

Oxidation of Nickel(II) and Copper(II) Macrocyclic Complexes by Chlorine Radical Anions and Monochlorocobalt(III) Ions

M. A. KHALIFA

Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt.

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Summary: Strong oxidants such as chlorine radical anions and monochlorocobalt(III) ions are generated by flash photolysis. Oxidation of nickel(II) and copper(II) tetraazamacrocyclic complexes are reported. The nickel(III) and copper(III) complexes are stable in strongly acidic aqueous solutions. Axial coordination of chloride stabilizes the copper(III) state of copper macrocyclic complexes; while nickel(III) state are stabilized at low chloride ion concentration. Thus, an outer-sphere electron-transfer mechanism was proposed for the oxidation of copper macrocyclic complexes. On the other hand, both rate patterns and spectra of the oxidation products of nickel(II) macrocyclic complexes indicate that Cl^- -bridged-inner sphere reaction pathways do occur. The mechanistic considerations were discussed and the rate law was derived for the two cases.

Introduction

One of the most fascinating features of macrocyclic ligands is the stabilization of unusual oxidation states of transition metals. Ligand effects on the thermodynamic stabilization of copper(0) [1], copper(III) and nickel(III) [2-6] and ruthenium(IV) and iron(IV) [7,8] macrocyclic complexes via chemical and electrochemical techniques has been reported. Flash photolysis of copper(II) macrocyclic complexes in solutions containing Cl^- , Br^- or NCS^- also produced longlived copper(III) transients [9,10]. Similar copper(III) transients were produced by the reaction of copper(II) complexes with radicals [9,10] such as $\text{Cl}_2\cdot$ and $\text{Br}_2\cdot$. Pulse radiolysis of nickel(II) macrocyclic complexes suggested the oxidation of nickel complexes by anion radicals [11-15] such as $\text{Br}_2\cdot^-$, $\text{Cl}_2\cdot^-$ and $(\text{SCN})_2\cdot^-$.

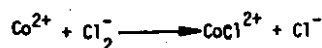
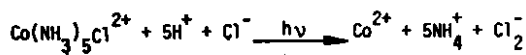
The presence of Br^- ion in the axial position of intermediates of the type $\text{Ni(III)(N}_4\text{)Br}^-$ was reported. Witburn and Laurence [13] suggested oxidation of Br^- by nickel(III) in acidic solutions.

This work is designed to study in some details the oxidation of nickel(II) and copper(II) macrocyclic complexes by chlorine radical anions and monochlorocobalt(III) ions generated by the flash photolysis. It is the goal of these studies to elucidate the reaction pathways initiated by the different oxidants and to determine the mechanisms by which these reaction pathways proceeds.

Experimental

The nickel complex of Tim was prepared as described in the literature [16] and isolated as hexafluorophosphate salt. The nickel complexes of cyclam [17], ATH_2 [18-20] as well as the nickel and the copper complexes of trans [14] diene [21] were prepared by literature procedures and were isolated as perchlorate salts. Solutions of $\text{Co(ClO}_4\text{)}_2$ and CoCl_2 were prepared from 99.999% Co powders (Aldrich).

The jacket of the photolysis cell (20 cm path-length) was filled with 0.015 M toluene in hexane to obtain a cut off at λ 265 nm. The kinetics were measured at the desired wavelength using a band pass filter to avoid the decomposition of $\text{Ni(N}_4\text{)Cl}^{2+}$, $\text{Cu(N}_4\text{)Cl}^{2+}$ and $\text{Co(NH}_3\text{)}_5\text{Cl}^{2+}$ by the xenon lamp. The oxidants were generated *in situ* using flash photolysis techniques. Chlorine radical anion $\text{Cl}_2\cdot^-$ was generated by flash photolysis of $\text{Co(NH}_3\text{)}_5\text{Cl}^{2+}$ in HCl; CoCl^{2+} was generated by flash photolysis of $\text{Co(NH}_3\text{)}_5\text{Cl}^{2+}$ in HCl and Co^{2+} .



*Ligand abbreviations: cyclam = [14] 1,4,8,11-tetraazacyclotetradecane; Tim = $\text{Me}_4[14]$ 1,4,8,11-tetraazacyclotetradeca 1,3,8,10-tetraene; ATH_2 = $\text{Me}_2[14]$ 1,4,8,11-tetraazacyclotetradeca 4,7-diene; trans[14] diene = $\text{Me}_6[14]$ 1,4,8,11-tetraazacyclotetradeca - 4,11 - diene.

The transient transmittance changes generated in the Xenon Corp. flash photolysis apparatus were stored in a Nicolet Explorer(III) digital oscilloscope. The digital data were then transmitted for analysis at a computer network using standard least squares programs.

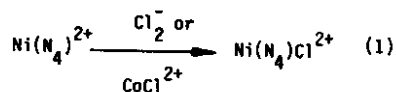
The spectra associated with Cl_2^- and CoCl_2^+ oxidation of $\text{Ni}(\text{trans [14]diene})^{2+}$, $\text{Ni}(\text{ATH}_2)^{2+}$, and $\text{Ni}(\text{Tim})^{2+}$ are given in Figure 2 showing λ_{max} at 310 - 350 nm. This spectra is similar to the $\text{Ni}(\text{cyclam})\text{Cl}^{2+}$ spectrum. Accordingly, the product of the oxidation of $\text{Ni}(\text{trans [14]diene})^{2+}$, $\text{Ni}(\text{ATH}_2)^{2+}$ and $\text{Ni}(\text{Tim})^{2+}$ in acidic media in presence of chloride by Cl_2^- and CoCl_2^+ is the monochlorocomplexes $\text{Ni}(\text{trans [14]diene})\text{Cl}^{2+}$, $\text{Ni}(\text{ATH}_2)\text{Cl}^{2+}$ and $\text{Ni}(\text{Tim})\text{Cl}^{2+}$ as showing by equation 1. These monochlorocomplexes hereafter will be referred to as $\text{Ni}(\text{N}_4)\text{Cl}^{2+}$ and their precursor macrocyclic complexes as $\text{Ni}(\text{N}_4)^{2+}$.

Results and Discussion

α -Nickel Complexes:

For each macrocyclic system investigated, the kinetics were monitored through the following sequential steps: (a) formation of Cl_2^- or CoCl_2^+ (b) disappearance of Cl_2^- or CoCl_2^+ by reaction with the macrocyclic complex to form a transient oxidation product; (c) transformation of this transient

product into a relatively long - lived intermediate. Transmittance against time curves for the flash photolysis of $\text{Ni}(\text{trans[14]diene})^{2+}$ complex at (a) 0.001 M $[\text{Cl}^-]$ and (b) 0.90 M $[\text{Cl}^-]$ is shown in Figure 1. These kinetic runs indicate, that, at low chloride concentration the nickel(III) complex is much more stable than at high chloride concentration. Oxidation of $\text{Ni}(\text{cyclam})^{2+}$ by either Cl_2^- or CoCl_2^+ produces a transient with λ_{max} at 308 nm. The shape of the spectrum and the position of λ_{max} are similar to those previously reported by Haines and McAuley [22] for the $\text{Ni}(\text{cyclam})\text{Cl}^{2+}$. Thus, the product of oxidation of $\text{Ni}(\text{cyclam})^{2+}$ by Cl_2^- or CoCl_2^+ is consistent with the formation of $\text{Ni}(\text{cyclam})\text{Cl}^{2+}$.



The oxidation reactions of $\text{Ni}(\text{N}_4)^{2+}$ complexes by Cl_2^- and CoCl_2^+ are sufficiently rapid for the mechanisms of the reactions to be established from observations of the initial Ni^{3+} products. Moreover, the initial products of the reactions between Cl_2^- or CoCl_2^+ and the $\text{Ni}(\text{N}_4)\text{Cl}^{2+}$ complexes are shown to be $\text{Ni}(\text{N}_4)\text{Cl}^{2+}$ complexes. Therefore reaction (1) must be written as in (2) and (3).

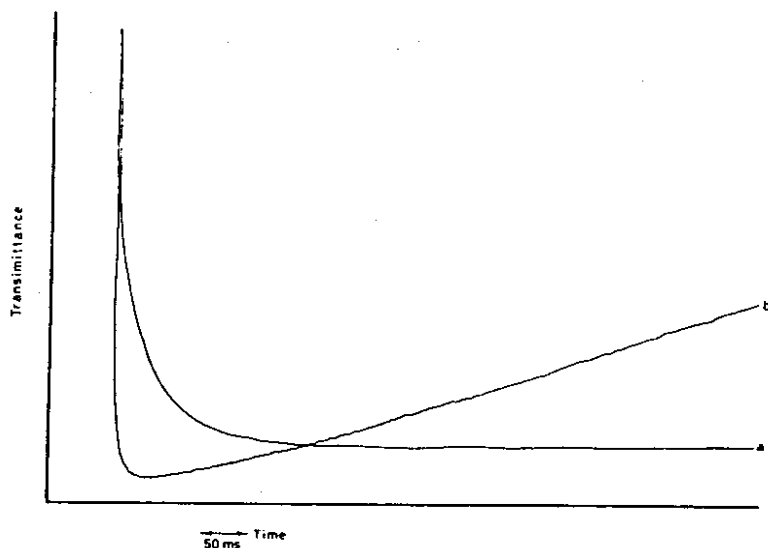
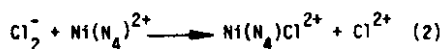


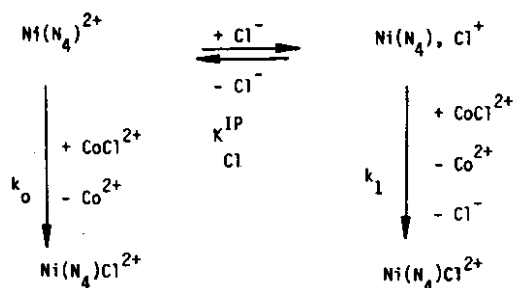
Fig. 1: Transmittance against time curves for flash photolysis of solutions (5×10^{-5} M $\text{Ni}(\text{trans[14]diene})^{2+}$, 0.1 M Co^{2+} , 1×10^{-4} M $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, and 0.7 M H^+) at 375 nm, $t = 25^\circ\text{C}$ and $\mu = 1.0$ (ClO_4^-) a: $[\text{Cl}^-] = 0.001$ M, b: $[\text{Cl}^-] = 0.9$ M.



The formation of the nickel(III) macrocyclic monochlorocomplexes as the predominant products of the oxidation by Cl_2^- and CoCl^{2+} suggested that the reaction proceeds by an inner-sphere mechanism. For electron-transfer reactions which proceed by an inner-sphere mechanism, electron transfer is preceded by substitution step in which the inner coordination sphere of one of the reactants is penetrated, and new primary bonds are formed and old ones disrupted in the path up to and through the transition state. The maximum rate of the electron transfer process cannot exceed the substitution rate at the determining metal center and may be much slower than this rate. For reactions in which one oxidation state of one of the reactants is labile but the other is inert, if the reaction follows an inner-sphere path, it is possible to demonstrate experimentally that ligand transfer accompanies electron transfer and that the mechanism is indeed inner-sphere [23].

The rate constant for oxidation of some saturated and unsaturated nickel(II) macrocyclic complexes by Cl_2^- is reported to span a range $2.0 \times 10^9 - 9.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (11). Thus, the rate constants for the reaction of $\text{Ni}(\text{cyclam})^{2+}$, $\text{Ni}(\text{ATH}_2)^{2+}$, $\text{Ni}(\text{Tim})^{2+}$ and $\text{Ni}(\text{trans [14]diene})^{2+}$ with Cl_2^- are $109 \text{ M}^{-1} \text{ s}^{-1}$. Therefore a large excess (103) of Co^{2+} toward $\text{Ni}(\text{N}_4)^{2+}$ had to be used to observe reaction (3). Some $\text{Ni}(\text{N}_4)\text{Cl}^{2+}$ was still formed by reaction (2). Since reaction (2) occurs within a much faster time scale than (3), the oxidation with CoCl^{2+} was not disturbed by the reaction of Cl_2^- .

The mechanism by which the inner-sphere oxidation of $\text{Ni}(\text{N}_4)^{2+}$ complexes by CoCl^{2+} takes place can be represented by Scheme-1.



Scheme-1

For all the investigated $\text{Ni}(\text{N}_4)^{2+}$ complexes the rate law (4) was observed

$$\text{rate} = k[\text{Ni}(\text{N}_4)^{2+}][\text{CoCl}^{2+}] \quad (4)$$

$$k = k_o + k'[\text{Cl}^-] \quad (5)$$

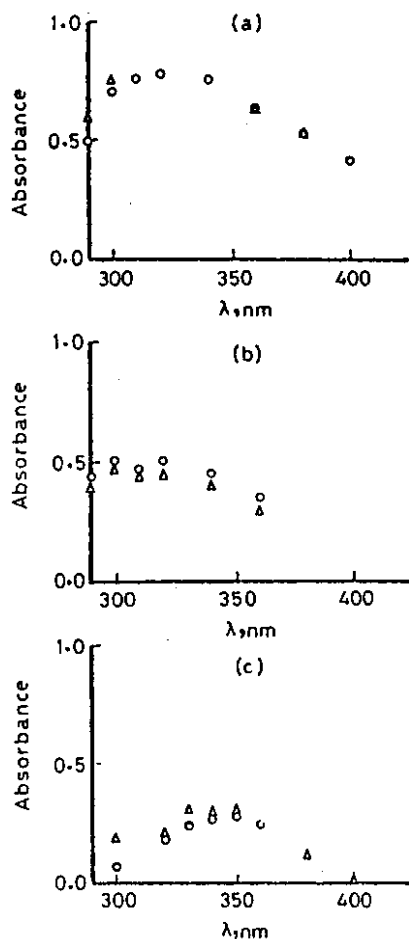


Fig.2: Transient absorbance spectra of (a) $\text{Ni}(\text{trans[14]diene})\text{Cl}_2^{2+}$, (b) $\text{Ni}(\text{ATH}_2)\text{Cl}_2^{2+}$ and (c) $\text{Ni}(\text{Tim})\text{Cl}_2^{2+}$. O: generated by Cl_2^- ($5 \times 10^{-5} \text{ M Co}(\text{NH}_3)_5\text{Cl}_2^{2+}$, 1.0 HCl , $1 \times 10^{-5} \text{ M Ni}(\text{N}_4)^{2+}$; (a): 1.5 ms, (b): 3.5 ms, (c): 0.2 ms after flash). D: generated by CoCl^{2+} ($5 \times 10^{-5} \text{ M Co}(\text{NH}_3)_5\text{Cl}_2^{2+}$, 0.1 M Co^{2+} , 0.7 M H^+ , 0.9 M Cl^- , $1 \times 10^{-5} \text{ (Ni}(\text{N}_4)^{2+})$; (a): 0.6 s, (b): 3.3 ms, (c): 6.45 after flash).

The chloride dependance is interpreted in terms of the oxidation of an ion pair of $\text{Ni}(\text{N}_4)^{2+}$, $\text{Ni}(\text{N}_4), \text{Cl}^+$ (Scheme-1). Table-1 and Fig. 3 shows the dependance of the second order rate constant k on $[\text{Cl}^-]$ for various compounds. The calculated rate law for Scheme 1, is linear over the $[\text{Cl}^-]$ range

$$\text{rate} = \frac{k_o + k_1 K_{\text{Cl}}^{\text{IP}} [\text{Cl}^-]}{1 + K_{\text{Cl}}^{\text{IP}} [\text{Cl}^-]} [\text{Ni}(\text{N}_4)^{2+}][\text{CoCl}^{2+}] \quad (6)$$

Table-1: Dependence of the Second Order Rate Constant $k(\text{M}^{-1} \text{s}^{-1})$ on $[\text{Cl}^-]$ and $[\text{H}^+]$ for nickel macrocyclic complexes, $\mu = 1.0(\text{NaClO}_4)$, 25°C .

$[\text{Cl}^-], \text{M}$	$[\text{H}^+], \text{M}$	$\text{Ni}(\text{cyclam})^{2+}$ $10^{-7}.k$	$\text{Ni}(\text{trans}/14)\text{diene}^{2+}$ $10^{-6}.k$	$\text{Ni}(\text{TIM})^{2+}$ $10^{-5}.k$	$\text{Ni}(\text{ATH})_2^{2+}$ $10^{-7}.k$
0.1	0.7	6.1 ± 0.5	1.0 ± 0.1	3.6 ± 0.7	2.0 ± 0.3
0.3	0.7	8.0 ± 0.1	1.4 ± 0.0	6.7 ± 0.7	2.1 ± 0.1
0.3	0.1	-	-	-	2.3 ± 0.6
0.5	0.7	9.4 ± 0.6	1.8 ± 0.1	9.3 ± 0.4	2.9 ± 0.2
0.7	0.7	10.8 ± 0.4	2.3 ± 0.1	12.5 ± 1.0	2.7 ± 0.3
0.9	0.7	13.1 ± 1.2	2.7 ± 0.3	17.2 ± 1.0	4.6 ± 0.5
0.9	0.1	-	-	-	5.1 ± 0.5

studied. The values of k_0 and k' are summarized in Table-2.

The oxidation of $\text{Ni}(\text{ATH}_2)^{2+}$ is slightly pH dependant, Table-1 and Fig. 2. This dependance is due to the oxidation of the deprotonated ligand [24]. Since the pH dependance is so small, the rate constant at $[\text{H}^+] = 0.7 \text{ M}$ represent the pH independent pathway very well. The inner - sphere oxidation of the metal center by CoCl^{2+} seems to be strongly favoured than the outer - sphere oxidation of the deprotonated ligand.

b-Copper Complexes:

The copper complex of *trans* [14]-diene exist in two distinct, but interconvertible, isomers namely $[\text{Cu}(\text{meso-trans}[14]\text{diene})]^{2+}$ and $[\text{Cu}(\text{dl-trans}[14]\text{diene})]^{2+}$. Transmittance against time curves for the flash photolysis of $[\text{Cu}(\text{meso-trans}[14])]^{2+}$ complex is shown in Figure 4 which indicates that at high $[\text{Cl}^-]$ the copper (III) complex is much more stable than at low $[\text{Cl}^-]$. At $[\text{Cl}^-] 0.01 \text{ M}$ the oxidation of $\text{Cu}(\text{N}_4)^{2+}$ cannot be observed. The clear implication of Figure 4 is that $\text{Cu(III)} (\text{N}_4)$ is greatly stabilized by axial coordination to chloride. Thus, demonstrating that the $\text{Cu}(\text{N}_4)\text{Cl}^{2+}$ complexes are

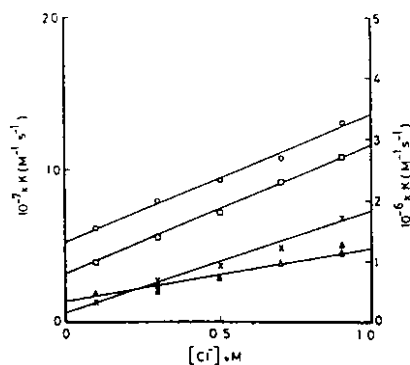


Fig.3: Dependence of the second order rate constant k on $[\text{Cl}^-]$ ($\mu = 1.0(\text{NaClO}_4)$, 25°C). Left Scale: O : $\text{Ni}(\text{Cyclam})^{2+}$; Δ, Δ : $\text{Ni}(\text{ATH}_2)^{2+}$ at 0.7 and 0.1 M H^+ . Right Scale : $\text{Ni}(\text{trans}[14]\text{diene})^{2+}$; X : $\text{Ni}(\text{TIM})^{2+}$.

very stable. Stabilization of copper(III) macrocyclic complexes by axial coordination of the chloride *via* chemical and electrochemical techniques has been previously reported [2-6]. Furthermore, the electrochemical behavior of such complexes suggested that only $\text{Cu}(\text{N}_4)\text{Cl}_2$ complexes are easily oxidized. Thus oxidation of $\text{Cu}(\text{N}_4)^{2+}$ complexes by CoCl^{2+} proceed by an outer - sphere mechanism. In such case the primary coordination spheres of the reactants remain intact during the

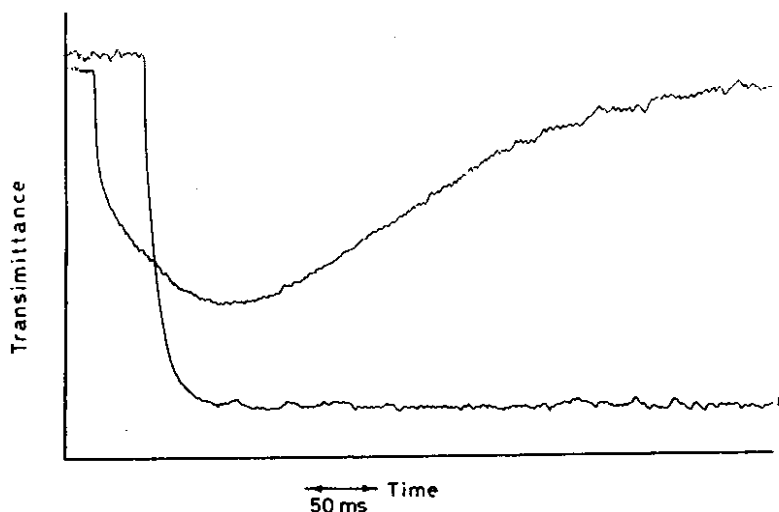


Fig.4: Transmittance against time curves for flash photolysis of solutions (2×10^{-4} M Cu(meso-trans[14]dien) $^{2+}$, 0.1 M Co^{2+} , 1×10^{-4} M $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ and 0.7 M H^+) at 380 nm, at 25°C and $\mu = 1.0$ (ClO_4^-) a: $[\text{Cl}^-] = 0.1$ M, b: $[\text{Cl}^-] = 0.9$ M.

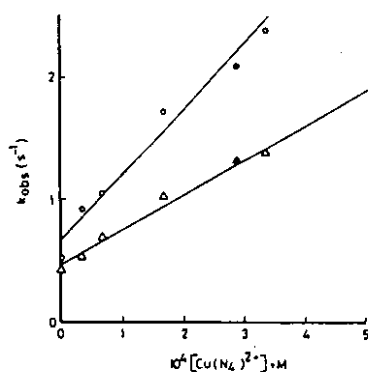


Fig.5: Plot of k_{obs} (s^{-1}) as a function of $[\text{Cu}(\text{meso-trans}[14]\text{diene})^{2+}]$ at 25°C , $m = 1.0$ (ClO_4^-); O, Δ ; at 0.8 M Cl^- and 0.4 M Cl^- ; and O, D: $[\text{Cu}(\text{dl-trans}[14]\text{dien})^{2+}]$.

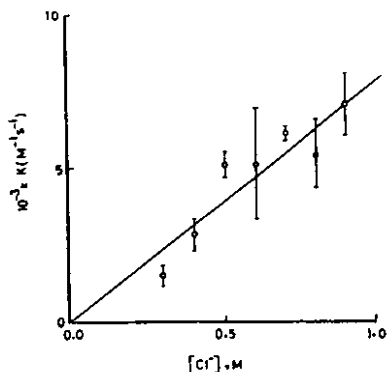


Fig.6: Dependence of the second order rate constant k on $[\text{Cl}^-]$ ($\mu = 1.0$ -(NaClO_4), 25°C) for oxidation of $\text{Cu}(\text{meso-trans}[14]\text{diene})^{2+}$.

Table-2: Rate constants for the chloride independent (k_0 , $\text{M}^{-1} \text{s}^{-1}$) and chloride dependent (k' , $\text{M}^{-2} \text{s}^{-1}$) oxidation of $\text{Ni}(\text{N}_4)^{2+}$ by CoCl_2^{2+} ($\mu = 1.0$ (NaClO_4), 25°C).

	$k_0, \text{M}^{-1} \text{s}^{-1}$	$k', \text{M}^{-2} \text{s}^{-1}$
$\text{Ni}(\text{cyclam})^{2+}$	$(5.3 \pm 0.6) \cdot 10^7$	$(8.4 \pm 1.1) \cdot 10^7$
$\text{Ni}(\text{trans}[14]\text{diene})^{2+}$	$(8.0 \pm 1.1) \cdot 10^5$	$(2.1 \pm 0.2) \cdot 10^6$
$\text{Ni}(\text{ATH}_2)^{2+}$	$(1.4 \pm 0.6) \cdot 10^7$	$(3.5 \pm 1.1) \cdot 10^7$
$\text{Ni}(\text{TlM})^{2+}$	$(1.6 \pm 1.5) \cdot 10^5$	$(1.7 \pm 2.6) \cdot 10^5$

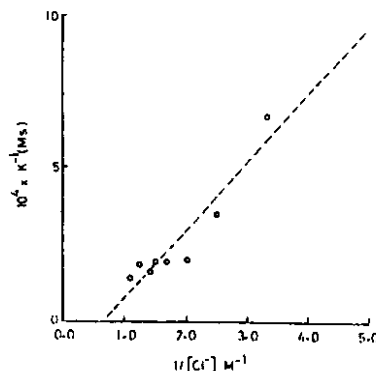


Fig.7: Plot of $1/k$ vs. $1/[\text{Cl}^-]$ for oxidation of $\text{Cu}(\text{meso-trans}[14]\text{diene})^{2+}$ at $\mu = 1.0$ (NaClO_4) and 25°C .

approach to electron transfer, although rearrangements of secondary solvation spheres and of ligand-metal bond lengths and geometries can occur.

The kinetic data for the oxidation of Cu(*trans* [14]diene)²⁺ by CoCl²⁺ at 25°C are depicted in Table-3. Since the reaction of Cu(N₄)²⁺ with CoCl²⁺ is so slow, the decay of CoCl²⁺ has to be taken into account. The decay of CoCl²⁺ is a complex function of [Co²⁺], [Cl⁻] and [H⁺] [25]. This decay was treated approximately as a first order reaction ([Cu(N₄)²⁺]_{total} >> [CoCl²⁺]):

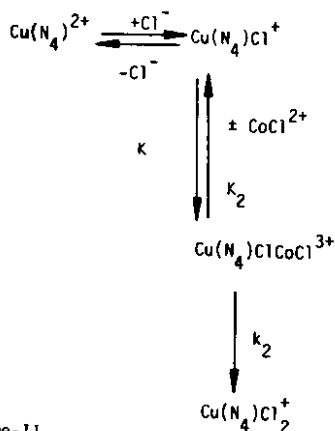
$$-\frac{d[\text{CoCl}^{2+}]}{dt} = k_0[\text{CoCl}^{2+}] + k[\text{Cu(N}_4\text{)}^{2+}][\text{CoCl}^{2+}] \quad (7)$$

Figure 5 shows a graphic representation for two selected [Cl⁻]. This is an indication that both [Cu(*meso-trans* [14]diene)]²⁺ and Cu(*dl-trans* [14]diene)]²⁺ show the same reactivity. The dependence of the second order rate constant K on the [Cl⁻] are shown in Table-4 and Fig. 6. Thus, the second order rate constant may be represented as

$$k = k_2' [\text{Cl}^-] \quad (8)$$

$$k_2' = (7.7 \pm 1.2) \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$$

The intercept equals zero as the straight line pass through the origin. This is an indicative that Cu(N₄)²⁺ is not oxidized in significant amount by CoCl²⁺. However, Cu(N₄)Cl⁺ and Cu(N₄)Cl₂ are oxidized by CoCl²⁺. This is consistent with our findings and others that axial coordination of halides stabilizes the copper(III) oxidation state of macrocyclic complexes [2-6]. The mechanism by which oxidation of Cu(N₄)²⁺ complexes by CoCl²⁺ takes place can be represented by Scheme-2



Scheme-11

Table-3: Oxidation of copper macrocyclic complexes by CoCl²⁺ at 25°C, $\mu = 1.0$ (NaClO₄) and [H⁺] = 0.70 M.

[Cl ⁻], M	[Cu(<i>meso</i> -(N ₄)) ²⁺], M	k _{obs} , s ⁻¹	k _{calc} , (M ⁻¹ s ⁻¹)
0.30	0.0	0.374	0.41
0.30	3.09.10 ⁻⁵	0.449	0.46
0.30	6.17.10 ⁻⁵	0.536	0.50
0.30	1.54.10 ⁻⁴	0.670	0.64
0.30	3.09.10 ⁻⁴	0.851	0.87
0.30	1.23.10 ⁻⁴	0.608	0.60
0.40	0.0	0.432	0.46
0.40	3.34.10 ⁻⁵	0.523	0.55
0.40	6.68.10 ⁻⁵	0.672	0.65
0.40	1.67.10 ⁻⁴	1.01	0.93
0.40	3.34.10 ⁻⁴	1.37	1.41
0.40	2.88.10 ^{-4**}	1.30	-
0.50	0.0	0.454	0.43
0.50	6.17.10 ⁻⁵	0.708	0.75
0.50	1.54.10 ⁻⁴	1.23	1.21
0.50	3.09.10 ⁻⁴	2.00	2.00
0.60	0.0	0.487	0.57
0.60	3.34.10 ⁻⁵	0.607	0.74
0.60	6.68.10 ⁻⁵	0.984	0.91
0.60	1.67.10 ⁻⁴	1.70	1.42
0.60	3.34.10 ⁻⁴	2.14	2.28
0.60	2.88.10 ^{-4**}	1.62	-
0.70	0.0	0.423	0.55
0.70	3.00.10 ⁻⁵	0.663	0.73
0.70	6.00.10 ⁻⁵	1.09	0.91
0.70	1.5.10 ⁻⁴	1.56	1.46
0.70	3.00.10 ⁻⁴	2.30	2.38
0.80	0.0	0.532	0.67
0.80	3.34.10 ⁻⁵	0.918	0.85
0.80	6.68.10 ⁻⁵	1.05	1.03
0.80	1.67.10 ⁻⁴	1.71	1.57
0.80	3.34.10 ⁻⁴	3.39	2.47
0.80	2.88.10 ^{-4**}	2.09	-
0.90	0.0	0.501	0.63
0.90	1.50.10 ⁻⁵	0.628	0.74
0.90	3.00.10 ⁻⁵	0.693	0.84

Table-3: continued.

[Cl ⁻], M	[Cu(meso-(N ₄) ²⁺), M	k _{obs} , s ⁻¹	k _{calc} , (M ⁻¹ s ⁻¹) ^a
0.90	6.00.10 ⁻⁵	1.14	1.05
0.90	1.50.10 ^{-4a}	1.53	1.69
0.90	1.50.10 ⁻⁴	2.17	1.69
0.90	1.50.10 ^{-4b}	1.91	1.69
0.90	3.00.10 ⁻⁴	2.58	2.74
0.90	6.36.10 ^{-5c}	1.06	1.08
0.90	7.95.10 ^{-6c}	0.316	0.69
0.90	4.77.10 ⁻⁴	3.74	3.98
0.90	1.59.10 ^{-4a}	2.25	1.75
0.90	1.59.10 ⁻⁴	1.83	1.75
0.90	1.59.10 ^{-4b}	1.71	1.75

^ak_{calc} = k₀ + k[CuI²⁺]_{total}; ^{**} Cu(dI-(N₂)²⁺).

a) 5 x 10⁻⁵ M Co(NH₃)₅Cl²⁺, b) 2x10⁻⁴ M Co(NH₃)₅Cl²⁺,

c) 10⁻³ M Co(NH₃)₅Cl²⁺.

The calculated rate law for Scheme-II is

$$\text{rate} = \frac{k_2 K_2 K [\text{Cl}^-]}{1 + K [\text{Cl}^-]} [\text{Cu}(\text{N}_4)^{2+}] [\text{CoCl}^{2+}] \quad (9)$$

A plot of 1/K vs. 1/[Cl⁻] has negative intercept as not significant Figure 7. Therefore the assumption is made that K < 0.1 M⁻¹, k₂ = K K₂k₂.

The outer-sphere electron-transfer mechanism observed for the oxidation of copper(II) macrocyclic complexes takes place at a slower rate than does the chloride-bridged-inner-sphere mechanism observed for the oxidation of the corresponding nickel(II) macrocyclic complexes. This is a general feature of the inner - sphere electron transfer reactions.

Table-4: Dependence of the second order rate constant k(M⁻¹ s⁻¹) on [Cl⁻] for copper macrocyclic complexes, μ = 1.0 (NaClO₄), 25°C.

[Cl ⁻], M	1/[Cl ⁻], M ⁻¹	10 ⁻³ , k, M ⁻¹ s ⁻¹	k/[Cl ⁻], M ⁻² s ⁻¹	10 ⁴ .k ⁻¹ M s
			(= k' ₂)	
0.3	3.33	1.5 ± 0.3	5000	6.67
0.4	2.50	2.8 ± 0.5	7100	3.52
0.5	2.00	5.1 ± 0.4	10200	1.97
0.6	1.67	5.1 ± 1.8	8520	1.95
0.7	1.43	6.1 ± 0.2	8700	1.64
0.8	1.25	5.4 ± 1.1	6730	1.84
0.9	1.11	7.0 ± 1.0	7810	1.42

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