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Oxidations of hydrogen peroxide by bis(1,4,7-triazacyclononane)-nickel(III), bis(1,4,7-trithiacyclononane)iron(III) and tris(2,2′-bipyridine)ruthenium(III) ions in acidic aqueous solutions‡

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The oxidations of hydrogen peroxide by typical outer-sphere oxidizing reagents, bis(1,4,7-triazacyclononane)nickel(III) [$Ni(tacn)_2^{3+}$], bis(1,4,7-trithiacyclononane)iron(III) [$Fe(ttcn)_2^{3+}$], and tris(2,2′-bipyridine)ruthenium(III) [$Ru(bipy)_3^{3+}$], were studied in acidic aqueous solution [ionic strength $I = 0.10$ mol dm^{-3} ($NaClO_4$)]. The stoichiometry was determined iodometrically as 2 : 1 ([M^{III}] : [H_2O_2]) for the reactions of $[Ni(tacn)_2]^{3+}$ and $[Fe(ttcn)_2]^{3+}$. Kinetic measurements with an excess of H_2O_2 revealed that HO_2^- is the only redox-active species for the reaction with $[Ni(tacn)_2]^{3+}$ under the conditions $2 < -\log[H^+] < 5.5$, while the participation of both HO_2^- and H_2O_2 was observed for the reactions with $[Fe(ttcn)_2]^{3+}$ and $[Ru(bipy)_3]^{3+}$. The second-order rate constant for the oxidation reaction of HO_2^- by $Ni(tacn)_2^{3+}$ was $(6.15 \pm 0.06) \times 10^6$ dm^3 mol^{-1} s^{-1} at 25 °C with $\Delta H^‡ = 46.9 \pm 0.4$ kJ mol^{-1} and $\Delta S^‡ = 42 \pm 1$ J K^{-1} mol^{-1}. The rate constants for the oxidation of HO_2^- and H_2O_2 by $[Fe(ttcn)_2]^{3+}$ at 25 °C were $(2.63 \pm 0.18) \times 10^9$ dm^3 mol^{-1} s^{-1} with $\Delta H^‡ = 26.7 \pm 4.1$ kJ mol^{-1} and $\Delta S^‡ = 25 \pm 14$ J K^{-1} mol^{-1}, and 3.12 ± 0.03 dm^3 mol^{-1} s^{-1} with $\Delta H^‡ = 40.1 \pm 0.9$ kJ mol^{-1} and $\Delta S^‡ = -101 \pm 3$ J K^{-1} mol^{-1}, respectively. The rate constants for the oxidation reaction of HO_2^- and H_2O_2 by $[Ru(bipy)_3]^{3+}$ at 25 °C were $(3.70 \pm 0.26) \times 10^7$ and 3.57 ± 0.19 dm^3 mol^{-1} s^{-1}, respectively. It was confirmed from the Marcus-type cross-relation that the oxidations of HO_2^- by $[Fe(ttcn)_2]^{3+}$ and $[Ru(bipy)_3]^{3+}$ proceed through the outer-sphere mechanism with $k_{ex}(HO_2^{\bullet}-HO_2^-) = 3.8 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}. The second-order rate constant for the oxidation of HO_2^- by $[Ni(tacn)_2]^{3+}$ was *ca.* 10^3 times faster than the predicted rate constant from the other outer-sphere reactions. The kinetic isotope effect ($k_H/k_D = 2.8$) indicates that the reaction of HO_2^- with $[Ni(tacn)_2]^{3+}$ proceeds *via* a transition state (shown in Scheme 1). The difference in the reactivity of small ions is discussed in relation to the electronic coupling in the precursor complex and the solvation structures of small ions.

Reactions of hydrogen peroxide in aqueous acidic solutions have been intensively studied for the elucidation of the reaction mechanism of this analytically and biochemically important reagent.[1–4] Most of these studies concern the inner-sphere reactions of hydrogen peroxide with metal aqua complexes, in which the electron-transfer processes were significantly accelerated by the formation of metal–peroxide bonds.

Wells and Fox[5] investigated the one-electron oxidation reaction of hydrogen peroxide with the substitution-inert tris(2,2′-bipyridine)nickel(III) ion $[Ni(bipy)_3]^{3+}$ in aqueous acidic solutions, which was independent of $[H^+]$ (> 0.5 mol dm^{-3}) and no replacement of the ligand on the nickel(III) center by H_2O_2 was observed. As the pK_a value of hydrogen peroxide is 11.52 at 298 K, the species which reacted with $[Ni(bipy)_3]^{3+}$ was supposed to be H_2O_2 rather than the more reactive HO_2^- below pH 0.3.[6] Macartney and Sutin[7] investigated the electron-exchange reaction for the $[Ni(bipy)_3]^{3+/2+}$ couple in acidic aqueous solutions, and reported that the redox potential and the electron-exchange rate constant for this couple were 1.72 V ([CF_3SO_3H] = 1 mol dm^{-3}) and 1.5×10^3 dm^3 mol^{-1} s^{-1}, respectively. Using the redox potential of 1.44 V for the H_2O_2–$HO_2^{\bullet}$ couple,[6] a value of 2.5×10^{-9} dm^3 mol^{-1} s^{-1} can be estimated for the electron-exchange reaction between $H_2O_2^{\bullet +}$ and H_2O_2 at $[H^+] = 1$ mol dm^{-3}, by assuming the pK_a value of equilibrium (1) to be 1.0.[8a]

$$H_2O_2^{\bullet +} \rightleftharpoons H^+ + HO_2^{\bullet};\ pK_a = -10^{8b} \text{ or } 1.0 \qquad (1)$$

More recently, Macartney[9] reported that the oxidation reactions of H_2O_2 by tris(polypyridine)metal(III) complexes (M = Fe, Ni or Os) occur *via* an outer-sphere mechanism under neutral or basic conditions, by carrying out careful experiments at 6 < pH < 9. Although a possible decomposition of polypyridine ligands by OH^- has been suggested,[10] his precise experiments revealed that the reduction of the metal(III) center by HO_2^- takes place more rapidly compared with ligand decomposition in the basic media. Macartney estimated the electron self-exchange rate constant for the $HO_2^{\bullet}$–HO_2^- couple as *ca.* 0.01 dm^3 mol^{-1} s^{-1}.

We have studied the reactions of hydrogen peroxide with $[Ni(tacn)_2]^{3+}$ and $[Fe(ttcn)_2]^{3+}$ (tacn = 1,4,7-triazacyclononane, ttcn = 1,4,7-trithiacyclononane) to examine the possible reaction pathways for the oxidation of hydrogen peroxide in acidic solutions. The reaction of HO_2^- with the latter complex is expected to proceed through an outer-sphere mechanism while that with the $[Ni(tacn)_2]^{3+}$ complex may take place through a pathway involving the interaction between HO_2^- and the amino hydrogen atom on the tacn ligand. By the use of two structurally similar complexes, $[Ni(tacn)_2]^{3+}$ and $[Fe(ttcn)_2]^{3+}$, the involvement of the hydrogen atom in the electron-transfer process may be examined. The stoichiometries of the reactions were determined iodometrically. The oxidation of hydrogen peroxide by $[Ru(bipy)_3]^{3+}$ was also studied for direct comparison of the kinetic data with those reported by Macartney.[9] The kinetic isotope effect was also examined to confirm the interaction of HO_2^- with the amino hydrogen atom on the tacn ligand during the electron-transfer process. This provides an opportunity to investigate the reactivity of H_2O_2 and HO_2^- ions in detail.

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‡ *Supplementary data available* (No. SUP 57287, 6 pp.): rate constants for the oxidations. See *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.

Experimental

Syntheses

The complex $[Ni(tacn)_2][ClO_4]_3$ was synthesized according to the literature method[11] (Found: C, 23.77; N, 13.75; N, 4.88. Calc. for $C_{12}H_{30}Cl_3N_6NiO_{12}$: C, 23.42; N, 13.66; H, 4.91%). The complexes $[Fe(ttcn)_2][ClO_4]_2$ and $[Fe(ttcn)_2][ClO_4]_3$ were synthesized by the literature methods[12,13] (Found: C, 23.99; N, 0.03; H, 3.99. Calc. for $C_{12}H_{24}Cl_2FeO_8S_6$: C, 23.42; N, 0; H, 3.93. Found: C, 21.02; N, 0; H, 3.53. Calc. for $C_{12}H_{24}Cl_3FeO_{12}S_6$: C, 20.16; N, 0; H, 3.38%) and $[Ru(bipy)_3][ClO_4]_3$ was synthesized by oxidizing $[Ru(bipy)_3]Cl_2$ with Cl_2.[10] By the addition of sodium perchlorate solution, dark green crystals were obtained, which were washed with ethanol and diethyl ether, and dried *in vacuo* (Found: C, 39.04; N, 8.97; H, 3.25. Calc. for $C_{30}H_{24}Cl_3N_6O_{12}Ru$: C, 41.51; N, 9.68; H, 2.79%). The poor microanalysis results for the $[Fe(ttcn)_2][ClO_4]_3$ and $[Ru(bipy)_3][ClO_4]_3$ were caused by the existence of unchanged $[Fe(ttcn)_2][ClO_4]_2$ or $[Ru(bipy)_3][ClO_4]_2$.[14] However, under the pseudo-first-order conditions used in this study, the existence of iron(II) or ruthenium(II) species (up to 23% was determined spectrophotometrically[14]) did not interfere in the oxidation reactions of hydrogen peroxide.

Chemicals

Stabilizer-free hydrogen peroxide (Mitsubishi Gas Co.) was used without further purification. Analyses by standardized permanganate solution revealed that the solution supplied contained 31.10% H_2O_2. Sodium perchlorate was prepared by mixing perchloric acid (SSG grade, Wako Pure Chemicals) and sodium carbonate (AR grade, Wako). After two recrystallizations, a stock solution was prepared by dissolving the solid in doubly distilled water. Its concentration was determined gravimetrically. Deuterium oxide (99.8 atom %) and deuteriated perchloric acid (68%, D_2O) were obtained from Aldrich. Other chemicals (AR grade, Wako) were used without further purification.

Physical measurements

Kinetic measurements of the oxidation of hydrogen peroxide by $[Ni(tacn)_2]^{3+}$ were carried out with excess amounts of hydrogen peroxide by using a Unisoku RA-401 stopped-flow apparatus ($4 < -\log[H^+] < 6$) and by using a JASCO Ubest V-570 UV/VIS spectrophotometer ($2 < -\log[H^+] < 3$). The temperatures of the cell compartments of each apparatus were controlled to ± 0.1 °C by a Hetofrig 04-PT-623 and by a Neslab RTE-111 temperature controller, respectively. Hydrogen-ion concentrations of sample solutions were adjusted either by the addition of perchloric acid or by acetic acid–sodium acetate buffer solutions (0.04 mol dm^{-3}). The decrease in the absorption of $[Ni(tacn)_2]^{3+}$ was monitored at 312 nm. The oxidation of hydrogen peroxide by $[Fe(ttcn)_2]^{3+}$ was monitored at 340 nm in acidic solutions ($[H^+] = 8.12 \times 10^{-3}$–$3.05 \times 10^{-2}$ mol dm^{-3}). The reaction of hydrogen peroxide with $[Ru(bipy)_3]^{3+}$ was studied in the range $3.91 < -\log[H^+] < 6.63$ by using acetic acid–sodium acetate (0.04 mol dm^{-3}) and phosphoric acid–sodium phosphate buffer solutions (0.04 mol dm^{-3}) by monitoring the absorbance change at 452 nm.

A kinetic isotope effect was observed for the oxidation of hydrogen peroxide by $[Ni(tacn)_2]^{3+}$ in D_2O at $[D^+] = 1.00 \times 10^{-2}$ mol dm^{-3} ($DClO_4$). The pK_D value for reaction (3) was

$$H_2O_2 \xrightleftharpoons{K_H} H^+ + HO_2^- \qquad (2)$$

$$D_2O_2 \xrightleftharpoons{K_D} D^+ + DO_2^- \qquad (3)$$

estimated from the linear relationship between K_H and K_D for various acids and bases reported to date.[15]

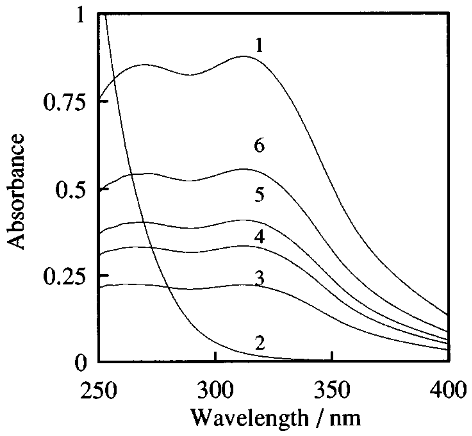

Fig. 1 Recovery of $[Ni(tacn)_2]^{3+}$ by re-oxidation of a solution containing $[Ni(tacn)_2]^{2+}$ with peroxodisulfate. 1; Original absorption spectrum before the reaction with H_2O_2. 2; Spectrum after completion of reduction of 1 by H_2O_2 (30 min after the reduction under neutral conditions). 3–6; Reappearance of $[Ni(tacn)_2]^{3+}$ at 20, 40, 60 and 260 min after the addition of excess of peroxodisulfate to 2 at pH 1 (perchloric acid), respectively. Spectra 3–6 were calculated by subtracting 2 from the absorption spectra recorded at each time interval. $[Ni(tacn)_2{}^{3+}]_0 = 9.03 \times 10^{-5}$ mol dm^{-3}, $[H_2O_2]$ added $= 5.96 \times 10^{-2}$ mol dm^{-3}

As the 31.10% solution of H_2O_2 in H_2O was used to prepare the D_2O_2 solution, the formation of deuteriated hydrogen peroxide was not complete (maximum molar ratio of $H_2O:D_2O$ 1 : 30). However, after 1 h, the deuterium oxide solution containing H_2O_2 gave reproducible kinetic data for the reaction with $[Ni(tacn)_2]^{3+}$, which suggests that the substitution of hydrogen ion for deuterium ion was in complete equilibrium within an hour. It has been reported by McAuley *et al.*[11] that the amino protons on co-ordinated tacn rapidly exchange with deuterium ions in solution. Therefore, the kinetic isotope effect can be successfully observed if there is any significant interaction between hydrogen peroxide and the hydrogen atom on the amino nitrogen of the tacn ligand.

Determination of the stoichiometries

The stoichiometry of the oxidation of hydrogen peroxide by $[Ni(tacn)_2]^{3+}$ was determined by the following method. To a hydrogen peroxide solution, the concentration of which was determined iodometrically, was added a weighed amount of solid $[Ni(tacn)_2][ClO_4]_3$. After the reaction was complete (up to 1 h which corresponds to more than 100 half-lives), the amount of excess of hydrogen peroxide was determined iodometrically. This procedure was repeated three times and the stoichiometry determined as 2.01 ± 0.01 : 1 for $[Ni(tacn)_2{}^{3+}]:[H_2O_2]$. Therefore, the overall reaction is expressed by equation (4).[5]

$$2[Ni(tacn)_2]^{3+} + H_2O_2 \longrightarrow 2[Ni(tacn)_2]^{2+} + O_2 + 2H^+ \qquad (4)$$

The reversibility of the reaction was examined by the spectrophotometric method. After completion of the reaction, the reaction mixture was treated with an excess amount of peroxodisulfate. The increase of the absorption bands at 270 and 310 nm in Fig. 1 indicates the recovery of the $[Ni(tacn)_2]^{3+}$ species. A spectrophotometric determination of $[Ni(tacn)_2{}^{2+}]$ at 799 nm (molar absorption coefficient = 7.41 dm^3 mol^{-1} cm^{-1}) revealed that more than 96% of $[Ni(tacn)_2]^{3+}$ in the original solution was reduced to $[Ni(tacn)_2]^{2+}$ by H_2O_2. The observation that only 63% of the original $[Ni(tacn)_2]^{3+}$ was recovered by the re-oxidation of Ni^{II} by peroxodisulfate (Fig. 1) may be attributed to the decomposition of $[Ni(tacn)_2]^{3+}$ during the oxidation by peroxodisulfate.[11] Therefore, it was concluded that the reduction of nickel(III) species by H_2O_2 occurs not at the ligand but at the metal center.

An attempt was made to determine the stoichiometry for the reaction of hydrogen peroxide with $[Fe(ttcn)_2]^{3+}$. The purity of $[Fe(ttcn)_2][ClO_4]_3$ was found spectrophotometrically to be 77.6% by dissolving the crystals in 2 mol dm^{-3} H_2SO_4.[14] By using the same procedure applied to the reaction of hydrogen peroxide with $[Ni(tacn)_2]^{3+}$, the stoichiometry of this reaction was determined as 2.2 : 1 for $[Fe(ttcn)_2{}^{3+}]$: $[H_2O_2]$, which may be taken as 2 : 1, by considering the instability of $[Fe(ttcn)_2]^{3+}$ in solution.[14] All the reactions were observed at a constant ionic strength of $I = 0.10$ mol dm^{-3} ($NaClO_4$).

Results

Oxidation of hydrogen peroxide by $[Ni(tacn)_2]^{3+}$

The reactions with excess amounts of hydrogen peroxide were excellently first order up to 4 half-lives. No rapid spectral change at the initial stage of the reaction was observed. The conditional second-order rate constant ($k = k_{obs}/[H_2O_2]_0$ where $[H_2O_2]_0$ is the total concentration of hydrogen peroxide) increased with decreasing hydrogen-ion concentration. This dependence of k on $[H^+]$ indicates the following dual pathways for reaction (4) (M = Ni). As the resulting superoxide radical is

$$H_2O_2 \overset{K_a}{\rightleftharpoons} HO_2^- + H^+ \qquad (1)$$

$$H_2O_2 + M^{3+} \xrightarrow{k_2} H_2O_2^{\bullet +} + M^{2+} \qquad (5)$$

$$HO_2^- + M^{3+} \xrightarrow{k_1} HO_2^{\bullet} + M^{2+} \qquad (6)$$

a moderately weak acid, $HO_2^{\bullet}$ is the predominant species under the experimental conditions.[6] Superoxide ions formed by reactions (5) and (6) are then consumed either by reaction (9) with Ni^{III} or by the disproportionation reaction (8).[5,6] In either case

$$HO_2^{\bullet} \rightleftharpoons O_2^{\bullet -} + H^+;\ pK_{a2} = 4.89 \qquad (7)$$

$$2\,HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \qquad (8)$$

$$HO_2^{\bullet} + M^{3+} \longrightarrow O_2 + M^{2+} + H^+ \qquad (9)$$

the stoichiometry of the reaction is 2 : 1 as determined in this study. As the reactivity of superoxide radicals is very high, reactions (5) and (6) are the rate-determining steps and the rate law is given in equation (10). Plots of log k *vs.* $-\log[H^+]$ gave straight lines with unit slope as shown in Fig. 2. Therefore, reaction (6) is the dominant process under the experimental conditions. Although an attempt was made to obtain the k_2 value by applying equation (10) for the results obtained at $[H^+] > 1 \times 10^{-3}$ mol dm^{-3}, the intercept of the plot of k_{obs} *vs.* $[H^+]^{-1}$ was not meaningful within the experimental uncertainty $[(-4.83 \pm 3.19) \times 10^{-4}]$.

$$-\frac{d[M^{3+}]}{dt} = 2\left(\frac{k_1K_a}{[H^+]} + k_2\right)[H_2O_2][M^{3+}] \qquad (10)$$

$$k_{obs} = 2\left(\frac{k_1K_a}{[H^+]} + k_2\right)[H_2O_2]_0 \qquad (11)$$

Oxidation of hydrogen peroxide by $[Fe(ttcn)_2]^{3+}$ and $[Ru(bipy)_3]^{3+}$

As $[Fe(ttcn)_2]^{3+}$ decomposes at high pH, measurements were carried out under acidic conditions ($8.12 \times 10^{-3} < [H^+] < 3.05 \times 10^{-2}$ mol dm^{-3}), where the iron complex is stable for more than 30 min. As the range of hydrogen-ion concentration was narrow, the conditional second-order rate constant ($k = k_{obs}/[H_2O_2]_0$) was plotted against $[H^+]^{-1}$ by assuming equations (10) and (11) for this reaction (Fig. 3). The linear dependence of k on the reciprocal hydrogen-ion concentration indicates the dual pathways expressed by equations (5) and (6). The second-order rate constants, k_1 and k_2, corresponding to (5) and (6), are listed in Table 1, together with the activation parameters for each process.

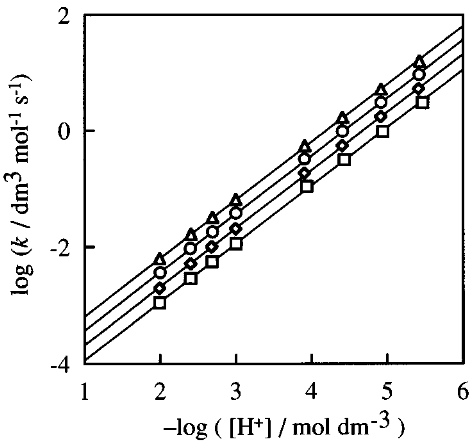

Fig. 2 Plots of log k *vs.* $-\log[H^+]$ for the reaction of H_2O_2 with $[Ni(tacn)_2]^{3+}$. The symbols represent the data obtained at 303.2(△), 298.2(○), 293.2(◇) and 288.8 K(□). $[Ni(tacn)_2{}^{3+}]_0 = (0.500–1.00) \times 10^{-4}$ mol dm^{-3}, $[H_2O_2] = 0.02–0.19$ mol dm^{-3}

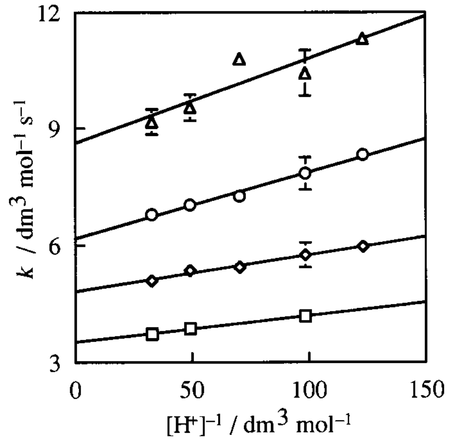

Fig. 3 Plots of k *vs.* $[H^+]^{-1}$ for the reaction of H_2O_2 with $[Fe(ttcn)_2]^{3+}$. Symbols as in Fig. 2. $[Fe(ttcn)_2{}^{3+}]_0 = 1.40 \times 10^{-3}$ mol dm^{-3}, $[H_2O_2] = 0.025–0.21$ mol dm^{-3}

The oxidation reaction of hydrogen peroxide by $[Ru(bipy)_3]^{3+}$ was observed at 3.91 < pH < 6.63, to confirm the previous results reported by Macartney.[9] A plot of log k ($k = k_{obs}/[H_2O_2]_0$) against $-\log[H^+]$ at 25 °C (Fig. 4) appears to be a straight line, indicating that reaction (6) is the dominant process. The solid line in Fig. 4 was obtained by non-linear least-squares analysis on the basis of equation (11). The obtained rate constants, k_1 and k_2, were $(3.70 \pm 0.26) \times 10^7$ and 3.57 ± 1.19 dm^3 mol^{-1} s^{-1}, respectively. These results suggest that reaction (5) is negligibly slow compared with the k_1 process. A value of 3×10^7 dm^3 mol^{-1} s^{-1} was reported for k_1 in the previous study,[9] which seems in satisfactory agreement with the present value considering the difference in the experimental conditions: measurements in ref. 9 were made at $[LiCF_3SO_3] = 0.50$ mol dm^{-3} while our measurements were carried out at $[NaClO_4] = 0.10$ mol dm^{-3}.

Kinetic isotope effect for the oxidation of hydrogen peroxide by $[Ni(tacn)_2]^{3+}$

The conditional rate constant, k_D ($= k_{obs}/[D_2O_2]_0$), was determined at various temperatures at the constant concentration of

Table 1 Rate constants and activation parameters obtained for oxidation reactions of H_2O_2

Oxidant	Rate constant */dm^3 mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
$[Ni(tacn)_2]^{3+}$	k_1 (6.15 ± 0.06) × 10^6	46.9 ± 0.4	42 ± 1
$[Fe(ttcn)_2]^{3+}$	k_1 (2.63 ± 0.18) × 10^9	26.7 ± 4.1	25 ± 14
	k_2 3.12 ± 0.03	40.1 ± 0.9	−101 ± 3
$[Ru(bipy)_3]^{3+}$	k_1 (3.70 ± 0.26) × 10^7		
	k_2 3.57 ± 1.19		

* At 298.2 K.

Table 2 Rate constants obtained for the oxidation reaction of HO_2^- by $[Ni(tacn)_2]^{3+}$ at various temperatures in water and D_2O *

Solvent		288.2 K	293.2 K	298.2 K	303.2 K
water	$-\log(K_H/\text{dm}^3\ \text{mol}^{-1})$	11.73	11.62	11.52	11.42
	$k_{1H}/10^6$ dm^3 mol^{-1} s^{-1}	3.08 ± 0.28	4.35 ± 0.04	6.15 ± 0.06	8.49 ± 0.08
D_2O	$-\log(K_D/\text{dm}^3\ \text{mol}^{-1})$	12.37	12.16	12.26	12.06
	$k_{1D}/10^6$ dm^3 mol^{-1} s^{-1}	1.05 ± 0.04	1.56 ± 0.05	2.25 ± 0.06	3.21 ± 0.09

* The equilibrium constant, K_D, at 298.2 K was estimated from reported values of K_H by using the following equation,[15] from the fourteen acid–base equilibria for which both K_H and K_D values have been reported, $\log(K_H/K_D) = C \log K_H$, where C is a constant. The K_D values at other temperatures were calculated by assuming that the reaction enthalpy is identical for H_2O_2 and D_2O_2.[16]

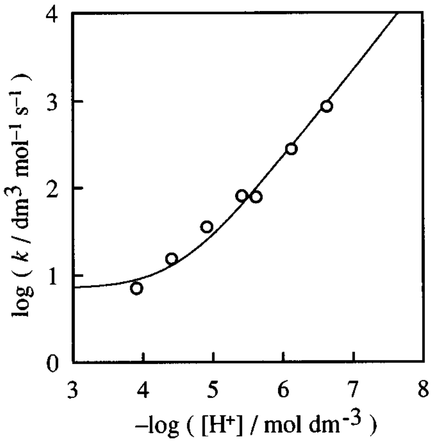

Fig. 4 Plot of log k *vs.* −log $[H^+]$ for the reaction of H_2O_2 with $[Ru(bipy)_3]^{3+}$. The solid line is the best-fit curve estimated by the non-linear least-squares analysis on the basis of equation (11). $[Ru(bipy)_3^{3+}]_0 = 2.00 \times 10^{-5}$ mol dm^{-3}, $[H_2O_2]_0 = 0.0067$–0.092 mol dm^{-3}

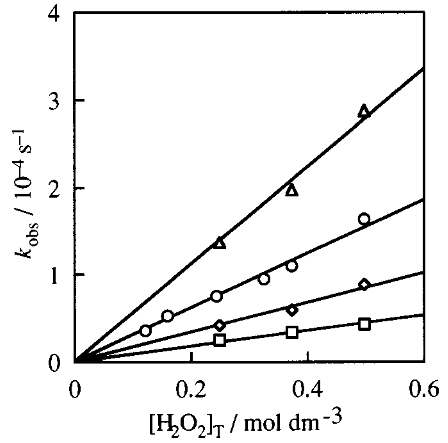

Fig. 5 Plots of k_{obs} *vs.* initial concentration of hydrogen peroxide in D_2O. $[D^+] = 1.00 \times 10^{-2}$ mol dm^{-3}. $[H_2O_2]_T$ on the horizontal axis denotes the initial concentration of H_2O_2 dissolved in D_2O. Symbols as in Fig. 2

$[D^+] = 1.00 \times 10^{-2}$ mol dm^{-3} in D_2O. The results are shown in Fig. 5, and k_D was (3.12 ± 0.08) × 10^{-4} dm^3 mol^{-1} s^{-1} at 25 °C, which is significantly smaller than that obtained in water [(3.61 ± 0.03) × 10^{-3} dm^3 mol^{-1} s^{-1}]. On the basis of the treatment by Bell,[15] the K_a value for D_2O_2 was estimated at 298.2 K. The values of K_a in D_2O at other temperatures were calculated by assuming that the enthalpy for reaction (3) is identical to that for (2).§ In Table 2 are listed the values of thus calculated K_{aD} and k_{1D} (the subscript D indicates that the values were obtained in D_2O while $k_{1H} = k_1$). The net isotope effect, k_{1H}/k_{1D}, at 25 °C was 2.28 ± 0.05. The isotope effect for the pre-exponential factor A_H/A_D, expressed by equation (12), was

$$\ln(k_{1H}/k_{1D}) = \ln(A_H/A_D) + [(\Delta E_D - \Delta E_H)/RT] \qquad (12)$$

calculated as 2.2 ± 0.3, which is much larger than the limiting value of 0.7–1.4 expected for the existence of proton tunnelling;[16] here ΔE denotes the activation energy for the reactions in water and D_2O.

Discussion

Redox potentials for the reactions of $H_2O_2^{\bullet +}$–H_2O_2 and $HO_2^{\bullet}$–HO_2^- couples are expressed by equations (13) and 14).[6,9]

$$HO_2^{\bullet} + H^+ + e^- \rightleftharpoons H_2O_2;\ E^\circ = 1.44\ \text{V} \qquad (13)$$

$$HO_2^{\bullet} + e^- \rightleftharpoons HO_2^-;\ E^\circ = 0.74\ \text{V} \qquad (14)$$

The relation between the rate constants for the cross-reaction and the self-exchange reactions can be described by the Ratner-type cross-relations (15)–(17), regardless of the reaction

$$k_{12} = (k_{11}k_{22}K_{12})^{\frac{1}{2}}W_{AB} \qquad (15)$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \qquad (16)$$

$$w_{ij} = 4.225 \times 10^3\, z_iz_j/r(1 + 0.329\, r\, I^{\frac{1}{2}}) \qquad (17)$$

mechanism.[17,18] where k_{11}, k_{22}, k_{12} and K_{12} are the self-exchange rate constants, the rate constant for the cross-reaction, and the equilibrium constant of the cross-reaction, respectively; z_i, z_j, and r are the ionic charges and the sum of the ionic radii of each reacting species. Equation (15) is valid for every type of reaction if the following two requirements are fulfilled:[17] (1) the activation process for each reactant is independent of the other reactant and (2) the activated species are the same for the self-exchange and cross-reaction.

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§ This assumption may not be valid for these reactions. However, the ratio of A_H/A_D is not affected by this assumption, as the difference in the reaction free energies for equations (2) and (3) is attributed to the second term of the right-hand side of equation (12). A value of 2.2 ± 0.3 for A_H/A_D estimated from k_{1H}/k_{1D} is identical to that estimated from the gross rate constants, k_H/k_D.

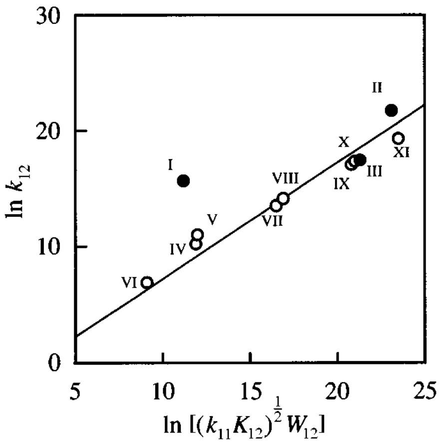
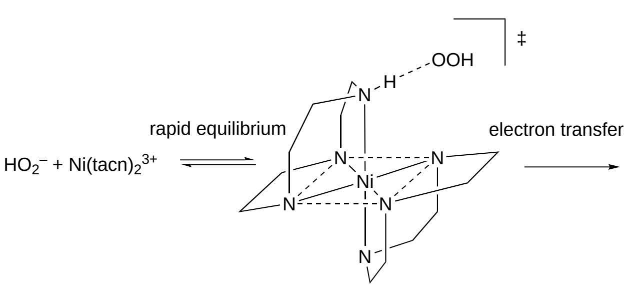


Fig. 6 Plot of ln k_{12} *vs.* ln$[(k_{11}K_{12})^{\frac{1}{2}}W_{12}]$ on the basis of equation (17). The Roman numbers denote that each circle represents the reaction of HO_2^- with: $[Ni(tacn)_2]^{3+}$, **I**; $[Fe(ttcn)_2]^{3+}$, **II**; $[Ru(bipy)_3]^{3+}$ (this work), **III**; $[Os(dmbipy)_3]^{3+}$, **IV**; $[Os(bipy)_3]^{3+}$, **V**; $[Fe(dmbipy)_3]^{3+}$, **VI**; $[Fe(bipy)_3]^{3+}$, **VII**; $[Ru(dmbipy)_3]^{3+}$, **VIII**; $[Ru(bipy)_3]^{3+}$ (ref. 9), **IX**; $[Ni(dmbipy)_3]^{3+}$, **X**; $[Ni(bipy)_3]^{3+}$, **XI** (dmbipy = 4,4′-dimethyl-2,2′-bipyridine)



Scheme 1

In Fig. 6 a plot of ln k_{12} *vs.* ln $[(k_{11}K_{12})^{\frac{1}{2}}W_{12}]$ is shown for the oxidations of HO_2^- by various tris(polypyridine)metal(III) complexes in aqueous solution,[9] together with the results obtained in this study. All the reactions except the oxidation of HO_2^- by $[Ni(tacn)_2]^{3+}$ fit on a straight line with unit slope. Therefore, it may be concluded that the oxidations of HO_2^- by $[Fe(ttcn)_2]^{3+}$ and $[Ru(bipy)_3]^{3+}$, and those by **IV–XI**, proceed through an outer-sphere mechanism.[9] On the other hand, the rate constant for the oxidation of HO_2^- by $[Ni(tacn)_2]^{3+}$ ion is much larger than that predicted by the outer-sphere reactions. In such a case a specific interaction between HO_2^- and the amino proton on the tacn ligand may be indicated.[19] The involvement of the amino proton is supported by the fact that the oxidation of HO_2^- by $[Fe(ttcn)_2]^{3+}$, which has a similar structure to that of $[Ni(tacn)_2]^{3+}$ with no reactive (or labile) hydrogen atom, occurs *via* the outer-sphere mechanism.

deMaine and Stanbury reported that the reaction of $[Ni(tacn)_2]^{3+}$ with NO involved N-deprotonated $[Ni^{III}(tacn)(tacn-H)]^{2+}$ species and did not produce $[Ni(tacn)_2]^{2+}$ $\{[Ni^{III}(tacn)(tacn-H)]^{2+}$ represents the N-deprotonated conjugate base form of $[Ni(tacn)_2]^{3+}\}$. A pK_a value for the deprotonation of the co-ordinated tacn was estimated as *ca.* 11.[20] Therefore, the degree of deprotonation of the co-ordinated tacn ligand should be very small under the experimental conditions. Moreover, the stoichiometric yield of $[Ni(tacn)_2]^{2+}$ observed in this study (Fig. 1) indicates that such a species suggested by deMaine and Stanbury was not involved in the reaction of $[Ni(tacn)_2]^{3+}$ with HO_2^-. Instead, the kinetic isotope effect observed for the oxidation of HO_2^- by $[Ni(tacn)_2]^{3+}$ strongly indicates an interaction between the amino proton on the tacn ligand and HO_2^- during the activation process (Scheme 1). The relatively small value of k_{1H}/k_{1D}(= 2.28 ± 0.05 at 25 °C) indicates that this interaction may not lead to a proton-transfer reaction or that the transfer of a proton in the transition state occurs to a much lower extent compared with the 50% transfer assumed for the maximum isotope effect ($k_{1H}/k_{1D} = 8$).[16,19] As the proton exchange on the amino nitrogen atom of tacn is reported to be very fast,[11] it is possible to consider that electron transfer takes place coupled with a proton-transfer reaction, followed by rapid protonation of the amino nitrogen atom. Therefore the mechanism in equations (18)–(20) similar to that

$$[Ni^{III}(tacn)_2]^{3+} + HO_2^- \overset{K'}{\rightleftharpoons} [Ni^{III}(tacn)(tacn{-}O_2H)^{2+}]^* \quad (18)$$

$$[Ni^{III}(tacn)(tacn{-}O_2H)^{2+}]^* \xrightarrow{k} [Ni^{II}(tacn)(tacn-H)]^+ + H^+ + HO_2^{\bullet} \quad (19a)$$

$$\text{or } [Ni(tacn)_2]^{2+} + HO_2^{\bullet} \quad (19b)$$

$$[Ni(tacn)(tacn-H)]^+ + H^+ \xrightarrow{\text{fast}} [Ni(tacn)_2]^{2+} \quad (20)$$

$$[Ni(tacn)_2]^{3+} + HO_2^{\bullet} \xrightarrow{\text{fast}} [Ni(tacn)_2]^{2+} + O_2 + H^+ \quad (21)$$

for the reaction of $[Co(sep)]^{2+}$ (sep = sepulchrate,1,3,6,8,10,-13,16,19-octaazabicyclo[6.6.6]eicosane) with $O_2^{\bullet-}$ is suggested for the oxidation of HO_2^- by $[Ni(tacn)_2]^{3+}$,[19] where $[Ni^{III}(tacn)(tacn{-}O_2H)^{2+}]^*$ is the species shown in Scheme 1, and the species $[Ni^{II}(tacn)(tacn-H)]^+$ is the N-deprotonated conjugate base form of $[Ni(tacn)_2]^{2+}$. If K' is not very large ($\leqslant 10^6$ dm^3 mol^{-1}), the rate law can be expressed by equation (10) with $k_1 = kK'$. It seems reasonable to assume that K' is smaller than 10^6, considering that the maximum value for an outer-sphere association constant is 5 dm^3 mol^{-1} for $[Ni(tacn)_2]^{3+}$ and HO_2^- under the experimental conditions.[21] However, the possibility of other proton-mediated mechanisms, such as the double exchange or superexchange-type mechanism,[22] may not be ruled out, as the ratio of the pre-exponential factors (A_H/A_D) indicates no proton tunnelling expected for the ordinary proton-transfer reactions.[16]

From the intercept of the plot in Fig. 6, a value of (3.8 ± 0.3) × 10^{-3} dm^3 mol^{-1} s^{-1} was calculated as the electron self-exchange rate constant of the $HO_2^{\bullet}$–HO_2^- couple, $k_{ex}(HO_2^{\bullet}-HO_2^-)$, which is consistent with the value reported by Macartney.[9] Eriksen *et al.*[23] reported the reaction of $ClO_2^{\bullet}$ with HO_2^-. From their results, 3 × 10^4 dm^3 mol^{-1} s^{-1} was calculated as $k_{ex}(HO_2^{\bullet}-HO_2^{\bullet})$, which is about 10^7 times larger than (3.8 ± 0.3) × 10^{-3} dm^3 mol^{-1} s^{-1} estimated here. It may be reasonable to consider that the reaction studied by Eriksen *et al.* may not proceed through the simple outer-sphere mechanism. For the electron-transfer reactions between small molecules such as those of HO_2^- and $ClO_2^{\bullet}$, a specific intermediate (or a precursor complex) which causes strong interaction between the electronic orbitals of the reactants has been proposed.[24,25] Unlike the oxidation of HO_2^- by $[Ni(tacn)_2]^{3+}$, a strong acid–base interaction between HO_2^- and $ClO_2^{\bullet}$ takes place as the anion affinity of $ClO_2^{\bullet}$ is very large.[23] Therefore, the oxidation of HO_2^- by $ClO_2^{\bullet}$ probably occurs, with a somewhat inner-sphere character, through strong electronic coupling caused by the acid–base (donor–acceptor) interaction between these two molecules in the transition state.

For reactions involving small molecules such as the O_2–$O_2^{\bullet-}$ couple, strong solvation of anions was suggested to explain the relatively slow self-exchange rate constants.[17] The small rate constant of the outer-sphere electron-exchange reaction for the $HO_2^{\bullet}$–HO_2^- couple may also be attributed to the strong solvational interaction for HO_2^-. Macartney[9] tried to explain the slow electron-exchange rate constant for this couple on the basis of a semiclassical model. His calculation using the hard-sphere radii of HO_2^- and $HO_2^{\bullet}$ species yielded a *ca.* 10^2 times larger value for the self-exchange rate constant than the experimentally obtained value. The application of semiclassical theory to the electron-exchange reactions of the $ClO_2^{\bullet}$–ClO_2^- and $NO_2^{\bullet}$–NO_2^- couples[26,27] led to the conclusion that the calculated interaction distances between each redox pair were *ca.* 100 pm larger than the sum of the hard-sphere radii of each species,[9] which suggests that electron-transfer reactions involving small ions take place through the solvational sheath around the ions. On this basis, the relative slowness of the electron transfer for the $HO_2^{\bullet}$–HO_2^- couple may be explained by the non-adiabatic effect originating from the lower electronic interaction between the reactants. The relations have been derived from the semiclassical treatment for the non-adiabatic electron-transfer reactions,[28,29] where κ_{el} and ν_n are the electronic transmission

$$k = \nu_{el}\exp[(\Delta G_{OS}^* + \Delta G_{IS}^*)/RT] \tag{22}$$

$$\kappa_{el} = 2[1 - \exp(-\nu_{el}/2\nu_n)]/[2 - \exp(\nu_{el}/2\nu_n)] \tag{23}$$

$$\nu_{el} = (H_{AB}{}^2/h)(\pi^3/RT\Delta G_{OS}^*)^{\frac{1}{2}} \tag{24}$$

$$H_{AB} = H_{AB}{}^0\exp[-\alpha(\sigma - \sigma_0)] \tag{25}$$

coefficient and the nuclear frequency, H_{AB} and $H_{AB}{}^0$ are the electronic coupling factors for the non-adiabatic and adiabatic cases, α, σ and σ_0 are the distance scaling factor and the separations between the reactants for the non-adiabatic and adiabatic cases, and ΔG_{OS}^* and ΔG_{IS}^* denote the outer- and inner-sphere reorganization free energies, respectively. As the electronic coupling factor decreases exponentially with increasing distance between the reactants [equation (25)], the separation of two reactants by the solvation sheath significantly reduces the rate of the electron-transfer reaction.

By assuming the pK_a value for reaction (1) is 1.0,[8a] the electron self-exchange rate constant for the $H_2O_2^{\bullet+}$–H_2O_2 couple was calculated as 3×10^{-7} dm^3 mol^{-1} s^{-1} from the cross-reaction with $[Fe(ttcn)_2]^{3+}$. The self-exchange rate constant for this couple was estimated as 2.5×10^{-9} dm^3 mol^{-1} s^{-1} from the reaction of H_2O_2 with $[Ni(bipy)]^{3+}$ reported by Wells and Fox.[5] These two self-exchange rate constants may be in good agreement with each other, considering the accuracy of the calculation and the difference in the experimental conditions.[5] However, the self-exchange rate constant for the $H_2O_2^{\bullet+}$–H_2O_2 couple is more than 10^4 times smaller than that for the $HO_2^{\bullet}$–HO_2^- couple. The very small self-exchange rate constant for the $H_2O^{\bullet+}$–H_2O_2 couple cannot be explained by the difference in the thickness of the solvational sheaths of these ions as the solvation of the HO_2^- ion is supposed to be greater compared with that of $H_2O_2^{\bullet+}$ in water.[30] Moreover, the estimated inner-sphere contribution to the activation free energy for the $H_2O_2^{\bullet+}$–H_2O_2 couple is almost identical to that for the $HO_2^{\bullet}$–HO_2^- couple.[9,17] Therefore, it may be assumed that the self-exchange rate constant for the $H_2O_2^{\bullet+}$–H_2O_2 couple is comparable to or faster than that for the $HO_2^{\bullet}$–HO_2^- couple.[9] In such a case, a maximum value of −4.8 was estimated as the pK_a value for reaction (1) from the relation given in equation (15). Kustin and co-workers[8a] used 1.0 as the pK_a value for reaction (1) for the analysis of the reaction of H_2O_2 with Mn^{III}. More recently, Schwarz[8b] argued that the pK_a value for reaction (1) should be less than −10 and that $H_2O_2^{\bullet+}$ is an unlikely participant in reactions in water considering the stability of $H_3O_2^+$. The value of $pK_a < -4.8$ for reaction (1) estimated in this study is, therefore, closer to that postulated by Schwarz, and this result supports the involvement of the solvational sheath in the electron-transfer reactions of small ions or molecules such as hydrogen peroxide.

Conclusion

It may be summarized that the redox reactions involving HO_2^- proceed in the following three ways: (1) an outer-sphere mechanism with inert metal complexes (however, the reactions may be non-adiabatic), (2) electron transfer coupled with proton transfer or through the double exchange/superexchange-type interaction, and (3) strong electronic coupling by direct donor–acceptor interaction between the reacting species.

The slow electron-transfer rate constants for the reactions involving small ions may be explained by the non-adiabatic effect originating from the strong solvation of these small ions. Such speculation was also made previously by Jordan and Macartney.[9,17] A maximum value of −4.8 was estimated as the pK_a value for reaction (1) from the limiting self-exchange rate constant for the $H_2O^{\bullet+}$–H_2O_2 couple.

Acknowledgements

This research was supported by Grants-in-Aid for Scientific Research (Nos. 7554061 and 7504003) from the Ministry of Education, Science and Culture of Japan.

References

1 R. D. Jones, D. A. Summerville and F. Basolo, *Chem. Rev.*, 1979, **79**, 139.
2 A. Bakac, *Prog. Inorg. Chem.*, 1995, **43**, 267 and refs. therein.
3 C. F. Wells, *Prog. React. Kinet.*, 1995, **20**, 1 and refs. therein.
4 S. A. Mirza, B. Bocquet, C. Robyr, S. Thomi and A. F. Williams, *Inorg. Chem.*, 1996, **35**, 1332.
5 C. F. Wells and D. Fox, *J. Chem. Soc., Dalton Trans.*, 1977, 1498.
6 D. T. Sawyer, *Oxygen Chemistry*, Oxford University Press, New York, 1991.
7 D. H. Macartney and N. Sutin, *Inorg. Chem.*, 1983, **22**, 3530.
8 (*a*) G. Davies, L. J. Kirschenbaum and K. Kustin, *Inorg. Chem.*, 1968, **7**, 146 and refs. therein; (*b*) H. A. Schwarz, *J. Chem. Educ.*, 1981, **58**, 101.
9 D. H. Macartney, *Can. J. Chem.*, 1986, **64**, 1936.
10 P. K. Gosh, B. S. Brunschwig, M. Chou, C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, 1984, **106**, 4772.
11 A. McAuley, P. R. Norman and O. Olubuyide, *Inorg. Chem.*, 1984, **23**, 1938; *J. Chem. Soc., Dalton Trans.*, 1984, 1051.
12 H. J. Kuppers, K. Wieghardt, B. Nuber, J. Weiss, E. Bill and A. X. Trautwein, *Inorg. Chem.*, 1987, **26**, 3762.
13 K. Wieghardt, H. J. Kuppers and J. Weiss, *Inorg. Chem.*, 1985, **24**, 3067.
14 H. D. Takagi and T. W. Swaddle, *Can. J. Chem.*, 1990, **68**, 2228.
15 R. P. Bell, *The Proton in Chemistry*, Methuen, London, 1959.
16 W. H. Sauders, jun., *Techniques of Chemistry*, Wiley, New York, 1986, vol. 6.
17 R. B. Jordan, *Reaction Mechanism of Inorganic and Organometallic Systems*, Oxford University Press, New York, 1991.
18 M. A. Ratner and R. D. Levine, *J. Am. Chem. Soc.*, 1980, **102**, 6898.
19 A. Bakac, J. H. Espenson, I. I. Creaser and A. M. Sargeson, *J. Am. Chem. Soc.*, 1983, **105**, 7624.
20 M. M. deMaine and D. M. Stanbury, *Inorg. Chem.*, 1991, **30**, 2104.
21 R. M. Fuoss, *J. Am. Chem. Soc.*, 1958, **80**, 5059.
22 J. Halpern and L. E. Orgel, *Discuss. Faraday. Soc.*, 1960, **29**, 32.
23 T. E. Eriksen, J. Lind and G. Merenyi, *J. Chem. Soc., Faraday Trans. 1*, 1981, 2115.
24 K. Zahir, J. H. Espenson and A. Bakac, *J. Am. Chem. Soc.*, 1988, **110**, 5059.
25 D. M. Stanbury, M. M. deMaine and G. Goodloe, *J. Am. Chem. Soc.*, 1989, **111**, 5496.
26 O. Knop and P. A. Giguere, *Can. J. Chem.*, 1959, **37**, 1794.
27 W. K. Wilmarth, D. M. Stanbury, J. E. Byrd, H. N. Po and C. P. Chua, *Coord. Chem. Rev.*, 1983, **51**, 155.
28 N. Sutin, *Prog. Inorg. Chem.*, 1983, **30**, 441.
29 H. Doine and T. W. Swaddle, *Can J. Chem.*, 1988, **66**, 2763.
30 Y. Marcus, *Introduction to Liquid State Chemistry*, Wiley, New York, 1977.

Received 28*th May* 1997; *Paper* 7/03670A