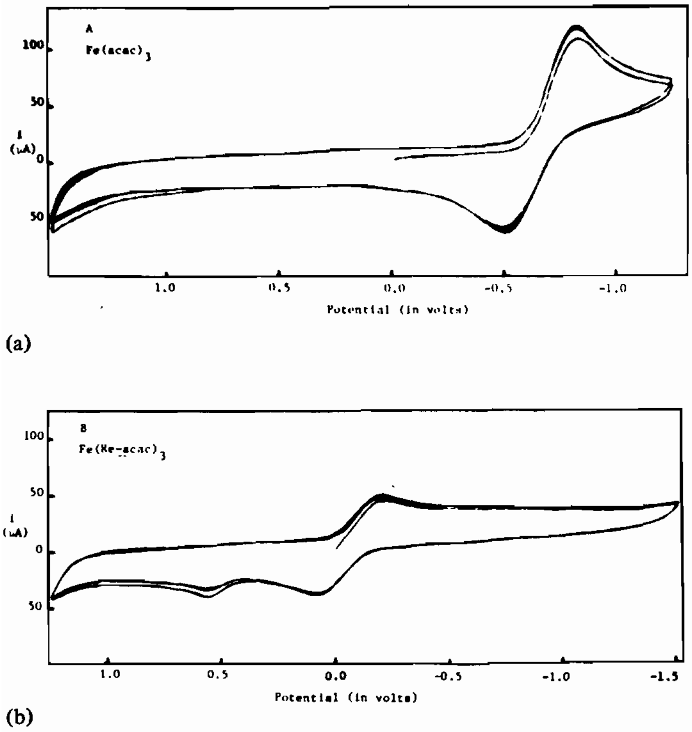
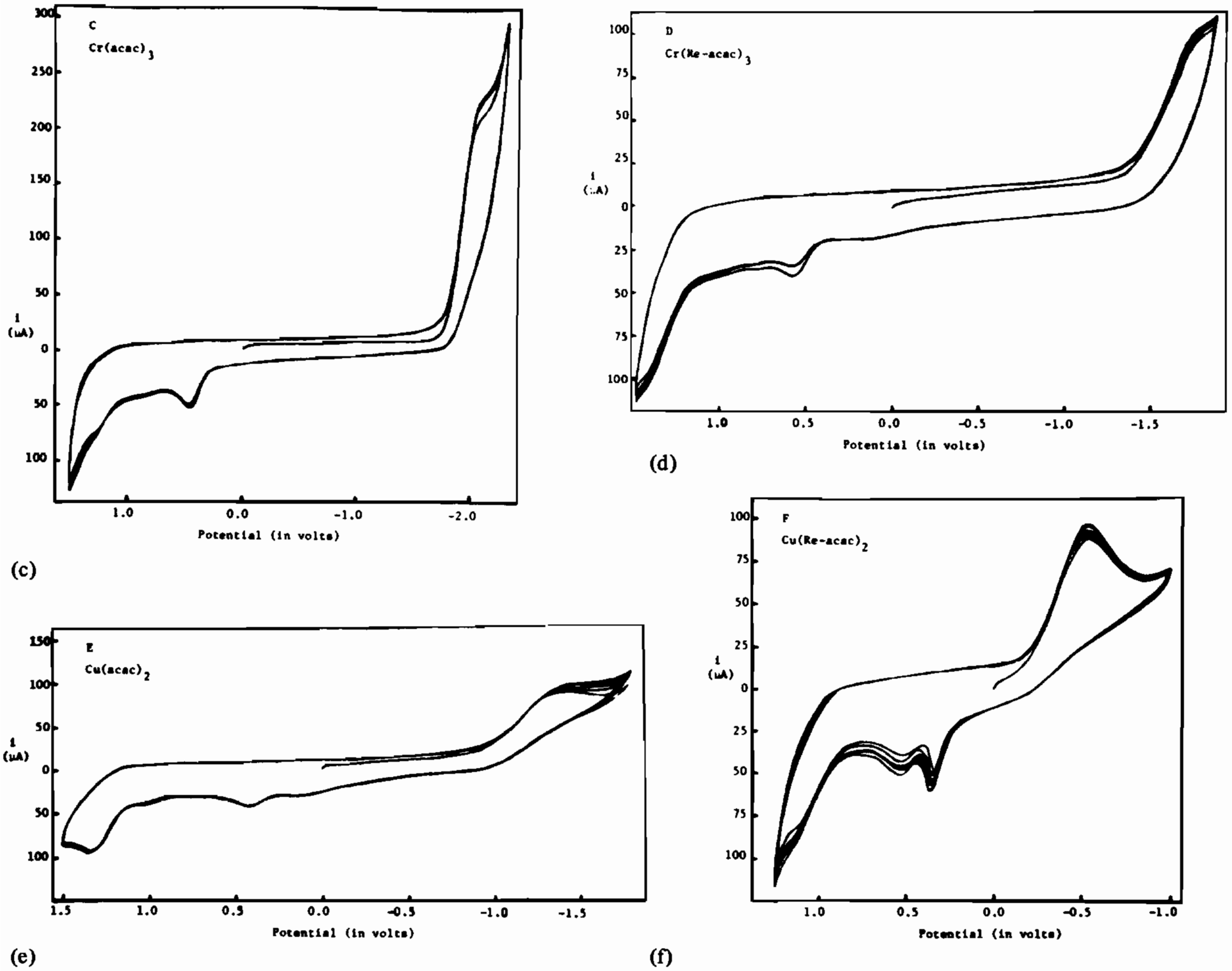


Fig. 1. *(For legend please see on facing page)*



(c) (d) (e) (f)

Fig. 1. The cyclic voltammograms at 24 °C in methylene chloride solution using 0.1 *M* [$(butyl)_4N$]ClO_4 as supporting electrolyte of 5 × 10^{-3} *M* solutions of: (A) Fe$(acac)_3$, (B) Fe(Re-acac$)_3$, **1**, (C) Cr$(acac)_3$, (D) Cr(Re-acac$)_3$, **2**, (E) Cu$(acac)_2$, and (F) Cu(Re-acac$)_2$, **3**. Potentials are measured *vs.* the Ag/AgCl electrode and at a scan speed of 300 mV/sec. Repetitive scans are shown.

The tris-(rhena-acetylacetonato)iron complex, Fe(Re-acac$)_3$, **1**, undergoes a one-electron reduction at –0.20 V with a nearly reversible reoxidation of the reduction product at +0.05 V. The greater reversibility of the redox reaction of **1** compared to Fe$(acac)_3$ may reflect the greater kinetic stabilization of the anionic reduction potential product by the more electronegative metalla-acetylacetonate ligands. The shift of +0.63 V in the reduction of **1** compared to Fe$(acac)_3$ reflects the greater electronegativity of the rhena-acetylacetonate ligands. The anodic peak at +0.55 V appears in the cyclic voltammograms of **2** and **3**, also. The assignment of this oxidation process, which is discussed below, may be related to a similar electrochemical reaction observed for the acetylacetonate complexes.

The highly irreversible reduction of Cr$(acac)_3$ occurs at –2.08 V, and the reoxidation wave of the reduction product is not observed. The polarographic $E_{1/2}$ reduction potentials of Cr$(acac)_3$ in 30% ethanol or acetonitrile solutions occur at –1.55 V and –1.81 V *vs.* SCE, respectively [7, 12]. The more negative reduction potential in methylene chloride solution appears to be a solvent effect resulting from the low dielectric constant of the solvent. A one-electron reduction has been postulated for this reaction [12].

Complex **2** undergoes reduction at –1.74 V which is 0.34 V more positive than the reduction of Cr$(acac)_3$. This shift is attributed to the greater electronegativity of the rhena-acetylacetonate ligands. If the faint anodic wave at +0.1 V is attributed to the reoxidation of Cr(Re-acac$)_3^-$, then the electron step is highly irreversible. The interpretation of this weak anodic wave is not obvious. The anodic reduction product may either exhibit irreversible electron transfer or be involved with a subsequent chemical

TABLE I. Cyclic Voltammetric Data for the Acetylacetonate and Rhena-Acetylacetonate Complexes of Fe(III), Cr(III) and Cu(II).

Complex/wave	E_p (±0.05 V)[a]	$E_{p/2}$ (±0.05 V)[b]	i_p (±5 μA)
$Fe(acac)_3$			
cathodic	−0.83	−0.69	100
anodic[c]	−0.50	−0.65	70
$Fe(Re\text{-}acac)_3$, 1			
cathodic	−0.20	−0.09	30
anodic	+0.05	−0.05	30
	+0.55	+0.48	7
$Cr(acac)_3$			
cathodic	−2.08	−1.96	10
anodic	+0.45	+0.36	30
	+1.24	+1.17	5
$Cr(Re\text{-}acac)_3$, 2			
cathodic	−1.74	−1.65	5
anodic	+0.10	−0.02	2
	+0.56	+0.49	10
	+1.40	+1.31	10
$Cu(acac)_2$			
cathodic	−1.34	−1.19	30
anodic	+0.11	−0.04	6
	+0.43	+0.36	10
	+1.01	+0.96	4
	+1.34	+1.24	30
$Cu(Re\text{-}acac)_2$, 3			
cathodic	−0.54	−0.35	55
anodic	+0.35	+0.30	35
	+0.54	+0.44	20
	+1.09	+1.02	5

[a] Recorded in methylene chloride solutions at 24 °C with 0.1 *M* tetrabutylammonium perchlorate as supporting electrolyte. All potentials are measured *vs.* the Ag/AgCl electrode. [b] Concentration of metal complex is 5×10^{-3} *M* and sweep rate is 300 mV/sec. [c] At faster scan speeds another anodic wave appears at +0.40 V (see text).

kinetic process or both. By whichever mechanism, the rhena-acetylacetonate ligand produces an observable anodic step.

The shift in reduction potential between $Cr(acac)_3$ and $Cr(Re\text{-}acac)_3$ is *ca.* one-half of the shift observed between the corresponding iron complexes. One possible explanation for this difference is that Cr(III), a d^3 metal ion, is a high-spin complex [2], which could add an electron to the d_{z^2} or $d_{x^2-y^2}$ orbitals upon reduction. These primarily σ-bonding orbitals accept electron density from the six oxygen donor atoms. However, the d^5 high-spin Fe(III) ion [2] would add an electron to one of the d_{xy}, d_{xz} or d_{yz} orbitals which have π-symmetry relative to the metal–oxygen σ bonds. Since the highly electronegative rhena moiety is presumably incorporated directly into both the σ- and π- molecular orbitals of the metalla-acetylacetonate ligand, the electronic influence of the rhena moiety would be greater in the iron complex than in the chromium complex.

Holtzclaw, *et al.*, has studied the electrochemistry of several bis(β-diketonato)copper complexes under a variety of conditions [8, 13–15]. $Cu(acac)_2$ apparently undergoes a two-electron highly irreversible reduction, as shown below.

$$Cu(acac)_2 + 2e^- \rightleftharpoons \{Cu(acac)_2^{-2}\} \longrightarrow Cu^0 + 2acac^-$$

Polarographic $E_{1/2}$ reduction potentials for $Cu(acac)_2$ as measured in water, aqueous ethanol and aqueous dioxane solutions range from −0.184 V to −0.49 V *vs.* SCE. When electronegative substituents were attached to the β-diketonate ligand the reduction potentials for the complexes became more positive. For example, the difference in reduction potential between $Cu(acac)_2$ and bis(hexafluoroacetylacetonato)copper is +0.527 V.

In methylene chloride solution we assign the cathodic wave of $Cu(acac)_2$ at −1.34 V to the two-electron irreversible reduction and the faint anodic wave at +0.11 V to the reoxidation of the reduction product. For the rhena-copper complex, **3**, the primary redox process becomes more reversible. The reduction and reoxidation waves appear at −0.54 V and +0.35 V, respectively. The cathodic to anodic peak current ratio changes from 5 for $Cu(acac)_2$ to 1.6 for complex **3**, thus indicating a more reversible process.

The very electronegative rhena moieties apparently enhance the kinetic stability of the dianionic reduction product by inhibiting reduction to copper metal and cause a +0.80 V shift in reduction potential upon replacing the acetylacetonate ligands with the rhena analogues. The difference in reduction potential between $Cu(acac)_2$ and **3** is 0.17 V greater than the difference in reduction potential between $Fe(acac)_3$ and **1**. This difference may reflect a greater influence by the electronegative rhena moieties in delocalizing the negative charge on the copper atom of **3** than on the iron atom of **1** relative to the analogous acetylacetonate complexes. A molecular orbital calculation of bis(dipivaloylmethanido)copper [16] indicates that, upon reduction, the first electron would enter a predominantly copper d orbital, but that the second electron would occupy an out-of-plane ligand orbital. The rhena groups of **3** should significantly stabilize the second electron if a similar orbital population occurs upon reduction of **3**.

As mentioned above, an anodic wave of unknown origin appears at *ca.* +0.44 V for the acetylacetonate complexes and at *ca.* +0.55 V for the rhena-acetylacetonate complexes. The constancy of the peak potentials suggests a common and closely related redox process within each class of molecule.

A study of the cyclic voltammograms of **1** and **2** at various potential-sweep widths reveals that the +0.55 V peak appears only after the reduction product is formed. Variation of the scan rate for $Fe(acac)_3$ indicated that the current associated with the +0.40 V anodic wave increased with increasing scan rate with a concomitant decrease in the current of the associated reoxidation wave. Presumably a kinetic stability factor is involved in this electrochemical redox process.

The experimental data obtained for these oxidation waves indicate that; (1) the species oxidized originates from the initial reduction reaction, (2) the concentration of the oxidized species decreases with time and the unknown species apparently converts into the orignal reduction product at the same rate, (3) the oxidation potential is independent of the central coordinating metal ion, and (4) the oxidized species derived from the acetylacetonate complexes is similar to but slightly different from that species derived from the rhena-acetylacetonate complexes.

We tentatively assign these anodic waves to a ligand-oxidation reaction. When the initial neutral complexes, ML_n, are reduced, the kinetically-controlled reduction products produced are presumed to be ML_{n-1} and L^-. These products then combine at various rates to form the thermodynamically preferred reduction product ML_n^-. With $Fe(acac)_3$ a slow scan rate permits a nearly complete formation of $Fe(acac)_3^-$ and reoxidation of this anion affords a quasi-reversible cyclic voltammogram. The difference in reversibility between $Fe(acac)_3$ and $Cr(acac)_3$ may be related to the relative stabilities of the neutral ML_{n-1} complexes. $Fe(acac)_2$ is unstable as a monomer and will polymerize in solution, while $Cr(acac)_2$ exists as a planar monomeric complex.

The copper complexes presumably undergo a two-electron reduction which complicates the above analysis. The species L^- appears to be present in the solutions of $Cu(acac)_2$ and **3**, although the kinetically-controlled reduction products may be CuL^- and L^- in this system. The anodic waves at *ca.* +1.05 V may represent the oxidation of the CuL^- species.

Using this explanation, the anodic peaks at *ca.* +0.45 V and *ca.* +0.55 V are assigned to the oxidation of $acac^-$ and Re-$acac^-$, respectively. The greater electronegativity of the rhena moiety accounts for the higher oxidation potential.

The cyclic voltammogram of Li[*cis*-$(OC)_4Re(CH_3CO)_2$] in methylene chloride solution using $[(butyl)_4N]ClO_4$ as supporting electrolyte shows an anodic wave at +0.94 V. Although a shift to more positive potentials is expected from lithium ion coordination to the Re-$acac^-$ anion [7], the observed shift of 0.39 V seems too large. An equimolar mixture of $Fe(acac)_3$ and $LiClO_4$ shifts the $Fe(acac)_3$ reduction wave only 0.27 V to more positive potential. The unexpectedly high oxidation potential for the (rhena-acetylacetonato)lithium complex makes the above assignment of the +0.45 V and +0.55 V anodic waves somewhat uncertain.

Another possibility is to assign these anodic waves to the oxidation of the neutral ML_{n-1} species generated from the dissociation of L^- from the initial reduction product ML_n^-. The ML_{n-1}^+ ion formed would then recombine with L^- to afford ML_n. This mechanism has been proposed to explain a similar anodic peak for $Fe(acac)_3$ when $LiClO_4$ is present in the solution [7]. We favor the previous assignment of these anodic waves since a coordinating cation is not present in these methylene chloride solutions, and the oxidation potentials should be dependent upon the central coordinating metal ion according to this latter assignment.

This electrochemical study does reveal a significant positive shift of reduction potential for the rhena-acetylacetonate complexes of Fe(III), Cr(III) and Cu(II) in comparison to the analogous acetylacetonate complexes. This shift is attributed to the weaker Lewis basicity of the metalla-β-diketonate ligand due to the presence of the very electronegative rhena moiety. A detailed study of the electrochemical processes following the initial reduction was not undertaken, although some tentative peak assignments are postulated. Further study of these reactions is warranted, but we do not anticipate continuing this investigation.

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References

1 Research Fellow of the Alfred P. Sloan Foundation (1979–81).

2 C. M. Lukehart and G. P. Torrence, *Inorg. Chem.*, *18*, 3150 (1979).

3 C. M. Lukehart and G. P. Torrence, *Chem. Comm.*, 183 (1978).

4 C. M. Lukehart and J. V. Zeile, *J. Amer. Chem. Soc.*, *98*, 2365 (1976).

5 P. G. Lenhert, C. M. Lukehart and L. T. Warfield, *Inorg. Chem.*, *19*, 311 (1980).

6 W. C. Fernelius and B. E. Bryant, *Inorg. Syn.*, *5*, 105 (1957).

7 R. W. Murray and L. K. Hiller, Jr., *Anal. Chem.*, *39*, 1221 (1967).

8 E. R. Nightingale, Jr. and H. F. Holtzclaw, Jr., *J. Amer. Chem. Soc.*, *81*, 3523 (1959).

9 W. R. Heineman, J. N. Burnett and R. W. Murray, *Anal. Chem.*, *40*, 1970 (1968).

10 B. K. Afghan, R. M. Dagnall and K. C. Thompson, *Talanta*, *14*, 715 (1967).

11 M. Petek and M. Branica, *J. Polarog. Soc.*, *9*, 1 (1963).

12 G. Costa and A. Puxeddu, *J. Inorg. Nucl. Chem.*, *8*, 104 (1958).

13 H. F. Holtzclaw, Jr., K. W. R. Johnson and F. W. Hengeveld, *J. Amer. Chem. Soc.*, *74*, 3776 (1952).

14 H. F. Holtzclaw, Jr., A. H. Carlson and J. P. Collman, *J. Amer. Chem. Soc.*, *78*, 1838 (1956).

15 R. L. Lintvedt, H. D. Russell and H. F. Holtzclaw, Jr., *Inorg. Chem.*, *5*, 239 (1966).

16 F. A. Cotton, C. B. Harris and J. J. Wise, *Inorg. Chem.*, *6*, 909 (1967).