Kinetics and mechanism of the oxidation of sulfite by *trans*-[Ru(tmc)O$_2$]$^{2+}$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)

Tai-Chu Lau,* Kwok-Ho Chow, Kent W. C. Lau and Wenny Y. K. Tsang

Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon Tong, Hong Kong

The kinetics of the oxidation of SO$_3^{2-}$ by *trans*-[Ru(tmc)O$_2$]$^{2+}$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) has been studied in aqueous solution at 25.0 °C. The reaction has the following stoichiometry: *trans*-[Ru^{VI}(tmc)O$_2$]$^{2+}$ + SO$_3^{2-}$ + H$_2$O ⟶ *trans*-[Ru^{IV}(tmc)O(OH$_2$)]$^{2+}$ + SO$_4^{2-}$. Sulfite and sulfur-containing products were analysed by ion chromatography. No S$_2$O$_6^{2-}$ could be detected. The rate law is $-$d[Ru^{VI}]/dt = k/{1 + ([H$^+$]/K)}[Ru^{VI}][S^{IV}] with k = (7.0 ± 1.4) × 10^4 dm^3 mol^{-1} s^{-1} and K = (3.4 ± 1.0) × 10^{-7} mol dm^{-3} at I = 1.0 mol dm^{-3}. The value of k is more than two orders of magnitude greater than predicted by Marcus theory, and an inner-sphere mechanism involving the intermediate [O=Ru^{VI}=O–SO$_3$] is proposed. This may decompose by one- or two-electron pathways.

Ruthenium forms an extensive series of oxo complexes with oxidation states ranging from IV to VIII.[1] These are in general potent oxidants and there have been many reports on their reactions with organic substrates.[1,2] We have been studying the reactions of oxoruthenium complexes, especially *trans*-dioxo-ruthenium(VI) complexes, with simple inorganic substrates since much less is known in this area. We are particularly interested in *trans*-[Ru^{VI}(tmc)O$_2$]$^{2+}$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) for the following reasons. The presence of the macrocyclic tertiary amine tmc makes this complex particularly stable, hence complications arising from ligand exchange or decomposition can be eliminated. It is also a mild oxidant (E^o = 0.56 V),[3] thus reactions would be likely to occur at convenient rates for most substrates. The kinetics of the reduction of this complex with PPh$_3$,[4] Fe^{2+}(aq),[5] and I$^-$ [6] have been reported. We describe here kinetic studies of its reduction with sulfite. Although the oxidation of sulfite by transition-metal complexes has been extensively studied,[7] most of these reactions are either outer sphere involving substitution-inert oxidants, or inner sphere involving labile oxidants. In the present study an additional pathway such as oxygen-atom transfer is possible.

Experimental

Materials

The complex *trans*-[Ru^{VI}(tmc)O$_2$][PF$_6$]$_2$ was prepared by a literature method.[8] Sodium sulfite (AR grade) was obtained from BDH and used as received. Ionic strength was maintained with sodium trifluoroacetate. Water for kinetic experiments was distilled twice from alkaline permanganate, and was deaerated with argon for 30 min before use for preparation of solutions. Sodium sulfite solutions were standardized by iodometry.

Kinetics

Kinetic experiments were performed under pseudo-first-order conditions using either a Hewlett-Packard 8452A diode-array spectrophotometer or an Applied Photophysics DX-17MV stopped-flow spectrophotometer. The progress of the reaction was monitored by measuring absorbance changes at 260 nm (λ_{max} of Ru^{VI}). Pseudo-first-order rate constants, k_{obs}, were obtained by non-linear least-squares fits of A_t *vs.* time t accord-

tmc
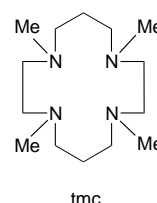
ing to the equation $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$, where A_0 and A_∞ are the initial and final absorbances, respectively.

Products

The SO$_3^{2-}$ and sulfur-containing products were analysed by ion chromatography (IC) with a Wescan ICM 300 ion chromatograph equipped with a 335 suppressor module and an Anion/R column. The mobile phase was 1.8 mmol dm^{-3} Na$_2$CO$_3$ and 1.7 mmol dm^{-3} NaHCO$_3$. In a typical experiment a 1.5 × 10^{-4} mol dm^{-3} solution (2.5 cm^3) of [Ru(tmc)O$_2$]$^{2+}$ in water was added to a 2.4 × 10^{-3} mol dm^{-3} solution (2.5 cm^3) of Na$_2$SO$_3$ in acetate buffer (pH 4.52 and I = 0.01 mol dm^{-3}) at 25 °C. After a reaction time of 5 min the solution was diluted to 10.0 cm^3 with water and analysis by ion chromatography indicated that the final solution contained 5.6 × 10^{-4} mol dm^{-3} SO$_3^{2-}$ and 3.5 × 10^{-5} mol dm^{-3} SO$_4^{2-}$. Thus, 1 mol of SO$_3^{2-}$ reacted with 1 mol of Ru^{VI} to produce 1 mol of SO$_4^{2-}$. No S$_2$O$_6^{2-}$ was detected.

Results and Discussion

Spectral changes and stoichiometry

Preliminary repetitive scanning indicated rapid spectral changes when a solution of Ru^{VI} was mixed with a solution of S^{IV}-(HSO$_3^-$ + SO$_3^{2-}$). A well defined isosbestic point at 290 nm was maintained throughout the reaction (Fig. 1). The final spectrum showed quantitative formation of *trans*-[Ru^{IV}(tmc)O(OH$_2$)]$^{2+}$ [λ_{max}/nm(ε/dm^3 mol^{-1} cm^{-1}): 420 (150), 280 (1600) and 210 (9800)].[9] Analysis by ion chromatography indicated that 1 mol of Ru^{VI} reacted with 1 mol of SO$_3^{2-}$ to produce 1 mol of SO$_4^{2-}$. Thus the stoichiometry of the reaction is as in equation (1).
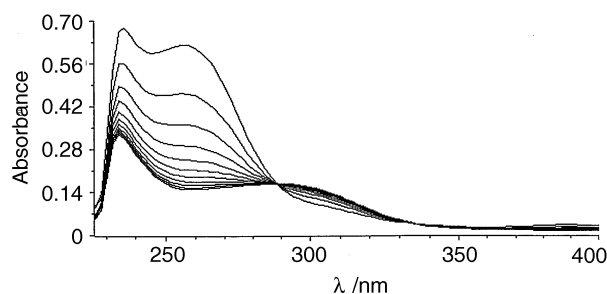
$$[Ru^{VI}(tmc)O_2]^{2+} + SO_3^{2-} + H_2O \longrightarrow [Ru^{IV}(tmc)O(OH_2)]^{2+} + SO_4^{2-} \quad (1)$$
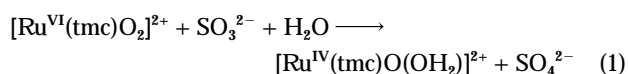
Fig. 1 Spectral changes during the reduction of $[Ru^{VI}(tmc)O_2]^{2+}$ ($\approx 5 \times 10^{-5}$ mol dm^{-3}) by S^{IV} ($\approx 5 \times 10^{-4}$ mol dm^{-3}) at pH 3.8, $I = 0.5$ mol dm^{-3} and $T = 298.0$ K. Spectra were recorded at 4 s intervals

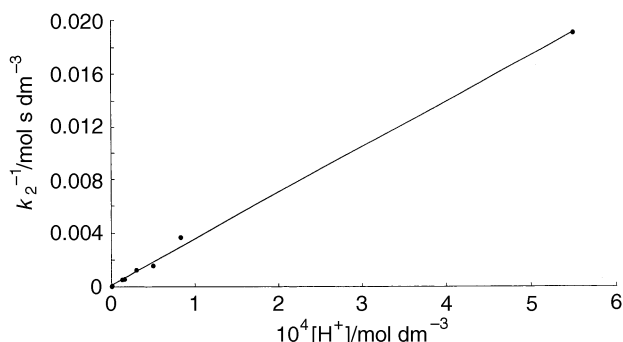**Fig. 2** Plot of $1/k_2$ vs. [H$^+$] for the reduction of $[Ru^{VI}(tmc)O_2]^{2+}$ by S^{IV} at 298.0 K and $I = 1.0$ mol dm^{-3}

Kinetics

In the presence of at least 10-fold excess of S^{IV} clean pseudo-first-order kinetics was observed for over three half-lives. The kinetics was followed at 260 nm (λ_{max} of Ru^{VI}). The pseudo-first-order rate constants, k_{obs}, were independent of [Ru^{VI}] from 2.5×10^{-5} to 1×10^{-4} mol dm^{-3}. Most kinetic runs were done under anaerobic conditions using syringe techniques to transfer degassed solution to the stopped-flow spectrophotometer, since oxidation of SO_3^{2-} by certain metal complexes is known to be highly sensitive to contamination by atmospheric dioxygen.[7b,d] A few experiments were done by mixing ruthenium(VI) solutions saturated with air with degassed sulfur(IV) solutions in the stopped-flow apparatus. The rate constants were found to be identical to those obtained when both solutions were degassed. The effect of Cu^{II} on the reaction was investigated at pH 4.52. When reactions were carried out with solutions containing up to 2.6×10^{-4} mol dm^{-3} CuSO$_4\cdot$5H$_2$O the rate constants were similar to those obtained when there was no added Cu^{II}. The reaction is first order in [S^{IV}] up to 2000 [Ru^{VI}]. Thus the experimentally determined rate law is as in equation (2).

$$-\text{d}[Ru^{VI}]/\text{d}t = k_{obs}[Ru^{VI}] = k_2[Ru^{VI}][S^{IV}] \qquad (2)$$

Representative results are summarized in Table 1; k_2 increases with decreasing ionic strength, as expected for a bimolecular reaction between ions of opposite charges; a plot of log k_2 versus $I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ was linear with slope $= -3.6 \pm 0.2$ and intercept $= 4.5 \pm 0.1$.

The kinetics of the oxidation of S^{IV} by Ru^{VI} were studied over the range pH 3.26–6.28. A plot of $1/k_2$ against [H$^+$] gave a straight line (Fig. 2) consistent with the relationship (3). A non-

$$k_2 = k/\{1 + ([H^+]/K)\} \qquad (3)$$

linear least-squares fit of the data using equation (3) yielded $k = (7.0 \pm 1.4) \times 10^4$ dm^3 mol^{-1} s^{-1} and $K = (3.4 \pm 1.0) \times 10^{-7}$ mol dm^{-3} at 25 °C and $I = 1.0$ mol dm^{-3}.

Mechanism

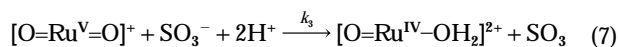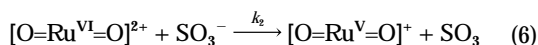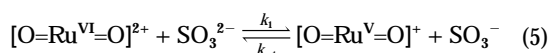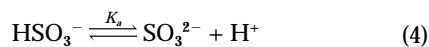The mechanism for the outer-sphere oxidation of sulfite by metal complexes is well established.[7a,b] A similar outer-sphere

Table 1 Representative rate constants at 25.0 °C for the oxidation of sulfite by $[Ru(tmc)O_2]^{2+}$ *

I/mol dm^{-3}	pH	$[S^{IV}]$/mol dm^{-3}	k_{obs}/s^{-1}	k_2/dm^3 mol^{-1} s^{-1}
1.0	3.26	4.60×10^{-4}	3.19×10^{-2}	$(5.25 \pm 0.01) \times 10$
1.0	3.26	1.59×10^{-3}	5.32×10^{-2}	
1.0	3.26	2.30×10^{-3}	1.33×10^{-1}	
1.0	3.26	3.40×10^{-3}	1.67×10^{-1}	
1.0	3.26	4.60×10^{-3}	2.65×10^{-1}	
1.0	3.26	9.20×10^{-3}	4.16×10^{-1}	
1.0	3.26	4.69×10^{-2}	2.46	
1.0	4.08	1.59×10^{-3}	2.63×10^{-1}	$(2.72 \pm 0.01) \times 10^2$
1.0	4.08	2.30×10^{-3}	5.85×10^{-1}	
1.0	4.08	3.40×10^{-3}	8.12×10^{-1}	
1.0	4.08	4.60×10^{-3}	1.08	
1.0	4.08	9.20×10^{-2}	2.49×10	
1.0	4.30	5.00×10^{-4}	1.69×10^{-1}	$(6.40 \pm 0.05) \times 10^2$
1.0	4.30	1.20×10^{-3}	5.78×10^{-1}	
1.0	4.30	2.30×10^{-3}	1.32	
1.0	4.30	3.50×10^{-3}	2.06	
1.0	4.30	5.00×10^{-3}	3.10	
1.0	4.30	9.20×10^{-3}	5.71	
1.0	4.52	4.60×10^{-4}	2.16×10^{-1}	$(8.03 \pm 0.10) \times 10^2$
1.0	4.52	1.16×10^{-3}	6.08×10^{-1}	
1.0	4.52	2.30×10^{-3}	1.29	
1.0	4.52	3.40×10^{-3}	1.94	
1.0	4.52	4.60×10^{-3}	2.93	
1.0	4.52	9.20×10^{-3}	5.44	
1.0	4.52	2.76×10^{-2}	2.14×10	
1.0	4.52	3.68×10^{-2}	2.87×10	
1.0	4.52	4.66×10^{-2}	3.69×10	
1.0	4.80	1.16×10^{-3}	3.02	$(1.77 \pm 0.06) \times 10^3$
1.0	4.80	2.30×10^{-3}	3.61	
1.0	4.80	3.40×10^{-3}	4.38	
1.0	4.80	4.60×10^{-3}	1.00×10	
1.0	4.80	9.20×10^{-3}	1.35×10	
1.0	4.80	1.84×10^{-2}	3.07×10	
1.0	4.80	2.76×10^{-2}	4.79×10	
1.0	4.80	3.68×10^{-2}	6.94×10	
1.0	4.80	4.60×10^{-2}	7.66×10	
1.0	4.88	4.60×10^{-4}	2.47×10^{-1}	$(1.88 \pm 0.04) \times 10^3$
1.0	4.88	1.16×10^{-3}	1.15	
1.0	4.88	2.30×10^{-3}	2.86	
1.0	4.88	3.40×10^{-3}	4.48	
1.0	4.88	4.60×10^{-3}	6.33	
1.0	4.88	9.20×10^{-3}	1.22×10	
1.0	4.88	4.64×10^{-2}	8.60×10	
1.0	5.93	4.60×10^{-4}	4.59	$(1.37 \pm 0.03) \times 10^4$
1.0	5.93	1.16×10^{-3}	1.48×10	
1.0	5.93	2.30×10^{-3}	3.21×10	
1.0	5.93	3.40×10^{-3}	4.43×10	
1.0	5.93	4.60×10^{-3}	6.78×10	
1.0	5.93	9.20×10^{-3}	1.13×10^2	
1.0	5.93	1.84×10^{-2}	2.59×10^2	
1.0	5.93	2.76×10^{-2}	3.73×10^2	
1.0	6.28	4.60×10^{-4}	7.95	$(2.78 \pm 0.08) \times 10^4$
1.0	6.28	1.16×10^{-3}	2.89×10	
1.0	6.28	2.30×10^{-3}	6.53×10	
1.0	6.28	3.40×10^{-3}	1.02×10^2	
1.0	6.28	4.60×10^{-3}	1.31×10^2	
1.0	6.28	9.20×10^{-3}	2.52×10^2	
0.10	4.40	4.60×10^{-4}	2.39	$(4.96 \pm 0.10) \times 10^3$
0.10	4.40	1.15×10^{-3}	5.96	
0.10	4.40	3.45×10^{-3}	1.77×10	
0.10	4.40	4.60×10^{-3}	2.28×10	
0.08	4.40	4.60×10^{-4}	2.51	$(5.60 \pm 0.10) \times 10^3$
0.08	4.40	1.15×10^{-3}	5.76	
0.08	4.40	3.45×10^{-3}	1.87×10	
0.08	4.40	4.60×10^{-3}	2.56×10	
0.036	4.40	4.60×10^{-4}	3.21	$(6.45 \pm 0.10) \times 10^3$
0.036	4.40	1.15×10^{-3}	6.42	
0.036	4.40	3.45×10^{-3}	2.11×10	
0.036	4.40	4.60×10^{-3}	2.98×10	

*The pH was maintained with acetate buffer (below 5.5) and phosphate buffer (above 5.5). Ionic strength was adjusted with NaO$_2$CCF$_3$. Each k_{obs} value is the average of at least two determinations. Results were reproducible to within 5%.

mechanism for the present reaction that is consistent with the experimental results is shown in equations (4)–(9). This

$$HSO_3^- \xrightleftharpoons{K_a} SO_3^{2-} + H^+ \qquad (4)$$

$$[O=Ru^{VI}=O]^{2+} + SO_3^{2-} \xrightleftharpoons[k_{-1}]{k_1} [O=Ru^V=O]^+ + SO_3^- \quad (5)$$

$$[O=Ru^{VI}=O]^{2+} + SO_3 \xrightarrow{k_2} [O=Ru^V=O]^+ + SO_3 \quad (6)$$

$$[O=Ru^V=O]^+ + SO_3^- + 2H^+ \xrightarrow{k_3} [O=Ru^{IV}-OH_2]^{2+} + SO_3 \quad (7)$$

$$2[O=Ru^V=O]^+ + 2H^+ \xrightarrow{k_4} [O=Ru^{VI}=O]^{2+} +$$
$$[O=Ru^{IV}-OH_2]^{2+} \quad (8)$$

$$SO_3 + H_2O \xrightarrow{k_5} 2H^+ + SO_4^{2-} \qquad (9)$$
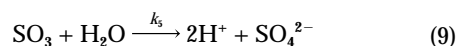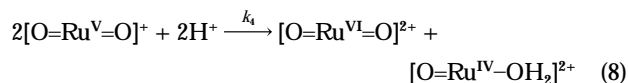
mechanism leads to the observed rate law with $k = k_1$ and $K = K_a$ under the conditions that the equilibrium K_a is established rapidly and that the k_2, k_3 and k_4 steps compete efficiently with the back electron-transfer step k_{-1}. In an acidic medium dioxoruthenium(v) is a stronger oxidant than dioxoruthenium(vi), and would rapidly oxidize SO_3^- (k_3 step) or undergo disproportionation[3] (k_4 step). The measured value of K_a (3.4×10^{-7} mol dm^{-3}) is in reasonable agreement with a literature value[10] (1.2×10^{-7} mol dm^{-3}).

If the oxidation of SO_3^{2-} by Ru^{VI} is indeed a simple outer-sphere reaction as shown above then the rate constant k_1 should be comparable to the theoretical value k_{12} obtained by the Marcus cross-relation[11] (neglecting the work term) (10) and the relationship of f_{12} is given in equation (11). The

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{\frac{1}{2}} \qquad (10)$$

$$\log f_{12} = (\log K_{12})^2/4\log(k_{11}k_{22}/10^{22}) \qquad (11)$$

equilibrium constant K_{12} is calculated from the reduction potentials for the Ru^{VI}–Ru^V (0.56 V[12]) and the SO_3^-–SO_3^{2-} (0.72 V[7a]) couples. A value of 1×10^5 dm^3 mol^{-1} s^{-1} is used for k_{11}, the self-exchange rate for Ru^{VI}–Ru^V;[3] k_{22}, the self-exchange rate for SO_3^-–SO_3^{2-}, is 4 dm^3 mol^{-1} s^{-1}.[7a] The value of k_{12} obtained in this manner is 6.3×10^2 dm^3 mol^{-1} s^{-1}, lower than the observed one by a factor of more than 10^2. This suggests that the oxidation of SO_3^{2-} probably goes through an inner-sphere pathway. A one-electron inner-sphere pathway involving co-ordination of SO_3^{2-} to the metal centre is common for substitution-labile metal complexes as oxidants. Since the ruthenium(vi) complex is substitution inert and the bulky macrocyclic ligand would prevent formation of a seven-co-ordinate complex, this pathway is highly unlikely. Moreover, $S_2O_6^{2-}$, which is usually produced in such pathways, is not detected in our system. A more reasonable inner-sphere pathway involves the intermediate $[O=Ru^{VI}=O-SO_3]$, in which the S atom in SO_3^{2-} is bonded to an oxygen atom of a ruthenium–oxo bond. This intermediate may undergo subsequent decomposition in two ways, namely by one-electron transfer (12) or by oxygen-atom transfer, which is
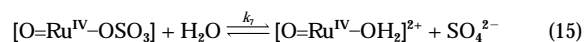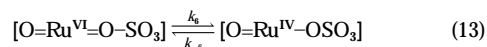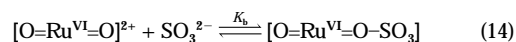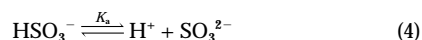
$$[O=Ru^{VI}=O-SO_3] \rightleftharpoons [O=Ru^V=O]^+ + SO_3^- \qquad (12)$$
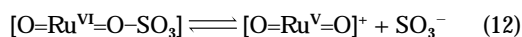
a two-electron process (13). The inner-sphere one-electron

$$[O=Ru^{VI}=O-SO_3] \rightleftharpoons [O=Ru^{IV}-OSO_3] \qquad (13)$$
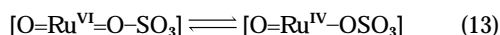
pathway would have a rate law similar to that of the outer-sphere pathway. The mechanism for the proposed oxygen-atom transfer pathway is shown in Scheme 1. By applying the steady-state approximation to $[O=Ru^{IV}-OSO_3]$, the rate law (16) is

$$-d[Ru^{VI}]/dt = K_b k_6 k_7 [Ru^{VI}][S^{IV}]/(k_{-6} + k_7) \times$$
$$\{1 + ([H^+]/K_a)\} \qquad (16)$$

$$HSO_3^- \xrightleftharpoons{K_a} H^+ + SO_3^{2-} \qquad (4)$$

$$[O=Ru^{VI}=O]^{2+} + SO_3^{2-} \xrightleftharpoons{K_b} [O=Ru^{VI}=O-SO_3] \qquad (14)$$

$$[O=Ru^{VI}=O-SO_3] \xrightleftharpoons[k_{-6}]{k_6} [O=Ru^{IV}-OSO_3] \qquad (13)$$

$$[O=Ru^{IV}-OSO_3] + H_2O \xrightleftharpoons{k_7} [O=Ru^{IV}-OH_2]^{2+} + SO_4^{2-} \qquad (15)$$

Scheme 1

obtained. This agrees with the observed rate law with $k = K_b k_6 k_7/(k_{-6} + k_7)$ and $K = K_a$.

Although our kinetic results cannot distinguish between the two inner-sphere pathways, we tend to favour the oxygen-atom-transfer mechanism for the following reasons. First the kinetics is not very sensitive to the presence of O_2, suggesting that the SO_3^- radical may not be an intermediate. Secondly the oxygen-atom-transfer pathway is rather common for oxoruthenium complexes, *e.g* oxidation of PPh$_3$[4] and olefins.[13] It has also been proposed for the oxidation of I$^-$.[6]

Similar intermediates have also been proposed for the oxidations of S^{IV} by other oxometal species. In the oxidation by Cr^{VI} in acidic solution $[O_3CrOSO_3]^{2-}$ was proposed to be an intermediate.[7g] In a detailed study of the oxidation of sulfite by MnO$_4^-$ in alkaline solution the initial step was suggested to be outer-sphere reduction of Mn^{VII} to Mn^{VI}. However, in a more recent and similar study, the intermediate $[O_3MnOSO_3]^-$ was proposed, which may decompose by one- or two-electron mechanisms.[7e] The rate constants obtained in the two studies were comparable, but much higher than predicted by Marcus theory,[7a] so the inner-sphere mechanism seems to be more reasonable.

Acknowledgements

References

1 C. M. Che and V. W. W. Yam, *Adv. Inorg. Chem. Radiochem.*, 1992, **39**, 233.
2 W. P. Griffith, *Transition Met. Chem.*, 1990, **15**, 251; *Chem. Soc. Rev.*, 1992, **21**, 179.
3 C. M. Che, K. Lau and T. C. Lau, *J. Am. Chem. Soc.*, 1990, **112**, 5176.
4 K. Y. Wong and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1989, 2056.
5 T. C. Lau, K. W. C. Lau and C. K. Lo, *Inorg. Chim. Acta*, 1993, **209**, 89.
6 T. C. Lau, K. W. C. Lau and K. Lau, *J. Chem. Soc., Dalton Trans.*, 1994, 3091.
7 (*a*) R. Sarala, M. A. Islam, S. B. Rabin and D. M. Stanbury, *Inorg. Chem.*, 1990, **29**, 1133; (*b*) R. Sarala and D. M. Stanbury, *Inorg. Chem.*, 1990, **29**, 3456; (*c*) L. I. Simandi, M. Jaky, C. R. Savage and Z. A. Schelly, *J. Am Chem. Soc.*, 1985, **107**, 4220; (*d*) J. M. Anast and D. W. Margerum, *Inorg. Chem.*, 1981, **20**, 2319; (*e*) T. Ernst, M. Cyfert and M. Wilgocki, *Int. J. Chem. Kinet.*, 1992, **24**, 903; (*f*) E. S. Gould, *Acc. Chem. Res.*, 1986, **19**, 66; (*g*) G. P. Haight, jun., E. Perchonock, F. Emmenegger and G. Gordon, *J. Am. Chem. Soc.*, 1965, **87**, 3835.
8 C. M. Che, K. Y. Wong and C. K. Poon, *Inorg. Chem.*, 1985, **24**, 1797.
9 C. M. Che, T. F. Lai and K. Y. Wong, *Inorg. Chem.*, 1987, **26**, 2289.
10 R. M. Smith and A. E. Martell, *Critical Stability Constants*, Plenum, New York, 1989, vol. 6.
11 R. A. Marcus, *Annu. Rev. Phys. Chem.*, 1964, **15**, 155.
12 C. M. Che, K. Y. Wong and F. C. Anson, *J. Electroanal. Chem. Interfacial Electrochem.*, 1987, **226**, 211.
13 C. M. Che, W. H. Leung, C. K. Li and C. K. Poon, *J. Chem. Soc., Dalton Trans.*, 1991, 379.