CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, WAYNE STATE UNIVERSITY, DETROIT, MICHIGAN 48202,
AND BOSTON UNIVERSITY, BOSTON, MASSACHUSETTS 02215

Oxidation–Reduction Behavior of Complexes Containing Macrocyclic Ligands. An Electrochemical Comparison of Complexes with the Metals Iron through Zinc[1]

BY D. PAUL RILLEMA, JOHN F. ENDICOTT,*[2] AND ELIAS PAPACONSTANTINOU

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Complexes of macrocyclic nitrogen donor ligands (of the Curtis type) with metals iron through copper undergo one-electron oxidations or reductions in nonaqueous solvent systems. Cyclic voltammetry has been used to demonstrate that the redox couples $M^{II}L \rightleftarrows M^{I}L$ and $M^{III}L \rightleftarrows M^{II}L$ are quasi-reversible to irreversible. For $Ni^{II}L$ complexes the potential for reduction of the metal center shifts to very negative values when the ligand and metal are linked in a conjugated unsaturated system. For simpler unconjugated ligand systems (which may contain imine groups), the half-wave potentials for oxidation of $M^{I}L$ and $M^{II}L$ parallel the variations of the ionization potential of the metal. In the case of cobalt(III) complexes, values of $E_{1/2}$ for $Co^{III}LX_2 \rightarrow Co^{II}LX_2$ vary with the spectrally determined ligand field strength of X in a largely predictable manner. Complexes of the type $Co^{I}L$ have been prepared in nonaqueous solution and some of their properties are discussed.

Coordination complexes containing macrocyclic ligands play significant chemical roles in biological systems,[3] yet the chemical behavior of metal ions fixed in a more or less constant coordination environment is still poorly explored. That metals so "trapped" can behave differently from the more labile complexes has been demonstrated very recently by the preparation of nickel(I)[4] and nickel(III)[4,5] complexes containing the cyclic Schiff base and cyclic tetramine ligands (Figure 1) discovered by Curtis.[6,7] These nickel complexes were found to be sufficiently "stable" that rather complete characterization has been possible.[4] It is natural to inquire whether such behavior is characteristic of any metal in a similar coordination "trap" and whether, in such systems, the possibility of generating complexes containing metals in unusual oxidation states depends on the extent of unsaturation of the ligand.

In an earlier study we[8] noted that stereochemical stabilization of one oxidation state over another can alter reduction potentials of the $Cu(trans[14]diene)^{2+}$ [7] complexes. The possibility that unusual oxidation states may be "stabilized" by interaction of the metal center with π-ligand orbitals has recently been considered by Busch and coworkers for some related ligand systems.[9] It has also been noted that reduction potentials of metal complexes should vary with the ligand field strength of the coordinated ligands.[10–12]

The present study was undertaken with the above questions in mind. We have chosen to extend the oscillopolarographic technique described earlier[8] due to its convenience and to the detailed information which it provides concerning the reversibility of the electrochemical oxidations and reductions.

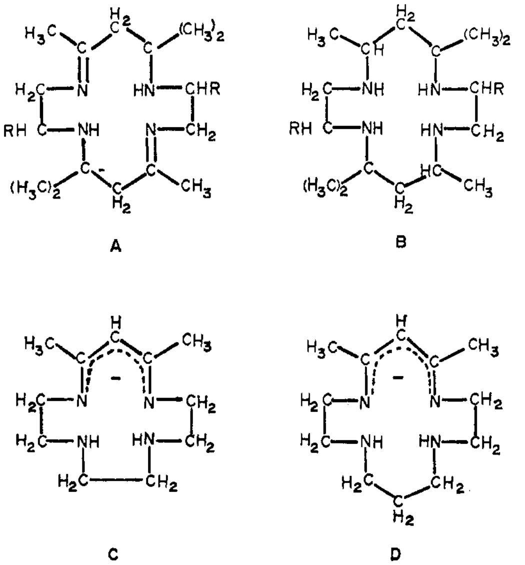

Figure 1.—Macrocyclic ligands: (A) R = H, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (*trans*[14]-diene); R = CH_3, 2,5,7,7,9,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene ($(CH_3)_2$-*trans*[14]diene); (B) R = H, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet*a* or tet*b*); R = CH_3, 2,5,7,7,9,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane ($(CH_3)_2$-tet*a*); (C) 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-diene (A[13]T); (D) 12,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-11,13-diene (A[14]T).

Experimental Section

A. **Preparation of Complexes.**—The *trans*[14]diene, tet*a*, and tet*b* ligands and their complexes with Cu^{2+}, Ni^{2+}, and Co^{3+} were prepared as described in the literature.[5, 13–17]

Ni(A[13]T)ClO_4[18] was prepared by the method of Cummings

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[2] Author to whom correspondence may be addressed at Wayne State University.

[3] For examples see (a) E. Bonnett, *Chem. Rev.*, **63**, 573 (1963); (b) J. E. Falk and J. N. Phillips in "Chelating Agent and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964; (c) J. Persall, P. Hisen, and W. E. Blumberg, Ed., "The Biochemistry of Copper, Proceedings of the Symposium on Copper in Biological Systems (1965)," Academic Press, New York, N. Y., 1966.

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[6] N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

[7] These ligands are 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (*trans*[14]diene) and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet*a* or tet*b*). See also Figure 1.

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[18] $A[13]T^-$ = 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-diene; $A[14]T^-$ = 12,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-11,13-diene. See also Figure 1.

TABLE I

HALF-WAVE POTENTIALS FROM CYCLIC VOLTAMMETRY AND POLAROGRAPHIC DIFFUSION CURRENTS AT THE RPE FOR REDUCTION AND OXIDATION OF CYCLIC COMPLEXES IN ACETONITRILE[a]

	Reduction					Oxidation			
		Cyclic voltammetry		Rpe[b]				Rpe[b]	
L	Assignment[c]	$E_{1/2}$(hde)[d]	$E_{1/2}$(spe)[e]	$E_{1/2}$	Diffusion current, μA	Assignment[c]	Cyclic voltammetry $E_{1/2}$(spe)[e]	$E_{1/2}$	Diffusion current, μA
				$Fe^{II}L^{2+}$					
trans[14]diene[f]	II → I	−1.90	−1.86			II → III[g]	0.16		
	I → II					III → II	0.15		
teta[h]	II → I	−1.92				II → III	0.18		
	I → II					III → II	0.18		
				$Co^{II}L^{2+}$ [i]					
trans[14]diene	II → I	−1.59	−1.39	−1.40	70	II → III	0.72		
	I → II	−1.19	−1.36			III → II	0.40		
trans[14]diene·$2H_2O$	II → I	−1.55	−1.40	−1.42	72	II → III	0.94	1.21	68
	I → II	−1.29	−1.39			III → II	0.31		
trans[14]diene·2py	II → I	−1.46	−1.42	1.43	76	II → III	1.06	1.44	80
	I → II	−1.25	−1.41			III → II	0.25		
teta	II → I	−1.90	−1.76			II → III	0.51		
	I → II	−1.66	−1.63			III → II	0.37		
$(CH_3)_2$-*trans*[14]diene	II → I	−1.37	−1.36	−1.33	70	II → III	0.75		
	I → II	−1.24	−1.36			III → II	0.53		
				$Ni^{II}L^{n+}$					
trans[14]diene	II → I	−1.26	−1.22	−1.23	80	II → III	1.76	2.06	76
	I → II	−1.24	−1.21			III → II	1.03		
cis[14]diene	II → I	−1.25	−1.25	−1.25	80	II → III	1.73		
	I → II	−1.24	−1.25			III → II	1.12		
$(CH_3)_2$-*trans*[14]diene	II → I	−1.21	−1.17	−1.20	80	II → III	1.92		
	I → II	−1.19	−1.16			III → II	1.22		
A[13]T^-	II → I	−2.26[j]				II → III	0.69[k]	0.73	80
	I → II	−2.15				III → II			
A[14]T^-	II → I	−2.02[j]	−2.00[j]			II → III	0.61[k]		
	I → II	−1.99	−2.00			III → II			
teta	II → I	−1.25	−1.24	−1.29	80	II → III	1.25		
	I → II	−1.22	−1.23			III → II	1.21		
tetb	II → I	−1.30	−1.25	−1.25	72	II → III	1.80		
	I → II	−1.17	−1.24			III → II	1.28		
$(CH_3)_2$teta	II → I	−1.21	−1.21	−1.22	88	II → III	1.42		
	I → II	−1.20	−1.19			III → II	1.36		
				$Cu^{II}L^{n+}$ [l]					
α-*trans*[14]diene	II → I	−0.65	−0.73			II → III	1.60		
	I → II	−0.61	−0.53			III → II	1.52		
β-*trans*[14]diene	II → I	−0.65	−0.70	−0.77	80	II → III	1.64		
	I → II	−0.59	−0.55			III → II	1.52		
teta	II → I		−0.82	−0.83	80	II → III	1.68	1.54	80
	I → II					III → II	1.54		
				$Zn^{II}L^{2+}$					
trans[14]diene[m]	II → 0	−1.64							
				$Co^{III}LX_2^{n+}$					
X				L = *trans*[14]diene					
Br	III → II		+0.17	+0.10	80	II → I	−1.45 (−1.47)[n]		
	II → III		+0.17			I → II	−1.45 (−1.31)		
Cl	III → II		−0.20	−0.20	72	II → I	−1.55	−1.80	70
	II → III		−0.17			I → II	−1.47		
N_3	III → II	−0.42	−0.45			II → I	(−1.73)		
	II → III	−0.42	−0.42			I → II	(−1.64)		
H_2O	III → II		+0.32,[o] −0.27	(+0.40	50)[q]	II → I	−1.53 (−1.61)		
	II → III		−0.23[p]	(−0.26	30)[q]	I → II	−1.50 (−1.28)		
NCS	III → II		+0.44, −0.40	−0.45	80	II → I	−1.46 (−1.54)	−1.48	70
	II → III		+0.59, +0.02			I → II	−1.45 (−1.44)		
OH, O_2CCH_3	III → II	−0.58	−0.60			II → I	−1.78 (−1.84)		
	II → III	−0.44	−0.55			I → II	−1.70		
NO_2	III → II	−0.40	−0.48			II → I	−1.66 (−1.72)		
	II → III	−0.38				I → II	−1.64		
CN	III → II	−1.10	−1.10	−1.09	80	II → I	−1.78	−1.80	60
	II → III	−1.10	−1.10			I → II	−1.68		
NH_3	III → II		−0.91			II → I	−1.45		
	II → III		−0.91			I → II	−1.43		

TABLE I (*Continued*)

	Reduction					Oxidation			
		Cyclic voltammetry		Rpe[b]				Rpe[b]	
X	Assignment[c]	$E_{1/2}$(hde)[d]	$E_{1/2}$(spe)[e]	$E_{1/2}$	Diffusion current, μA	Assignment[c]	Cyclic voltammetry $E_{1/2}$(spe)[e]	$E_{1/2}$	Diffu. current, μA
				$Co^{III}LX_2{}^{n+}$					
				L = tet*a*					
Cl[h]	III → II		−0.14	−0.08	70	II → I	(−1.94)		
	II → III		−0.14			I → II			
Br[r]	III → II		+0.06	+0.05	80	II → I			
	II → III		+0.06			I → II			
CN	III → II	−1.00[s]	−1.00[s]						
	II → III	−1.00[s]	−1.00[s]						
				L = tet*b*					
Cl	III → II		−0.17	−0.05	75				
	II → III		−0.17						

[a] $E_{1/2}$ values given in volts *vs.* sce. Anion is ClO_4^- except as indicated. [b] Rotating platinum electrode. [c] Roman numerals indicate oxidation state change of metal assigned to the polarographic wave. [d] Hanging drop mercury electrode. [e] Stationary platinum electrode. [f] Thiocyanate salt. [g] Possible ligand oxidation at ∼1.8 V. [h] Chloride salt. [i] Interference on anodic sweep due to adsorption phenomena causes a large wave at ∼−1.0 V and a weaker component at ∼−0.8 V. [j] In DMF. [k] Possible oxidation waves of ligands were observed at 1.71 V for $Ni(A[14]T)^+$ with a weak cathodic component at 1.34 V. [l] For copper complexes, reduction of the metal of I → 0 occurred at −1.37, −1.95, and −1.90 V at the spe and at −1.31, −1.38, and −0.97 V at the hde for the ligand complexes from top to bottom. Amalgam waves are ill defined but in the vicinity of −0.4 V whereas copper stripping waves are observed at −0.2 to −0.3 V. For $Cu(tet\textit{a})^{2+}$ at the hde, the reduction appears to be Cu(II) → Cu(Hg). The second reduction of Cu(tet*a*) at the rotating platinum electrode occurred at −1.5 V with a diffusion current of 80 μA. [m] Reduction of Zn(II) → Zn(Hg). Amalgam waves of Zn occurred at −0.86 V. [n] Values in parentheses were determined at the hde. Note that for cobalt(III) complexes we have listed reduction waves in this column. [o] Note similarity of potential to that obtained in the analogous cobalt(II) complex. [p] Broad peak. Peak potential was not well defined. [q] Both waves in parentheses, observed for the III → II reduction. To be compared with reductions at +0.40 and −0.26 V at spe. [r] Bromide salt. [s] DMF.

and Sievers.[19] $Ni(A[14]T)ClO_4$[18] was obtained by an extension of their procedure.[20]

[Fe(*trans*[14]diene)Cl]ClO$_4$.[21]—Anhydrous $FeCl_2$ (3.2 g), prepared by treatment of the hydrate with 2,2′-dimethoxypropane, was dissolved in 50 ml of anhydrous DMF under N_2. After the addition of 9.6 g of (*trans*[14]diene)·2HClO$_4$, the solution was heated to ∼70° for 1 hr during which time the color of the solution changed from yellow to red. The solvent was removed by vacuum distillation until a thick suspension remained. The precipitate was filtered, washed with a 1:5 methanol–ether mixture, and then dried under vacuum. An insoluble product was removed and discarded after 25 ml of DMF was added to the original material. The solvent was again removed under vacuum. Maximum product was obtained by addition of methanol followed by enough ether to cause a curdy precipitate to form. It was filtered, washed with ether, and dried under vacuum. This procedure was continued until pure product was obtained. *Anal.* Calcd for $FeCl_2C_{16}H_{32}O_4N_4$: Cl, 15.04; C, 40.77; H, 6.86; N, 11.89. Found: Cl, 14.94; C, 40.44; H, 6.70; N, 11.80.

Fe(*trans*[14]diene)(SCN)$_2$.—One gram of [Fe(*trans*[14)diene)-Cl]ClO$_4$ was suspended in 20 ml of methanol. As a 2:1 ratio of SCN^- to Fe^{II} was added, a brown precipitate formed and the solution turned from yellow to violet. The precipitate was washed with methanol and then ether before drying under vacuum. *Anal.* Calcd for $FeC_{18}H_{32}N_6S_2$: C, 47.77; H, 7.14; N, 18.58. Found: C, 47.36; H, 7.03; N, 18.19.

Fe(tet*a*)Cl$_2$.—Two grams of $FeCl_2 \cdot 4H_2O$ was added to a solution (at 70°) of 3.2 g of tet*a*·2H$_2$O in 25 ml of DMF. As the solution was allowed to cool to room temperature, a tan precipitate formed, was washed with ether, and was dried under vacuum. Failure to heat the solution resulted in the formation of a tan product which contained water as indicated by the infrared spectrum. *Anal.* Calcd for $FeCl_2C_{16}H_{36}N_2$: Cl, 17.24; C, 46.72; H, 8.88; N, 13.62. Found: Cl, 17.48; C, 45.45; H, 8.71; N, 13.16.

Co(*trans*[14]diene)(CoCl$_4$).—$CoCl_2 \cdot 4H_2O$ was dehydrated by heating at 180°. Excess $CoCl_2$ (5.1 g) was added to a 60° solution of 14.4 g of (*trans*[14]diene)·2HClO$_4$ in 60 ml of DMF. A green precipitate slowly formed. The suspension was heated for 1 additional hr before it was cooled to room temperature. The product was filtered and washed twice with a 1:2.5 methanol–ether mixture and then ether and dried under vacuum. *Anal.* Calcd for $Co_2Cl_2C_{16}H_{32}N_4$: Cl, 26.20; C, 35.60; H, 6.00; N, 10.38. Found: Cl, 26.60; C, 35.74; H, 6.17; N, 10.70.

Co(*trans*[14]diene)(ClO$_4$)$_2$.—Two grams of Co(*trans*[14]diene)-(CoCl$_4$) was dissolved in 20 ml of H_2O. Excess NH_4ClO_4 was added until precipitation of a yellow compound was complete. The compound was filtered. It was washed twice with a 1:1 ether–methanol solution and then ether. The compound was dried under vacuum. *Anal.* Calcd for $CoCl_2C_{16}H_{32}N_4O_8$: Cl, 13.17; C, 35.69; H, 6.00; N, 10.41. Found: Cl, 13.18; C, 35.86; H, 6.28; N, 10.32.

Co(*trans*[14]diene)(ClO$_4$)$_2$·2H$_2$O.—Recrystallization of Co-(*trans*[14]diene)(ClO$_4$)$_2$ from hot water resulted in the formation of the hydrated compound. *Anal.* Calcd for $CoCl_2C_{16}H_{36}N_4O_{10}$: Co, 10.26; Cl, 12.34; C, 33.45; H, 6.33; N, 9.76. Found: Co, 10.25; Cl, 12.53; C, 33.98; H, 6.16; N, 9.49.

Co(*trans*[14]diene)(ClO$_4$)$_2$·2py.—One gram of Co(*trans*[14]-diene)(ClO$_4$)$_2$ was dissolved in 10 ml of pyridine. Ten milliliters of methanol was added followed by 50 ml of ether. A yellow curdy product formed. The compound was filtered, washed with ether, and dried under vacuum. *Anal.* Calcd for $CoCl_2C_{26}H_{42}N_6O_8$: Cl, 10.18; C, 44.83; H, 6.09; N, 12.07. Found: Cl, 10.07; C, 44.17; H, 6.49; N, 11.92.

Co(tet*a*)(CoCl$_4$).—A 1.7-g sample of $CoCl_2$ was added to an ∼70° solution of tet*a*·2H$_2$O in 25 ml of DMF. During a period of 1 hr, a blue precipitate formed. The suspension was cooled to room temperature and the product was filtered. It was washed with a 1:2.5 methanol–ether solution and then ether. The compound was dried under vacuum. *Anal.* Calcd for $Co_2Cl_4C_{16}H_{36}N_4$: Cl, 26.00; C, 35.34; H, 6.67; N, 10.30. Found: Cl, 26.05; C, 35.39; H, 6.66; N, 10.24.

Co(tet*a*)(ClO$_4$)$_2$.—One gram of Co(tet*a*)(CoCl$_4$) was dissolved in 25 ml of hot H_2O. Excess NH_4ClO_4 was added until precipitation of a red compound was complete. The product was filtered from the hot solution, washed with a 1:5 methanol–ether solution and then ether, and dried under vacuum. *Anal.* Calcd for $CoCl_2C_{16}H_{36}N_4O_4$: Cl, 14.82; C, 40.17; H, 7.60; N, 11.71. Found: Cl, 14.76; C, 39.88; H, 7.33; N, 11.83.

Co((CH$_3$)$_2$-*trans*[14]diene)(ClO$_4$)$_2$.[22]—A 10.2-g sample of

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(19) (a) S. C. Cummings and R. E. Sievers, *J. Amer. Chem. Soc.*, **92**, 215 (1970); (b) S. C. Cummings and R. E. Sievers, *Inorg. Chem.*, **9**, 1131 (1970).

(20) We are indebted to Dr. S. D. Malone for the preparation of this complex.

(21) Evidence that this complex is five-coordinate has recently been reported by P. H. Merrell, V. L. Goedkin, D. H. Busch, and J. A. Stone, *J. Amer. Chem. Soc.*, **92**, 7590 (1970).

(22) (CH$_3$)$_2$-*trans*[14]diene = 2,5,7,7,9,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; (CH$_3$)$_2$tet*a* = 2,5,7,7,9,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane. See Figure 1.

$((CH_3)_2$-*trans*[14]diene)$\cdot 2HClO_4$[6] was dissolved in 50 ml of DMF. To this solution 3.4 g of $CoCl_2$ was added. As the solution was heated to 60°, a small amount of blue precipitate formed. The blue precipitate dissolved and the solution color changed from blue to red upon the addition of 35 ml of H_2O. Excess NH_4ClO_4 was added followed by 75 ml of H_2O which caused the yellow complex to precipitate. It was filtered, washed with a 1:5 methanol–ether solution and then ether, and dried under vacuum. *Anal.* Calcd for $CoCl_2C_{18}H_{38}N_4O_8$: Cl, 12.47; C, 38.03; H, 6.75; N, 9.86. Found: Cl, 12.57; C, 37.99; H, 6.52; N, 10.15.

[Co(*trans*[14]diene)$(NH_3)_2$]$Cl_2ClO_4\cdot H_2O$.—One gram of [Co(*trans*[14]diene)Cl_2]ClO_4 was added to 25 ml of liquid ammonia. The ammonia was allowed to distil off and a yellow solid remained. The infrared spectrum of the compound showed an OH stretch at 3450 cm^{-1} and two N–H stretches at 3000 cm^{-1}, plus other frequencies. The compound is stable in solution of pH 2 or less but rapidly forms a red solution above pH 3. The visible spectrum is also consistent with the formulation Co(*trans*-[14]diene)$(NH_3)_2^{3+}$ since two d–d absorptions occur at 450 and 333 nm. *Anal.* Calcd for $CoC_{12}H_{40}N_6O_5Cl_3$: C, 34.20; H, 7.19; N, 14.96; Cl, 18.92. Found: C, 34.18; H, 7.77; N, 14.38; Cl, 18.54.

Ni($(CH_3)_2$teta)$(ClO_4)_2$.[22]—Ni($(CH_3)_2$-*trans*[14]diene)$^{2+}$ formed by the addition of 2.5 g of $Ni(C_2H_3O_2)_2\cdot 4H_2O$ to 5.2 g of $(CH_3)_2$-*trans*[14]diene$\cdot 2HClO_4$,[6] in 25 ml of hot DMF. The solution was heated until the color changed from green to yellow. After the solution cooled, it was added to a saturated sodium perchlorate–water solution and the yellow Ni($(CH_3)_2$-*trans*[14]-diene)$(ClO_4)_2$ separated. The compound was dissolved in water and the ligand was reduced with sodium borohydride.[6] Curtis'[23] method was used in an attempt to separate isomers $(CH_3)_2$tet*a* and $(CH_3)_2$tet*b*. Only a small amount of Ni($(CH_3)_2$tet*b*)$(C_2O_4)_{1/2}$ (ClO_4) was obtained. Thus, the compound is predominantly the Ni($(CH_3)_2$tet*a*) isomer. *Anal.* Calcd for $NiCl_2C_{18}H_{38}N_4O_8$: Cl, 12.39; C, 37.78; H, 7.42; N, 9.79. Found: Cl, 12.45; C, 37.79; H, 7.29; N, 9.98.

B. Electrochemistry.—Oscillographic polarography was performed with a Chemtrix Model SSP-2 oscillographic polarograph. The instrument is equipped to scan the voltage ranges of 0.5, 1.0, and 2.0 V in 0.2–20 sec. The electrode system consisted of a saturated calomel reference electrode, a Brinkmann Instruments hanging drop mercury electrode (for reproducible drop size) or a platinum electrode (stationary for cyclic voltammetry; rotating for conventional polarography), and a platinum wire functioned as the third electrode. Measurements were made at 25° and in a closed vessel which was flushed with nitrogen prior to addition of the solution. Contact of the solution to the bridge compartment, which was separated from the reference electrode and solution by two medium glass frits, was made through a glass tube with a capillary tip. The solution was forced up the tube under N_2 pressure. Complex compounds were dissolved in 0.1 *M* $(CH_3CH_2)_4NClO_4$ solution. The salt bridge contained 0.1 *M* $(CH_3CH_2)_4NClO_4$ in the solvent used for electrolysis.

Conventional polarography was performed using the Sargent XXI polarograph as described previously[8] or (in nonaqueous solutions) with the Chemtrix (three-electrode) unit using a Sargent rotating platinum electrode.

Controlled-potential electrolyses were performed under N_2 and in a special H-type cell. The anode compartment consisted of a Pt wire and N_2 was bubbled through the 1 *M* LiCl solution in DMF or 0.5 *M* tetraethylammonium chloride in acetonitrile to remove O_2. The potential was controlled by a Heathkit Model IP-27 power supply. A Pt wire gauze functioned as the cathode. Electrolyzed solutions were transferred into an evacuated flask or spectophotometric cell *via* stopcocks and ground-glass joints. The flask was filled with N_2 and removed under N_2 pressure. Only a slight amount of decomposition of the most reactive species was noted.

Values of $E_{1/2}$ were obtained from cyclic voltammograms using the expression $E_{1/2} = {}^1/_2(E_p + E_{p/2})$. The "peak" potential, E_p, is the potential at maximum diffusion current and the "half-peak" potential, $E_{p/2}$, is the potential determined at half the maximum diffusion current. Half-wave potentials determined this way generally compared well with $E_{1/2}$ values from the rotating platinum electrode.

C. Experimental Techniques.—All solutions of cobalt(II) and iron(II) complexes and all solutions for electrochemical studies of the complexes were prepared under purified nitrogen. DMF and acetonitrile were dried by distillation in the presence of calcium hydride. Methanol was dried by distillation over magnesium. Solvents and air-sensitive compounds were stored under dry nitrogen.

D. Materials.—All chemicals were reagent or spectral grade. Eastman tetraethylammonium perchlorate was recrystallized six times from distilled water and once from a 1:1 acetone–methanol mixture. The purified compound was dried in a vacuum oven at 80°.

Results

A. Polarography of $M^{II}L$ Complexes.

—Our polarographic observations in nonaqueous solvents are summarized in Table I. For comparison purposes a few systems have been examined in water and these data are summarized in Table II.

TABLE II

POLAROGRAPHY OF SOME CYCLIC COMPLEXES IN AQUEOUS SOLUTION[a]

Complex	$-E_{1/2}$, V^b	Ratio of diffusion currents[c]
Cu(*trans*[14]diene)$^{2+}$	0.57	2.0
	1.43	3.7
Cu(teta)$^{2+}$	0.62	2.0
Ni(*trans*[14]diene)$^{2+}$	*d*	0
Zn(*trans*[14]diene)$^{2+}$	1.32	1.8
	1.41	2.0
Co(*trans*[14]diene)$(CN)_2^+$	0.725[e]	1.1

[a] Conventional polarography using dme, 0.1 *M* $NaClO_4$, and a citrate–biphosphate buffer (pH 6.0). [b] *Vs.* sce. [c] Relative to $Zn(NO_3)_2$ and $Cd(NO_3)_2$ standards under the same conditions. See also ref 8 for a discussion of the polarography of the copper complexes in water. [d] No reduction wave was observed for $E > -1.4$ V. In the cyclic voltammogram for this complex in water we observed a small-amplitude very irreversible wave at about -1.2 V. [e] A catalytic hydrogen wave was observed for $E < -1.2$ V.

The basis for the assignment of the polarographic waves (or "peaks" in the case of cyclic voltammetry) is largely a comparison of wave heights (*i.e.*, differences in limiting diffusion currents) as noted in Table I. Some of the nickel[4] and copper[8] systems have been rather thoroughly characterized previously. Ni(*trans*[14]diene)$^{2+}$ and Ni(teta)$^{2+}$ have been shown to undergo a one-electron reduction in acetonitrile.[4] These well-defined processes and the 2-equiv reductions of simple cadmium and zinc salts were used as standard references for the limiting diffusion currents expected for 1-equiv and 2-equiv processes, respectively. In the cases of the copper(II) and zinc(II) complexes, 2-equiv reductions were accompanied by production of the free metal (*i.e.*, an amalgam at the mercury electrode or a plate on Pt) and the anodic return sweep showed stripping (on Pt) or amalgam (on Hg) peaks characteristic of the metal (as demonstrated in similar reductions of simple salts of these metals). The observation of these stripping or amalgam waves greatly assists in assigning the observed reduction waves, particularly in the case of copper(II) complexes where one may observe a two-step reduction to the metal or a one-step reduction to the metal depending on the electrode and the solvent. In the case of cobalt complexes we have found that the stripping and amalgam waves are not well characterized and (in nonaqueous solution) depend on the salt used. For reductions of many of the cyclic complexes of cobalt(II) and nickel(II) at the mercury electrode we have observed a spike in the an-

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(23) N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).

TABLE III

VISIBLE–ULTRAVIOLET SPECTRA OF SOME COBALT AND IRON COMPLEXES[a]

Species	Absorption bonds, $10^{-3}\nu$, cm^{-1} (ϵ_{max})[a]
Co(*trans*[14]diene)(ClO_4)$_2$	6.3 (35), 22.4 (130), 29.8 (2.5×10^3), 34.5 sh
Co(*trans*[14]diene)(ClO_4)$_2$·$2H_2O$	6.3 (44), 22.3 (120), 30.3 (2.4×10^3), 34.6 (2.3×10^3)
Co(*trans*[14]diene)(ClO_4)$_2$·2py	6.3 (49), 22.3 (130), 29.0 (2.8×10^3)
Co((CH_3)$_2$-*trans*[14]diene)(ClO_4)$_2$	6.2 (20), 21.8 (100), 28.7 (2.5×10^3), 33.9 sh
Co(tet*a*)(ClO_4)$_2$	5.7 (6), 20.7 (70), 30.3 sh
Co(tet*b*)Cl(ClO_4)	5.7 (11), 16.0 (22), 19.5 (49), 20.7 (39)
[Fe(*trans*[14]diene)Cl]ClO_4	12.8 sh, 30.2 (830)
Fe(*trans*[14]diene)(SCN)$_2$	11.4 (18), 15.7 (80), 18.6 sh, 29.6 (4.8×10^3), 34.9 sh, 36.0 (3.5×10^3)
Fe(*trans*[14]diene)(SCN)$_2$[b]	17.5 (1.5×10^3), 19.1 sh, 27.0 (3.2×10^3)
Fe(tet*a*)Cl_2	16.6 (77), 18.9 (88), 28.7 (2.5×10^3)
Co(*trans*[14]diene)$^+$[c]	14.4 (2.5×10^3), 22.0 (1.2×10^3)
Co(tet*a*)$^+$[c]	14.1 (755), 19.6 (125), 23.2 sh
Fe(tet*a*)$^+$[c]	16.5 (98), 24.2 sh
Fe(*trans*[14]diene)$^+$[c]	12.4 (35), 31.8 sh

[a] In DMF except as indicated. [b] In CH_3CN. [c] ϵ values are approximate and less than or equal to actual values since the species was generated electrolytically.

odic return sweep which can be associated with a definite (more negative than −1.8 V) potential region of the cathodic sweep. However, these "spikes" which do resemble the Cu(Hg) → Cu^{2+} peak do not occur on platinum, become very large only at the slowest sweep times, are not reproducible (varying with electrode geometry), and are not associated with irreversible decomposition of the macrocyclic complexes on successive sweeping of the potential range. It must be concluded that such anomalous "spikes" are associated with an electrode or an adsorption phenomenon. We have no evidence for reduction of any of the iron, cobalt, or nickel complexes to the metal (in the nonaqueous solvents) at potentials less than about −2.5 V. In our preparative electrolysis studies we have observed that after passage of sufficient current to reduce 1 equiv of CoL^{2+} a reactive black metallic deposit, apparently cobalt metal, forms at the electrode. At about −2.5 V with the M(*trans*[14]diene)$^{2+}$ complexes we have frequently observed an extremely irreversible wave of anomalous shape. We have not determined whether these waves correspond to further reduction of the metal or the ligand or are another adsorption phenomenon.

Considerable care must be exercised in the interpretation of the Fe(*trans*[14]diene)(SCN)$_2$ systems. The visible spectra are different in DMF from what they are in acetonitrile (see Table III). Consequently one can envision different coordination environments for the complex in these solutions. Thus the values in Table I for oxidation and reduction of FeL^{2+} in acetonitrile may be for a species different from those for the same processes in DMF.

B. Direct-Current Electrolysis of $M^{II}L$ Complexes. —The electrolysis of DMF solutions of ML^{2+} with a platinum electrode has produced powerful and facile reducing agents. Solutions were approximately 0.02 *M* in complex and the current was adjusted (10–20 mA) to allow calculation of the faradays by keeping time with a stopwatch. There was always some diffusion from the cathode into the anode compartment as noted by the appearance of the respective ML^{3+} colors. Electrolysis of Co compounds beyond 1 equiv led to deposition of free cobalt at the electrode surface. Free iron was not noted under similar circumstances. In solution the color of reduced species ML^+ appears to depend upon the metal to ligand[8] charge-transfer band. For *trans*[14]diene, the Co^I species is deep blue-green compared to the yellow Co^{II} complex and the Fe^I complex is darker brown than the yellow-brown complex of Fe^{II}. The tet*a* compounds did not undergo noticeable color changes presumably because there is no low-energy charge-transfer band.

C. Oscillopolarography of *trans*-$Co^{III}LX_2$ Complexes. The cyclic voltammograms of several $Co^{III}LX_2$ complexes indicate that the $Co^{III \rightarrow II}$ reductions are far more reversible[24] than one might have expected (Table I). In general the $Co^{III \rightarrow II}$ reductions are not quite as reversible as the $M^{II \rightarrow I}$ couples reported in Table I.[24] Furthermore the peak area may be somewhat smaller for the anodic sweep than for the cathodic sweep (*e.g.*, Figure 2) indicating a slow reaction following reduction. Nevertheless, the electrochemical behavior is sufficiently reversible to argue strongly that the $Co^{III}LX_2 \rightarrow Co^{II}LX_2$ couples are involved in each half-cycle; *i.e.*, on reduction to cobalt(II) in acetonitrile, the ligands X^- are not rapidly replaced by solvent molecules. This conclusion is reinforced by our observation that the values of $E_{1/2}$ depend very strongly on the ligands X^-. In fact, one may take the oxidation peaks (—∼0.5 V) for the CoL^{2+} complexes as an indication of values of $E_{1/2}$ expected for the solvolyzed cobalt(III) complexes (*i.e.*, for CoL(AN)$_2^{3+}$).

It appears that the $Co^{II \rightarrow I}$ potential varies somewhat with ligands X^-. One extreme case is illustrated by the cyclic voltammogram of Co(*trans*[14]diene)(CN)$_2^+$ in Figure 2. The apparent $Co^{II \rightarrow I}$ wave for this com-

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[24] It should be noted however that most of the polarographic waves reported in this study are at best quasi-reversible when judged by any rigorous criterion.[25] Furthermore, the reversibility (*i.e.*, as judged by separation of peak potentials) is a function of scan time (becoming more reversible at slower sweep times) as would be expected.[25] We have recorded potentials in Table I for the slowest sweep times ($\leq$2 V sec^{-1}) in those cases that the peak positions were noticeably frequency dependent. As would be expected this dependence of peak potential on scan time was a serious problem only for the cobalt(III) complexes. However, it is very important to observe that ethylenediamine or ammine complexes of cobalt(III) generally exhibit totally irreversible reductions with no evidence for well-defined anodic peaks. (Several of these latter systems were examined by us using the same techniques as described above.) This striking difference in behavior between the cyclic amine complexes and their simpler ethylenediamine or ammine analogs suggests either a higher thermodynamic stability of the $Co^{II}LX_2$ (L a cyclic ligand) complexes or that the solvolysis reactions of the $Co^{II}LX_2$ complexes are relatively slow. We suspect that the latter is the case and are investigating the phenomenon further.

[25] R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

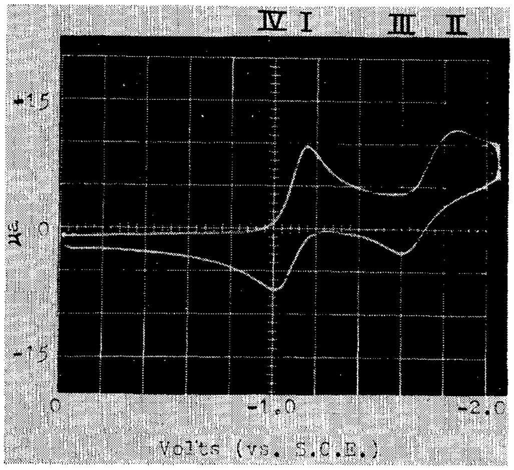

Figure 2.—Cyclic voltammogram of Co(*trans*[14]diene)$(CN)_2^+$ in acetonitrile solution, with $2.5 \times 10^{-3} M$ Co(*trans*[14]diene)-$(CN)_2^+$, 20-sec sweep time, and 0.1 *M* tetraethylammonium perchlorate. Key to waves: I, cobalt(III → II); II, cobalt(II → I); III, cobalt(I → II); IV, cobalt(II → III).

plex is more than 0.3 V more negative than the similar wave for Co(*trans*[14]diene)$^{2+}$ (Table I).[26]

In the case of *trans*-Co(*trans*[14]diene)$(OH_2)_2^{3+}$ we found what appear to be two components (Table I) to the $Co^{III \rightarrow II}$ wave. The most positive of these occurs near the potential for the $Co^{II \rightarrow III}$ wave obtained from Co(*trans*[14]diene)$^{2+}$ (Table I). Thus it seems likely that acetonitrile replaces water in the cobalt(III) coordination sphere in the time required to prepare the solutions for polarographic studies.

D. The Reduced Species, ML^+.—Dark blue solutions of (*trans*[14]diene)Co^I were produced electrolytically in DMF. Similar intensely colored solutions have been reported for vitamin B_{12s} and the cobaloxime systems which both react with alkyl halides to give cobalt(III) alkyls.[27,28] In marked contrast addition of CH_3I to (*trans*[14]diene)Co^I results in the evolution of a gas and formation of (*trans*[14]diene)Co^{II}. This behavior occurs even in the dark. At −78°, the same reaction takes place more slowly. The reaction of (*trans*[14]diene)Co^I with methyl iodide is much slower in acetonitrile requiring about 2 hr for complete reappearance of the yellow-orange cobalt(II) color.

The formation of iodide in the reaction mixture was demonstrated by addition of Ag^+ and additionally by isolation of a product from the reaction of (tet*a*)Co^I with methyl iodide in DMF. The compound gave a good analysis. *Anal.* Calcd for Co(tet*a*)I_2: C, 32.17; H, 6.08; N, 9.38; I, 42.49. Found: C, 32.45; H, 6.29; N, 9.29; I, 42.24.

Discussion

A. Polarography of ML^{2+} Complexes.—Some of our electrochemical observations suggest that caution should be exercised in making generalizations. In particular it appears that even the qualitative aspects of the electrochemistry of CuL^{2+} and NiL^{2+} depend on the solvent system and the electrode used. Our observations on the nickel(II) complexes in acetonitrile and DMF are very similar to those of Olson and Vasilevskis.[4] It appears the nickel(II) → nickel(I) potential is much more negative[29] in water than in the nonaqueous solvents. On the other hand the copper(II) reductions can occur in two 1-equiv steps at one electrode or in one 2-equiv step at a different electrode. This observation was implicit in our previous study[8] of the copper complexes but can now be clearly documented. A final point to note is that the reversibility, especially for the cobalt(II)[24] complexes, varies a great deal depending again both on the solvent and the electrode. It is also to be noted that adsorption processes were found to be a more frequent problem on mercury than on platinum in the nonaqueous solvents. Our observations with platinum electrodes in nonaqueous solvents seem more reversible and more consistent.

With the above reservations in mind, it seems evident that the larger variations in values of $E_{1/2}$ (in DMF and acetonitrile) parallel the ionization potentials of the reduced electrode species (Table IV); *i.e.*, the more readily ionizable the metal in the reduced state, the more negative is the observed value of $E_{1/2}$.

TABLE IV

COMPARISON OF IONIZATION AND HALF-WAVE POTENTIALS FOR M(*trans*[14]diene)$^{2+}$ COMPLEXES IN NONAQUEOUS SOLUTIONS

M	Ionization potential (I → II),[a] eV	$E_{1/2}$,[b] V	Ionization potential (II → III),[a] eV	$E_{1/2}$,[b] V
Fe	16.2	−1.9	30.6	0.16
Co	17.1	−1.4	33.5	0.7
Ni	19.2	−1.2	35.2	1.8
Cu	20.3	−0.6	36.8	1.6

[a] Ionization potentials taken from F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Wiley, New York, N. Y., 1966, p 797. [b] *Vs.* sce.

As a general rule it appears that the cyclic tetramine complexes are only very slightly more difficult to reduce than the Curtis diene complexes. A striking shift of $E_{1/2}$ to very negative potentials occurs for Ni(A[13]T)$^+$ and Ni(A[14]T)$^+$. This may be a manifestation of metal electron delocalization in these complexes; however, if this is the case the polarographic evidence indicates that there can be very little stabilization of nickel(II) due to this effect in Ni(*trans*[14]diene)$^{2+}$. It is further to be noted that Busch and coworkers[9a] argued that electron delocalization can account for the 0.5 V more positive value of $E_{1/2}$ of Ni(TAAB)$^{2+}$ compared to its hydrogenated analog. Since these "delicalization" effects are in opposite directions, it seems most likely that the added electron enters qualitatively different orbitals in the two cases. That is if the metal is reduced at about −2.0 V in Ni(A[13]T)$^+$, then the reduction must be mostly of the ligand in Ni(TAAB)$^{2+}$. In this regard it is of interest that we have been unable to hydrogenate the ligand of the Ni(A[13]T)$^+$ complex while Ni(TAAB)$^{2+}$ is reported[9a] to be very easily hydrogenated.

B. The ML^+ Complexes.—The CoL^+ and FeL^+ complexes are exceptionally reactive species. These

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[26] A negative shift in potentials might be expected on complexing the metal to anionic ligands. A shift of this magnitude (a few tenths of 1 V) might not be reasonable for such a change in complex charge type (as a referee suggested); however, $E_{1/2}$ for Cd^{2+} is not very sensitive to the anions present which would lead us to expect such electrostatic effects to contribute less than 0.1 V to $E_{1/2}$.

[27] G. N. Schrauzer and J. Kohnle, *Chem. Ber.*, **97**, 3056 (1966).

[28] G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, **88**, 3838 (1966).

[29] Note that our values of $E_{1/2}$ are consistently more negative (by 0.5 ± 0.1 V) in nonaqueous solvents than in water, apparently due to differences in junction potentials. There is a similar shift in the $Cd^{2+ \rightarrow 0}$ potential.

reduced species react very rapidly with O_2, protolytic solvents, and alkyl halides. Most of our observations have been on the CoL^+ complexes. It is clear that these cobalt(I) complexes do not readily react with alkyl halides to form isolable cobalt(III)–alkyl complexes. Although the failure of this reaction may be a result of insufficient electron delocalization in the cobalt complex to stabilize the cobalt(III)–alkyl bond,[27,28] the rapidity and seeming simplicity of these reactions seems more consistent with a radical reaction scheme[30]

$$CoL^+ + RX \xrightarrow{\text{fast}} CoL^{2+} + R\cdot + X^-$$

$$R\cdot + HS \xrightarrow{\text{fast}} HR + S\cdot$$

$$2R\cdot \xrightarrow{\text{fast}} R_2$$

$$CoL^{2+} + R\cdot \xrightarrow{\text{slow}} RCo^{III}L$$

where HS is a solvent species.

As noted previously[8] the low-energy charge-transfer bands of many $M(\textit{trans}[14]\text{diene})^{n+}$ ($n = 1$ or 2) complexes appear to be metal to ligand in character. Thus, for example, the $Co(\textit{trans}[14]\text{diene})^+$ species has an intense absorption band at 14.4×10^3 cm^{-1} while the $Co(\text{teta})^+$ complex does not absorb strongly in this region. It is significant that the reduced $Fe(\textit{trans}[14]\text{diene})^{2+}$ complex does not exhibit such intense absorption bands at such low energies. This suggests that it may not be possible to produce useful amounts of $(\textit{trans}[14]\text{diene})Fe^I$ by a simple electrolysis procedure. This also seems to correlate with our polarographic observations that the iron(II)–iron(I) couples are relatively irreversible.

C. A Polarographic Comparison of Cobalt(III) Complexes.—The quasi-reversibility of the $Co^{III}LX_2$ reductions (Table I) suggests that the observed values of $E_{1/2}$ vary largely as the corresponding reversible electrode potentials $E°$. The range of potentials spanned by variation of the axial ligands X is more than 1 V. The complexes in which the ligands X have relatively low ligand field strengths are reduced at relatively positive potentials. This is the qualitative trend one would expect for variations in $E°$.[10-12]

The approach of Rock[10] may be modified to allow a semiquantitative comparison of values of $E_{1/2}$ with ligand field parameters. If we adopt Rock's hypothesis that variations in $\Delta H°$ arise largely from variation in ligand field splitting energies, at least in a series of very similar complexes, then[31]

$$\Delta G° = -FE° \simeq (-2.40\Delta + 2P) - (-1.80\Delta' + P') - T\Delta S \quad (1)$$

where we have assumed the cobalt(II) species formed is spin paired.[32,33] In order to simplify Rock's expression for the present comparison we have made the following rather drastic assumptions: (1) $2\Delta' \simeq \Delta$ for the same ligands (based on comparisons of estimated ligand field strengths of cobalt(II) and cobalt(III) complexes, respectively); (2) for complexes of the type *trans*-$CoLX_2$ the total ligand field splitting parameter, Δ, is simply related to the splitting parameters for octahedral complexes with ligands X and L, respectively; thus $\Delta = {}^1/_3\Delta_X + {}^2/_3\Delta_L$; and (3) $E_{1/2} \simeq E° +$ constant. With these assumptions and setting $\Delta = 10Dq$ (so that the Wentworth and Piper[34,35] treatment may be used directly), eq 1 may be put in the form (2) where C is a

$$Dq^z \simeq 1.6E_{1/2} + C \quad (2)$$

collection of terms insensitive to changes in ligand field strength along the z axis.[36] The slope of a plot of Dq^z *vs.* $E_{1/2}$ (Figure 3) is 1.7 ± 0.2 cm^{-1} mV^{-1}.[37] The agreement is certainly satisfactory considering the assumptions involved. It is to be noted that similar data for the octahedral complexes $Co(OH_2)_6^{3+}$, $Co(NH_3)_6^{3+}$, and $Co(CN)_6^{3-}$ [38,39] are consistent with the theoretical analog of (2) with a slope of 0.5 cm^{-1} mV^{-1} and that a plot of $E_{1/2}$ *vs.* Dq^z for $Co^{III}(NH_3)_5X$ complexes[38,40] is consistent with the theoretical slope of 3.2 cm^{-1} mV^{-1}. Although Rock's correlation is not completely satisfactory in its application to a variety of cobalt(II)–

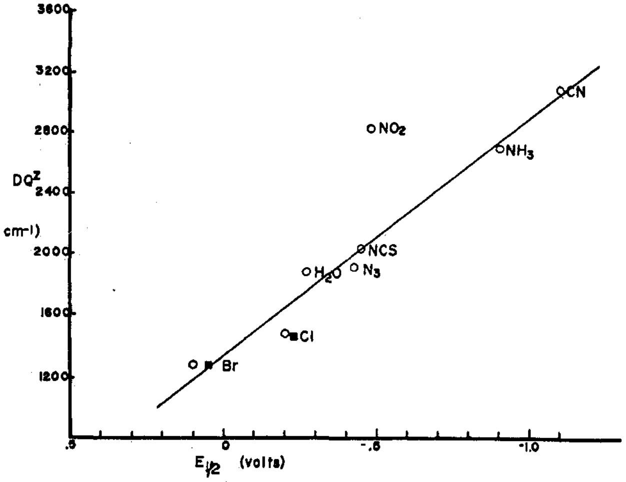

Figure 3.—Ligand field stabilization energy of X, Dq^z, *vs.* the half-wave potential, $E_{1/2}$: $Co(\textit{trans}[14]\text{diene})X_2^+$, ○; $Co(\text{teta})X_2^+$, ■.

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[30] See also L. G. Marzilli, P. A. Marzilli, and J. H. Halpern, *J. Amer. Chem. Soc.*, **92**, 5752 (1970).

[31] The primed quantities Δ' and P' are for the cobalt(II) complexes; the unprimed quantities are for cobalt(III).

[32] We have independently confirmed Warner's[33] observations that $[Co(\textit{trans}[14]\text{diene})](ClO_4)_2$ and $[Co(\text{teta})](ClO_4)_2$ are spin paired.

[33] L. E. Warner, Ph.D. Dissertation, The Ohio State University, 1968.

[34] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

[35] To obtain the values of Dq^z plotted in Figure 3, we have used the spectra of the corresponding cyclic complexes as reported in ref 6 and 14 and in this paper (note that there were some errors in the spectra reported in ref 14[6]). To extract these values of Dq^z we have set $Dq_{xy} = 2480$ and 2429 cm^{-1} for the *trans*[14]diene and teta ligands, respectively (J. A. Kernohan, Ph.D. Dissertation, Boston University, 1969), and set $C = 3800$ cm^{-1}.[33] We have also assigned the low energy absorption maximum as the energy of ^1E_a transition (Wentworth and Piper's second approximation[33]) for each complex. Our Co^{III} spectra indicate N_3^- has a crystal field strength comparable with that of Cl^-. A $Co(N_3)_4^{2-}$ complex prepared in our laboratories also has an absorption maximum at slightly higher energy than $Co(Cl_4)^{2-}$. Calculations using the ^1E_a absorption maximum produce $Dq^z = 1580$ cm^{-1} for N_3^-. A similar recalculation for NO_2^- gave it a crystal field parameter of 2800 cm^{-1}. These were the values used for N_3^- and NO_3^- in Figure 3.

[36] Note that for $Co^{III}LX_2$ and $Co^{III}(NH_3)_5X$ complexes C contains terms resulting from ligand field interactions in the xy plane (Dq_{xy}). Thus the slope in each case is a measure of the change in ligand field strength per ligand changed required to cause the potential to shift 1 mV.

[37] If one uses directly the Dq^z values listed in ref 33 for ethylenediamine complexes, there is more scatter in the correlation; the slope in this case is 1.8 ± 0.4 cm^{-1} mV^{-1}.

[38] A. A. Vleck, *Progr. Inorg. Chem.*, **5**, 270 (1963).

[39] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1952.

[40] A. A. Vleck, *Discuss. Faraday Soc.*, **26**, 164 (1958).

cobalt(III) couples,[41] it does appear that the greater part of variations in potentials of these couples as the ligands are changed does arise from the concomitant variation in ligand field stabilization energies.

The nitro complex deviates significantly from the above pattern. The discrepancy may arise partly from the use of incorrect values of Dq^z for this ligand.[35] However, it seems more likely that the above treatment is no longer even approximately true when the ligands X are not predominantly σ donors.

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CONTRIBUTION NO. 2886 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

Bismuth(I) Tetrachloroaluminate. A Spectrophotometric Study of Its Equilibrium Formation in the Gas Phase[1]

BY RICHARD A. LYNDE AND JOHN D. CORBETT*

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A new absorption band at 723 nm in the ternary system Bi(l)–BiCl$_3$(g)–AlCl$_3$(g) is shown to originate from BiAlCl$_4$(g). A value of -28.1 ± 0.5 kcal mol^{-1} for $\Delta H°_{1050}$ for the reaction BiCl(g) + AlCl$_3$(g) = BiAlCl$_4$(g) is obtained from spectral data obtained between 650 and 900° together with known data pertaining to the BiCl and AlCl$_3$ reactants. An estimated value of -42.8 ± 4 eu for $\Delta S°$ gives $K_p(1050°\text{K}) = 3.1 \times 10^{-4}$ and $\epsilon = 5.4 \times 10^4$ l. mol^{-1} cm^{-1}. Species of the type Bi$_x$AlCl$_4$, $x > 1$, are eliminated on the basis of entropy considerations and the implausibly large values of ϵ obtained. The enthalpy change for the above reaction can be accounted for well in terms of known data and a simple ionic model for Bi$^+$-AlCl$_4^-$. Several new, low-intensity bands for BiCl were observed between 1350 and 1620 nm.

Introduction

The simple bismuth(I) oxidation state has a relatively limited stability in condensed systems. The Bi$^+$ ion has been well established in dilute solution in BiCl$_3$[2,3] and in NaAlCl$_4$[4] but the simple ion evidently polymerizes at higher concentration to form Bi$_4^{4+}$ [2,3] (or Bi$_3^+$ [5]) in chloride media and Bi$_5^{3+}$ and Bi$_8^{2+}$ with tetrachloroaluminate anions.[6,7] The so-called "BiCl" which separates from concentrated solutions of metal in liquid BiCl$_3$ has been shown to be a complex structure with the stoichiometry BiCl$_{1.167}$, *viz.*, $(\text{Bi}_9^{5+})_2(\text{BiCl}_5^{2-})_2(\text{Bi}_2\text{Cl}_8^{2-})$.[8] The only example of a Bi$^+$ ion in a solid compound is in the recently discovered $\text{Bi}^+(\text{Bi}_9^{5+})(\text{HfCl}_6^{2-})_3$.[9]

The simple monochloride BiCl has a well-documented existence in the vapor phase as a minor product on reduction or decomposition of BiCl$_3$. The BiCl band system at 450 nm was first observed and correctly identified by Saper,[10] while the thermodynamics of the equilibrium of gaseous BiCl with BiCl$_3$(g) and liquid metal have been studied by Cubicciotti by transpiration techniques.[11,12]

A spectral examination of the gaseous products in the Bi–BiCl$_3$ system was originally undertaken in order to determine whether there were unreported BiCl transitions in the visible or near-ir region. This possibility was raised[13] by a tentative application of the theory of $p^2 \leftrightarrow p^2$ intraconfigurational transitions which was developed for Bi$^+$ in NaCl–AlCl$_3$ melts.[14] When such new features were not readily discernible, the study was extended to include the Bi–BiCl$_3$–AlCl$_3$ system in order to examine the possible formation of reduced bismuth tetrachloroaluminate species in the gas phase which might be important in the transport reaction of Bi$_5$(AlCl$_4$)$_3$(s).[15] Quantitative studies on the formation of gaseous adducts with aluminum chloride have been reported for neodymium(III)[16] and uranium(IV)[17] chlorides and, more recently, for calcium, magnesium, manganese, cobalt, and nickel dichlorides.[18] The principal driving force for such reactions is presumably the rather large chloride ion affinity of AlCl$_3$, $\sim 78 \pm 7$ kcal/mol.[19]

Experimental Methods

Materials.—The bismuth employed and the preparation of the trichloride were previously described.[7] The salt after three vacuum distillations was white and free of carbonaceous impurities. The aluminum trichloride was prepared from high-purity aluminum and "transistor grade" HCl as before.[20] All transfers

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