Notes

Contribution from the Department of Chemistry,
Kuwait University, P.O. Box 5969, Safat, Kuwait

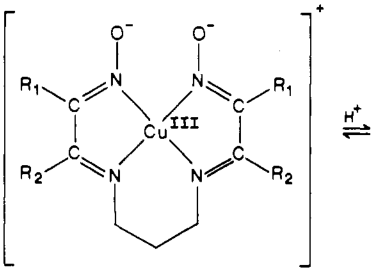
Outer-Sphere Electron Transfer between $[Ni^{II}(cyclam)]^{2+}$ and Copper(III) Imine–Oxime Complexes

Ashiq Hussein, Yousif Sulfab,* and Mohamed Nasreldin

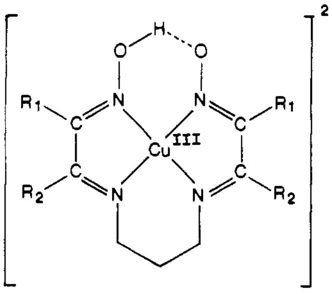
Received March 4, 1988

In recent years a number of Cu(III) and Ni(III) complexes have been characterized both in solutions and as solids.[1-4] Both electrochemical and chemical methods were used to generate these oxidation states.[5-9] The Cu(III) complexes of *o*-phenylenebis(biuret),[10] tri-α-aminoisobutyric acid,[11] dithiocarbamate,[2] and a macrocyclic ligand[12] were isolated and their crystal structures have been determined. Margerum and co-workers[1,2,13] have carried out extensive studies on electron-transfer reactions involving Cu(III) peptide complexes. Both outer- and inner-sphere mechanisms seem to be operative depending upon the nature of the reductant. In the oxidation of both $Ir^{III}Cl_6^{3-}$ [14] and $Fe^{II}(CN)_6^{4-}$,[15] where the chloro and cyano ligands are capable of axial coordination to the Cu(III) complexes, a bridged mechanism was invoked, whereas in the oxidation of $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_5py^{2+}$ (py = pyridine), an outer-sphere mechanism was suggested.[16]

From this laboratory we have also reported that the trivalent oxidation state of copper is stabilized by imine–oxime ligands.[6,17] The Cu(III) complexes of the ligands L^1, L^2, and L^4 have been isolated, and that of L^3 has been characterized in solution. These Cu(III) complexes undergo facile electron transfer with iodide,[18] $Co^{II}EDTA$[19] (EDTA = ethylenediaminetetraacetate), catechol, and hydroquinone,[17,20] giving the initial Cu(II) complex. Kinetic studies showed that both unprotonated (I) and protonated (II) forms of these complexes are present in aqueous acidic solutions.[17-20]



$[Cu^{III}L^n]^+$ (I)



$[Cu^{III}HL^n]^{2+}$ (II)

L^1: $R_1 = R_2 = CH_3$
L^2: $R_1 = CH_3$, $R_2 = C_2H_5$
L^3: $R_1 = C_6H_5$, $R_2 = CH_3$
L^4: $R_1 = CH(CH_3)_2$, $R_2 = CH_3$

Ni(III) complexes are also well documented, and a few have been isolated;[4] they are generally more stable in nonaqueous media than in aqueous solutions.[8,21] The $[Ni^{III}(cyclam)]^{3+}$ complex (cyclam = 1,4,8,11-tetraazacyclotetradecane) is relatively stable in aqueous solutions containing >1 M $HClO_4$. Kinetic studies of the oxidation of $[Ni^{II}(cyclam)]^{2+}$ by Co(III),[22] Ni(IV),[23] and Ag(II)[24] have been reported. An outer-sphere mechanism is believed to be operative in all of these reactions.

Here we report the results of the kinetic studies of the oxidation of $[Ni^{II}(cyclam)]^{2+}$ by four Cu(III) imine–oxime complexes, $[Cu^{III}L^n]^+$ (n = 1–4). The square-planar structure of both the reductant and the oxidants as well as the absence of bridging atoms (only a protonated form of copper(III) complexes is reactive) warrants the accommodation of an outer-sphere electron-transfer process. Application of the Marcus theory[25] to these reactions gives a value for the self-exchange rate constant for the $[Cu^{III/II}HL^n]^{2+/+}$ couples that can be compared with other Cu(III/II) exchange rates.

Experimental Section

Materials. $[Ni^{II}(cyclam)](ClO_4)_2$ was prepared by reacting $Ni(ClO_4)_2 \cdot 6H_2O$ and cyclam (Strem Chemicals) and recrystallized from a methanol–water solvent. The Cu(II) imine–oxime complex with L^1 was prepared according to the method of Addison et al.[26] and recrystallized from water. Anal. Calcd for $[Cu^{II}HL^1]ClO_4 \cdot 2H_2O$: C, 30.14; H, 5.29; N, 12.78; Cl, 8.28; Cu, 14.50. Found: C, 30.33; H, 4.90; N, 12.80; Cl, 8.11; Cu, 14.70. The ligands L^2, L^3, and L^4 were prepared first by nitrosation of diethyl ketone, benzyl methyl ketone, and 4-methyl-2-pentanone, respectively, and then by condensation of the nitroso ketone with 1,3-diaminopropane in the ratio of 2:1.[17] The Cu(II) complexes of

---

[1] Margerum, D. W.; Owens, G. D. *Metal Ions in Biological Systems*; Marcel Dekker: New York, 1981; Vol. 12, p 75.
[2] Levason, W.; Spicer, M. D. *Coord. Chem. Rev.* **1987**, *76*, 45.
[3] Nag, K.; Chakravorty, A. *Coord. Chem. Rev.* **1980**, *33*, 87.
[4] Haines, R. I.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77.
[5] Margerum, D. W.; Chellappa, K. L.; Bossu, F. P.; Burce, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 6894.
[6] (a) Sulfab, Y.; Hussein, M. A.; Al-Shatti, N. I. *Inorg. Chim. Acta* **1982**, *67*, L33. (b) Sulfab, Y.; Al-Shatti, N. I. *Inorg. Chim. Acta* **1984**, *87*, L32.
[7] Bossu, F. P.; Margerum, D. W. *J. Am. Chem. Soc.* **1976**, *98*, 4003.
[8] Cook, C. F.; Curtis, N. F. *J. Chem. Soc., Chem. Commun.* **1967**, 9626.
[9] Olsen, D. C.; Vasileviskis, J. *Inorg. Chem.* **1969**, *8*, 1611.
[10] Birker, P. J. M. W. L. *Inorg. Chem.* **1977**, *16*, 2478.
[11] Diaddario, L. L.; Robinson, W. R.; Margerum, D. W. *Inorg. Chem.* **1983**, *22*, 1021.
[12] Clark, G. R.; Skelton, B. W.; Waters, T. N. *J. Chem. Soc., Dalton Trans* **1976**, 1528.
[13] Margerum, D. W. *Pure Appl. Chem.* **1983**, *55*, 23.
[14] Owens, G. D.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 1446.
[15] Anast, J. M.; Margerum, D. W. *Inorg. Chem.* **1982**, *21*, 3493.
[16] Anast, J. M.; Hamburg, A. W.; Margerum, D. W. *Inorg. Chem.* **1983**, *22*, 2139.
[17] Al-Sogair, F.; Sulfab, Y. To be submitted for publication.
[18] Al-Shatti, N. I.; Hussein, M. A.; Sulfab, Y. *Transition Met. Chem.* **1984**, *9*, 31.
[19] Al-Shatti, N. I.; Hussein, M. A.; Sulfab, Y. *Inorg. Chim. Acta* **1985**, *99*, 129.
[20] Sulfab, Y.; Al-Sogair, F.; Naseldin, M.; Hussein, M. A.; Al-Shatti, N. I. *Abstracts of Papers*, 30th IUPAC Conference, Manchester, England, 1985.
[21] Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109.
[22] Bordovitch, J. C.; McAuley, A. *Inorg. Chem.* **1981**, *20*, 1667.
[23] Macartney, D. H.; McAuley, A. *Inorg. Chem.* **1983**, *22*, 2062.
[24] Mentasti, E.; Kirschenbaum, L. J. *Inorg. Chim. Acta* **1987**, *129*, 97.
[25] Marcus, R. A. *J. Phys. Chem.* **1963**, *67*, 853.
[26] Addison, A. W.; Carpenter, M.; Lau, L. K.-M.; Wicholas, M. *Inorg. Chem.* **1978**, *17*, 1545.

0020-1669/89/1328-0157$01.50/0

Table I. Variation of the Pseudo-First-Order Rate Constant with $[Ni^{II}(cyclam)]^{2+}$ Complex Concentration[a]

$10^4[[Ni^{II}(cyclam)]^{2+}]$, M	k_{obs}, s^{-1}			
	$[Cu^{III}L^1]^{+}$[b]	$[Cu^{III}L^2]^{+}$	$[Cu^{III}L^3]^{+}$[c]	$[Cu^{III}L^4]^{+}$[d]
8.0	15.0 ± 0.6		15.33 ± 1.3	4.4 ± 0.4
10.0		44.8 ± 1.8	19.6 ± 2.2	5.6 ± 0.4
12.0	22.5 ± 0.8			
20.0		87.0 ± 4.7	37.4 ± 2.0	10.4 ± 0.8
30.0	56.0 ± 2.7			
40.0		172.3 ± 9.7	69.0 ± 5.5	19.9 ± 1.4
50.0			97.5 ± 9.3	
56.0	115.0 ± 1.0			
60.0		270.0 ± 8.5		31.0 ± 3.6
80.0	159.2 ± 6.9		138.0 ± 9.5	211.8 ± 3.8

[a] Unless otherwise stated, $[[Cu^{III}L^n]^+]_T = 1.0 \times 10^{-4}$ M, $[H^+] = 0.10$ M, $\mu = 0.50$ M ($NaClO_4$), and $T = 25.0 \pm 0.1$ °C. [b] $[H^+] = 0.05$ M. [c] $[[Cu^{III}L]^{\beta+}] = 5.0 \times 10^{-5}$ M. [d] $[[Cu^{III}L]^{4+}] = 2.5 \times 10^{-5}$ M.

the ligands L^2, L^3, and L^4 were prepared by reacting copper(II) acetate with the corresponding ligand in 1:1.1 mole ratio in methanol and were precipitated by addition of solid $NaClO_4$. The crude products were recrystallized from water or methanol–water solvent. Anal. Calcd for $[Cu^{II}HL^2]ClO_4{\cdot}H_2O$: C, 34.83; H, 5.62; N, 12.49; Cu, 14.17; Cl, 7.90. Found: C, 34.53; H, 5.38; N, 12.27; Cu, 14.15; Cl, 7.81. Calcd for $[Cu^{II}HL^3]ClO_4$: C, 47.91; H, 4.40; N, 10.64; Cu, 12.07; Cl, 6.73. Found: C, 47.79; H, 4.34; N, 10.54; Cu, 11.95; Cl, 6.48. Calcd for $[Cu^{II}HL^4]ClO_4{\cdot}5H_2O$: C, 37.12; H, 6.23; N, 11.54; Cu, 13.09; Cl, 7.30. Found: C, 37.34; H, 6.81; N, 11.49; Cu, 13.05; Cl, 7.22.

Solutions of the Cu(III) complexes were prepared immediately before each kinetic experiment by addition of PbO_2 to an acidified solution (10^{-3} M $HClO_4$) of the desired complex. At this acid concentration the Cu(III) complexes were stable for several hours. However, at $[H^+] \geq 0.1$ M decomposition is accelerated. Decomposition of Cu(III) peptide complexes is also reported to be catalyzed by acid.[27] A stock solution of $[Ni^{II}(cyclam)]^{2+}$ (0.012 M) was prepared by weight, and solutions for kinetic runs were made up by dilution from this stock. When high concentrations of the Ni(II) complex were used, these were made up by weight. A stock solution of $HClO_4$ was prepared by dilution of AR grade concentrated $HClO_4$ and standardized against a standard NaOH solution. A stock solution of $NaClO_4$ was standardized, after passing a known volume through Amberlite IR-120 H resin, against a standard NaOH solution.

Stoichiometric Studies. The stoichiometry of the reaction of the $[Ni^{II}(cyclam)]^{2+}$ complex with each of the $[Cu^{III}L^n]^+$ complexes was determined by using a Unicam SP 8000 UV–visible spectrophotometer. Solutions with known concentrations of both the reductant and the oxidants were reacted at $[H^+] = 0.01$ M. Various concentrations of the oxidants and the reductant were used with the initial ratio of [oxidant]:[reductant] being 1:1, 2:1, and 3:1.

Kinetic Procedure. Kinetic measurements were made with a Hi-Tech stopped-flow spectrophotometer, Model SF-3L. The signal and the trigger pulse from the spectrophotometer was fed into a DL 901 transient recorder, where the information was stored in digital form and was displayed continuously on an oscilloscope. The transient recorder was interfaced to a HP 9825B minicomputer, which was used to analyze the absorbance data. The consumption of the Cu(III) complexes $[Cu^{III}L^1]^+$, $[Cu^{III}L^2]^+$, and $[Cu^{III}L^4]^+$ was followed at $\lambda_{max} = 515$ nm. The disappearance of $[Cu^{III}L^3]^+$ was monitored at $\lambda_{max} = 527$ nm. The molar absorption of each of these complexes is $>10^4$ M^{-1} cm^{-1}. All kinetic experiments were performed under pseudo-first-order conditions with $[[Ni^{II}(cyclam)]^{2+}] \geq 10[[Cu^{III}L^n]^+]_T$. $[H^+]$ was varied over the concentration range 0.025–0.250 M. The ionic strength was maintained at 0.50 M ($NaClO_4$) and the temperature at 25.0 ± 0.1 °C.

Results

The ratio of the concentration of $[Cu^{III}L^n]^+$ consumed to that of $[Ni^{II}(cyclam)]^{2+}$ initially present is in agreement with eq 1, indicating a stoichiometry of 1:1.

$$[Ni^{II}(cyclam)]^{2+} + [Cu^{III}L^n]^+{}_T \xrightarrow{H^+} [Ni^{III}(cyclam)]^{3+} + [Cu^{II}HL^n]^+ \quad (1)$$

Pseudo-first-order plots were linear to beyond 3 half-lives, and the magnitude of the pseudo-first-order rate constant, k_{obs}, does not vary with variation of the initial concentration of the Cu(III) complex.

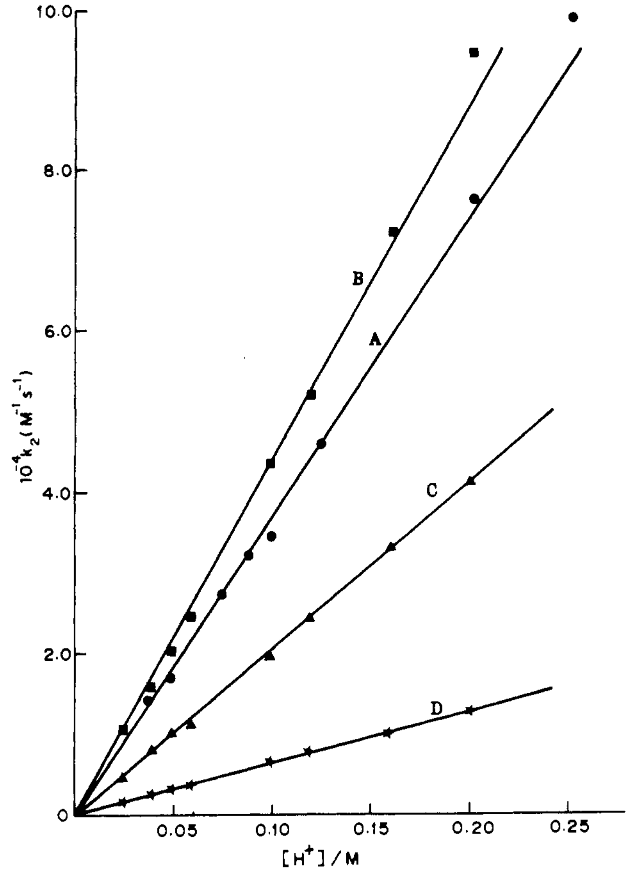


Figure 1. Plot of the second-order rate constant (k_2, M^{-1} s^{-1}) against $[H^+]$ ($T = 25.0 \pm 0.1$ °C, ionic strength $\mu = 0.50$ M ($NaClO_4$)): (A) $[Cu^{III}L^1]^+$; (B) $[Cu^{III}L^2]^+$; (C) $[Cu^{III}L^3]^+$; (D) $[Cu^{III}L^4]^+$.

Table II. Formal Electrode Potentials of $[Cu^{II}L^n]^+$ Complexes at pH 0 and the Rate Constants for Their Reduction by $[Ni^{II}(cyclam)]^{2+}$ at 25.0 ± 0.1 °C

complex	$E°$, V[a]	$10^{-5}k_3$, M^{-2} s^{-1}	complex	$E°$, V[a]	$10^{-5}k_3$, M^{-2} s^{-1}
$[Cu^{III}L^1]^+$	1.16	3.67 ± 0.20	$[Cu^{III}L^3]^+$	1.10	1.82 ± 0.15
$[Cu^{III}L^2]^+$	1.17	4.47 ± 0.30	$[Cu^{III}L^4]^+$	1.05	0.62 ± 0.02

[a] $\mu = 0.10$ M ($NaClO_4$).

The results in Table I show that the magnitude of k_{obs} varies linearly with the concentration of the Ni(II) complex. This is consistent with a first-order dependence on the Ni(II) complex concentration as expressed in eq. 2.

$$k_{obs} = k_2[[Ni^{II}(cyclam)]^{2+}] \quad (2)$$

The pseudo-first-order rate constant varies with $[H^+]$, and a plot of the second-order rate constant k_2 ($k_2 = k_{obs}/2[[Ni^{II}(cyclam)]^{2+}]$) against $[H^+]$ is shown in Figure 1. A first-order dependence of k_2 on $[H^+]$ is deduced. From these findings the

---

(27) Rybka, J. S.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 1452.

rate law for the reduction of each of the four Cu(III) complexes by $[Ni^{II}(cyclam)]^{2+}$ is given by eq 3. The values of the third-order

$$-\frac{d[[Cu^{III}L^n]^+]_T}{dt} = k_3[[Ni^{II}(cyclam)]^{2+}][[Cu^{III}L^n]^+]_T[H^+] \tag{3}$$

rate constant k_3, obtained from the slopes of the plots of Figure 1, are collected in Table II.

Discussion

The dependence of the $[Ni^{II}(cyclam)]^{2+}$–$[Cu^{III}L^n]^+$ reactions on H^+ concentration, almost certainly, arises from protonation of oxime oxygens, possibly with formation of hydrogen bonding (structure II) as is known for the Cu(II) analogues.[26] $[Ni^{II}(cyclam)]^{2+}$ could not be held responsible for the H^+ dependence as this complex does not enter into deprotonation–protonation equilibria over the employed H^+ concentration.[22]

The responsibility of the $[Cu^{III}L^n]^+$ complexes for the H^+ dependence finds support in electrochemical studies. The peak potential average values E_p ($E_p = {}^1/_2(E_{pa} + E_{pc})$) of all of the $[Cu^{III}L^n]^+$ complexes are pH-dependent. E_p varies with the pH according to eq 4, where a plot of E_p vs pH is linear with a slope

$$E_p = E° - 0.059\text{pH} \tag{4}$$

$$[Cu^{III}L^n]^+ + H^+ + e^- \rightleftharpoons [Cu^{II}HL^n]^+ \tag{5}$$

of −59 ± 3 mV for the four complexes.[6,17] This clearly indicates that one proton is involved in the electrode reaction (eq 5). Linearity of plots of E_p vs pH hold over the pH 1.2–5.0 range. The electrode reaction (eq 5) could be divided into steps, fast protonation of a $[Cu^{III}L^n]^+$ complex followed by electron transfer. In the oxidation of iodide[18] by $[Cu^{III}L^1]^+$ a proton-dependent pathway was found, and the protonation of $[Cu^{III}L^1]^+$ is the only alternative. The absence of a reaction pathway independent of H^+ shows that the reaction between $[Ni^{II}(cyclam)]^{2+}$ and an unprotonated $[Cu^{III}L^n]^+$ complex is an uphill reaction. This is in agreement with the decrease in the electrode potential of these complexes with increasing pH. The pK_a of $[Cu^{II}HL^n]^+$ is ~10 as indicated by their spectrophotometric titrations.[17] This value is close to the pK_a of ~10.6 reported for $Cu^{II}((DMG)H)_2$[28] ($(DMG)H_2$ = dimethylglyoxime).

A reaction sequence that is compatible with the observed kinetics may be described by eq 6 and 7. From eq 6 and 7 the rate

$$[Cu^{III}L^n]^+ + H^+ \rightleftharpoons [Cu^{III}HL^n]^{2+} \quad K_1 \tag{6}$$

$$[Cu^{III}HL^n]^{2+} + [Ni^{II}(cyclam)]^{2+} \xrightarrow{k_4} [Cu^{II}HL^n]^+ + [Ni^{III}(cyclam)]^{3+} \tag{7}$$

law given in eq 8 could be derived. Equation 8 reduces to the form

$$-\frac{d[[Cu^{III}L^n]^+]_T}{dt} = \frac{k_4K_1[[Ni^{II}(cyclam)]^{2+}][[Cu^{III}L^n]^+]_T[H^+]}{1 + K_1[H^+]} \tag{8}$$

of eq 9 if $1 \gg K_1[H^+]$, and by comparison of eq 3 and 9 it would seem that $k_3 = k_4K_1$.

$$-\frac{d[[Cu^{III}L^n]^+]_T}{dt} = k_4K_1[[Ni(cyclam)]^{2+}][[Cu^{III}L^n]^+][H^+] \tag{9}$$

An alternative reaction sequence may involve the reaction between the diprotonated Cu(III) complex and the Ni(II) reductant (eq 6, 10, and 11).

$$[Cu^{III}HL^n]^{2+} + H^+ \rightleftharpoons [Cu^{III}H_2L^n]^{3+} \quad K_2 \tag{10}$$

$$[Cu^{III}H_2L^n]^{3+} + [Ni^{II}(cyclam)]^{2+} \xrightarrow{k_5} [Cu^{II}H_2L]^{2+} + [Ni^{III}(cyclam)]^{3+} \tag{11}$$

From eq 6, 10, and 11 the rate law of eq 12 is derived.

$$-\frac{d[[Cu^{III}L^n]^+]_T}{dt} = \frac{k_5K_1K_2[[Ni^{II}(cyclam)]^{2+}][[Cu^{III}L^n]^+]_T[H^+]^2}{1 + K_1[H^+] + K_1K_2[H^+]^2} \tag{12}$$

Under the conditions of the $[H^+]$ employed it seems that $K_1[H^+] \gg 1 + K_1K_2[H^+]^2$ and eq 12 reduces to the form of eq 13, which is of the same form as the experimental rate law. By comparison of eq 3 and 13 it can be seen that $k_3 = k_5K_2$.

$$-\frac{d[[Cu^{III}L^n]^+]_T}{dt} = k_5K_2[[Ni^{II}(cyclam)]^{2+}][[Cu^{III}L^n]^+]_T[H^+] \tag{13}$$

Attempts were made to determine K_1 and K_2, but these have been unsuccessful so far. The slow decomposition of $[Cu^{III}L^n]^+$ complexes as well as $[Cu^{II}HL^n]^+$ complexes at relatively high acid concentration made these attempts fruitless. However, it seems that K_1 is very small as indicated by the linearity of the k_2 vs $[H^+]$ plots up to $[H^+]$ = 0.25 M.

The reductant $[Ni^{II}(cyclam)]^{2+}$ is known to have a square-planar structure in aqueous acidic solutions.[29] A change to octahedral geometry, however, seems to be induced in basic media.[30] Under the conditions of acid concentrations employed here, the square-planar structure is likely to be maintained. A square-planar structure is also known for Cu(III) complexes in the solid state.[10-12] The structure of the Cu(III) imine–oxime complex $[Cu^{III}L^2]^+$, isolated from an acidic solution (pH 3.7) as a perchlorate salt, has been determined.[31] The copper ion is bound to the four N atoms, but the Cu–N bond lengths are not significantly shorter than those determined for the $[Cu^{II}HL^1]^+$ complex.[32] Support for the square-planar geometry in solution is usually derived from the absence of ESR signals for these complexes. Axial coordination to Cu(III) complexes, however, seems to operate in electron-transfer reactions when the reductant is capable of offering a bridging ligand as has been shown in the oxidation of $Ir^{III}Cl_6^{3-}$ [14] and $Fe^{II}(CN)_6^{4-}$.[15] The formation of a five-coordinate species in the transition state of these reactions is not surprising as low-spin d^8 complexes, more often than not, undergo substitution by an associative mechanism.[33] In the reactions dealt with here, since only the protonated forms of the Cu(III) complexes, $[Cu^{III}HL^n]^{2+}$, are reactive, it is likely that the two oxime oxygens are hydrogen-bonded, as in the corresponding Cu(II) complexes,[26] and are thus not available for bridging the two reaction centers. These arguments seem to make an outer-sphere mechanism for the $[Ni^{II}(cyclam)]^{2+}$–$[Cu^{III}L^n]^+$ reactions a plausible suggestion. An outer-sphere mechanism was also suggested for the oxidation of $[Ni^{II}(cyclam)]^{2+}$ by $[Co^{III}OH]^{2+}$ and $[Ni^{IV}L]^{2+}$ [23] (H_2L = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime) in spite of the hydroxo ligand and unprotonated oxime oxygens on the two oxidants, respectively.

It may also be argued that an inner-sphere mechanism in which the two reactants are bridged by a water molecule could operate. However, both complexes showed no tendency to be pentacoordinated even in the solid state.[31]

The outer-sphere nature of the electron transfer between $[Ni^{II}(cyclam)]^{2+}$ and the protonated forms of the $[CuL^n]^+$[21] complexes may be tested by applying the Marcus theory[25] as shown in eq 14 and 15, where K_{12} is the equilibrium constant of the redox

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \tag{14}$$

$$\log f = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2) \tag{15}$$

reaction, k_{11} and k_{22} are the self-exchange rate constants for the

---

(28) Dyrssen, D.; Hennichs, M. *Acta Chem. Scand.* **1961**, *15*, 47.

(29) Anichini, A.; Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *Inorg. Chim. Acta* **1977**, *24*, L21.

(30) Kaden, T. A.; Lotz, T. J. *Helv. Chim. Acta* **1978**, *61*, 1376.

(31) Al-Sogair, F.; Sulfab, Y.; Ito, T. Unpublished results.

(32) Bertrand, J. A.; Smith, J. H.; VanDerveer, D. G. *Inorg. Chem.* **1977**, *16*, 1484.

(33) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions. A Study of Metal Complexes in Solution*; Wiley: New York, 1967; Chapter 4.

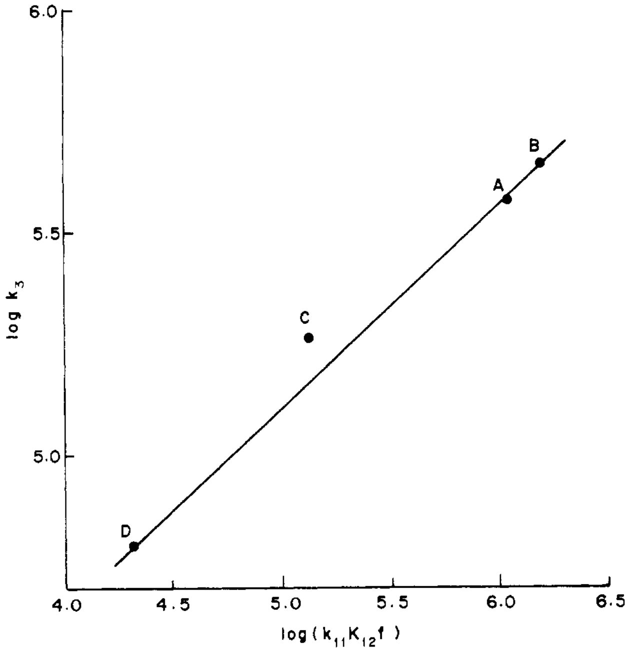


Figure 2. Plot of log k_3 vs log ($k_{11}K_{12}f$) for the oxidation of $[Ni^{II}(cyclam)]^{2+}$ by copper(III) imine–oxime complexes: (A) $[Cu^{III}L^1]^+$; (B) $[Cu^{III}L^2]^+$; (C) $[Cu^{III}L^3]^+$; (D) $[Cu^{III}L^4]^+$.

redox couples of each reagent, Z is the collision frequency in solution, usually taken as 10^{11} s^{-1}, and f is given by the expression in eq 15. This form of the Marcus relationship was found to be suitable for reactions between redox couples of the same charge type, as the reactions described here, because the work terms to a large extent cancel each other.

The self-exchange rate constant k_{11} of $[Ni^{III/II}(cyclam)]^{3+/2+}$ has been measured, and a value of $\sim 10^3$ M^{-1} s^{-1} is reported.[34] The self-exchange rate constant k_{22} of $[Cu^{III/II}HL^n]^{2+/+}$ is not known. The value of K_{12}, for each cross-reaction, is calculated by using the standard electrode potential $E°$, calculated from eq 4 for the Cu(III/II) couples at pH 0 (Table II), and the reported redox potential of the Ni(III/II) cyclam couple (0.97 V vs NHE).[35] In the application of the Marcus theory the value for k_3 (the second-order constant at $[H^+] = 1$ M) was used. A value for k_{22} was calculated by using the log form of eq 10 assuming $f = 1$. The value of k_{22} was then used to calculate f and k_{22} until the best fit of log k_3 vs log ($k_{11}K_{12}f$) was obtained as shown in Figure 2. This plot has a slope of 0.46, which is in reasonable agreement with the predicted value of 0.5. The self-exchange rate constant of the $[Cu^{III/II}HL^n]^{2+/+}$ couples with alkyl substituents is calculated as $\sim 5 \times 10^5$ M^{-1} s^{-1}. A value of $\sim 7 \times 10^5$ M^{-1} s^{-1} is estimated for the phenyl-substitued Cu(III/II) couple. The higher value of the self-exchange of the phenyl-substituted complexes probably results from the π system of the aromatic ring, which may facilitate electron transfer. This may explain the deviation shown by this complex from the linear free energy relationship shown in Figure 2. However, when the values of k_{22} calculated for the alkyl- and the phenyl-substituted complexes were used to plot log k_3 vs log ($k_{11}k_{22}K_{12}f$), the point falls on the line, and the linear plot has a slope of 0.46 ± 0.02 and an intercept of 0.22 ± 0.19. The involvement of the aromatic ring in electron transfer has become more evident in the reactions of $[Cu^{III}L^n]^+$ with $Co(phen)_3^{2+}$ (phen = 1,10-phenanthroline). Only the reaction involving the Cu(III) complex with the phenyl substituent was too fast to follow on the stopped-flow instrument.[17] It is to be observed that the self-exchange rate constant of the $[Cu^{III/II}HL^n]^{2+/+}$ complexes is about 1 order of magnitude higher than the self-exchange constant of the Cu(III/II) peptide complexes determined by ^{1}H NMR line broadening (5.5×10^4 M^{-1} s^{-1}).[36] These differences in rate, probably, reflect the small changes in Cu–N bond lengths (<0.02 Å) in the copper imine–oxime complexes compared to the large changes in the bond length (>0.1 Å) of the copper peptide complexes between the +2 and +3 oxidation states.[11] The self-exchange rate constant calculated for $[Cu^{III/II}HL^1]^{2+/+}$ was used to calculate its cross-reaction rate constant with catechol, and a fairly good agreement between the calculated ($\sim 4 \times 10^6$ M^{-2} s^{-1}) and the observed values (5.2×10^6 M^{-2} s^{-1}) was found.[17]

Acknowledgment. Financial support for this work provided by the Research Council of Kuwait University under Grant No. SC030 is greatly appreciated.

Registry No. $[Ni^{II}(cyclam)]^{2+}$, 46365-93-9; $[Cu^{III}L^1]^+$, 89230-27-3; $[Cu^{III}L^2]^+$, 117733-88-7; $[Cu^{III}L^3]^+$, 117687-05-5; $[Cu^{III}L^4]^+$, 117687-06-6.

Supplementary Material Available: A table of rate constant determinations using different Cu(III) complex concentrations and various H$^+$ concentrations (2 pages). Ordering information is given on any current masthead page.

---

(34) McAuley, A.; Macartney, D. H.; Oswald, T. *J. Chem. Soc., Chem. Commun.* **1982**, 274.

(35) Brodovitch, J. C.; McAuley, A.; Oswald, T. *Inorg. Chem.* **1982**, *21*, 3442.

(36) Koval, C. A.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 2311.

Contribution from the Departamento de Química
Inorgânica, Facultad de Farmacia, Universidad de Valencia,
46010 Valencia, Spain, and Institut de Ciência
de Materials, CSIC Barcelona, Barcelona, Spain

Coordination Behavior of Acetazolamide (5-Acetamido-1,3,4-thiadiazole-2-sulfonamide): Synthesis, Crystal Structure, and Properties of Bis(acetazolamidato)tetraamminenickel(II)

S. Ferrer,[†] J. Borrás,*,[†] C. Miratvilles,[‡] and A. Fuertes[‡]

Received April 23, 1988

Acetazolamide (Acm) (Figure 1) is one of the most potent inhibitors of carbonic anhydrase enzyme.[1] It is used as a diuretic drug and in the treatment of glaucoma. Although the mechanism whereby Acm inhibits the carbonic anhydrase is not well understood, direct binding studies using [^{3}H]Acm showed that Acm acts by coordinating the Zn atom of the active site. The $-SO_2-NH_2-$ seems to be the obvious candidate as the metal-chelating group.[2] The sulfonamide N atom must occupy the fourth coordination site at the Zn environment, replacing the Zn-bound water molecule in the native enzyme. One oxygen atom of the sulfonamide group links weakly the metal to give a distorted (4 + 1) "tetrahedron".[3]

We have initiated studies on the coordination chemistry of Acm and derivatives with transition-metal and d^{10} metal ions in an attempt to examine their mode of binding. As this ligand possesses the both character of thiadiazolyl and sulfonamide derivatives, a goal of our current investigation is the understanding of the coordination behavior of a compound with both groups. We have reported previously the synthesis and characterization of $M(Acm)_2(NH_3)_2$ (M = Zn or Co).[4] The complex described here is the first structurally characterized complex of Acm.

Finally, the crystal structure of this complex allows us to know where the deprotonation of the Acm takes place, since the literature indicates there are two ionizable hydrogens in the Acm, but

---

* To whom correspondence should be addressed.

[†] Universidad de Valencia.

[‡] CSIC Barcelona.