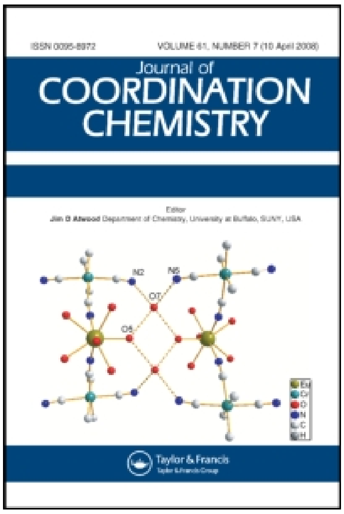

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Kinetics of oxidation of phenylhydrazine by a μ-oxo diiron(III,III) complex in acidic aqueous media

Ritam Mukherjee[a]; Basab Bijayi Dhar[a]; Rupendranath Banerjee[a]; Subrata Mukhopadhyay[a]
[a] Department of Chemistry, Jadavpur University, Calcutta 700 032, India

To cite this Article Mukherjee, Ritam , Dhar, Basab Bijayi , Banerjee, Rupendranath and Mukhopadhyay, Subrata(2006) 'Kinetics of oxidation of phenylhydrazine by a μ-oxo diiron(III,III) complex in acidic aqueous media', Journal of Coordination Chemistry, 59: 10, 1157 — 1165

To link to this Article: DOI: 10.1080/00958970500410614

URL: http://dx.doi.org/10.1080/00958970500410614

Journal of Coordination Chemistry
Vol. 59, No. 10, 10 July 2006, 1157–1165

Taylor & Francis
Taylor & Francis Group

Kinetics of oxidation of phenylhydrazine by a μ-oxo diiron(III,III) complex in acidic aqueous media

RITAM MUKHERJEE, BASAB BIJAYI DHAR,
RUPENDRANATH BANERJEE and SUBRATA MUKHOPADHYAY*

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

(*Received in final form 31 August 2005*)

Phenylhydrazine (R) quantitatively reduces $[Fe_2(\mu\text{-}O)(phen)_4(H_2O)_2]^{4+}$ (**1**) (phen = 1,10-phenanthroline) and its conjugate base $[Fe_2(\mu\text{-}O)(phen)_4(H_2O)(OH)]^{3+}$ (**2**) to $[Fe(phen)_3]^{2+}$ in presence of excess 1,10-phenanthroline in the pH range 4.12–5.55. Oxidation products of phenylhydrazine are dinitrogen and phenol. The reaction proceeds through two parallel paths: $\mathbf{1} + R \rightarrow$ products (k_1), $\mathbf{2} + R \rightarrow$ products (k_2); neither RH^+ nor the doubly deprotonated conjugate base of the oxidant, $[Fe_2(\mu\text{-}O)(phen)_4(OH)_2]^{2+}$ (**3**) is kinetically reactive though both are present in the reaction media. At 25.0°C, $I = 1.0\,M$ ($NaNO_3$), the rate constants are $k_1 = 425 \pm 10\,M^{-1}\,s^{-1}$ and $k_2 = 103 \pm 5\,M^{-1}\,s^{-1}$. An inner-sphere, one-electron, rate-limiting step is proposed.

Keywords: Kinetics; Oxidation; Redox; Iron(III); Phenylhydrazine

1. Introduction

The μ-oxo diiron(III,III) unit, $\{Fe–O–Fe\}^{4+}$, is unavoidable in iron chemistry, both in abiological and biological environments. Several diiron complexes having oxo- or hydroxo-bridges were structurally known by the late 1970s [1] though the first knowledge of their biological relevance came later with the single-crystal X-ray structures of two naturally occurring proteins, hemerythrin [2] and ribonucleotide reductase [3] (dinuclear oxo iron sites). With this in mind, chemists and biochemists prepared many synthetic models for the latter species (mostly structural) involving di- and multinuclear oxo/carboxylato-bridged iron complexes of intriguing diversity [4]. Despite the availability of a large number of such synthetic polyiron species, their reactivity and mechanism of reaction have received little detailed attention [5].

The chosen oxidant for the present study, $[Fe_2(\mu\text{-}O)(phen)_4(H_2O)_2]^{4+}$ (phen = 1,10-phenanthroline, figure 1), is a Raman spectroscopic model [6] for the binuclear iron site in ribonucleotide reductase and methemerythrin, the oxidised form of the oxygen transport protein hemerythrin. The complex is quite soluble in water and its solutions

---

*Corresponding author. E-mail: subrataju@vsnl.net

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970500410614

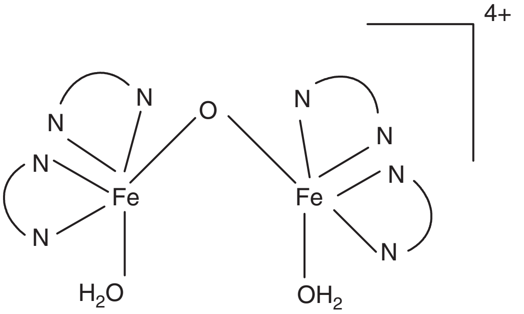

Figure 1. Graphical structure of $[Fe_2(\mu\text{-}O)(phen)_4(H_2O)_2]^{4+}$.

are fairly stable towards self-decomposition in the pH range 3.0–7.0 in the presence of excess 1,10-phenanthroline.

Phenylhydrazine is a common reducing agent with a broad spectrum of oxidised products depending on oxidizing agents and intermediate species formed during oxidation [7]. Phenylhydrazine may offer much greater versatility than hydrazine with respect to reaction products and pathways leading to them. However, detailed studies of the oxidation of phenylhydrazine are known with only a limited number of oxidants. In striking contrast to hydrazine, phenylhydrazine has poorly defined redox chemistry and it is difficult to speculate on reaction products with a new oxidant. We report here the oxidation kinetics of phenylhydrazine by $[Fe_2(\mu\text{-}O)(phen)_4(H_2O)_2]^{4+}$, an overall 2 electron oxidant.

2. Experimental

2.1. *Materials*

Crystals of $[Fe_2(\mu\text{-}O)(phen)_4(H_2O)_2](NO_3)_4 \cdot 5H_2O$ were prepared by a known method [6]. Samples gave satisfactory electronic spectra [6] and elemental analyses Anal. Calcd for $C_{48}H_{32}Fe_2O_{13}N_{12} \cdot 7H_2O$ (%): C, 47.15; H, 3.8; N, 13.75; Fe, 9.1. Found: C, 47.1; H, 3.7; N, 13.7; Fe, 9.0. Stock solutions of phenylhydrazine were prepared from phenylhydrazine hydrate (Merck, G. R.) with appropriate dilution and standardised spectrophotometrically [8] at 730 nm using excess phosphomolybdic acid and ca 0.03 M HCl. Preparation, storage and standardisation of $NaNO_3$, $[Fe(phen)_3](NO_3)_3$, and $[Fe(phen)_3](NO_3)_2$ were described earlier in detail [5e]. All reported kinetic and equilibrium data are for 25.0°C, $I = 1.0$ M ($NaNO_3$). Doubly distilled and then freshly boiled water was used throughout.

2.2. *Physical measurements and kinetics*

All absorbance values and electronic spectra were recorded with a Shimadzu 1601 PC spectrophotometer with 1.00 cm quartz cells as described earlier [5e]. Excess 1,10-phenanthroline, C_{phen} (=$[Hphen]^+ + [phen]$), 3–10 mM, was used in all kinetic runs. Solution pH values were measured using an Orion 710A pH meter with a combined electrode, details of which can be found elsewhere [9]. For faster reactions, mixing of reactants (pre-equilibrated at desired pH) was carried out in the spectrophotometer cells [10].

2.3. *Equilibrium measurements*

Acid dissociation constants of phenylhydrazine were determined by pH-metric titration of several aliquots with carbonate-free standard NaOH solution using a Metrohm 736 GP Titrino autotitrator.

2.4. *Stoichiometry and reaction products*

Under kinetic conditions electronic spectra of product solutions confirmed quantitative (99 ± 2%) formation of 2 moles of $[Fe(phen)_3]^{2+}$ as the only iron product per mole of oxidant. The gaseous product formed during the reaction was collected over a saturated sodium chloride solution and analysed by gas chromatography using a Chemito (India) GC 8610 equipped with TCD, a Porapack Q and molecular sieve 13X column as described earlier [11]. The oven, injector and detector temperatures were kept at 40, 110 and 150°C, respectively. The carrier hydrogen gas flow was adjusted to $30\,cm^3\,min^{-1}$. Formation of aniline, benzene or phenol as phenylhydrazine oxidation products was qualitatively analysed by HPLC. A reaction mixture initially containing 0.2 mM of diiron(III) complex was reacted with 2.0 mM phenylhydrazine at pH 4.0 in the presence of 3.0 mM of 1,10-phenanthroline. After completion of the reaction, excess $NaClO_4$ was added to the reaction solution. Precipitated $[Fe(phen)_3](ClO_4)_2$ was removed by filtration and the colourless filtrate applied to a HPLC system at 25.0°C (Shimadzu LC 8A) using a Phenomenex C_{18} column (length 25 cm, diameter 4.6 mm) with $MeOH/H_2O$ (60/40, v/v) as mobile phase [12], a flow rate of $1.0\,cm^3\,min^{-1}$ and detection at 270 nm.

3. Results and discussion

3.1. *Stoichiometry and reaction products*

Results of at least five determinations yielded $\Delta[N_2]:\Delta[Fe_2^{III}] = 0.47 \pm 0.04$ as determined by GC analysis after complete reduction of the iron complex. Retention times found in HPLC experiments confirmed phenol (5.003 min, observed in the product mixture; 4.995 min for pure phenol) as the only oxidation product present with unreacted phenylhydrazine (2.885 min, observed in the product mixture; 2.799 min for pure phenylhydrazine). These results, along with the quantitative formation of $[Fe(phen)_3]^{2+}$ confirmed an overall 4e oxidation of phenylhydrazine (**1**).

$$\begin{aligned} &2[Fe_2^{III}(\mu - O)(phen)_4(H_2O)_2]^{4+} + C_6H_5NHNH_2 + 4phen \\ &\quad \rightarrow 4[Fe(phen)_3]^{2+} + 5H_2O + C_6H_5OH + N_2 \end{aligned} \tag{1}$$

3.2. *Equilibrium studies*

The built-in program of the autotitrator yielded a pK_a of 5.20 ± 0.10 for monoprotonated phenylhydrazine (defined as RH^+), in excellent agreement with reported values [13] under similar conditions (5.20 at 25.0°C, $I = 1.0$ M [13a], 5.20 at 25.0°C, $I = 0.5$ M, 20% EtOH + 80% H_2O [13b]). Complex **1** behaves as a mild dibasic acid in aqueous solution and its acid dissociation constants are $pK_{a1} = 3.71 \pm 0.05$ and $pK_{a2} = 5.28 \pm 0.10$ (both at 25.0°C, $I = 1.0$ M) [5e].

$$\underset{\mathbf{1}}{[Fe_2(\mu\text{-}O)(phen)_4(H_2O)_2]^{4+}} \overset{K_{a1}}{\rightleftharpoons} \underset{\mathbf{2}}{[Fe_2(\mu\text{-}O)(phen)_4(H_2O)(OH)]^{3+}} + H^+ \tag{2}$$

$$\underset{\mathbf{2}}{[Fe_2(\mu\text{-}O)(phen)_4(H_2O)(OH)]^{3+}} \overset{K_{a2}}{\rightleftharpoons} \underset{\mathbf{3}}{[Fe_2(\mu\text{-}O)(phen)_4(OH)_2]^{2+}} + H^+ \tag{3}$$

3.3. *Kinetics*

In weakly acidic solution, the pH interval chosen for the present study, the oxo-bridge in **1** is stable and self-decomposition is negligible. We used excess 1,10-phenanthroline in all kinetic measurements to suppress any hydrolysis and thus minimized the number of reactive iron(III) species. High C_{phen} also sequesters foreign metal ion impurities and excludes any possible metal-catalysed degradation of phenylhydrazine [14]. Excess C_{phen} also buffers the reacting solutions to well within 0.05 units.

The reaction follows excellent first-order decay of **1** as evidenced by good linear plots ($r \geq 0.99$) of $\log(A_{\propto} - A_t)$ *versus* time, where $A_{\propto}$ and A_t stand respectively for the absorbance of final $[Fe(phen)_3]^{2+}$ ($=2[\mathbf{1}]_{Total}$) and $[Fe(phen)_3]^{2+}_t$ ($=2[\mathbf{1}]_{consumed}$ at time t), whence first-order rate constants, k_0, were evaluated (table 1). In the investigated pH range the k_0 versus pH plot has an inverted bell shape that indicates the presence of more than one acid-base equilibrium (figure 2) [15]. The k_0 values remained invariant in the presence of $C_{phen} = 3.0$–10.0 mM and this clearly indicates no phen dissociation

Table1. Representative first-order rate constants[a] at 25.0°C, $I = 1.0$ M ($NaNO_3$).

pH	T_R (mM)	C_{phen} (mM)	$10^4 k_0$ (s^{-1})
4.12	0.50	3.0	65
4.30			80
4.51			115
4.72			139
4.92			146
5.10			163
5.31			146
5.55			132
4.30	0.35		50
4.31	1.0		145
4.30	1.5		212
4.30	2.0		295
5.11	0.50	10.0	161
5.55	0.50	3.0	136[b]
4.50	0.50	6.0	118[c]

[a] [diiron complex] = 0.05 mM. [b]At $I = 0.5$ mM ($NaNO_3$) $10^4 k_0 = 135\ s^{-1}$.
[c] In the presence of added 0.05 mM ferroin $10^4 k_0 = 113\ s^{-1}$.

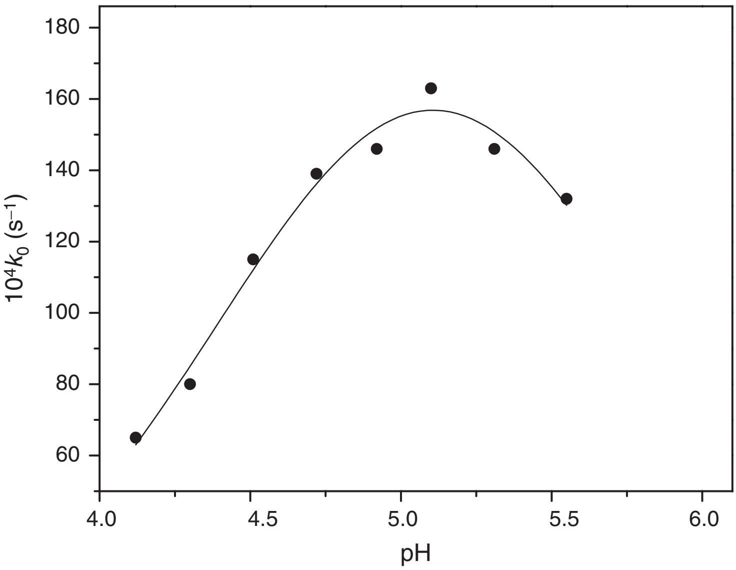

Figure 2. Plot of k_0 (s^{-1}) *vs.* pH at [complex] = 0.05 mM, $T_{R=}$0.50 M, C_{phen} = 3.0 mM, T = 25.0°C, I = 1.0 M ($NaNO_3$).

$$RH^+ \underset{}{\overset{K_a}{\rightleftharpoons}} R + H^+ \tag{4}$$

$$\mathbf{1} + R \xrightarrow{k_1} \text{Products} \tag{5}$$

$$\mathbf{2} + R \xrightarrow{k_2} \text{Products} \tag{6}$$

$$\mathbf{3} + R \xrightarrow{k_3} \text{Products} \tag{7}$$

Scheme 1. Possible rate steps of the oxidation of phenylhydrazine by the Fe_2^{III} dimer.

from the complex under the experimental condition chosen; at a particular [H^+] we observed a purely linear dependence of k_0 on T_R (=[$C_6H_5NHNH_3^+$] + [$C_6H_5NHNH_2$]). On increasing pH, the concentration of deprotonated $C_6H_5NHNH_2$ increases, with the expected superior reactivity over its conjugate acid $C_6H_5NHNH_3^+$, whereas the less reactive deprotonated form of the oxidant [16] continually increases. At upper pH values a substantial decrease in rate is observed. It was also found that k_0 did not depend on ionic strength in the range 0.1–1.5 M (table 1) and this supports reaction of an uncharged species ($C_6H_5NHNH_2$). Equilibria (2)–(4) along with the rate steps in scheme 1 describe the kinetic observations.

The scheme leads to the rate law

$$[k_0\alpha(K_a + [H^+])]/K_aT_R = k_1 + k_2K_{a1}/[H^+] + k_3K_{a1}K_{a2}/[H^+]^2 \tag{8}$$

where

$$\alpha = (1 + K_{a1}/[H^+] + K_{a1}K_{a2}/[H^+]^2) \tag{9}$$

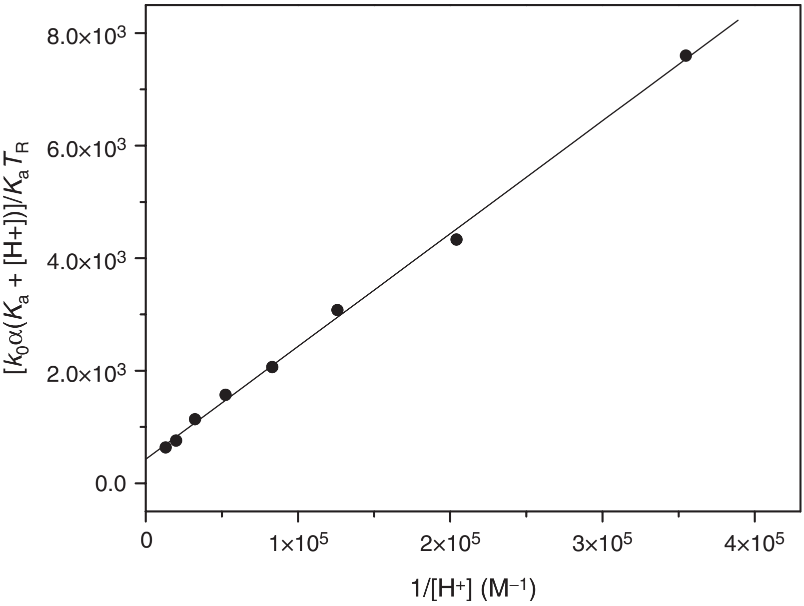

Figure 3. Plot of $[k_0\alpha(K_a + [H^+])]/K_aT_R$ *vs.* $1/[H^+]$; $[\text{complex}] = 0.05\,\text{M}$, $T_R = 0.50\,\text{M}$, $C_{\text{phen}} = 3.0\,\text{mM}$, $T = 25.0^\circ\text{C}$, $I = 1.0\,\text{M}$ ($NaNO_3$).

Equation (8) shows the left-hand-side would be a second-order polynomial in $[H^+]^{-1}$ but the left-hand-side of (8) *versus* $1/[H^+]$ plot yielded an excellent straight line with a statistically significant intercept (figure 3, $r > 0.99$), which indicates essentially zero reactivity of **3**. Thus we find the rate steps (5) and (6) are sufficient to predict the observed behaviour of rate dependence on pH. The rate equation in this way simplifies to (10).

$$[k_0\alpha(K_a + [H^+])]/K_aT_R = k_1 + k_2K_{a1}/[H^+] \tag{10}$$

The intercept and slope (divided by K_{a1}) of the plot in figure 3 yielded $k_1 = 425 \pm 10\,\text{M}^{-1}\,\text{s}^{-1}$ and $k_2 = 103 \pm 5\,\text{M}^{-1}\,\text{s}^{-1}$. These second-order rate constants generate observed k_0 values satisfactorily. It is of note that with the stoichiometric factor 2, these rate constants are twice that of the proposed one-electron rate determining steps $\{Fe_2O\}^{4+} + C_6H_5NHNH_2 \rightarrow \{Fe_2O\}^{3+} + C_6H_5NHNH_2^+$ (*vide infra*).

3.4. *Mechanism*

The reactivity order $k_1 > k_2$ and non-reactivity of $C_6H_5NHNH_3^+$ support the well-accepted view that protonated oxidants reacts faster than their conjugate bases and the reverse is true for reducing species [16]. In comparison to the N_2H_4 reduction [5e] of the oxidant, we find phenylhydrazine reacts much faster. This may be attributed to the availability of much higher concentrations of reactive $C_6H_5NHNH_2$ than N_2H_4 under the experimental condition as the conjugate acid $C_6H_5NHNH_3^+$ ($pK_a = 5.20$) is far more acidic than $N_2H_5^+$ ($pK_a = 8.18$) [17].

The unidentate ligand bound to each high-spin iron(III) in the iron(III) dimer is labile as evidenced from the rapid aquation of $[L_4Cl_2(\mu\text{-}O)Fe_2^{III}]^{2+}$

to produce $[L_4(H_2O)_2(\mu\text{-O})Fe_2^{III}]^{4+}$ [18], which also instantaneously produces $[L_4(SCN)_2(\mu\text{-O})Fe_2^{III}]^{2+}$ on adding KSCN (L = 2,2′-bipyridine or 1,10-phenanthroline) [18, 19]. An inner-sphere attachment of moderately basic $C_6H_5NHNH_2$ to the iron(III) centre is thus anticipated. Stynes *et al.* [20] noted that weakly basic amines form adducts (equilibrium constants $\sim 10^3$) with the oxo-bridged diiron(III) complex $[AFe(dmgBF_2)_2]_2O$ ($dmgBF_2$ = difluoro(dimethylglyoximato)borate, A = CH_3CN, which is axially bound). This ligation was also established with donors like pyridine or methylimidazole, which are not easily oxidized [21]. Phenylhydrazine is a much stronger base than amines or NH_2OH and is expected to form strong adducts with iron(III). Holding the inequality $K_i[C_6H_5NHNH_2] \ll 1$ (K_i = pre-equilibrium constant for adduct formation, $i = 1$, 2 for the oxidant species **1** and **2**), an estimated upper limit of K_i is around 10^4, with no definite lower limit.

A net 2e change is necessary per iron(III) dimer to completely reduce it to $[Fe(phen)_3]^{2+}$ in the presence of 1,10-phenanthroline. We propose the rate-determining steps to be one-electron changes in the intermediates to form the respective Fe^{II}–O–Fe^{III} dimers that quickly transform to products either by aquation or by further reduction to Fe(II) and Fe(III) monomers. The Fe(III) monomer is further reduced to Fe(II) monomer and ultimately forms ferroin where all subsequent steps are kinetically silent. The $[Fe_2O]^{4+}$ core in the Fe_2^{III} dimer gains stability from the superexchange of the two high-spin iron(III) centres linked by an oxo-bridge [22]. However, high-spin iron(II) and iron(III) are probably less strongly bound to O^{2-}, since both the oxidation states having two antibonding electrons are directed towards bond axes that would impart weaker Fe^{II}–O–Fe^{III} or Fe^{II}–O–Fe^{II} bonds and the oxo-bridge in the mixed-valence system Fe^{II}–O–Fe^{III} is in generally putative outside a protein environment [23]. This thus substantiates our one-electron proposal to form $[Fe_2O]^{3+}$ and $C_6H_5NHNH_2^{+}$ in the rate-determining step. Existence of very highly reactive short-lived phenylhydrazyl radicals formed from phenylhydrazine has been established by fast-flow EPR spectroscopy [24].

We have only phenol as the organic product in the reaction, along with N_2, and there is no indication of even minor amounts of benzene or aniline in the products. We thus conclude that the $C_6H_5NHNH_2^{\bullet +}$ radical leads to products *via* the intermediate formation of the diazonium cation $C_6H_5N_2^{+}$, though we could not trap any such intermediate with alkaline β-napthol. This suggests fast hydrolysis of $C_6H_5N_2^{+}$, leading to phenol with evolution of N_2.

Acknowledgements

This work was financially supported by the Council of Scientific and Industrial Research, New Delhi (India). We gratefully acknowledge Dr. Joydeep Mukherjee, Lecturer, Environmental Science Programme of Jadavpur University for HPLC measurements.

References

[1] (a) K.S. Murray. *Coord. Chem. Rev.*, **12**, 1 (1974) and references therein; (b) D.M. Kurtz. *Chem. Rev.*, **90**, 585 (1990).

[2] (a) R.E. Stenkamp, L.C. Sieker, L.H. Jensen. *Acta Crystallogr.*, **B38**, 784 (1982); (b) J.B. Vincent, G.L. Oliver-Lilley, B.A. Averill. *Chem. Rev.*, **90**, 1447 (1990).

[3] (a) T. Joelson, U. Uhlin, H. Eklund, B.-M. Sjoberg, S. Hahve, M.J. Karlsson. *J. Biol. Chem.*, **259**, 9076 (1984); (b) P. Norlund, B.-M. Sjoberg, H. Eklund. *Nature*, **345**, 593 (1990).

[4] (a) K. Wieghardt, K. Pohl, D. Ventur. *Angew. Chem. Int. Ed. Engl.*, **24**, 392 (1985); (b) J.R. Hartman, R.L. Rardin, P. Chaudhuri, K. Pohl, K. Weighardt, B. Nuber, J. Weiss, G.C. Papaefthymiou, R.B. Frankel, S.J. Lippard. *J. Am. Chem. Soc.*, **109**, 7387 (1987); (c) S. Yan, D.D. Cox, L.L. Pearce, C. Juarez-Garcia, L. Que, J.H. Zhang, C.J. O'Connor. *Inorg. Chem.*, **28**, 2507 (1989); (d) S. Ménage, J.M. Vincent, C. Lambeaux, G. Chottard, A. Grand, M. Fontecave. *Inorg. Chem.*, **32**, 4766 (1993); (e) R.M. Buchanan, S. Chen, J.F. Richardson, M. Bressan, L. Forti, A. Morvillo, R.H. Fish. *Inorg. Chem.*, **33**, 3208 (1994); (f) A. Hazell, K.B. Jensen, C.J. McKenzie, H. Toftlund. *Inorg. Chem.*, **33**, 3127 (1994); (g) Y.-G. Wei, S.-W. Zhang, M.-C. Shao. *Polyhedron*, **16**, 2307 (1997); (h) D.F. Xiang, X.S. Tan, S.W. Zhang, Y. Han, K.B. Yu, W.X. Tang. *Polyhedron*, **17**, 2095 (1998); (i) A.G.J. Lightenbarg, P. Oosting, G. Royelfes, R.M. La Crois, M. Lutz, A.L. Spek, R. Hage, B.L. Feringa. *J. Chem. Soc., Chem. Commun.*, 385 (2001); (j) C. Stadler, J. Daub, J. Kohler, R.W. Saalfrank, V. Coropceanu, V. Schunemann, C. Ober, A.X. Trautwein, S.F. Parker, M. Poyraz, T. Inomata, R.D. Cannon. *J. Chem. Soc., Dalton Trans.*, 3373 (2001); (k) D. Lee, S.J. Lippard. *J. Am. Chem. Soc.*, **123**, 4611 (2001); (l) M. Scarpellini, A. Neves, A.J. Bortoluzzi, I.V.V. Drago, A.W. Ortiz, C. Zucco. *J. Chem. Soc., Dalton Trans.*, 2616 (2001); (m) R.F. Moreira, E.Y. Tshuva, S.J. Lippard. *Inorg. Chem.*, **43**, 4427 (2004); (n) S.V. Kryatov, S. Taktak, I.V. Korendovych, E.V. Rybak-Akimova, J. Kaizer, S. Torelli, X. Shan, S. Mandal, V.L. MacMurdo, A. Payeras Jr, L. Que. *Inorg. Chem.*, **44**, 85 (2005).

[5] See for example: (a) T.G. Traylor, W.A. Lee, D.V. Stynes. *J. Am. Chem. Soc.*, **106**, 755 (1984); (b) P.N. Balasubramanian, J.R.L. Smith, M.J. Davies, T.W. Kaaret, T.C. Bruice. *J. Am. Chem. Soc.*, **111**, 1477 (1989); (c) B. Chaudhuri, R. Banerjee. *Can. J. Chem.*, **76**, 350 (1998); (d) B. Chaudhuri, R. Banerjee. *J. Chem. Soc., Dalton Trans.*, 3451 (1998); (e) J. Bhattacharyya, K. Dutta, S. Mukhopadhyay. *J. Chem. Soc., Dalton Trans.*, 2910 (2004); (f) L. Keeney, M.J. Hynes. *J. Chem. Soc., Dalton Trans.*, 1524 (2005); (g) J. Bhattacharyya, S. Mukhopadhyay. *Helv. Chim. Acta*, **88** (2005) (In press).

[6] J.E. Plowman, T.M. Loehr, C.K. Schaner, O.P. Anderson. *Inorg. Chem.*, **23**, 3553 (1984).

[7] (a) G. Stedman, N. Uysal. *J. Chem. Soc., Perkin Trans. 2*, 667 (1977); (b) U.S. Banthiya, B.C. Joshi, Y.K. Gupta. *Indian J. Chem.*, **20A**, 43 (1981); (c) A.K. Gupta, B.C. Joshi, Y.K. Gupta. *Indian J. Chem.*, **20A**, 276 (1981); (d) A.K. Gupta, B. Gupta, A.K. Gupta, Y.K. Gupta. *J. Chem. Soc., Dalton Trans.*, 2599 (1984).

[8] P.C. Schlecht, P.F. O'Connor (Eds). *NIOSH Manual of Analytical Methods*, 4th Edn, Method No. 3518, New York, USA (1994).

[9] (a) S. Banerjee, U. Roy Choudhury, B.C. Roy, R. Banerjee, S. Mukhopadhyay. *Anal. Lett.*, **34**, 2797 (2001); (b) H.N. Irving, M.G. Miles, L.D. Pettit. *Anal. Chim. Acta*, **38**, 475 (1967).

[10] B.B. Dhar, R. Mukherjee, S. Mukhopadhyay, R. Banerjee. *Eur. J. Inorg. Chem.*, 2950 (2004).

[11] K. Dutta, S. Bhattacharjee, B. Chaudhuri, S. Mukhopadhyay. *J. Environ. Monit.*, **4**, 754 (2002).

[12] The composition of solvent mixture was chosen according to the following: (a) S.V. Galushko. *J. Chromatogr.*, **552**, 91 (1991); (b) S.V. Galushko. *J. Chromatogr.*, **36**, 93 (1993); (c) S.V. Galushko, A.A. Kamenchuk, G.L. Pit. *J. Chromatogr. A*, **660**, 47 (1994); (d) R.J.M. Vervoort, E. Ruyter, A.J.J. Debets, H.A. Claessens, C.A. Cramers, G.J. de Jong. *J. Chromatogr. A*, **931**, 67 (2001).

[13] (a) A. Fisher, D.A.R. Harper, J. Vaughan. *J. Chem. Soc.*, 4060 (1964); (b) L. Do Amaral, W.A. Sandstron, E.H. Cordes. *J. Am. Chem. Soc.*, **88**, 2225 (1996).

[14] (a) D.M. Stanbury. *Prog. Inorg. Chem.*, **47**, 511 (1998); (b) L.F. Audrieth, B.A. Ogg. *The Chemistry of Hydrazine*, John Wiley, New York (1951).

[15] R.G. Wilkins. *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes*, Allyn and Bacon, Boston (1974).

[16] Protonation normally increases the reactivity of the oxidizing agents whereas it decreases reactivity of reductants. See for example (a) K. Lemma, A.M. Sargeson, L.I. Elding. *J. Chem. Soc., Dalton Trans.*, 1167 (2000); (b) P. Bandyopadhyay, S. Mukhopadhyay. *Polyhedron*, **21**, 1893 (2002); (c) P. Bandyopadhyay, B.B. Dhar, J. Bhattacharyya, S. Mukhopadhyay. *Eur. J. Inorg. Chem.*, 4308 (2003); (d) A. Das, S. Mukhopadhyay. *Polyhedron*, **23**, 895 (2004).

[17] R.M. Smith, A.E. Martell. *Critical Stability Constants*, Vol. 4, p. 43, Plenum, New York (1976).

[18] P.G. David, P.C. de Mello. *Inorg. Chem.*, **12**, 2188 (1964).

[19] P.G. David. *J. Inorg. Nucl. Chem.*, **35**, 1463 (1973).

[20] H. Noglik, D.W. Thompson, D.V. Stynes. *Inorg. Chem.*, **30**, 4571 (1991) and references therein.

[21] D.V. Stynes, H. Noglik, D.W. Thompson. *Inorg. Chem.*, **30**, 4567 (1991).

[22] (a) G. McLendon, R.J. Motekaitis, A.E. Martell. *Inorg. Chem.*, **15**, 2306 (1976); (b) P. Chaudhuri, K. Weighardt, B. Nuber, J. Weiss. *Angew. Chem. Int. Ed. Engl.*, **24**, 778 (1985); (c) R.C. Reem, E.I. Solomon. *J. Am. Chem. Soc.*, **109**, 1216 (1987).

[23] E. Tshuva, S.J. Lippard. *Chem. Rev.*, **104**, 987 (2004); (b) S. Yoon, S.J. Lippard. *Inorg. Chem.*, **42**, 8606 (2003); (c) S. Zhang, R.E. Shepherd. *Inorg. Chem.*, **33**, 5262 (1994); (d) F. Arena, C. Floriani, A. Chiesi-Villa, C. Guastini. *J. Chem. Soc.*, *Chem. Commun.*, 1369 (1986).

[24] (a) H.J. Sipe Jr, A.R. Jaszewski, R.P. Mason. *Chem. Res. Toxicol.*, **17**, 226 (2004); (b) P. Smith, K.R. Maples. *J. Magn. Reson.*, **65**, 491 (1985).