

**KINETICS OF OXIDATION OF β -DIIMINE MACROCYCLIC COMPLEXES
AND ACCESSIBILITY OF SIX-COORDINATE
COPPER(III) COMPLEXES GENERATED BY ELECTROCHEMICAL
OXIDATION OF COPPER(II) COMPLEXES.**

Mohamed A. Khalifa

Chemistry Department, Science & Mathematics Center
Makkah, P.O. Box 2064, Saudi Arabia

(Received April 3, 1989; revised December 7, 1989)

ABSTRACT. The kinetics of oxidation of macrocyclic β -diimine cobalt, nickel and copper complexes with Fe(phen) were investigated. Two reaction pathways have been found: one pathway involves electron transfer from the metal, the other electron transfer from the ligand. In solutions of moderate acidity, $1.0 \text{ M} > [\text{H}^+] > 0.01 \text{ M}$ rates are first order in each reactant and $k_{\text{obs}} = k_{\text{M}} + k_{\text{L}}/[\text{H}^+]$. Thus the site of oxidation may be either the anionic ligand (k_{L} pathway) leading to C-C coupled bis-macrocyclic, binuclear complexes, or the metal center (k_{M} pathway), depending on the relative redox potentials and the reorganization barriers for electron transfer to the metal center. In the course of this study it has been found that axial coordination of halides stabilizes the copper(III) state of copper macrocyclic complexes.

INTRODUCTION

Consideration of known substituent effects, geometry requirements, charge effects and solvent interactions were reported to be the requirements of the stabilization of unusual oxidation states of copper(0) (1) and ruthenium(IV) (2,3) macrocyclic complexes. However, π -cation radical ligand states were proposed to mediate electron transfer reactions of some cyclochromes (4). Evidence that the site of oxidation, ligand or metal, of ruthenium porphyrins can be altered by changing the axial ligands was also reported (5).

The tetraaza- β -diimine macrocyclic complexes (6) are simple class of molecules with two sites, ligand or metal, for electron transfer. The preferred site may be manipulated by protonating or deprotonating the ligand (7). To gain insight into the extent of electron delocalization and the possibilities of identification of the site of oxidation of β -diimine complexes, simple outer sphere electron transfer reactions were investigated. One of the most fascinating features of the one electron oxidized β -diimine complexes is that the highest occupied molecular orbital may be sufficiently delocalized to exhibit both metal and ligand properties.

EXPERIMENTAL

Synthesis. Cobalt, nickel and copper complexes were prepared according to literature procedures (8-13). The perchlorate salt of Fe(phen) $_3^{3+}$ (phen = 1,10-phenanthroline) was obtained by PbO $_2$ oxidation of Fe(phen) $_3^{2+}$. Other materials were reagent grade chemicals or purified solvents.

Kinetic measurements. Reactions of Fe(phen) $_3^{3+}$ with Co $^{3+}$, Ni $^{2+}$, Cu $^{2+}$ complexes of (Me $_2$ [14] 1,11-diene N $_4$) and Ni $^{2+}$ complex of (Me $_2$ [13]1,10-diene N $_4$),

were followed on an Aminco stopped flow spectrophotometer. The reactions were monitored by following the appearance of $\text{Fe}(\text{phen})_3^{2+}$ at 510 nm ($\epsilon = 1.11 \times 10^4$); and they were run under pseudo-first-order conditions with the macrocyclic complex in excess. The reactions were also examined for pH dependencies. The pseudo-first order rate constants were evaluated from plot of $-\ln(A_\infty - A_t)$ versus time. A_∞ was determined after 8-10 reaction half-lives. For stopped-flow reactions which involved small spectral changes ($\Delta A = 0.05$), $\ln(T_\infty - T_t)$ was plotted versus time (16,17). ΔT was determined by measuring the distance between T_∞ and T_t on a photomultiplier (RCA IP28) output. Standard deviations of the least-squares slope and intercept were calculated by literature methods (18).

Electrochemical measurements. Cyclic voltammetric experiments at platinum and glassy carbon disk electrodes were undertaken with a Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer as described before (1,2). A sodium chloride calomel reference electrode was employed and tetraethylammonium perchlorate, or reagent grade acids were used as supporting electrolytes.

RESULTS AND DISCUSSION

Electrochemistry. The results of the electrochemical measurements are depicted in Table 1. Oxidation of the copper(II) macrocyclic complexes have exhibited several surprising features. In trying to work out the assignments of oxidation waves and to come to terms with the shifts of these waves in different media, the electrochemical behaviour of a series of related macrocyclic copper complexes, were also examined (19). These additional complexes behaved in a manner similar to that reported here for $\text{Cu}(\text{Me}_2[14]1,11\text{-dieneN}_4)^{2+}$; details of the remaining systems will be presented elsewhere. The pattern of behaviour may be summarized: (i) in reasonably non-complexing media (e.g. aqueous perchlorate or DMF-perchlorate solutions) the $\text{Cu}(\text{II})(\text{N}_4)/\text{Cu}(\text{I})(\text{N}_4)$ couple appears to be strongly oxidizing ($E_{1/2} \geq 1.2$ V) (Fig. 1) and the $\text{Cu}(\text{II})(\text{N}_4)/\text{Cu}(\text{I})(\text{N}_4)$ couple

Table 1. Cyclic voltammetry of β -diimine complexes at 25.0 \pm 0.2°C.

Complex	Solvent	Electrolyte	Electrode	$E_p, c-E_p, a^a$ (mV)	$E_{1/2}^a$ (NHE)	E_p, a^b (SCE)
$\text{Ni}(\text{Me}_2[13]1,11\text{-dieno(-)N}_4)$	DMF	0.1 M TEAP ^c	Pt	-	-	+0.62
$\text{Ni}(\text{Me}_2[14]1,11\text{-dieneN}_4)^{2+}$	H ₂ O	1 M HCl	Pt	-	-	+0.80(0.72) ^d
	H ₂ O	3 M HCl	Pt	-	-	+0.72 ^e
$\text{Ni}(\text{Me}_2[14]1,11\text{-dieno(-)N}_4)^+$	DMF	0.1 M TEAP ^c	Pt	-	-	+0.55 ^d
$\text{Cu}(\text{Me}_2[14]1,11\text{-dieneN}_4)^{2+}$	DMF	0.1 M TEAP	Pt	-	-	+0.51
	H ₂ O	1 M HCl	Pt	-	-	+0.38(0.30) ^d
	H ₂ O	3 M HCl	Pt	-	-	+0.36(0.30) ^d
	H ₂ O	6 M HCl	Pt	58	+0.54	-
	H ₂ O	6 M HCl	GC	80	+0.526	-
$\text{Cu}(\text{Me}_2[14]1,11\text{-dieneN}_4)^+$	H ₂ O	1.0 M HClO ₄	Pt			1.08
						1.28

^aFor quasi-reversible cyclic voltammograms for which anodic and cathodic peaks had similar amplitudes. Original measurements vs. SCE: $V(\text{SCE}) = V(\text{NHE}) - 0.245$.

^bFor voltammograms with much smaller cathodic than anodic peak amplitudes. E_p, c in parenthesis. Sweep rate = 50 mv s^{-1} except as indicated.

^cTEAP = tetraethylammonium perchlorate. ^dCalomel ref. electrode with 1 M NaCl. ^eSweep rate = 100 mv s^{-1} .

is strongly reducing ($E_{1/2} \approx -0.7\text{V}$) (20); (ii) in halide (Cl^- or Br^-) or pseudo-halide (NCS^-) solutions both couples are shifted to more negative values (Fig. 2). The

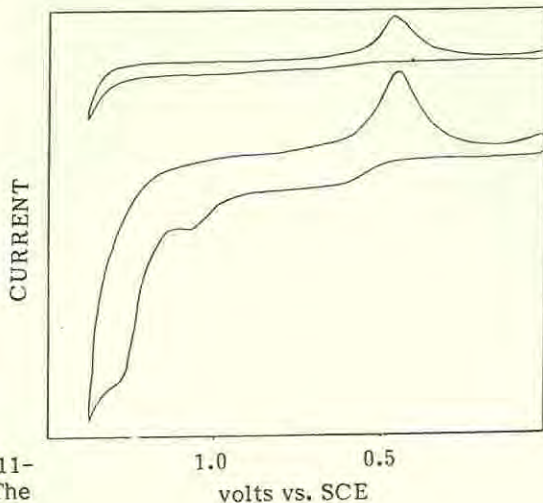


Fig. 1. Voltammograms (sweep rate, 50 mv s^{-1}) in 1.0 M HClO_4 : base line for oxidation in the perchlorate medium upper curve; $1.4 \times 10^{-3} \text{ M Cu}(\text{Me}_2[14]1,11\text{-dieneN}_4)^{2+}$, lower curve. The feature at 0.3 V on the return (cathodic) sweep in both curves is associated with the intense solvent wave at high potentials. Volts vs. SCE(NaCl).

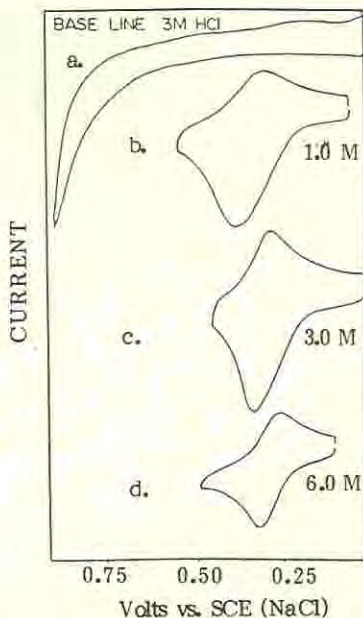


Fig. 2. Voltammograms in hydrochloric acid media (from top to bottom): base line is 3.0 M HCl (sweep rate 50 mv s^{-1}) upper curve; $2.3 \times 10^{-3} \text{ M Cu}(\text{Me}_2[14]1,11\text{-dieneN}_4)^{2+}$ in 1 M HCl (sweep rate, 50 mv s^{-1}); $2.1 \times 10^{-3} \text{ M Cu}(\text{Me}_2[14]1,11\text{-dieneN}_4)^{2+}$ in 3.0 M HCl (sweep rate, 20 mv s^{-1}); $2.4 \times 10^{-3} \text{ M Cu}(\text{Me}_2[14]1,11\text{-dieneN}_4)^{2+}$ in 6.0 M HCl (sweep rate, 20 mv s^{-1}). Volts vs. SCE (NaCl).

huge shift of the $\text{Cu(III)(N}_4\text{)}/\text{Cu(II)(N}_4\text{)}$ couple in acidic halide media was quite unexpected. The clear implication of Fig. 2 is that $\text{Cu(III)(N}_4\text{)}$ is greatly stabilized by axial coordination to Cl^- . That the $\text{Cu(III)(N}_4\text{)}/\text{Cu(II)(N}_4\text{)}$ wave becomes reversible only at high Cl^- concentration (greater than 3 M) and the large shift of $E_{1/2}$ to 0.29 V imply that the formation constants for the chloro complexes of $\text{Cu(II)(N}_4\text{)}$ are relatively small. That the $\text{Cu(II)(N}_4\text{)}/\text{Cu(I)(N}_4\text{)}$ potential also shifts to more negative potentials indicates much stronger association of

Cu(II)(N₄) than of Cu(I)(N₄) with chloride. It thus appears that Cu(N₄)Cl₂ is only weakly oxidizing; i.e., Cu(N₄)Cl₂ is a weak reducing agent.

The very irreversible anodic wave in the range 0.65 to 0.85 V vs. SCE (Fig. 1) was assigned to ligand oxidation. In the Ni(Me₂[14]1,11-dieneN₄)²⁺ complex an additional quasi-reversible wave appears in this same potential range, and was attributed to the Ni(II)(N₄) couple. Thus the Ni(II) → Ni(III) oxidation is nearly degenerate with ligand oxidation. Assignment of the redox processes corresponding to anodic waves is clearly the most ambiguous for the nickel complexes. On the other hand, Busch and co-workers (21) have assigned very similar anodic waves of related nickel complexes as metal centered. The ligand centered waves suffer from a different irreversibility. The ligand oxidations of (Me₂[14]1,11-diene(-1)N₄) are all chemically irreversible in DMF. Since $i_{p,a} > i_{p,c}$, $E_{1/2}$ cannot be equated with E° ($E_{1/2} > E^{\circ}$). The metal centered oxidations of the nickel complexes in acidic solution are also chemically irreversible ($i_{p,a} > i_{p,c}$) (22). This irreversibility is consistent with rapid ligand oxidation following the metal oxidation. As noted above, oxidations of the copper complexes are well behaved in very strong hydrochloric solutions.

Kinetic data. In solutions of moderate acidity, 1.0 M > [H⁺] > 0.01 M and at $\mu = 1.0$, the reactions of Fe(phen)₃³⁺ with the β -diimine complexes involved in this study were first order in Fe(phen)₃³⁺, first order in the β -diimine complex and inverse order in [H⁺]. There is a well defined intercept in the plot of k_{obs} vs. 1/[H⁺]. This behavior is exemplified in Figs. 3 and 4 and Table 2 for the oxidation of Cu(Me₂[14]1,11-dieneN₄)²⁺. The other systems behaved in a similar fashion.

Table 2. Fe(phen)₃³⁺ oxidation of [Cu(Me₂[14]1,11-dieneN₄)²⁺]. Summary of kinetic parameter.^a

[H ⁺] M	[CuL ²⁺] x10 ³ , M	Fe(phen) ₃ ³⁺ x10 ⁴ , M	k_{obs} x10 ¹ (s ⁻¹)	$t_{1/2}$ x10 ¹ (s)
1.00	1.947	1.006	1.62	42.78
1.00	3.750	1.006	3.55	19.52
1.00	5.893	1.006	5.37	12.91
1.006	8.250	1.006	6.93	9.99
1.006	11.79	1.006	9.91	6.99
0.50	5.884	1.006	5.60	12.38
0.10	5.936	1.062	7.51	9.23
0.03	5.910	1.062	8.65	8.01

^aAt 25.0 ± 0.2°C, $\lambda = 510$ nm, [Cl⁻] = $\mu = 1.0$ (LiCl),
Rate = $d[\text{Fe(phen)}_3^{2+}]/dt = k_{obs} [\text{Fe(phen)}_3^{3+}]$.

Table 3. Summary of kinetic parameters for acid dependent Fe(phen)₃³⁺ oxidations of β -diimine complexes.

Reductant complex	$k_M(\text{M}^{-1}\text{s}^{-1})^a$	$k_L(\text{s}^{-1})^a$	$k_2(\text{M})$	$k_L/k_2(\text{M}^{-1}\text{s}^{-1})$
Co(Me ₂ [14]1,11-dieneN ₄ (NCS) ⁺	155 ± 2	11 ± 1	2.3 × 10 ⁻⁸ ($u=1.0$)	5 × 10 ⁸
Ni(Me ₂ [14]1,11-dieneN ₄) ²⁺	(3.4 ± 0.3) × 10 ⁵	(1.4 ± 0.3) × 10 ⁴	3.6 × 10 ⁻⁷ ($u=0.1$) ^b	3 × 10 ¹⁰
Ni(Me ₂ [13]1,10-dieneN ₄) ²⁺	(7.7 ± 0.7) × 10 ³	(5.4 ± 0.5) × 10 ²	2.8 × 10 ⁻⁷ ($u=0.1$) ^b	2 × 10 ⁹
Cu(Me ₂ [14]1,11-dieneN ₄) ²⁺	87 ± 10	4 ± 1	5.0 × 10 ⁻¹⁰ ($u=0.10$) ^b	8 × 10 ⁹

^a $\mu = 1.0 = [\text{Cl}^-]$; 25°C.

^b Reference 11.

The small pH dependence of the apparent first-order rate constant; k_{obs} , Table 2 is suggestive of a variation of k_{obs} with [H⁺] where $k_{obs} = k_{obs}(\text{M}^{\text{II}}\text{ATH}_2)$, as indicated in equation 1.

$$k_{obs} = k_0 + k_1/[H^+] \quad (1)$$

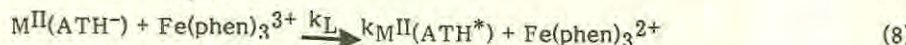
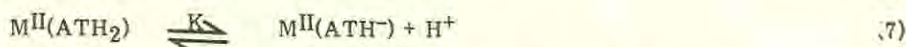
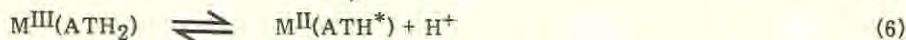
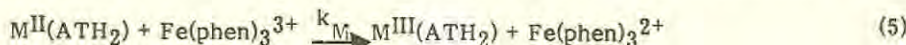
where ATH_2 represents the β -diimine moiety. A plot of k_{obs} versus $1/[\text{H}^+]$ is linear with a slope of k_1 , (s^{-1}) and intercept of k_0 , ($\text{M}^{-1}\text{s}^{-1}$) as shown in Fig. 3. The fit of this empirical rate law to these observations is described by the following rate law.

$$\frac{d(\text{Fe}(\text{phen})_3^{2+})}{dt} = (k_0 + k_1 / [\text{H}^+]) [\text{M}^{\text{II}}\text{ATH}_2] [\text{Fe}(\text{phen})_3^{2+}] \quad (2)$$

$$= k_{\text{obs}} [\text{Fe}(\text{phen})_3^{3+}] \quad (3)$$

$$k_{\text{obs}} = (k_{\text{M}} + k_{\text{L}} / [\text{H}^+]) [\text{M}^{\text{II}}(\text{ATH}_2)] \quad (4)$$

This behaviour, which falls in between the two limiting cases, metal oxidation and ligand oxidation is suggestive of the following reaction mechanism.



Hence, k_{obs} is the second order rate constant and should correspond to the slope of the linear plot of the pseudo-first order $k_{\text{obs}}(\text{s}^{-1})$ vs. $[\text{M}(\text{ATH}_2)]^{\text{II}}$, in Fig. 3, while k_{M} should correspond to the intercept of the linear plot of k_{obs} ($\text{M}^{-1}\text{s}^{-1}$) vs. $1/[\text{H}^+]$ and k_{L} correspond to the slope of this linear plot. Table 3 summarizes these kinetic parameters.

The simplest limiting interpretation of this behavior is that k_{M} corresponds to oxidation of the metal while the k_{L} pathway corresponds to oxidation of the β -diiminato moiety of the macrocyclic ligand. Thus, $k_{\text{L}} = k_{\text{L}}K$. Apparent values of k_{L} for the nickel and copper complexes, based on literature values of $\text{p}K_2$ (11), vary between $2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and $3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ as depicted in Table 3. Some of this variation may result from uncertainties in K and some from the inevitable variations in $E_{\frac{1}{2}}$ for ligand oxidation. In any case, these values of k_{L} are very near the expected diffusional limit ($\sim 6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for a 1+/3+ reaction) (23) and thus suggest only a small reorganizational barrier associated with the $\text{M}(\text{ATH})^{2+}/\text{M}(\text{ATH}^*)^{2+}$ couple (24). This is expected since the negative charge would be delocalized over the chelate ring, and bond lengths in the anionic and radical ligands should be similar.

The k_{M} pathway for the nickel and copper complexes is most readily attributed to oxidation of the metal center. Since the β -diiminato ligand tends to be oxidized in a potential range similar to that required for $\text{Ni}(\text{II}) \rightarrow \text{Ni}(\text{III})$, there is necessarily some ambiguity in assigning the site of oxidation. Nevertheless, the electrochemical oxidations do support the analysis of the kinetic data in terms of two sites for oxidation of the $\text{M}^{\text{II}}(\text{N}_4)$ complexes: (i) very irreversible oxidation in potential range 0.4 - 0.8 V vs. SCE are pH dependent and assigned as ligand centered; (ii) quasi-reversible, pH independent oxidation assigned as metal centered, cf. Table 1 and Figs. 1 and 2. These electrochemical observations indicate that $\text{Cu}(\text{Me}_2[14]1,11\text{-dieneN}_4)^{2+}$ is thermodynamically a stronger reducing agent than $\text{Ni}(\text{Me}_2[14]1,11\text{-dieneN}_4)^{2+}$ by approximately 0.4 V. Since k_{M} is larger for $\text{Ni}(\text{II})(\text{N}_4)$ than for $\text{Cu}(\text{II})(\text{N}_4)$, the electron transfer reactivity of the metal centers is reversed from the order expected on the basis of equilibrium constants for the $\text{Fe}(\text{phen})_3^{3+}$ oxidations. We entered into this study with the notion that nickel and copper couples were respectively low spin d^7/d^8 and d^8/d^9 , and that metal-axial ligand interactions would all be weak.

Fig. 3. Dependence of the Fe(phen)_3^{3+} oxidation of $\text{Cu(Me}_2[14]1,11\text{-dieneN}_4\text{)}^{2+}$ at the first-order limit ($[\text{H}^+] \gg [\text{Fe(phen)}_3^{3+}]$). Plot of $k_{\text{obs}}(\text{s}^{-1})$ vs. $\text{Cu(Me}_2[14]1,11\text{-dieneN}_4\text{)}^{2+}$.

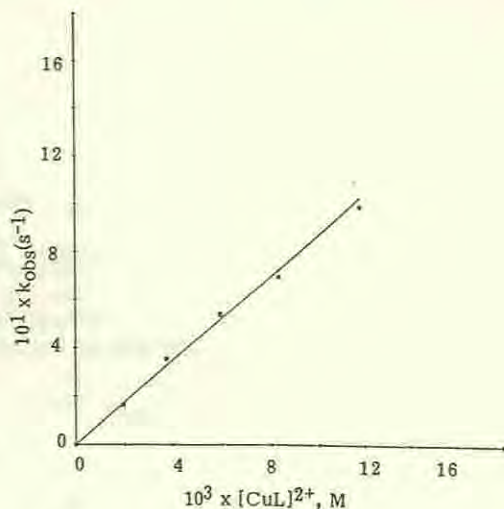
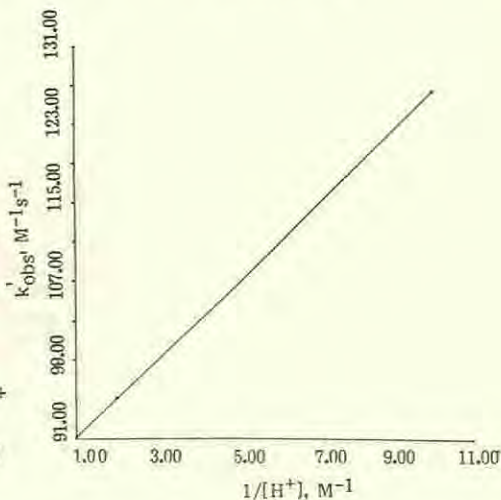


Fig. 4. pH dependence of the Fe(phen)_3^{3+} oxidation of $\text{Cu(Me}_2[14]1,11\text{-dieneN}_4\text{)}^{2+}$. Plot of $k_{\text{obs}}(\text{M}^{-1}\text{s}^{-1})$ vs. $1/[\text{H}^+]$.



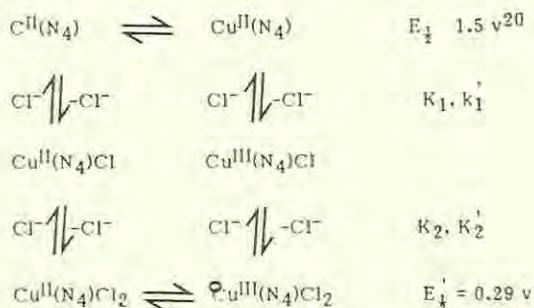
Such weak interactions would lead to small Franck-Condon barriers to electron transfer (24-27). Thus the observed values of k_M are smaller than predicted based on these assumptions. A similar situation arises for the $\text{Co(NH}_3\text{)}^{3+,2+}$ self-exchange and has been ascribed to the very small value of the two electron exchange integral $\langle V_{if} \rangle$ in a quantum mechanical model of electron transfer rates (28), $k = N_0 f(R) \cdot \langle V_{if} \rangle \cdot G(\text{F.C.})$, where $f(R)$ is a function of separation, and $G(\text{F.C.})$ is the Franck-Condon factor. The factors contributing to small values of $\langle V_{if} \rangle$ are not entirely clear at this time, but a major factor could be the effectiveness of coordinated ligands in preventing good spatial overlap of donor and acceptor orbitals. This should be a feature of the electron transfer behavior in complexes with σ^* donor and acceptor orbitals as exemplified in Co(III)-(II) couples or expected in low spin Ni(III)-(II) and Cu(III)-(II) couples. A second possible source of the large barrier to metal centered electron transfer in the nickel and copper complexes would be a large Franck-Condon factor resulting from very strong axial bonding interactions in the M(III) complexes.

Interpretation of $k_M = (3.4 \pm 0.3) \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ as the rate of metal centered oxidation of $\text{Ni}(\text{Me}_2[14]1,11\text{-dieneN}_4)^{2+}$ by $\text{Fe}(\text{phen})_3^{3+}$ leads to an apparent Ni(III)-(II) self-exchange rate constant, $k(\text{Ni}) \sim 10 \text{ M}^{-1}\text{s}^{-1}$ (24). As a consequence the Ni(III)-(II) self-exchange seems very similar to Co(III)-(II) self-exchange reactions in that the observed rate constant is a few orders of magnitude smaller than the rate constant based on Franck-Condon factor only. This is qualitatively satisfying result since both couples involve the exchange of electrons between nominally d_{z^2} orbitals.

The oxidations of $\text{Cu}(\text{Me}_2[14]1,11\text{-dieneN}_4)^{2+}$ are much more startling. The values of $k_M = 87 \pm 10 \text{ M}^{-1}\text{s}^{-1}$ and $E_1^0 = 0.34 \text{ V vs. SCE}$ imply that $k(\text{Cu}) \sim 10^{-13} \text{ M}^{-1}\text{s}^{-1}$. The dramatic inversion of reactivity from expectation, $k_M(\text{Ni}) \gg k_M(\text{Cu})$ even though $K(\text{Cu}) \gg K(\text{Ni})$ (equilibrium constants based on estimates of standard potentials), could have its source in either: (a) shielding of the $d_{x^2-y^2}$ orbital by the equatorial macrocyclic ligand resulting in an exceptionally large contribution from the electronic factor; or (b) an exceptional stability of the copper(III)-halide complexes which results in a large Franck-Condon barrier to electron transfer.

In fact the huge shift of the $\text{Cu(III)/(N}_4\text{)/Cu(II)(N}_4\text{)}$ potential in the presence of halides demonstrates that the $\text{Cu(N}_4\text{)X}_2$ complexes are very stable. A similar, but smaller, shift of the $\text{Cu(II)(N}_4\text{)/Cu(I)(N}_4\text{)}$ potential indicates that there is some halide-copper(II) axial complexation (19). That the cyclic voltammograms for the $\text{Cu(III)(N}_4\text{)/Cu(II)(N}_4\text{)}$ couples do not become reversible until the chloride concentration is very large (i.e., for $3 \text{ M} < [\text{Cl}^-] \leq 6 \text{ M}$) tends to verify that the large shift in potential in halide media is a consequence of a large difference in stability constants for axial ligation in $\text{Cu(II)(N}_4\text{)}$ and $\text{Cu(III)(N}_4\text{)}$. In terms of Scheme 1 for the $\text{Cu(III)(N}_4\text{)/Cu(II)(N}_4\text{)}$ couple in halide media, our observations demonstrate that $\beta = K_1 K_2 \ll \beta' = K_1' K_2'$; the shift in potential implies $\beta'/\beta \sim 10^{20}$. The electrochemical behavior suggests that only $[\text{Cu}^{\text{III}}(\text{N}_4)\text{Cl}_2]$ is easily oxidized. The ridiculously small value inferred for $k(\text{Cu})$ could thus be attributed to a very small $[\text{Cu}^{\text{II}}(\text{N}_4)\text{Cl}_2]$, with rapid axial exchange and larger double layer than bulk $[\text{Cl}^-]$ accounting for the observation of some electroactive species under these conditions as shown in Fig. 2. A value of $\beta < 10^{-6} \text{ M}^{-2}$ would be required to make $k(\text{Cu})$ comparable to $k(\text{Ni})$. Since K_1 must be greater than $\sim 10 \text{ M}^{-1}$ to effect a reasonable shift in the $\text{Cu(II)(N}_4\text{)/Cu(I)(N}_4\text{)}$ potential, this would suggest that $K_2 < 10^{-6}$. Since even the ion pair association constant for a +1, -1 association is larger than this, so small a value of K_2 does not provide an acceptable explanation of the small value of $k(\text{Cu})$. However, a small value ($\sim 10^{-2} \text{ M}^{-1}$) for K_2 in combination with a large $\text{Cu(N}_4\text{)Cl}_2/\text{Cu(N}_4\text{)Cl}_2$

Scheme 1.



reorganizational barrier could account for a great deal of the barrier to electron exchange in this couple. Even so, it seems likely that the $\text{Cu(N}_4\text{)Cl}_2^+/ \text{Cu(N}_4\text{)Cl}_2$ self-exchange electron transfer must be nearly as forbidden as electron exchange in the $\text{Co(en)}^{3+,2+}$ couples. Some of this forbiddenness may well derive from

in the $\text{Co(en)}_3^{3+,2+}$ couples. Some of this forbiddenness may well derive from shielding of the $d_{x^2-y^2}$ orbital. Any dependence of the intrinsic metal ion reactivity on the "stereochemistry" of the donor orbital implies a corresponding potential for selectivity in oxidation-reduction reactions. The selectivity of some metallo enzymes may have a related source. Additional studies of the redox behavior of these systems seems certainly warranted.

REFERENCES

1. A.M. Bond and M.A. Khalifa, *Inorg. Chem.*, **26**, 413 (1987).
2. A.M. Bond and M.A. Khalifa, *Aust. J. Chem.*, **41**, 1389 (1988).
3. M.A. Khalifa, *Polyhedron*, **8**(7), 851 (1989).
4. D. Dolphin, T. Niem, R.H. Felton and L. Fujita, *J. Am. Chem. Soc.*, **97**, 5288 (1975).
5. G.M. Brown, F.R. Hopf, T.J. Meyer and D.G. Whitten, *J. Am. Chem. Soc.*, **97**, 5383 (1975).
6. Ligand abbreviations:
 $\text{Me}_2[14]1,11\text{-dieneN}_4=12,14\text{-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,11-diene}$;
 $\text{Me}_2[14]1,11\text{-dieno(-1)N}_4=12,14\text{-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,11-dieno(-1)}$;
 $\text{Me}_2[13]1,10\text{-dieneN}_4=11,13\text{-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,10-diene}$;
 $\text{Me}_2[13]1,10\text{-diene; Me}_2[13]1,10\text{-dieno(-1)N}_4=11,13\text{-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,10-dieno(-1)}$.
7. C.J. Hipp, L.F. Lindoy and D.H. Busch, *Inorg. Chem.*, **11**, 1988 (1972).
8. G.W. Roberts, S.C. Cummings and J.A. Cunningham, *Inorg. Chem.*, **15**, 2503 (1976).
9. S.C. Cummings and R.E. Sievers, *J. Am. Chem. Soc.*, **92**, 215 (1970).
10. S.C. Cummings and R.E. Sievers, *Inorg. Chem.*, **9**, 1131 (1970).
11. J.G. Martin and S.C. Cummings, *Inorg. Chem.*, **12**, 1477 (1973).
12. W.H. Elfring and N.J. Rose, *Inorg. Chem.*, **14**, 2759 (1975).
13. J.C. Martin, R.M. Wei and S.C. Cummings, *Inorg. Chem.*, **3**, 475 (1972).
14. E. Pelizzetti, E. Mentastis and E. Pramauro, *Inorg. Chem.*, **15**, 2898 (1976).
15. M.H. Ford-Smith and N. Sutin, *J. Am. Chem. Soc.*, **83**, 1830 (1961).
16. R.G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes", Allyn and Bacon, Boston, p. 14, (1974).
17. A Weissberger Ed., "Techniques in Chemistry", Vol. VI Part 1, 3rd ed.; Wiley-Interscience, New York, p. 145 (1974).
18. H.D. Young, "Statistical Treatment of Experimental Data", McGraw-Hill, New York, p. 122 (1962).
19. M.A. Khalifa, unpublished work.
20. D.P. Rillema, J.F. Endicott and E. Papaconstantinou, *Inorg. Chem.*, **10**, 1739 (1971).
21. D.H. Busch, D.G. Pillsbury, F.V. Lovecchio, A.M. Tait, Y. Hung, S. Jackles, M.D. Rakowski, W.P. Schammel and L.Y. Martin, "Electrochemical Studies of Biological Systems", D.T. Sawyer Ed., American Chemical Society, Washington, D.C.; ACS Symp. Ser. No. 38, p. 32 (1977).
22. J.B. Headridge, "Electrochemical Techniques for Inorganic Chemists", Academic Press, New York, 1969.
23. V.J. Holzwarth and H. Jurgensen, *Ber. Bunsenges. Phys. Chem.*, **78**, 526 (1974).
24. (a) R.A. Marcus, *J. Chem. Phys.* **24**, 966 (1956); (b) *ibid*, *Discuss. Faraday Soc.*, **29**, 21 (1960); (c) *ibid*, *J. Phys. Chem.*, **67**, 853 (1963); (d) *ibid*, *J. Chem. Phys.*, **43**, 679 (1965); (e) *ibid*, *Annu. Rev. Phys. Chem.*, **15**, 155 (1966).
25. M.J. Heeg, M.D. Glick, J.F. Endicott and M.A. Khalifa, *Acta Cryst.*, **B 38**, 730 (1982).
26. K.H. Schmidt and A. Muller, *Inorg. Chem.*, **14**, 2183 (1975).
27. G.M. Brown and N. Sutin, *J. Am. Chem. Soc.*, **101**, 883 (1979).
28. E. Buhks, M. Bixon, J. Jortner and G. Navon, *Inorg. Chem.*, **18**, 2014 (1979).