Pergamon

PII: S0277–5387(97)00137–X

Polyhedron Vol. 16, No. 20, pp. 3493–3498, 1997
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0277–5387/97 $17.00+0.00

Oxidation of NO_2^- by $[Mn_2^{IV}(\mu\text{-}O)_2(\mu\text{-}OAc)(H_2O)_2(bipy)_2]^{3+}$ ion: a probable example of a two-electron transfer reaction

Swapan Chaudhuri and Rupendranath Banerjee*

Department of Chemistry, Jadavpur University, Calcutta 700 032, India

(Received 7 February 1997; accepted 3 April 1997)

Abstract—The title complex **1** coexists in equilibrium with $[Mn_2^{IV}(\mu\text{-}O)_2(H_2O)_4(bipy)_2]^{4+}$ (**2**) and $[Mn_2^{IV}(\mu\text{-}O)_2(\mu\text{-}OAc)(H_2O)_4(bipy)]^{3+}$ (**3**) in mixed (OAc^- + bipy) aqueous buffer. The complexes are quantitatively reduced to Mn^{II} by NO_2^-, which is itself oxidised to NO_3^-. There is no kinetic and UV–vis spectral evidence for any intermediate $Mn^{III,IV}$ complex, and the reactions appear to be two-electron transfer processes. The rate of reduction increases with increasing extent of hydrolysis in the sequence $\mathbf{1} < \mathbf{2} < \mathbf{3}$. A plausible interpretation has been presented. © 1997 Elsevier Science Ltd

Keywords: kinetics; nitrite; manganese; binuclear complex; electron transfer.

The identification [1] of a polynuclear manganese containing site in the water oxidation centre (WOC) in photosystem II has stimulated an intense research in the area of classical Werner-type dimeric and oligomeric compounds containing higher-valent manganese [2a]. However, greater emphasis has been placed on the preparative and structural aspects rather than the thermodynamic and kinetic properties in solution [2,3]. The title complex **1** satisfies [4] a crucial feature for a model of the WOC. Since water is the substrate for oxidation by WOC at its highest oxidative state [5], it is anticipated that water should be present in the coordination sphere of the Mn ions in the WOC.

1 is a rare example of a manganese complex in which water molecules are directly bound to the Mn^{IV} centres. Investigations on its chemical reactivity may be helpful to divulge ultimately the mechanism of stabilisation of the Mn—aqua bonds during oxidative charge buildup [6] on the WOC. We have recently determined the kinetics of oxidation of $S_2O_3^{2-}$ by the title complex (**1**, bipy is 2,2′-bipyridine and HOAc is ethanoic acid) and detected the one-electron reduced complex $[(bipy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bipy)_2]^{3+}$ as an intermediate [7]. Now, thiosulfate is a well known one-electron reductant and the intermediate is expected. But NO_2^- can act either as a one-electron or a two-electron reductant [8]. How it acts on **1** is an interesting question, which we have addressed in the present paper through the kinetic studies on the reduction of **1** with nitrite in aqueous solutions buffered with excess acetate and bipyridine ligands in the range pH 3.9–5.1.

EXPERIMENTAL

Materials

The complex $[Mn_2^{IV}(\mu\text{-}O)_2(\mu\text{-}OAc)(H_2O)_2(bipy)_2](ClO_4)_3 \cdot H_2O$ was prepared according to the method described by Reddy *et al.* [4a]. Its equivalent weight (215) found by iodometry is in good agreement with the calculated value (216). Solutions of $NaNO_2$ and $NaNO_3$ (both G.R., E. Merk) were prepared from recrystallised substances and were standardised as described earlier [9].

2,2′-Bipyridine,N-(1-napthyl)-ethylenediamime dihydrochloride and sulfanilamide were E. Merck products and used as received. Reagent grade chemi-

---

* Author to whom correspondence should be addressed.

cals, chromium(II) scrubbed nitrogen and triply distilled water were used throughout.

Physical measurements and kinetics

The reactions were measured *in situ* in the thermostatted cell housing of a Shimadzu (UV 1601 PC) spectrophotometer at 20.0°C. Ionic strength was maintained at 1.0 mol dm^{-3} by adding $NaNO_3$. Solutions were buffered with bipy + HOAc mixtures. The pH was measured with an Orion (710A) pH meter using a calibrated electrode [9a].

All kinetics were measured with the reductant in large excess. The faster reactions were initiated by mixing required volume of $NaNO_2$ from a microsyringe directly into the cell containing the complex solution stabilised with adequate concentrations of buffer. The complex solutions were always prepared fresh by adding the solid salt into the said buffers at a desired pH and ionic strength.

Decay in solution absorbance at 420 mm under the experimental conditions obeyed the first-order kinetics. At this wavelength the buffer mixture and the product solution do not absorb appreciably. The first-order constants, k_{obs} were obtained as usual from the least squares slope of log (absorbance) against time data for at least up to 90% reaction. Reported k_{obs} values are average of 2–3 determinations. They are reproducible within 5%. All reported errors are standard deviations.

Stoichiometric measurements

The reaction stoichiometry was determined by spectrophotometric titration (Fig. 1) at 420 nm of the oxidant complex **1** with $NaNO_2$. Stoichiometry in the presence of an excess of reductant was also determined by measuring the unreacted NO_2^- spectrophotometrically at 550 nm. The Griess–Ilsovey reaction was used for this purpose [10].

The NO_3^- ion produced in the reaction of **1** with excess $NaNO_2$ was quantified spectrophotometrically by the chromotropic acid method [11], for which the reaction between **1** and nitrite was carried out at pH 4.1–4.9. The Mn^{II} in the product solution was removed by eluting through a Dowex 50W X8 cation-exchanger resin bed in the Na^+ form. Unreacted NO_2^- was destroyed by addition of a sulfite–urea solution [11]. Chromotropic acid reagent was then added followed by concentrated H_2SO_4. A yellow colour developed. Its absorbance was measured at 410 nm to quantity NO_3^-. Bipyridine does not interfere with this method.

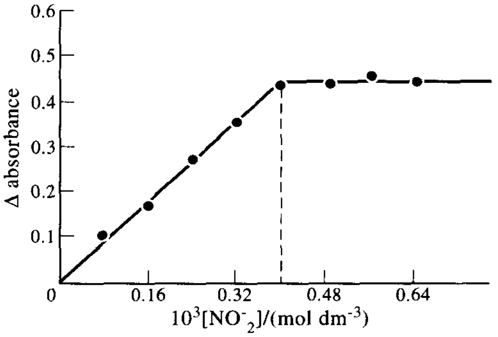

Fig. 1. A typical spectrophotometric titration curve at 420 mm. [complex], 0.20 mmol dm^{-3}; pH 4.5. The intersection seen is at 1 : 2 (complex : NO_2^-) ratio.

RESULTS AND DISCUSSION

Stoichiometry and reaction products

Stoichiometric measurements of NO_2^- and NO_3^- (Table 1 and Fig. 1) indicate a 1 : 2 stoichiometry and the overall reaction (1).

$$[Mn_2^{IV}(\mu\text{-}O)_2(\mu\text{-}OAc)(H_2O)_2(bipy)_2]^{3+} + 2NO_2^- + H^+ \rightarrow 2Mn^{II} + 2NO_3^- + HOAc + 2bipy + 2H_2O \quad (1)$$

Kinetics

First-order kinetics were obeyed at least up to 90% of the reaction. Any initial drop in absorbance (rarely more than 5%) is explicable by the first-order rate constant k_{obs} for the process. Hence, the first act of electron transfer appears to be rate determining in these reactions. The measured k_{obs} (Table 2) decreases with increasing pH, increasing $C_{bipy}(=[bipy]+[Hbipy^+])$ and decreasing $C_{OAc}(=[OAc^-]+[HOAc])$. k_{obs} increases linearly with increasing $[NO_2^-]$ and a plot of k_{obs} *vs* $[NO_2^-]$ is a straight line passing through the origin, with no indication for rate saturation up to 0.10 mol dm^{-3}.

Spectra of the complex **1** in aqueous buffer made of bipyridine and acetate agree satisfactorily with those reported earlier by Reddy *et al.* in the bipyridine buffer. They noted that the solution decomposes with time and nearly 80% of Mn is transformed to $[Mn_2O_2(bipy)_4]^{3+}$ after 72 h. We observed no appreciable decomposition of the complex solution within the time required for our kinetic measurements. But the complex spectra changes gradually to those for a mixture of Mn^{II}, bipyridine and acetate, if excess nitrite is added. The change is complete within an hour at the most. No UV–vis spectral evidence could be observed for the formation of any intermediate (III,IV) complex even when only half mole of the nitrite was added per mole of the complex (Fig. 2). The present spectral observations are different from those observed during reduction of **1** with thiosulfate, where $[Mn_2O_2(bipy)_4]^{3+}$ was detected as an intermediate and eventually as the final product, when one equivalent of thiosulfate was added to **1**. Since no detectable amount of the (III,IV) intermediate developed, following reac-

Table 1. Stoichiometry of reduction of $[Mn_2^{IV}(\mu\text{-}O)_2(\mu\text{-}OAc)(H_2O)_2(bipy)_2]^{3+}$ by NO_2^- in bipy + OAc^- mixed buffer[a]

$[Mn_2^{IV}]$	$[NO_2^-]$	pH	$\Delta[Mn_2^{IV}]/\Delta[NO_2^-]$	$\Delta[Mn_2^{IV}]/\Delta[NO_3^-]$
0.40	1.00	4.2	0.52	0.51
0.20[b]	0.80	4.4	0.47	0.50
0.80[b]	2.00	4.8	0.46	0.48
0.50	1.40	4.8	0.51	0.52
0.60	2.00	4.9	0.48	0.49
		Average	0.49 ± 0.03	0.50 ± 0.02

[a] Temp., 20°C. Concentrations are in mmol dm^{-3}.

[b] Reaction media purged with purified dinitrogen.

tion sequences may be conceived for the present reaction.

(a) A two-electron reduction of the Mn_2^{IV} complex by NO_2^- slowly produces a $Mn^{II,IV}$ species, which is quickly cleaved to Mn^{II} and a monomer Mn^{IV} complex. The latter, in turn, is rapidly reduced by another NO_2^- ion. It is known that $Mn^{II,IV}$ species are unstable in aqueous solutions [12].

(b) Nitrite reduces the Mn_2^{IV} complex to the $Mn^{III,IV}$ intermediate, itself being oxidised to NO_2. But the (III,IV) species is quickly depleted, without affecting the observed kinetics, and without accumulating to an extent sufficient for its spectrophotometric detection. The (III,IV) species may be lost (i) by reaction with a further equivalent of NO_2^-; (ii) by reaction with NO_2 generated in an earlier step or (iii) by way of disproportionation to Mn_2^{III} and Mn_2^{IV} complexes.

(c) Nitrite reduces the Mn_2^{IV} complex to Mn_2^{III} dimer, which is subsequently reduced to $2Mn^{II}$ by another equivalent of NO_2^-.

Among these possibilities, (b) (i) and (c) can be eliminated because the reactions of NO_2^- with the $Mn^{III,IV}$ complex, $[Mn_2O_2(bipy)_4]^{3+}$ and the Mn_2^{III}

Table 2. Representative k_{obs} (s^{-1}) for the reduction of Mn_2^{IV} complexes[a]

pH	C_{bipy}	C_{OAc}	$[NaNO_2]$	10^3k_{obs}
3.9	0.025	0.2	0.02	5.5 (5.33)
4.1				4.3 (4.29)
4.25				3.5 (3.66)
4.4				3.0 (3.16)
4.5[b]				2.9 (2.89)
4.6				2.8 (2.67)
4.8[b]				2.3 (2.33)
5.0				2.2 (2.11)
5.1				2.1 (2.03)
4.8	0.01	0.2	0.02	5.1 (5.02)
	0.0125			4.2 (4.16)
	0.015			3.5 (3.57)
	0.02			2.7 (2.81)
	0.03			2.0 (2.01)
5.0	0.01	0.01	0.02	3.6 (3.70)
		0.02		4.0 (3.99)
		0.04		4.25 (4.25)
		0.06		4.2 (4.37)
		0.08		4.5 (4.44)
		0.10		4.6 (4.48)
		0.50		4.65(4.65)
4.2[b]	0.025	0.2	0.01	2.0 (1.91)
			0.02	3.7 (3.83)
			0.03	5.6 (5.75)
			0.04	8.0 (7.67)
			0.05	9.9 (9.59)
			0.10	19.7 (19.1)
4.8[b]	0.025	0.2	0.01	1.1 (1.17)
			0.03	3.4 (3.50)
			0.04	4.8 (4.66)
			0.05	5.6 (5.83)
			0.10	11.7 (11.67)

[a] [complex], 10^{-4} mol dm^{-3}, Temp., 20.0°C; $I = 1.0$ mol dm^{-3} ($NaNO_3$); recalculated k_{obs} using eq. (13) are in parenthesis; all reagent concentrations are in mol dm^{-3}.

[b] Reaction media were purged with dinitrogen. No appreciable effect on rate is seen.

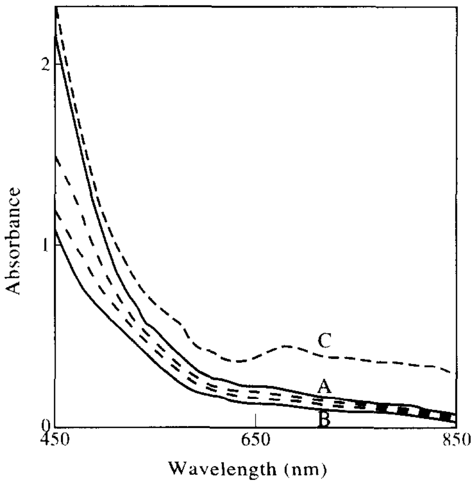

Fig. 2. Spectral observations. (A) spectra of 1.0 mmol dm^{-3} of **1** in the presence of C_{bipy}, 0.025 mol dm^{-3} and C_{OAc}, 0.15 mol dm^{-3} at pH, 5.0 and $I = 1.0$ mol dm^{-3}. (B) Solution A + 0.5 mmol dm^{-3} $NaNO_2$, after complete reaction. (C) Solution A with **1** replaced by $[Mn_2O_2(bipy)_4]^{3+}$. Spectra between (A) and (B) show how **1** changes with time to (B).

complex $[Mn_2O_2(bipy)_4]^{2+}$ are known to be slower [3a] than the reaction between **1** and NO_2^-. The path (b) (ii) also seems improbable because it is well known [13], that NO_2 produced in a one-electron oxidation by a metal complex does not attack another molecule of the metal complex. It rather diproportionates very rapidly to NO_3^- and NO_2^-. Such behaviour of NO_2^- has been detected also in its reaction with the non-metal oxidant $S_2O_8^{2-}$ [13c]. The path (b) (iii) is thermodynamically unfavourable under our conditions of pH. It is appreciable only below pH 2 [14]. Thus only path (a) seems probable and the rate determining step for the reaction of **1** with NO_2^- appears to involve two-electron transfer. The monomer Mn^{IV} product expected in this pathway should be a stronger oxidant than the parent dimer **1**, and be reduced rapidly by NO_2^-. We have not considered an oxygen atom transfer path, which seems impossible because N^{III} has no vacant acceptor orbital.

A reaction sequence in consonance with the observed kinetics and known [7] solution properties of **1** is given below

$$\mathbf{1}+2H_2O \overset{K_A}{\rightleftharpoons} \underset{\mathbf{2}}{[Mn_2^{IV}(O)_2(H_2O)_4(bipy)_2]^{4+}} + OAc^- \tag{3}$$

$$\mathbf{1}+2H_2O \overset{K_B}{\rightleftharpoons} \underset{\mathbf{3}}{[Mn_2^{IV}(O)_2(OAc)(H_2O)_4(bipy)]^{3+}} + bipy \tag{4}$$

$$Hbipy^+ \overset{K_{Hbipy}}{\rightleftharpoons} H^+ + bipy \tag{5}$$

$$HOAc \overset{K_{HOAc}}{\rightleftharpoons} H^+ + OAc^- \tag{6}$$

$$\mathbf{1}+NO_2^- \overset{k_1}{\rightarrow} \underset{\mathbf{4}}{[Mn^{IV}Mn^{II}(O)_2(OAc)(H_2O)_2(bipy)_2]^+} + NO_2^+ \tag{7}$$

$$\mathbf{2}+NO_2^- \overset{k_2}{\rightarrow} \underset{\mathbf{5}}{[Mn^{IV}Mn^{II}(O)_2(bipy)(H_2O)_4]^{2+}} + NO_2^+ \tag{8}$$

$$\mathbf{3}+NO_2^- \overset{k_3}{\rightarrow} \underset{\mathbf{6}}{[Mn^{IV}Mn^{II}(O)_2(OAc)(H_2O)_4]^+} + NO_2^+ \tag{9}$$

$$\mathbf{4,5,6} \overset{fast}{\rightarrow} Mn^{IV} + Mn^{II} \tag{10}$$

$$Mn^{IV} + NO_2^- \overset{fast}{\rightarrow} Mn^{II} + NO_2^+ \tag{11}$$

$$NO_2^+ + H_2O \overset{fast}{\rightarrow} 2H^+ + NO_3^- \tag{12}$$

Known values [7,15] for $K_A = 10^{-2}$, $K_B = 10^{-3}$, $K_{HOAc} = 1.8 \times 10^{-5}$ and $K_{Hbipy} = 3.8 \times 10^{-5}$ dm^3 mol^{-1} at 25°C. Again, the pK_a value (3.0) [9,16] for HNO_2 indicates that in the experimental pH range at least 97.7% of N^{III} exists as NO_2^-.

Further, HNO_2 is generally known to be kinetically less active [9] than NO_2^- and in the present study the kinetic contribution of HNO_2 may be neglected.

The above sequence leads to eq. (13a),

$$k_{obs} = k_0[NO_2^-] \tag{13a}$$

where,

$$k_0 = \frac{k_1[OAc^-][bipy] + k_2K_A[bipy] + k_3K_B[OAc^-]}{[OAc^-][bipy] + K_A[bipy] + K_B[OAc^-]} \tag{13b}$$

To test the validity of eq. (13b) and hence the scheme, it was rewritten as eq. (14)

$$k_0\{[OAc^-][bipy] + K_A[bipy] + K_B[OAc^-]\}$$
$$= k_1[OAc^-][bipy] + k_2K_A[bipy] + k_3K_B[OAc^-] \tag{14}$$

Now, two plots were constructed: (a) L.H.S. of equation (14) *vs* [bipy] at a fixed [OAc$^-$], and the same *vs* [OAc$^-$] at a fixed [bipy]. Excellent straight lines were obtained as expected for the proposed scheme.

An alternate form of eq. (13b) is (15), which demonstrates the pH dependence of k_0 more explicitly.

$$k_0D = A + B[H^+] \tag{15}$$

where,

$$A = K_{HOAc}K_{Hbipy}(k_1C_{OAc}C_{bipy} + k_2K_AC_{bipy} + k_3K_BC_{OAc})$$

$$B = K_2K_AK_{Hbipy} + k_3K_BC_{OAc}$$

and

$$D = K_{HOAc}K_{Hbipy}(C_{OAc}C_{bipy} + K_AC_{bipy} + K_BC_{OAc})$$
$$+ (K_AK_{Hbipy}C_{bipy} + K_BK_{HOAc}C_{OAc})[H^+]$$

Equation (15) is obtained when [OAc$^-$] and [bipy] in eq. (13b) are substituted by C_{OAc} and C_{bipy} using eqs (16) and (17),

$$[OAc^-] = (K_{HOAc}C_{OAc})([H^+] + K_{HOAc})^{-1} \tag{16}$$

$$[bipy] = (K_{Hbipy}C_{bipy})([H^+] + K_{Hbipy})^{-1} \tag{17}$$

A plot of k_0D against [H$^+$] at fixed C_{OAc} and C_{bipy} should be a straight line according to eq. (15) and this was actually observed.

In order to evaluate the rate constants k_1, k_2 and k_3, the k_{obs} values in Table 2 were fitted into eq. (14) using a program (LINEQ) to solve simultaneous linear equations. Only k_1, k_2, and k_3 were treated as unknowns, while known values for K_A, K_B, [OAc$^-$] and [bipy] were used. The best values for the rate constants thus found at 20.0°C and $I = 1.0$ mol dm^{-3} are $k_1 = (2.84 \pm 0.13) \times 10^{-3}$ dm^3 mol^{-1} sec^{-1}, $k_2 = (0.149 \pm 0.007)$ sec^{-1} and $k_3 = (2.07 \pm 0.12)$ sec^{-1}.

The observed sequence of rate constants $k_1 < k_2 < k_3$ indicates that the redox reactivity of the Mn-complexes increases with increased number of water molecules in the coordination sphere of a Mn centre. Increased redox reactivity with increased extent of aquation was found earlier in the case of mononuclear [17] and binuclear complexes of higher valent Mn. The likely reasons are:

(1) Progressive aquation increases the electron affinity of the metal centre and exposes it more and more towards extraneous reagents. Consequently, the complex becomes more reducible.

(2) Replacement of rigid chelate rings with monodentate, aqua ligands makes the complex more flexible. This means a lower Franck–Condon barrier for the reduction of an aqua complex than the parent chelate.

(3) Removal of bulky chelating agents reduces effective volume of the complex; internuclear distance between the redox partners in the activated state is thus reduced. This is expected to make the electron transfer more facile, when the oxidant and the reductant are oppositely charged, as in the present case.

The binuclear complex $[Mn_2O_2(bipy)_4]^{3+}$, its phenanthroline analogue and their aqua derivatives are known to adopt outer-sphere pathway for their reactions with several reducing agents [3,18]. It is also true that no evidence for the formation of any adduct is found between NO_2^- and the complexes **1**, **2** and **3**. Yet at this stage it is too early to say that a case has been made for an outer-sphere reaction.

Different *k*s for the NO_2^- system are $\sim 10^2$ times smaller than the corresponding values for $S_2O_3^{2-}$. Possible reasons for higher rate for $S_2O_3^{2-}$ are (a) high self-exchange rate [19] for the $S_2O_3^{2-/1-}$ couple and (b) the favourable potential for the $S_4O_6^{3-/2-}$ couple [20], which largely compensates for the high thermodynamic price for the one electron oxidation of $S_2O_3^{2-}$ to $S_2O_3^-$ and makes the thermodynamic driving force high for the reductions with $S_2O_3^{2-}$.

Two possible reasons as to why NO_2^- should prefer a two-electron pathway in the present system are:

(1) The potential for the two-electron couple, NO_2^-/NO_3^- is almost equal [13b] to that for the one-electron couple, NO_2^-/NO_2. Hence thermodynamically both the processes are equally favoured.

(2) Two-electron reduction of **1** should produce a $Mn^{II,IV}$ species. But such di(μ-oxo) bridged dimanganese species with one or more Mn^{II} are unstable and they easily cleave in aqueous solutions to monomer species [12] and thus provides extra thermodynamic driving force for the 2e⁻ reduction.

(3) One of the expected monomers in this path is a highly oxidising Mn^{IV} complex, which also makes the overall reduction favourable.

Acknowledgement—Financial assistance from the Department of Science and Technology (New Delhi) is gratefully acknowledged.

REFERENCES

1. Debus, R. J., *Biochim. Biophys. Acta*. 1992, **269**, 1102.
2. (a) Manchandra, R., Brudvig, G. W. and Crabtree, R. H., *Coord. Chem. Rev.* 1995, **1**, 144; (b) Weighardt, K., *Angew. Chem. Int. Ed. Engl.*, 1989, **28**, 1153.
3. (a) Chaudhuri, S., Mukhopadhyay, S. and Banerjee, R., *J. Chem. Soc., Dalton Trans.*, 1995, 621; (b) Kundu, S., Bhattacharya, A. K. and Banerjee, R., *J. Chem. Soc., Dalton Trans.*, 3951, 1996; (c) Mondal, B., Kundu, S. and Banerjee, R., *Polyhedron*, 1997, **16**, 2199.
4. (a) Reddy, K. R., Rajasekharan, M. V., Padhye, S., Dahan, F. and Tuchagues, J. P., *Inorg. Chem.*, 1994, **33**, 428; (b) Dave, B. C., Czernszewicz, R. S., Bond, M. C. and Carrans, C. J., *Inorg. Chem.*, 1993, **32**, 3593.
5. (a) Radmer, R. and Ollinger, O., *FEBS Lett.*, 1986, **195**, 285; (b) Sivaraja, M., Philo, J. S., Lary, J., Dismukes, G. C., *J. Am. Chem. Soc.*, 1989, **111**, 3221.
6. Kok, B., Forbush, B. and McGloin, M. P., *Photochem. Photobiol.*, 1970, **11**, 457.
7. Bhattacharya, A. K., Mondal, A. B. and Banerjee, R., *J. Chem. Soc., Dalton Trans.*, 1997, in press.
8. Fanning, J. C., *Coord. Chem. Rev.*, 1991, **110**, 235.
9. (a) Mukhopadhyay, S. and Banerjee, R., *J. Chem. Soc., Dalton Trans.*, 1994, 1349; (b) Wilmarth, W. K., Stanbury, D. W., Byrd, J. E., Po, H. N. and Chua, C., *Coord. Chem. Rev.*, 1983, **51**, 155.
10. Jeffery, G. H., Bassett, J., Mendham, J. and Deney, J. C., *Vogel's Textbook of Quantitative Chemical Analysis*, p. 702. Fifth edition, ELBS, Essex, U.K., 1994.
11. West, P. W. and Ramachandran, T. P., *Anal. Chim. Acta.*, 1966, **35**, 317.
12. Weighardt, K., Bossek, U., Nuber, B. and Weiss, J., Bonvoisim, J., *J. Am. Chem. Soc.*, 1988, **110**, 7398.
13. (a) Lee, Y. N. and Schwartz, S. E., *J. Phys. Chem.*, 1981, **85**, 840; (b) Ram, M. S. and Stanbury, D. M., *J. Am. Chem. Soc.*, 1984, **106**, 8136; (c) Ball, R. E., Chaco, A., Edwards, J. O. and Levey, G., *Inorg. Chim. Acta*, 1985, **49**, 999.
14. Sarneski, J. E., Thorp, H. H., Brudvig, G. W., Crabtree, R. H. and Shulte, G. K., *J. Am. Chem. Soc.*, 1990, **112**, 7255.
15. (a) Yamasaki, K. and Yasuda, M., *J. Am. Chem. Soc.*, 1956, **78**, 1324; (b) Harned, H. S. and Ehlers, R. W., *J. Am. Chem. Soc.*, 1933, **55**, 65.
16. (a) Lumme, P. and Tumnavuori, J., *Acta Chem. Scand.*, 1965, **19**, 617. (b) Zang, V. and Van Eldik, R., *Inorg. Chem.*, 1990, **29**, 4462.
17. (a) Mukhopadhyay, S. and Banerjee, R., *J. Chem. Soc., Dalton Trans.*, 1993, 933; (b) Banerjee, R., Das, R. and Chakraburtty, A. K., *J. Chem. Soc., Dalton Trans.*, 1990, 3277; (c) Banerjee, R., Das, R. and Chakraburtty, A. K., *J. Chem. Soc., Dalton Trans.*, 1991, 987; (d) Mukhopadhyay, S., Chaudhuri, S., Das, R. and Banerjee, R., *Can. J. Chem.*, 1993, **71**, 2155.
18. Ghosh, M. C., Reed, J. W., Bose, R. N. and Gould, E. S., *Inorg. Chem.*, 1994, **33**, 73.
19. (a) Ram, M. S. and Stanbury, D. M., *J. Phys. Chem.*, 1986, **90**, 3691; (b) Woodruff, W. and Margerum, D., *Inorg. Chem.*, 1974, **13**, 2578; (c) Rudgewick-Brown, N. and Cannon, R. D., *J. Chem. Soc., Dalton Trans.*, 1984, **17**, 2233; (d)

Nord, G., Padersen, B. and Farver, O., *Inorg. Chem.*, 1978, **17,** 2233; (e) Fairbank, M. G. and McAuley, A., *Inorg. Chem.*, 1987, **26,** 2844; (f) Stanbury, D. M., Wilmarth, W. K., Khalaf, S. K., Po, H. N. and Byrd, J. E., *Inorg. Chem.*, 1980, **19,** 2715.

20. (a) Sarala, R., Rasin, S. B. and Stanbury, D. M., *Inorg. Chem.*, 1991, **30,** 3999; (b) Wagman, D. D., Evans, W. H., Barker, V. B., Chusm, R. H., Halow, I., Baily, S. M., Churney, K. L. and Nuttal, R. L., *J. Phys. Chem. Ref. Data.*, 1982, **11,** Suppl. No. 2.