# The Rate of the Self-exchange Reaction of $Ni^{II}$ cyclam$^{2+}$/$Ni^{III}$ cyclam$^{3+}$ measured using $^{61}Ni$ E.S.R. and a Marcus Cross Correlation Reaction

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The e.s.r. spectra of labelled [$Ni^{III}$1,4,8,11-tetra-azacyclotetradecane]$^{3+}$ ($^{61}Ni$, $I$ = 3/2) complexes have been used to determine the first rates of electron exchange between $Ni^{II}$- and $Ni^{III}$-tetra-azamacrocycle complexes; independent measurements based on the reaction of $Fe^{III}$(tris-polypyridine) complexes provide a more accurate value for the self-exchange parameter.

There has been considerable recent interest in the characterization and spectroscopic properties of nickel(III) tetra-azamacrocycle complexes.[1–4] To date, however, there have been relatively few kinetic studies involving either complex formation or reduction to the nickel(II) state. The range of $E^\circ$ values for the $NiL^{3+/2+}$ couples [*ca.* 0.96 V where L = 1,4,8,11-tetra-azacyclotetradecane (cyclam) to 1.24 V where L = *meso*-5,5,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane ($Me_6$cyclam)] renders them attractive as reagents for electron-transfer studies involving linear free energy correlations such as those developed by Marcus[5] and Hush.[6] Recent investigations in these laboratories are consistent with an outer-sphere behaviour.[7] In order to make comparisons with other redox systems, however, it is necessary to know accurately values for the rate of the $Ni^{II}L/Ni^{III}L$ self-exchange reaction. No data of this kind are currently available. Also, the geometry change on transferring from a low-spin square planar $d^8$ $Ni^{II}$ to a low-spin tetragonally distorted $d^7$ $Ni^{III}$ ion may influence the rates.

In this study we have used $Ni^{III}(cyclam)^{3+}$ which of the aquo-complexes so far prepared is most stable with respect to intramolecular decomposition. Some kinetic experiments have also been made using the $Ni(Me_6cyclam)^{3+}$ complex. Two approaches have been made to evaluate the self-exchange parameters.

(i) The Marcus relationship may be expressed[5] as shown in equation (1), where $\lambda_{12} = 2(\Delta G^{*}_{11} + \Delta G^{*}_{22})$ and $W_{12}$, the work

$$\Delta G^{*}_{12} = W_{12} + \lambda_{12}/4 + \Delta G^{\circ}_{12}/2 + (\Delta G^{\circ}_{12})^2/4\lambda_{12} \qquad (1)$$

term, is small under the experimental conditions used ($I$ = 1.00 mol dm$^{-3}$).[8] The self-exchange activation energy, $\Delta G^{*}_{11}$, for $Ni(cyclam)^{2+/3+}$ may be determined from the activation parameters of reaction (2) where (LL) represents

$$Ni(cyclam)^{2+} + Fe(LL)_3^{3+} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} Ni(cyclam)^{3+} + Fe(LL)_3^{2+} \qquad (2)$$

a polypyridine ligand and where the reduction potentials of the complexes and self-exchange parameters are known.[9]

The rate constants and activation parameters for reaction (2) with Fe(4,4′-dimethyl-2,2′-bipyridine)$_3^{3+}$ ($E^\circ$ = 0.96 V) and Fe(4,7-dimethyl-1,10-phenanthroline)$_3^{3+}$ ($E^\circ$ = 1.00 V) in 1.00 mol dm$^{-3}$ toluene-*p*-sulphonic acid are presented in Table 1. Using $\Delta G^{*}_{22}$ = 14.6 ± 2 kJ mol$^{-1}$ for the iron(II) polypyridine complexes,[9] substitution in equation (1) yields a $\Delta G^{*}_{11}$ value for $NiL^{2+/3+}$ of 48.1 ± 9.0 kJ mol$^{-1}$. In the case of the reaction of $Ni(Me_6cyclam)^{2+}$, however, the higher oxidation potential of the nickel(III) species is evident from the fact that the $k_{obs}$ against $[Ni^{II}]_t$ plots (Table 2), although linear in the concentration range used, apparently do not pass through the origin, indicating reaction reversibility.

**Table 1.** Reaction of [$Ni^{III}$cyclam]$^{2+}$ with $Fe^{III}$ polypyridine complexes, [$H^+$] = $I$ = 1.00 mol dm$^{-3}$, toluene-*p*-sulphonic acid.

| | $T$/°C | $10^5k_{12}$/ mol$^{-1}$ dm$^3$ s$^{-1}$ | $\Delta H^‡$/ kJ mol$^{-1}$ | $\Delta S^‡$/ J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|
| $Fe(dmbpy)_3^{3+}$ | 9.9 | $2.2_0$ | 11 ± 6 | −105 ± 20 |
| | 18.6 | $2.2_5$ | | |
| | 25.0 | $2.9_5$ | | |
| $Fe(dmphen)_3^{3+}$ | 9.8 | $4.7_0$ | 6 ± 5 | −113 ± 22 |
| | 18.7 | $5.1_0$ | | |
| | 25.0 | $5.7_0$ | | |

(ii) All nickel(III) complexes so far studied show a characteristic e.s.r. spectrum with differing $g_\perp$ and $g_\parallel$ parameters owing to a distorted tetragonal geometry.[10] Sulphato-ligands co-ordinated axially to these centres stabilize the complexes with respect to intramolecular reduction.[3] Figure 1 shows the e.s.r. spectrum of $^{61}Ni(cyclam)(SO_4)_2^-$ (86% abundant $^{61}Ni$) at 77 K where the splitting of the $g_\parallel$ feature ($A_{11}$ = 37.7 G) is observed owing to the nuclear spin ($I$ = 3/2) of $^{61}Ni$. A similar spectrum is obtained for $^{61}Ni(cyclam)(OH_2)_2^{3+}$ in 1.0 mol dm$^{-3}$ $HClO_4$. The splitting is centro-symmetric around the $g_\parallel$ value observed for $^{58}Ni(cyclam)(OH_2)_2^{3+}$ also shown. Reaction of a solution of $^{61}Ni^{II}cyclam^{2+}$ prepared

**Table 2.** First-order rate constants for reaction of $Fe^{III}(phen)_3^{3+}$ and $Fe(bipy)_3^{3+}$ with [$Ni^{II}$-$Me_6$cyclam]$^{2+}$.[a]

| | | | | | |
|---|---|---|---|---|---|
| $Fe(phen)_3^{3+}$ | | | | | |
| | $10^4[Ni^{II}]$/mol dm$^3$ | 2.15 | 4.30 | 5.15 | 5.35 |
| | $k_{obs}$/s$^{-1}$ | 33.3 | 45.6 | 49.6 | 55.5 |
| $Fe(bipy)_3^{3+}$ | | | | | |
| | $10^4[Ni^{II}]$/mol dm$^3$ | 1.88 | 5.64 | 9.40 | 15.0 |
| | $k_{obs}$/s$^{-1}$ | 17.0 | 22.0 | 27.7 | 34.3 |

[a] $Fe^{III}(LL)_3^{3+}$ = *ca.* $10^5$ mol dm$^{-3}$, $Fe^{II}(LL)_3^{2+}$ = *ca.* 3 × $10^{-6}$ mol dm$^{-3}$, $I$ = 1.00 mol dm$^{-3}$.

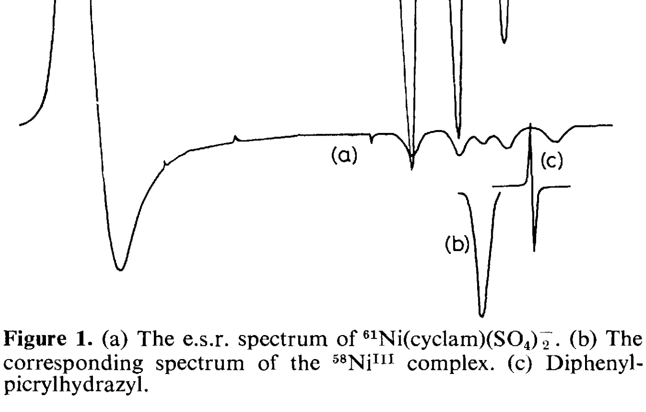

**Figure 1.** (a) The e.s.r. spectrum of $^{61}Ni(cyclam)(SO_4)_2^-$. (b) The corresponding spectrum of the $^{58}Ni^{III}$ complex. (c) Diphenylpicrylhydrazyl.

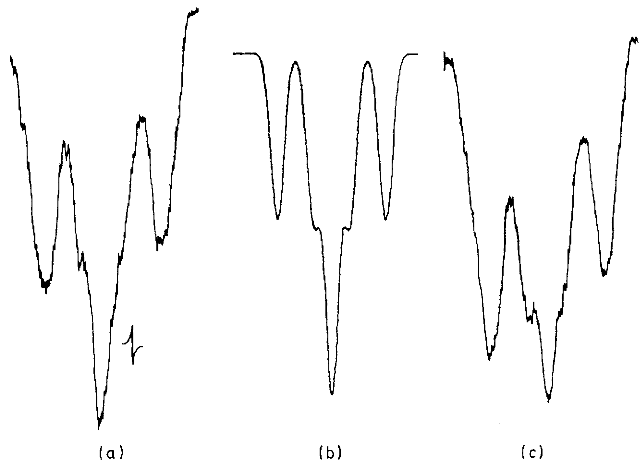

**Figure 2.** (a) E.s.r. spectrum of $1.16 \times 10^{-4}$ mol dm$^{-3}$ [$^{61}$Ni$^{II}$-(cyclam)]$^{2+}$ and $1.66 \times 10^{-5}$ mol dm$^{-3}$ [$^{58}$Ni$^{III}$(cyclam)]$^{3+}$ 9.5 s after mixing, $T$ = —16 °C. (b) Computer simulated spectrum of 2(a); see the text. (c) Equilibrium spectrum of 2(a), $t$ = 300 s.

from Ni metal (86.44% $^{61}$Ni) with a solution of $^{58}$Ni$^{III}$cyclam$^{3+}$ establishes the equilibrium (3), where $k_f = k_r$. The reaction

$$^{61}\mathrm{Ni^{II}(cyclam)^{2+}} + {}^{58}\mathrm{Ni^{III}(cyclam)^{3+}} \overset{k_f}{\underset{k_r}{\rightleftharpoons}} {}^{61}\mathrm{Ni^{III}(cyclam)^{3+}} + {}^{58}\mathrm{Ni^{II}(cyclam)^{2+}} \qquad (3)$$

rate may be deduced by observing the diminution of the $g_{\parallel}$ feature from the $^{58}$Ni$^{III}$ and the appearance of the quartet associated with the splitting by the $^{61}$Ni$^{III}$ nucleus. In our experiment, a 7:1 excess of $^{61}$Ni$^{II}$(cyclam)$^{2+}$ was mixed with $^{58}$Ni$^{III}$(cyclam)$^{3+}$. Solutions ([Ni$^{II}$] = $1.6 \times 10^{-4}$ M, [Ni$^{III}$] = $1.66 \times 10^{-5}$ M) were 1.00 mol dm$^{-3}$ in HClO$_4$ and at −16 °C. As soon as mixing was complete a sample was placed in an e.s.r. tube and frozen as quickly as possible in liquid nitrogen. The reaction time was measured reproducibly to ±1.0 s, the total time elapsed being 9.5 s. The e.s.r. spectrum was recorded [Figure 2(a)], the tube warmed to 25 °C for 5 min, and the equilibrium spectrum then measured [Figure 2(c)]. Each spectrum represents the addition of two signals from $^{61}$Ni$^{III}$ and $^{58}$Ni$^{III}$. Knowing the equilibrium concentrations accurately and the characteristics of the individual spectra, the equilibrium spectrum was simulated. The ratio of the central peak area ($^{58}$Ni$^{III}$) to that of the low-field peak ($^{61}$Ni$^{III}$) calculated from the simulation agrees with that of the experiment to within 15%. It is seen that the spectrum at $t$ = 9.5 s is closely similar to that at equilibrium, indicating that the reaction is largely completed within the time of measurement. This is consistent with a rate constant for the exchange where $k_f$ = *ca.* $10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$ since under the concentration conditions used, the reaction may be calculated to be >70% complete. The data were collected at −16 °C in an attempt to derive a more accurate value for $k_f$. Activation enthalpies for reactions of this type are known to be small, ≤10 kJ mol$^{-1}$,[8] so that the rate constant would not be expected to vary greatly in the range 250—295 K. These e.s.r. data are considered to provide independent support for a rapid self-exchange process.

The relatively rapid reaction rate suggests that any energy barrier associated with the geometry differences for d$^7$ and d$^8$ is small. There are reports, however, of some weak axial co-ordination of water in the Ni$^{II}$ complexes.[11] If such species were reactive the activation parameters would reflect only the electron transfer process. Owing to these uncertainties in the nature of the axial solvation of the nickel(II) complex and of the Ni$^{III}$–N bond lengths, we have not incorporated the work terms associated with the various free energy changes. These terms are such, however, as to change only slightly the value of $\Delta G^*_{11}$.

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Recent applications of the Marcus theory are consistent with values in the range 10—15 kJ mol dm$^{-3}$ (see E. Pelizzetti, E. Mentasti, and E. Pramauro, *Inorg. Chem.*, 1976, **15**, 2898; 1978, **17**, 1181).
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