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Oxidation-Reduction Reactions of Complexes with Macrocyclic Ligands. Kinetic and Electrochemical Studies of Metal-Ligand Synergism

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Abstract: Two reaction pathways have been found for oxidations of macrocyclic β-diimine cobalt, nickel, and copper complexes with $Fe(phen)_3^{3+}$: one pathway apparently involves electron transfer from the metal, the other electron transfer from the ligand. In solutions of moderate acidity, 1.0 M $\geq [H^+] <$ 0.01 M, rates are first order in each reactant and $k_{obsd} = k_M + k_L[H^+]^{-1}$. For $Co(N_4)Cl_2^{2+}$ $k_M \sim 0$ M^{-1} s^{-1} while for $Co(N_4)(NCS)_2^+$, $Ni(N_4)^{2+}$, and $Cu(N_4)^{2+}$ finite values of k_M are found. For $Co(N_4)(NCS)_2^+$ $k_M = 155 \pm 2$ M^{-1} s^{-1} and oxidation of NCS^- is implicated. For the nickel complexes: $k_M = (3.4 \pm 0.3) \times 10^5$ M^{-1} s^{-1}, N_4 = $Me_2[14]4,7$-dieneN_4; $k_M = (7.7 \pm 0.7) \times 10^3$ M^{-1} s^{-1}, N_4 = $Me_2[13]4,6$-dieneN_4). For $Cu(Me_2[14]$-4,7-diene$N_4)^{2+}$, $k_M = (9.3 \pm 1.0) \times 10^3$ M^{-1} s^{-1}. The k_M pathway for the nickel and copper complexes must involve oxidation of the metal center, while the acid-dependent pathway is associated with oxidation of the β-diiminato ligand. Values of pK_a for these coordinated ligands vary between 6 and 9, and $Fe(phen)_3^{3+}$ oxidation of the β-diiminato ligand is inferred to be approximately diffusion limited. Thus, the intrinsic barrier for oxidation of β-diiminato moieties must be very small, and ligand oxidation in these and analogous systems can be a very important electron-transfer pathway. The larger intrinsic barrier associated with electron transfer from the metal centers is attributed to Franck-Condon factors.

The properties of most coordination complexes are well described by considering the highest occupied orbitals and lowest unoccupied oribtals to be largely localized on the central metal, with the variations in their energies being a consequence of perturbations by ligand-centered electrons. This view that the metal and ligand electrons can be treated as approximately independent may not be useful when the metal has a large electron affinity (as in high formal oxidation states), when the ligand has a very small electron affinity (as in alkyl complexes) or when the ligand has low-energy unfilled orbitals. In some instances the mixing of metal and ligand orbital systems can be directly manifested in physical and chemical properties. Such behavior has even been found in saturated systems as in a macrocyclic tetraamine complex of nickel(III) that exhibits nickel(II)-radical ligand character when the ligand is deprotonated.[2] However, this dichotomous behavior is probably more common among complexes with unsaturated ligands. Thus, Dolphin[3] has proposed that π-cation radical ligand states mediate electron-transfer reactions of some cyclochromes and Brown et al.[4] have found some evidence that the site of oxidation (i.e., at the metal or ligand) of ruthenium porphyrins can be altered merely by changing the axial ligands.

We have recently found[5] nearly quantitative formation of a C-C-coupled binuclear cobalt(II) complex, 13,13′-[[$(Me_2[14]$-4,7-diene$N_4)_2Co^{II}$], following deprotonation of the β-diimine moiety of $[Co(Me_2[14]4,7\text{-diene}N_4)Cl_2]^+$.[6] This is clearly indicative of internal β-diiminato to cobalt(III) electron transfer followed by radical-radical coupling. The ready oxidation of the β-diiminato moiety by such a mild oxidant (the $Co(N_4)Cl_2^{+,0}$ couple has $E^\circ \sim 0.28$ V vs. NHE)[5] demonstrates the similarity in energy of the metal and ligand orbitals. More recently we have been investigating the use of mild oxidants to generate a series of binuclear complexes from β-diiminato complexes in order to gain further insight into the extent of electron delocalization and the possibilities of identification of the site of oxidation in these molecules. The macrocyclic complexes that we have chosen for study contain a single β-diimine moiety. This simplifies mechanistic considerations since these molecules contain two relatively well-defined reaction centers: the metal and the single β-diimine group. In limiting cases, it is possible that oxidation at ligand or metal sites could lead to very different products. Thus, metal oxidation has often been postulated as the initial step in oxidative dehydrogenation of a ligand[2,8,9] while ligand oxidation may lead to simple products of radical-radical coupling reactions.[5,10,11] One of the fascinating features of the one-electron-oxidized β-diiminato complexes is that the highest occupied molecular orbital may be sufficiently delocalized to exhibit both metal and ligand properties.

Since the inner ring structures of porphyrinato complexes contain the equivalent of four β-diimine (or β-diiminato) moieties, the simple β-diimine complexes can serve as limiting models for multiple-site reactivity in porphyrin complexes.

Experimental Section

A. Preparation of Complexes. 1. $[Co(Me_2[14]4,7\text{-diene}N_4)Cl_2]ClO_4$.[12,13] A solution of $Co(O_2CCH_3)_2 \cdot 4H_2O$ (750 cm^3) was heated to boiling and then allowed to cool under a $Cr^{2+}(aq)^-$ scrubbed nitrogen atmosphere. After cooling to approximately 40 °C, *N,N′*-bis(2-aminoethyl)-1,3-propanediamine, 2,3,2-tet (25 g, 0.16 mol), was deoxygenated and added. Oxygen-free 2,4-pentanedione (31 g, 0.31 mol) was added after 15 min and the solution was refluxed for 5 h under N_2. After the mixture was cooled to room temperature, concentrated HCl (100 cm^3) was added. This mixture was then poured into a large open beaker containing concentrated HCl (200 cm^3) and $HClO_4$ (100 cm^3) and

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(6) Ligand abbreviations: $Me_2[14]4,7$-dieneN_4 = 5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,7-diene; $Me_2[14]$ = 4,7-dieno(1−)N_4 = 5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,7-dieno(1−); $Me_2[13]4,7$-dieneN_4 = 5,7-dimethyl-1,4,8,11-tetraazacyclotrideca-4,7-diene; $Me_2[13]4,7$-dieno(1−)N_4 = 5,7-dimethyl-1,4,8,11-tetraazacyclotrideca-4,7-dieno(1−); *o*-phen = 1,10-phenanthroline; $Me_6[14]4,11$-dieneN_4 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; [14]aneN_4 = 1,4,8,11-tetraazacyclotetradecane.

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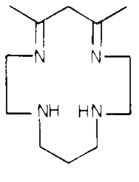
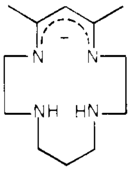
Table I. Electronic Absorption Spectra of Complexes

complex	solvent, M	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
$[Co(Me_2[14]4,7\text{-diene}N_4)Cl_2]ClO_4$	1.0, HCl	617 (34.4), 410 (68.8), 310 (2.22×10^3), 356 (1.87×10^4), 227 (1.72×10^4)
$[Co(Me_2[14]4,7\text{-diene}N_4)(OH_2)_2](PF_6)_2$	1.0, $HClO_4$ (N_2 satd.)	435 (86.8)
$[Co(Me_2[14]4,7\text{-diene}N_4)(NCS)_2]ClO_4$	1.0, $HClO_4$	522 (3.83×10^2), 340 (3.52×10^3), 222 (2.30×10^4)
$[Ni(Me_2[14]4,7\text{-diene}N_4)](ClO_4)_2$	0.1, $HClO_4$	434 (98)
	acetonitrile	435 (90), 355 (sh; 43)
$[Ni(Me_2[14]4,7\text{-dieno}(1-)N_4]ClO_4)_2$	H_2O	525 (91)
	acetonitrile	540 (101)
$[Ni(Me_2[13]4,7\text{-diene}N_4](ClO_4)_2$	0.1, $HClO_4$	400 (103)
$[Ni(Me_2[13]4,7\text{-dieno}(1-)N_4]ClO_4$	H_2O	480 (127)
	acetonitrile	490 (144)

aerated for 1 h. The green crystals (44 g, 77.8% yield) were collected and washed with 1.0 M $HClO_4$, 2-propanol, and ether.



$Me_2[14]4,7\text{-diene}N_4$



$Me_2[14]4,7\text{-dieno}(-1)N_4$

2. $[Co(Me_2[14]4,7\text{-diene}N_4)(NCS)_2]ClO_4$. A three-neck flash containing NaNCS (30 g, 0.37 mol) dissolved in 0.001 M $HClO_4$ (200 cm^3) was bubbled with nitrogen for 30 min, and $[Co(Me_2[14]4,7\text{-diene}N_4)Cl_2]ClO_4$ (15 g, 0.033 mol) was added under a stream of N_2. The solution was stirred under N_2 for 24 h at 50 °C and then allowed to cool to room temperature. Concentrated $HClO_4$ (20 cm^3) and $NaClO_4$ (50 g) were added, and the resulting red crystals (15.0 g, 0.030 mol, 90.9% yield) were washed with 1.0 M $HClO_4$, 2-propanol, and ether.

3. Nickel(II) and Copper(II) Complexes. Nickel(II) and copper(II) complexes were prepared according to literature procedures.[8,14,15] Elemental analyses of the compounds prepared are presented in Table S1.[16] Absorption spectra are summarized in Table I. The perchlorate salt of $Fe(phen)_3^{3+}$ (phen = 1,10-phenanthroline) was obtained by PbO_2[17] oxidation of $Fe(phen)_3^{2+}$.[18] Other materials were reagent-grade chemicals or purified solvents.

CAUTION. The perchlorate salts employed in this study are potentially explosive.

B. Kinetic Techniques. Solutions were prepared with water distilled in a Corning Mega-Pure still. The water was pretreated with Corning 3508-A Ultrahigh Purity Demineralizer. The resistivity of the water was monitored continuously with a glass-platinum electrode, and the demineralizer cartridge was discarded when the resistivity was less than 10^6 Ω cm.

Rate laws were determined using the isolation method.[19] The observed kinetics were pseudo first order or pseudo zero order in the rate-limiting reagent. Other reagents were either buffered or were initially at least in 5-fold excess and were systematically varied to determine the individual reaction orders. A linear regression analysis was used to resolve the actual rate constants from the appropriate concentration dependences. Standard deviations of the least-squares slope and intercept were calculated by literature methods.[20] Pseudo-first-order rate constants were obtained from the slope of $-\ln(|A_\infty - A_t|)$ vs. time plots: A_∞ was determined after 8–10 reaction half-lives. Reactions were run in an Aminco stopped-flow apparatus thermostated at 25 °C. Formation of $Fe(phen)_3^{2+}$ was monitored at 510 nm ($\epsilon_{max} = 1.11 \times 10^4$ M^{-1} cm^{-1}). For stopped-flow reactions that involved small spectral changes ($\Delta A \simeq 0.05$), $-\ln(|T_\infty - T_t|)$ was plotted vs. time. ΔT was determined by measuring the distance between T_∞ and T_t on a photograph of the oscilloscope trace of the stopped-flow photomultiplier (RCA IP28) output. When $\Delta A > 0.05$, the transmittance was converted to absorbance before plotting. Pseudo-zero-order rate constants were obtained from linear plots of absorbance vs. time. The slope of the line was divided by the difference between the molar absorptivities of the products and reactants to obtain the pseudo-zero-order rate constants.

C. Determination of Ligand pK_a for $[Co(Me_2[14]4,7\text{-diene}N_4)(X_2)]^+$ (X = Cl, NCS). The dichloro complex was dissolved in 1.0 M LiCl and the dithiocyanato complex in 1.0 M NaNCS. The Radiometer GK2321C semimicro combination electrode was fitted with a Teflon brand thermometer adapter, and a 10-cm^3 buret was inserted through a rubber serum cap in a 3-neck 100-cm^3 flask. The solution was bubbled with N_2 throughout the titration, and the temperature was maintained at 25.0 (±0.2) °C. The pH electrode was calibrated with pH 4 and 7 buffers for the dichloro complex and pH 6 and 9 buffers for the dithiocyanato complex. The titrant was aporoximately 0.1 M NaOH and 0.9 M NaX, where X is chloride or thiocyanate. The actual $[OH^-]$ was determined by titration of primary standard potassium hydrogen phthalate. The titrant was saturated with N_2 and was added in 0.2-cm^3 increments at 10-min intervals.

D. Electrochemistry. Half-wave potentials were determined by cyclic voltammetry with the Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer. Solutions were deaerated with Cr^{2+}-scrubbed N_2. Most of the studies employed a Pt-wire working electrode and a NaCl-calomel reference electrode. Purified tetraethylammonium perchlorate, or reagent grade acids were used as supporting electrolytes.

E. Photochemical Generation of Cl_2^- and $CoCl^{2+}$. These oxidants were generated in situ using flash photolysis techniques described previously.[21] Very briefly: Cl_2^- was generated by flash photolysis (xenon flash; unfiltered solution surrounding sample) of $Co(NH_3)_5Cl^{2+}$ in HCl; $CoCl^{2+}$ was generated by flash photolysis of $Co(NH_3)_5Cl^{2+}$ in HCl and Co^{2+}. Any of the thermal reactions subsequent to irradiation may be observed[21-23] by adjusting reactant concentration:

$$Co(NH_3)_5Cl^{2+} + h\nu \rightarrow Co^{2+} + 5NH_4^+ + Cl_2^-$$

$$2Cl_2^- \rightarrow Cl_2 + 2Cl^-$$

$$Cl_2^- + Co^{2+} \rightarrow CoCl^{2+} + Cl^-$$

$$Cl_2^- + M(N_4)^{2+} \rightarrow Cl\text{-}M(N_4)^{2+} + Cl^-$$

$$CoCl^{2+} + M(N_4)^{2+} \rightarrow Cl\text{-}M(N_4)^{2+} + Co^{2+}$$

In the present experiments transient transmittance changes generated in the Xenon Corp. flash photolysis apparatus have been stored in a Nicolet Explorer III digital oscilloscope. The digital data have been transmitted directly from the Explorer III to the departmental computer network for analysis using local variations on standard least-squares programs.

Results

A. Determination of Macrocyclic Ligand pK_a for $[Co(Me_2[14]4,7\text{-diene}N_4)X_2]ClO_4$ (X = Cl, NCS). The anaerobic pH titration curves for the two complexes are presented in Figures S1 and S2.[16] Kinetic measurements have implied a slow deprotonation rate ($t_{1/2} \sim 7$ s) for the dichloro complex, and it was often necessary to allow approximately 10 min for the pH reading to stabilize after each addition of base. The irregularities at the beginning of the $[Co(Me_2[14]4,7\text{-diene}N_4)(NCS)_2]^+$ titration curve are probably due to this kinetic inertness. Owing to the uncertainty of the pH in the vicinity of the half-equivalence point, the pK_a's were determined from the intercept of plots of pH vs.

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Table II. Cyclic Voltammetry of β-Diimine Complexes (25.0 ± 0.2° C)

complex	solvent	electrolyte	electrode	$E_{p,a} - E_{p,c}$,[a] mV	$E_{1/2}$,[a] V (NHE)	$E_{p,a}$,[b] V (SCE)	assignment
$[Co(Me_2[14]4,7\text{-dieneN}_4)Cl_2]^+$	H_2O	1.0 M HCl	Pt	69	+0.278		Co(III) → Co(II)
$[Co(Me_2[14]4,7\text{-dieneN}_4)(NCS)_2]^+$	H_2O	1.0 M NaNCS	Pt	120	−0.079		Co(III) → Co(II)
	H_2O	1.0 M NaNCS	HMD	73	−0.078		Co(III) → Co(II)
$Co(Me_2[14]4,7\text{-dieno}(1-)N_4)(NCS)_2$	H_2O	1.0 M NaNCS	Pt	190	−0.206		Co(III) → Co(II)
$[Co(Me_2[14]4,7\text{-dieneN}_4)(OH_2)_2]^{3+}$	H_2O	1.0 M $HClO_4$	Pt	80	+0.382		Co(III) → Co(II)
$Co(Me_2[14]4,7\text{-dieno}(1-)N_4)(NCS)_2$	DMF	0.1 M $NaClO_4$	Pt	145		⩽0.4	$L^- \to L$
	H_2O	1.0 M NaNCS	Pt	70		+0.20	$L^- \to L$
$Ni(Me_2[13]4,7\text{-dieno}(1-)N_4)^+$	DMF	0.1 M TEAP[c]	Pt			+0.62	
$Ni(Me_2[14]4,7\text{-dieneN}_4)^{2+}$	H_2O	1 M HCl	Pt			+0.80 (0.72)[d]	Ni(III) → Ni(II)
	H_2O	3 M HCl	Pt	96	1.07	+0.72[e]	Ni(III) → Ni(II)
	H_2O	6 M $HClO_4$	Pt			0.88 (0.79)[e]	Ni(III) → Ni(II)
$Ni(Me_2[14]4,7\text{-dieno}(1-)N_4)^+$	DMF	0.1 M TEAP[c]	Pt			+0.55[d]	
$Cu(Me_2[14]4,7\text{-dieneN}_4)^{2+}$	DMF	0.1 M TEAP	Pt			+0.51	
	H_2O	1 M HCl	Pt			+0.38 (0.30)[d]	
	H_2O	3 M HCl	Pt			+0.36 (0.30)[d]	
	H_2O	6 M HCl	Pt	58	+0.54	+0.320 (0.258)[d]	

[a] For quasi-reversible cyclic voltammograms for which anodic and cathodic peaks had similar amplitudes. Original measurements vs. SCE: V(SCE) = V(NHE) − 0.245. [b] For voltammograms with much smaller cathodic than anodic-peak amplitudes. $E_{p,c}$ in parentheses. Sweep rate = 50 mV s^{-1} except as indicated. [c] TEAP = tetraethylammonium perchlorate. [d] Calomel reference electrode with 1 M NaCl. [e] Sweep rate = 100 mV s^{-1}.

−log ([diene]/[dieno]) for the last 50% of the titration (Figures S3 and S4). The estimated pK_a values are 5.05 ± 0.03 and 7.64 ± 0.02 for the dichloro and dithiocyanato complexes, respectively.

B. Electrochemical (Cyclic Voltammetry) Characterization of Complexes. We have interpreted the voltammetric results (Table II) in terms of one equivalent processes. We have tended to assign the nearly acid independent, more or less quasireversible waves as largely metal centered: M(III) → M(II). The strongly pH dependent, very irreversible anodic waves have been assigned as equatorial ligand centered: $L\cdot \to L^-$. However, these "ligand"-centered anodic waves appear to be metal dependent as well as medium dependent, and the assignment must be regarded as somewhat ambiguous.

The Co(III)–Co(II) waves were found to be extremely sensitive to changes in the axial ligands as previously reported[24] and to substituents at the methine carbon of the macrocycle.[25,26] The results are listed in Table II. The Co(III)–Co(II) reduction potentials of complexes with H_2O as the axial ligands are all within the range of potentials (+0.4–+0.6 V, NHE) usually found for tetraaza-macrocyclic complexes.[9,27,28]

The electrochemical behavior of the $Cu(N_4)$ complexes has exhibited many peculiarities. In trying to work out the assignments of oxidation waves and to come to terms with the shifts of these waves in different media, we have also examined the electrochemical behavior of a series of related macrocyclic copper complexes.[30] These additional complexes all behaved in a manner similar to that reported here for $[Cu(Me_2[14]4,7\text{-dieneN}_4)]^{2+}$. The pattern of behavior may be summarized: (1) in reasonably noncomplexing media (e.g., aqueous perchlorate or DMF–perchlorate solutions) the $Cu(III)(N_4)/Cu(II)(N_4)$ couple appears to be strongly oxidizing ($E_{1/2} \geq 1.2$ V) (Figure S5) and the $Cu(II)N_4)/Cu(I)(N_4)$ couple is strongly reducing ($E_{1/2} \sim -0.7$ V)[24]; (2) in aqueous halide (Cl^- or Br^-) or pseudohalide (NCS^-) solutions the high-potential range is obscured by solvent electrochemistry, but a wave appears in the range 0.3–0.4 V vs. SCE when a platinum electrode is used. This low-potential wave approaches reversibility in concentrated halide solutions (>3 M HCl; Figure S6). However, such behavior was not observed when a carbon paste electrode was used, and similar waves were found for solutions of $CuCl_2$. We conclude that the anomalous waves at the Pt electrode are the result of complex decomposition at the electrode and that the $Cu^{III}(N_4)/Cu^{II}(N_4)$ couples are strongly oxidizing in all media. This conclusion is in accord with more extensive studies of Cu(III)–(II) couples to be published elsewhere.[32]

We attribute a very irreversible anodic wave in the range 0.65–0.85 V vs. SCE (see Table II and Figure S5) to ligand oxidation. In the $[Ni(Me_2[14]4,7\text{-dieneN}_4)]^{2+}$ complex, a quasi-reversible wave appears in this same potential range. The source of variations in this feature are not clear. Busch and co-workers have assigned very similar anodic waves of related nickel–β-diiminato complexes as "metal-centered", based in part on product ESR spectra.[33] We do detect a quasi-reversible Ni(III)–Ni(II) wave in strong acid at $E_{1/2}$ = 0.84 V vs. SCE (6 M $HClO_4$).

The metal-centered reductions of the cobalt complexes are all chemically reversible ($\Delta i_{p,c} \sim \Delta i_{p,a}$), but the cyclic voltammograms show scan rate dependent peak separations which exceed the theoretical 59 mV.[31] This irreversibility (or quasi-reversibility) is undoubtedly a consequence of the large reorganizational barriers that accompany electron transfer of the macrocyclic cobalt complexes.[8,25,31] The ligand-centered waves suffer from a different irreversibility. The ligand oxidations of $(Me_2[14]1,11\text{-dieno}(1-)N_4)M$(II or III) are all chemically irreversible in DMF. Since $i_{p,a} > i_{p,c}$, $E_{1/2}$ cannot be equated with $E°(E_{1/2} < E°)$.

C. Kinetics of $Fe(phen)_3{}^{3+}$ Oxidations of the β-Diimine Complexes. 1. $[Co(Me_2[14]4,7\text{-dieneN}_4)Cl_2]^{2+}$. The behavior of this system was quite extraordinary. At low pH the rate fitted pseudo-first-order plots very well (Figure S7), indicating that the reactions were first order in $Fe(o\text{-phen})_3{}^{3+}$. Reactions were also first order in $[Co(Me_2[14]4,7\text{-dieneN}_4)Cl_2]^+$ (Figure S8) and

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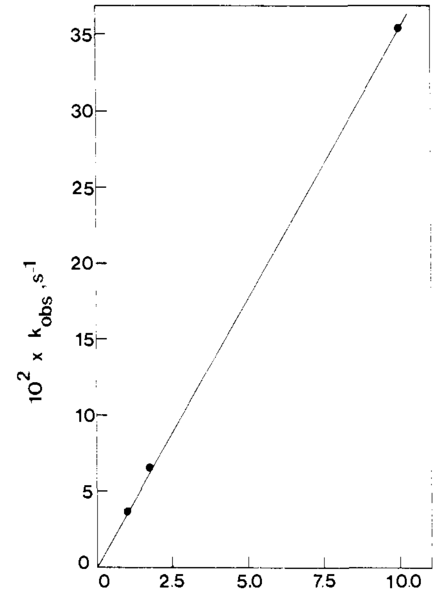

Figure 1. pH dependence of $Fe(o\text{-}phen)_3^{3+}$ oxidation of $[Co(Me_2[14]\text{-}4,7\text{-}dieneN_4)Cl_2]^+$. Plot of k_{obsd} (s^{-1}) vs. $1/[H^+]$, $[Fe(phen)_3^{3+}] = 1.0 \times 10^{-5}$ M; $[Co(Me_2[14]4,7\text{-}dieneN_4)Cl_2]^+ = 1.0 \times 10^{-4}$ M.

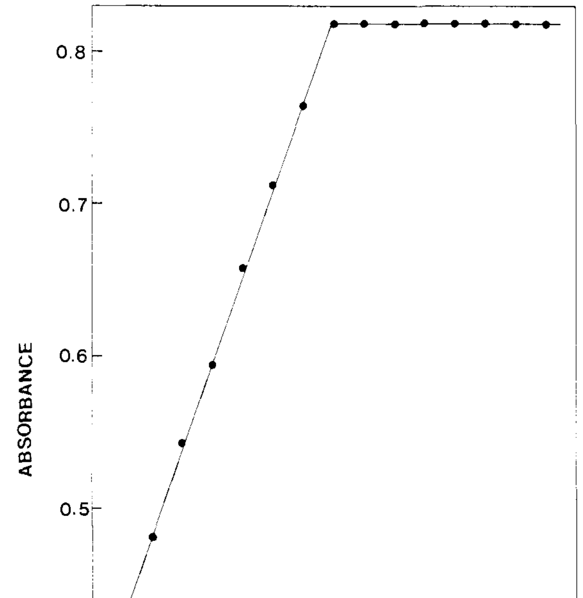

Figure 2. Sample pseudo-zero-order plot for $Fe(phen)_3^{3+}$ oxidation of $[Co(Me_2[14]4,7\text{-}dieneN_4)Cl_2]^+$. ($R = d[Fe(phen)_3^{2+}]/dt$), λ 510 nm, $[H^+] = [Fe(phen)_3^{3+}] = 10^{-4}$ M).

inverse order in $[H^+]$ (Figure 1).

As the pH was increased (pH 3–4), the reactions became zero order in $[H^+]$ and $[Fe(phen)_3^{3+}]$. A typical zero-order plot is shown in Figure 2, and the variation of the pseudo-zero-order k_{obsd} with $[Co(Me_2[14]4,7\text{-}dieneN_4)Cl_2]^+$ is shown in Figure 3. The kinetic data are summarized in Table S-II.[16]

2. **$[Co(Me_2[14]4,7\text{-}dieneN_4)(NCS)_2]^+$.** The kinetic behavior of this system was analogous to that of the dichloro complex except that there was a well-defined intercept in a plot of k_{obsd} vs. $1/[H^+]$ (Table S-IV). In the highly acidic region (1.00 M ≥ $[H^+]$ ≥ 0.10 M) $k_{obsd} = [(155 \pm 2) + (11 \pm 1)/[H^+]]\ M^{-1}\ s^{-1}$. We also found $Fe(phen)_3^{2+}$ to be formed with a pseudo-first-order rate constant of (0.9 ± 0.2) s^{-1} in a solution 1×10^{-2} M in NaNCS and 1.0×10^{-4} in $Fe(phen)_3^{3+}$ ($[HClO_4] = 1.0$ M; 25 °C).

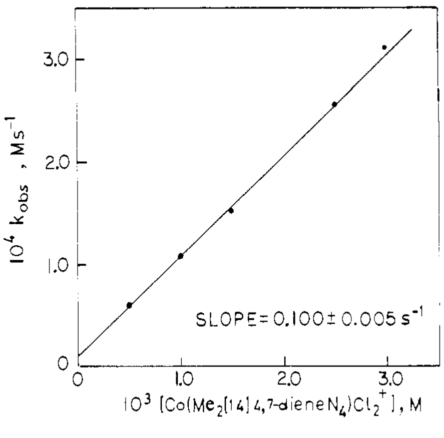

Figure 3. $[Co(L)Cl_2]^+$ dependence of $Fe(phen)_3^{3+}$ oxidation of $[Co(Me_2[14]4,7\text{-}dieneN_4)Cl_2]^+$ at zero-order limit ($[H^+] \sim [Fe(phen)_3^{3+}] = 10^{-4}$ M). Variation of pseudo-zero-order k_{obsd} with $[Co(N_4)Cl_2]^+$.

3. **$Cu^{II}(Me_2[14]4,7\text{-}dieneN_4)$.** The kinetics of the reaction of $Fe(phen)_3^{3+}$ with this complex were biphasic with a fast initial reaction ($k \sim 10^4\ M^{-1}\ s^{-1}$) and a slower ($t_{1/2} \sim 5$ s) final rate of formation of $Fe(phen)_3^{2+}$. The initial fast reaction seemed most consistant with oxidation of the copper complex while we suspect that the slower reaction corresponded to oxidation of the products of decomposition of the initial $Cu^{III}(N_4)$ species. Only a single reaction was observed for the $Ru(bpy)_3^{3+}$ oxidations of this copper(II) complex.

Discussion

The β-diimine complexes have been demonstrated to be reducing agents that are thermodynamically mild but kinetically labile. The $[Co(Me_2[14]4,7\text{-}dieneN_4)Cl_2]^+$ system has been the most thoroughly investigated. The pseudo-first-order rate constants fit well to an expression of the form

$$k_{obsd} = a[Co(N_4)Cl_2^+]/(b[H^+] + c[Fe(phen)_3^{3+}]) \quad (1)$$

Thus, for $b[H^+] > c[Fe(phen)_3^{3+}]$, the rates are first order in reactants and inversely dependent on $[H^+]$. For small $[H^+]$ the reaction rates become independent of oxidant. This behavior, and our previous observation of base-induced internal redox in this complex,[5,36] suggests that the reaction depends on ligand deprotonation to form $Co(Me_2[14]4,7\text{-}dieno(1-)N_4Cl_2$, and the following mechanistic scheme:

$$Co(N_4)Cl_2^+ \rightleftharpoons Co(N_4\text{-}H^+)Cl_2 + H^+ \qquad k_2, k_{-2}, K_2 \quad (2)$$

$$Co(N_4\text{-}H^+)Cl_2 + Fe(phen)_3^{3+} \rightleftharpoons Co(N\cdot_4)Cl_2^+ + Fe(phen)_3^{2+} \qquad k_3, k_{-3}, K_3 \quad (3)$$

$$2Co(N_4\cdot)Cl_2^+ \xrightarrow{\text{rapid}} \text{dimer} \quad (4)$$

Assuming a stationary state in $[Co(N_4\cdot)Cl_2]$,

$$k_{obsd} = k_2k_3[Co(N_4)Cl_2^+]/(k_{-2}[H^+] + k_3[Fe(phen)_3^{3+}]) \quad (5)$$

Since we have estimated $K_2 \simeq (8.9 \pm 0.4) \times 10^{-6}$ M, a fit of the kinetic parameters gives $k_2 = 0.100 \pm 0.002\ s^{-1}$, $k_{-2} = (1.1 \pm 0.1) \times 10^4\ M^{-1}\ s^{-1}$, and $k_3 = (3.9 \pm 0.3) \times 10^6\ M^{-1}\ s^{-1}$.

The derived value of k_2 seems relatively small as compared with the usual diffusion-controlled reactions of protons with bases.[37] In this case, however, the "lone pair" that interacts with the proton is delocalized over five atoms. Reactions of this type are always slower (the corresponding rate of protonation, k_{-1} for barbituric

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[36] We have also been using $FeCl_3$ as an oxidant for these complexes on a preparative scale (ref 5b and M. A. Khalifa, work in progress). The only products which we have been abble to isolate from these oxidations have been dimers coupled through carbon atoms of the macrocyclic ligands.

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Table III. Summary of Kinetic Parameters for Acid-Dependent Oxidations of β-Diimine Complexes

reductant complex	k_M, M^{-1} s^{-1} [a]	k_L, s^{-1} [a]	K_2 M	$k_3 = k_L/K_2$, M^{-1} s^{-1}
A. $Fe(phen)_3{}^{3+}$ Oxidant				
$[Co(Me_2[14]4,7\text{-diene}N_4)Cl_2]^+$	1 ± 2	34.8 ± 0.8	$\leqslant 8.9 \times 10^{-6}$ ($\mu = 1.0$)	$\geqslant 3.9 \times 10^6$
$[Co(Me_2[14]4,7\text{-diene}N_4)(NCS)_2]^+$	155 ± 2	11 ± 1	2.3×10^{-8} ($\mu = 1.0$)	5×10^8
$Ni(Me_2[14]4,7\text{-diene}N_4)^{2+}$	$(3.4 \pm 0.3) \times 10^5$	$(1.4 \pm 0.3) \times 10^4$	3.6×10^{-7} ($\mu = 0.1$)[b]	3×10^{10}
$Ni(Me_2[13]4,7\text{-diene}N_4)^{2+}$	$(7.7 \pm 0.7) \times 10^3$	$(5.4 \pm 0.5) \times 10^2$	2.8×10^{-7} ($\mu = 0.1$)[b]	2×10^9
$Cu(Me_2[14]4,7\text{-diene}N_4)^{2+}$	$(9.3 \pm 1.0) \times 10^3$ [c] (5×10^4)[c,d]		5.0×10^{-10} ($\mu = 0.10$)[b]	
B. $Co(OH_2)_5Cl^{2+}$ Oxidant				
$Ni(Me_2[14]4,7\text{-diene}N_4)^{2+}$	$(1.2 \pm 0.5) \times 10^7$ [e]	$\leqslant 2 \times 10^5$	3.6×10^{-7} ($\mu = 0.1$)	
$Cu(Me_2[14]4,7\text{-diene}N_4)^{2+}$	$\leqslant 10^6$	$\leqslant 10^6$		

[a] 1.0 M Cl^-; 25 °C. [b] Reference 14. [c] 1.5 M $HClO_4$; 25 °C. [d] $Ru(bpy)_3{}^{3+}$ oxidant. [e] Acid-independent, Cl^--independent rate constant; $k_{obsd} \times 10^{-7} = (1.2 \pm 0.5) + (3.9 \pm 0.8)[Cl^-]$ M^{-1} s^{-1}. Chloride-dependent term apparently originates from smaller charge of ion paired species in $ClO_4{}^-/Cl^-$ media.

acid, is 1×10^5 M^{-1} s^{-1}).[38] As noted below, the value of K_2 based on a simple titration $[Co(Me_2[14]4,7\text{-diene}N_4)Cl_2]^+$ may not be correct, and k_{-2} may be somewhat larger than we have estimated here.

Within the limits of experimental uncertainty, we have found no evidence for an acid-independent pathway for oxidation of $[Co(Me_2[14]4,7\text{-diene}N_4)Cl_2]^+$ ($k_M = 1 \pm 2$ M^{-1} s^{-1}). This contrasts to the behavior of most of the other β-diimine complexes. For these complexes we find

$$k_{obsd} = (k_M + k_L/[H^+])[M^{II}(N_4)] \tag{6}$$

The simplest, limiting interpretation of (6) is that k_M corresonds to oxidation of the metal while the k_L pathway corresponds to oxidation of the β-diiminato moiety of the macrocyclic ligand. Thus, $k_L = K_2k_3$; apparent values of k_3 for the nickel complexes, based on literature values of pK_2,[12] vary between 2×10^9 M^{-1} s^{-1} and 3×10^{10} M^{-1} s^{-1} (Table III). Some of this variation may result from uncertainties in K_2, some from the inevitable variations in $E_{1/2}$ for ligand oxidation. In any case, these values of k_3 are very near the expected diffusional limit ($\sim 6 \times 10^9$ M^{-1} s^{-1} for a 1+/3+ reaction)[39] and thus suggest only a small reorganizational barrier associated with the $M(N_4{-}H^+)^+/M(N_4\cdot)^{2+}$ couples.[40,41] This is expected since the negative charge would be delocalized over the chelate ring and, thus, bond lengths in the anionic and radical ligands should be similar.

While $Fe(phen)_3{}^{3+}$ oxidation at the deprotonated ligand site in $Ni(N_4)$ complexes appears to be nearly diffusion limited, one might infer that the k_L pathway involves a larger activation barrier for the cobalt complexes. The effect is not likely to be due to a relatively small magnitude for K_3, since the ligands appear to be somewhat more reducing when coordinated to cobalt than when they are coordinated to nickel (Table II). It is most likely that the discrepancy results from uncertainties in the magnitude and consistency of the values of pK_2; this is especially a problem for the $[Co(Me_2[14]4,7\text{-diene}N_4)Cl_2]^+$ complex since deprotonation is coupled with an internal redox reaction in this complex.[5] This would result in too small an estimate of pK_2 and a resulting underestimate of k_3. We believe the k_L pathway is most likely nearly diffusion limited for all these complexes.

The k_M pathway for the nickel and copper complexes is most readily attributed to oxidation of the metal center. However, the intrinsic reorganizational barriers for $Ni(N_4)^{3+,2+}$ and $Cu(N_4)^{3+,2+}$ couples seem to be relatively small, and these couples tend to be relatively oxidizing ($E^f > 1$ V). Data in Table II indicate an equilibrium constant for the $Fe(phen)_3{}^{3+}/Ni^{II}(N_4)$ reaction that implies the Ni(III)–Ni(II) self-exchange rate of $\sim 10^2$ M^{-1}/s^{-1},[42] comparable to that found for other $Ni([14]dieneN_4)^{3+,2+}$ couples.[32] On the basis of properties of the more stable $Cu(Me_6[14]4,11\text{-diene}N_4)^{3+,2+}$ couple,[32] the equilibrium constant of the $Fe(phen)_3{}^{3+}/Cu(Me_2[14]4,7\text{-diene}N_4)^{2+}$ reaction would be $\sim 10^{-5}$ and the Cu(III)–Cu(II) self-exchange rate would be 10^4–10^5 M^{-1} s^{-1}; this self-exchange parameter is similar to those found for other $Cu(N_4)^{3+,2+}$ couples. There seems little doubt that this reaction is driven by decomposition of the $Cu(N_4)^{3+}$ product. The proposed interpretation of the k_M pathway is certainly consistent with the redox properties of other nickel and copper macrocyclic complexes.

While the $CoCl^{2+}/Ni(N_4)^{2+}$ reactions appear to be inner sphere in mechanism,[32] the rapid $CoCl^{2+}/Ni(Me_2[14]4,7\text{-diene}N_4)^{2+}$ reaction does support facile metal-centered oxidations in the k_M pathway. The observed (lifetime $\sim$0.5 s in 1 M HCl) product of this and the $Cl_2{}^-$ reaction has the properties associated with Ni(III), consistent with this interpretation. Unfortunately, $Cu^{III}(N_4)$ complexes tend to be very unstable,[32] and $Cu^{III}(Me_2[14]4,7\text{-diene}N_4)$ has been the least tractable of the copper(III) complexes we have studied. The failure to observe any transients in this system leads us to believe that $Cu^{III}(N_4)$ redox chemistry dominates this system; we suspect that a substantial amount of ligand degradation occurs. Even so, the facility of $Cu(N_4)$-complex decomposition at mildly oxidizing Pt electrodes is surprising.

The two-site model for oxidation of metal–β-diiminato complexes is a useful basis for analysis of the kinetic data. However, our observations do not imply that the metal and ligand "sites" are wholly independent; this is especially a concern for the nickel and copper complexes. It appears that the final oxidation products are similar regardless of the initial electron-transfer "site".[5,7] In fact our observations (here and as reported in ref 5) argue that the $M^{III}(N_4{}^-) \rightleftharpoons M^{II}(N_4\cdot)$ equilibria are labile. A point to be noted is that, based in part on nonaqueous electrochemistry (ref 33 and this work), the $Fe(phen)_3{}^{3+}/Ni(N_4)^{2+}$ reaction appears to be nearly equipotential (we estimate $\Delta E° < 0.1$ V)[32] while the $Fe(phen)_3{}^{3+}$ $Cu(N_4)^{2+}$ reaction appears to be somewhat unfavorable ($\Delta E° \sim 0.3$ V). In order to observe the latter reactions it is necessary that the Cu(III) product be efficiently removed from the equilibrium mixture.

The existence of an alternative pathway, ligand oxidation, could greatly enhance the reactivity of complexes in which metal oxidation is associated with large reorganization barrier (e.g., cobalt complexes) or small donor–acceptor overlap. Both effects may be present in some electron-transfer enzymes.

Conclusions

One-electron oxidations of β-diiminato complexes of several metals are facile, leading to C–C coupled bis-macrocyclic, binuclear complexes. Kinetic studies with $Fe(phen)_3{}^{3+}$ as the oxidant have shown that the site of oxidation may be either the anionic ligand or the metal center, depending on the relative redox po-

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[42] Using $k(Fe) = 2 \times 10^9$ M^{-1} s^{-1} and $E° = 1.06$ V vs. NHE for $Fe(phen)_3{}^{3+,2+}$ and[40] $k_M = [k(Fe)k(Ni)Kf]^{1/2}$ where K is the equilibrium constant and $\log f = (\log K)^2/[4 \log [k(Fe)k(Ni)/Z^2]]$, $Z = 1 \times 10^{11}$ M^{-1} s^{-1}.

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tentials, the reorganizational barriers for electron transfer to the metal center, and the extent of deprotonation of the ligand. The metal-centered oxidations of $Co^{II}(N_4)$, $Ni^{II}(N_4)$, and $Cu^{II}(N_4)$ all involve appreciable barriers; in each case the barrier to electron transfer seems to be largely Franck–Condon in origin.

Registry No. $Fe(phen)_3^{3+}$, 13479-49-7; $[Co(Me_2[14]4,7\text{-diene }N_4]Cl_2]ClO_4$, 83916-53-4; $[Co(Me_2[14]4,7\text{-diene }N_4)(OH_2)_2](PF_6)_2$, 83862-34-4; $[Co(Me_2[14]4,7\text{-diene }N_4)(NCS)_2]ClO_4$, 83916-54-5; $[Ni(Me_2[14]4,7\text{-diene }N_4)](ClO_4)_2$, 83916-55-6; $[Ni(Me_2[14]4,7\text{-dieno }N_4](ClO_4)_2$, 83862-36-6; $[Ni(Me_2[13]4,7\text{-diene }N_4](ClO_4)_2$, 83862-37-7; $[Ni(Me_2[13]4,7\text{-dieno }N_4]ClO_4$, 30649-42-4; $Co(Me_2[14]4,7\text{-dieno }N_4)(NCS)_2$, 73104-21-9; $Co(Me_2[14]4,7\text{-diene }N_4)(OH_2)_2^{3+}$, 61359-48-6; $[Ni(Me_2[14]4,7\text{-diene }N_4)](PF_6)_2$, 39561-16-5; $Cu(Me_2[14]4,7\text{-diene }N_4)^{2+}$, 46754-89-6; $Co(OH_2)_5Cl^{2+}$, 83862-38-8; $[Ni(Me_2[14]4,7\text{-dieno }N_4)]PF_6$, 39042-83-6; $[Cu(Me_2[14]4,7\text{-diene }N_4)](PF_6)_2$, 39561-21-2; $[Cu(Me_2[14]4,7\text{-dieno }N_4)]PF_6$, 39561-20-1.

Supplementary Material Available: Tables of elemental analyses and kinetic data; figures of pH titrations, cyclic voltammograms, and kinetic plots (16 pages). Ordering information is given on any current masthead page.

Kinetics, Thermodynamics, and Mechanism of the Radical Chain Process for Ligand Substitution of Metal Carbonyls

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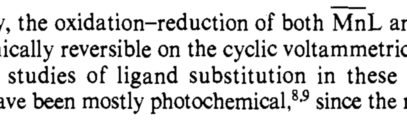
Abstract: The radical chain process for the ligand substitution of a variety of carbonylmanganese derivatives ($\overline{\text{MnL}}$) can be induced chemically or electrochemically with turnover numbers that can exceed 10^3. The catalytic cycle is initiated by electron transfer to afford the 17-electron carbonylmanganese cation $\overline{\text{MnL}}^+$. The propagation steps in the chain process are (1) the facile ligand exchange of $\overline{\text{MnL}}^+$ with the added nucleophile L to afford $\overline{\text{Mn}L}^+$ followed by (2) the reduction of $\overline{\text{Mn}L}^+$ by a homogeneous process involving cross electron exchange with $\overline{\text{MnL}}$ and/or heterogeneous electron transfer at the electrode. This carbonylmetal system is sufficiently well behaved to allow the kinetics and thermodynamics for each step of the catalytic cycle to be examined in quantitative detail by transient and bulk electrochemical techniques. Analysis of the reversible cyclic voltammograms of $\overline{\text{MnL}}$, both in the presence and in the absence of the nucleophile L, is achieved by Feldberg's digital simulation method. The computer simulation of the experimental cyclic voltammograms provides accurate values of the second-order rate constants for the rapid ligand exchange of $\overline{\text{MnL}}^+$ with a variety of added nucleophiles L. The unusual reactivity patterns for substitution in the paramagnetic $\overline{\text{MnL}}^+$ are presented in the context of previous studies with other metal carbonyls.

Ligand substitution of metal carbonyls plays a key role in the catalytic sequences of a variety of important processes leading to carbon monoxide fixation.[1,2] The conventional associative and dissociative mechanisms for such exchanges are usually considered to involve even-numbered, 16- and 18-electron intermediates.[3] Thus the recent reports of efficient chain mechanisms of ligand substitution in metal carbonyls involving odd-electron, radical intermediates merit special attention.[4,5]

Electrochemical techniques are well-suited for the study of radical chain mechanisms of ligand substitution, since the electron transfer to and from the diamagnetic metal carbonyls can be finely tuned to the electrode potential. Indeed we recently showed that electrocatalysis in the ligand substitution of a variety of otherwise stable group 6B metal carbonyls such as $(py)W(CO)_5$ is initiated by anodic oxidation to the 17-electron radical cation (i.e., $(py)W(CO)_5^+$), which is the species labile to substitution.[6] In order to probe the mechanistic details of this novel type of chain substitution, it is desirable to choose a metal carbonyl system of high catalytic efficiency and one in which the electrode process is well-behaved. Accordingly, we have focussed our attention in this paper on the carbonylmanganese derivatives $\eta^5\text{-MeCpMn(CO)}_2L$,[7] hereafter referred to as $\overline{\text{MnL}}$. The choice of this metal carbonyl was dictated by the high current efficiencies attainable for ligand substitution by various nucleophiles L at the electrode [E], i.e.:

 (1)

Importantly, the oxidation–reduction of both $\overline{\text{MnL}}$ and $\overline{\text{Mn}L}$ are electrochemically reversible on the cyclic voltammetric time scale.

Previous studies of ligand substitution in these manganese carbonyls have been mostly photochemical,[8,9] since the replacement

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