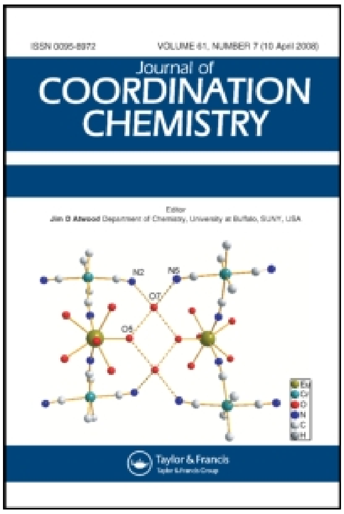

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KINETICS OF THE LIGAND EXCHANGE OF BIPYRIDINE IN TETRADENTATE NICKEL COMPLEXES

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An investigation into the ligand exchange reaction of bipyridine with Ni(EDDA) and Ni(trien) has led to proposed mechanisms based on steric and electronic effects. Kinetic studies show that the rate order dependence of bipyridine is different for the two reactions implying a slightly different mechanism for the bulkier trien. Both mechanisms involve unwrapping of the tetradentate ligand as the rate-determining step. This unwrapping is faster in acidic solution, because protonation of the amine groups inhibits recoordination of the ligand to the nickel. The rates for bipyridine exchange were significantly faster than for phenanthroline, suggesting an electronic ligand effect.

Keywords: Mechanism; Bipyridine; Nickel; Triethylenetetramine; Ethylenediaminediacetic acid; Steric effects

INTRODUCTION

Environmental chemists have expressed concern about the sources and environmental fate of strongly complexed nickel in water. Multidentate ligands lower nickel's affinity for surfaces thus enhancing its mobility in aquatic systems. This can lead to a greater risk of metal toxicity to organisms [1].

Kinetic measurements of the complexation process have become an important tool in determining the mechanism of ligand dissociation from nickel. Stability studies have provided an understanding of the thermodynamics, but kinetic studies concentrate on reaction rates and the mechanism for displacement reactions [2]. A comparison of the exchange rate between bipyridine (bpy) and the ligands ethylenediaminediacetic acid (EDDA) and triethylenetetramine (trien) in nickel complexes is explored in this article. The mechanism previously published for the exchange reactions between

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TABLE I Comparison of the stability constants for Ni complexes in this study

Compound	*Log K at 25°C*
$Ni(EDDA)(H_2O)_2$	13.65
$Ni(trien)(H_2O)_2$	14.4
$Ni(2,2'\text{-bipyridine})_3$	20.2

1,10-phenanthroline and the ligands in this study showed some differences [3,4]. In this article, dissociation from coordination compounds is explored in terms of steric hindrance and electronic structure. Ligands participate in bonding to metals by being σ-donors, π-acceptors, or π-donors to the metal. The steric and electronic properties of particular ligands are important for catalytic purposes [5].

The reaction investigated was the exchange of bipyridine with a tetradentate ligand:

$$NiL(H_2O)_2 + 3\ 2,2'\text{-bipyridine}\cdot Ni(2,2'\text{-bipyridine})_3 + L + H_2O \qquad (1)$$

where L represents a tetradentate ligand, either EDDA or trien. Analysis of the stability constants provided in Table I shows that the products are thermodynamically favored [6–8]. According to the chelate effect (entropy effect) products would not be favored because of the greater stability of the tetradentate ligands bound to the Ni compared to the bidentate ligand bipyridine. The higher stability of $Ni(bpy)_3$ is probably an electronic effect due to resonance stability of the pyridine ring attached to nickel [9].

The determined rate law will offer information leading to proposed mechanisms for the reaction of each tetradentate ligand. The mechanism involves a series of bond dissociation and bond formation steps with the central nickel ion, lending insight into steric and electronic effects.

EXPERIMENTAL

Reagents

All chemicals were reagent grade (98% purity or better) and used without further purification except EDDA, which was recrystallized from a hot basic solution. Solutions were made using distilled water passed through a Millipore Nanopure water purification system.

Preparation of Solutions

Solutions of Ni(EDDA) and Ni(trien) were prepared by adding a 5% molar excess of nickel(II) nitrate to the appropriate ligand solution followed by addition of NaOH to raise the pH to 11, causing the excess nickel to precipitate as nickel(II) hydroxide. After two days the solution was filtered to remove the $Ni(OH)_2$ precipitate.

Buffer solutions in the pH range 4.8 to 7.3 were made from a 50 μM concentration of HEPES (*N*-2-hydroxyethylpiperazine-*N*′-2-ethanesulfonic acid) with small quantities of dilute acid added to adjust the pH. HEPES buffers were advantageous for this study owing to the negligible metal binding constant [10]. Sodium chloride was added to control the ionic strength of each solution studied.

Standardization of Ni(EDDA) and Ni(trien)

The Ni(EDDA) and Ni(trien) concentrations were standardized spectrophotometrically through comparison with tetracyanonickelate solutions prepared from a standard nickel(II) nitrate solution and a 100-fold excess of KCN at pH 10.

Spectral Analysis

A Perkin-Elmer Lambda 20 spectrophotometer recorded the visible and ultraviolet absorption spectra of relevant coordination compounds. Beer's Law plots of absorbance readings at various concentrations provided molecular extinction coefficients.

Kinetic Measurements

Spectral study of the reaction showed the greatest variation in molar absorptivity of the metal–ligand charge transfer band at 308 nm. Time-dependent absorbance values at 308 nm for various concentrations of the reactants, 2,2′-bipyridine and Ni(EDDA) or Ni(trien), were recorded using a Perkin-Elmer Lambda 20 spectrophotometer. A series of kinetic experiments to determine the acid catalyst effect were performed over the pH range 5.2 to 7.0 using a boric acid–mannitol buffer. The solution's ionic strength was held constant at 0.1 M using a sodium chloride solution. A constant temperature of 25.0 ± 0.1°C was maintained throughout the experiments.

RESULTS

Spectral Data

The absorbance spectra of compounds involved in the reaction of Ni(EDDA) and 2,2′-bipyridine showed that the predominant absorbing species at 308 nm is Ni(2,2′-bipyridine)$_3$. Molar extinction coefficients for relevant species, presented in Table II, reveal that the three contributors to the absorbance at 308 nm during this reaction are the product, Ni(2,2′-bipyridine)$_3$, the intermediate species, Ni(trien)(2,2′-bipyridine) or Ni(EDDA)(2,2′-bipyridine), and protonated species of

TABLE II Extinction coefficients of relevant absorbing species at 308 nm

Compound	ε ($M^{-1}\,cm^{-1}$)
2,2′-bipyridine	412
Ni(trien)(2,2′-bipyridine)	9010
Ni(EDDA)(2,2′-bipyridine)	11 380
Ni(2,2′-bipyridine)$_3$	34 140
H(2,2′-bipyridine)	11 740

2,2′-bipyridine, which will contribute significant absorbance under more acidic conditions.

Kinetics of Bipyridine Exchange with Ni(trien)

Analysis of initial absorbance readings for the kinetic experiments confirms that formation of a ternary complex, shown in Eq. (2), occurs within a minute for these types of systems [11–13].

$$\mathrm{Ni(trien)} + 2,2'\text{-bipyridine} \rightarrow \mathrm{Ni(trien)}(2,2'\text{-bipyridine}) \tag{2}$$

The main reaction studied involves formation of products from this intermediate ternary species.

$$\mathrm{Ni(trien)}(2,2'\text{-bipyridine}) + 2(2,2'\text{-bipyridine}) \rightarrow \mathrm{Ni}(2,2'\text{-bipryridine})_3 + \mathrm{trien} \tag{3}$$

The absorbance value at 308 nm increased over time until the reaction went to completion as determined by the final absorbance measurement.

The rate of $\mathrm{Ni(bpy)_3}$ formation is equal to the rate of Ni(trien)(bpy) decay given by:

$$\mathrm{Rate} = \frac{-d[\mathrm{Ni(trien)(bpy)}]}{dt} = \frac{d[\mathrm{Ni(bpy)_3}]}{dt} = k^o[\mathrm{Ni(trien)(bpy)}]^m[\mathrm{bpy}]^n \tag{4}$$

where m and n are reaction orders with respect to the ternary complex and bipyridine, respectively, and k^o is the rate constant.

The rate order with respect to Ni(trien)(bpy) was determined by experiments with excess bipyridine to arrive at a pseudo rate law:

$$\mathrm{Rate} = \frac{-d[\mathrm{Ni(trien)(bpy)}}{dt} = \frac{d[\mathrm{Ni(bpy)_3}]}{dt} = k[\mathrm{Ni(trien)(bpy)}]^m \tag{5}$$

with $k = k^o[\mathrm{bpy}]^n$. The concentration of the mixed ligand complex Ni(trien)(bpy) was calculated from the absorbance data at 308 nm with consideration of the contribution of all relevant absorbing species. Equation (6) was derived to correct for overlapping absorbances of the species:

$$[\mathrm{Ni(trien)(bpy)}] = \frac{A_f - A_t}{b(\varepsilon_{\mathrm{Ni(bpy)_3}} - 2\varepsilon_{\mathrm{bpy}} - 2\varepsilon_{\mathrm{Hbpy}}[\mathrm{H}^+]/K_a - \varepsilon_{\mathrm{Ni(trien)(bpy)}})}, \tag{6}$$

where A_f is the final absorbance, A_t is the absorbance at time t, b is the cell path length, ε is the extinction coefficient of the relevant species and K_a is the acid dissociation constant for 2,2′-bipyridine which has a value of 3.98×10^{-5}. It should be noted that the protonated bipyridine species, which has a different spectral signature than the neutral bipyridine species, becomes an important species at pH values around 5 and below. A plot of the log[Ni(trien)(bpy)] *vs.* time is shown in Fig. 1.

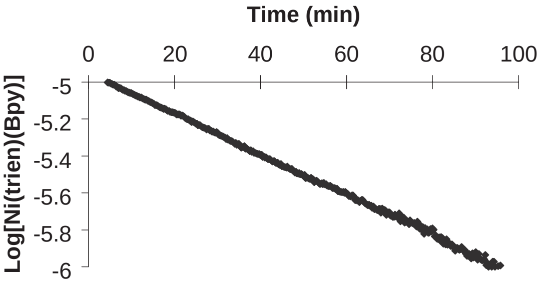

FIGURE 1 Kinetic rate data showing the first-order dependence of the ternary complex, Ni(trien)(bpy) at pH = 5.45.

TABLE III Rate constants for the dissociation of $Ni(trien)(bpy)^{2+}$

pH	*[Ni(trien)]* (μM)	*[2,2′-bipyridine]* (μM)	$10^4 k$ (s^{-1})
5.02	50	300	102
5.05	10	300	96
5.35	10	300	53
5.35	10	450	48
5.35	10	750	49
5.40	30	300	59
5.45	10	1000	50
5.69	10	500	18
5.69	20	100	17
5.74	10	300	20
5.74	10	450	22
5.98	10	1000	9.5
6.28	30	1000	7.6
6.40	10	750	7.9
6.40	10	450	7.7
6.50	10	1000	7.3
6.95	20	1500	6.9
7.00	10	300	6.7
7.30	10	500	5.0

A first-order rate dependence is clearly seen in this linear fit. Thus a transformation of the rate equation,

$$\log[\mathrm{Ni(trien)(bpy)}]_t = \log[\mathrm{Ni(trien)(bpy)}]_0 - kt/2.303 \qquad (7)$$

provides the pseudo rate constant, k, for the reaction.

Table III shows that the rate constant, k, at constant pH does not change over a five-fold variation of the ratio of bipyridine to Ni(trien) concentrations. At pH values of 5.0, 5.4, and 5.7 the rate constants have values 0.0100, 0.0060, and $0.0018\,\mathrm{s}^{-1}$ respectively, which are independent of the bipyridine concentration. Thus it can be concluded that the reaction is independent or zero order with respect to bipyridine, simplifying the rate law to:

$$\mathrm{Rate} = \frac{-d[\mathrm{Ni(trien)(bpy)}}{dt} = \frac{d[\mathrm{Ni(bpy)_3}]}{dt} = k^o[\mathrm{Ni(trien)(bpy)}]^m \qquad (8)$$

This ligand exchange reaction is strongly acid catalyzed as seen in Table III, such that a decrease in pH drastically increases the reaction rate constant from $0.00050\,\mathrm{s}^{-1}$ at a pH of 7.3 to $0.0100\,\mathrm{s}^{-1}$ at a pH of 5.0.

Kinetics of Bipyridine Exchange with Ni(EDDA)

This reaction has many similarities to the bipyridine exchange with Ni(trien). It proceeds through a ternary intermediate complex of Ni(EDDA)bipyridine that is formed within a minute:

$$\begin{aligned}&\mathrm{Ni(EDDA)(2,2'\text{-}bipyridine)} + 2(2,2'\text{-}\mathrm{bipyridine})\\&\quad\rightarrow \mathrm{Ni(2,2'\text{-}bipryridine)_3{+}EDDA}\end{aligned} \tag{9}$$

The kinetic data were analyzed as for Ni(trien). The rate law can be written as:

$$\mathrm{Rate} = \frac{-d[\mathrm{Ni(EDDA)(bpy)}}{dt} = \frac{d[\mathrm{Ni(bpy)_3}]}{dt} = k^o[\mathrm{Ni(EDDA)(bpy)}]^m[\mathrm{bpy}]^n \tag{10}$$

Excess bipyridine leads to pseudo-first-order conditions,

$$\mathrm{Rate} = \frac{-d[\mathrm{Ni(EDDA)(bpy)}}{dt} = \frac{d[\mathrm{Ni(bpy)_3}]}{dt} = k[\mathrm{Ni(EDDA)(bpy)}]^m, \tag{11}$$

where $k = k^o[\mathrm{bipyridine}]^n$. First-order behavior with respect to Ni(EDDA)(bpy) was observed from a linear plot of log[Ni(EDDA)(bpy)] *vs*. time.

Table IV shows that at fairly constant pH values of 4.84 and 5.50 with excess bipyridine the rate constant, k, increases linearly with the bipyridine concentration. Thus the reaction is first order with respect to bipyridine and first order with respect to the intermediate, Ni(EDDA)(bpy). The rate constant also increases markedly with acidity of the solutions from a value of $4.59\times10^{-4}\,\mathrm{s}^{-1}$ at a pH of 6.95 to $1.96\times10^{-3}\,\mathrm{s}^{-1}$ at a pH of 4.84 for a constant bipyridine concentration of 300 μM.

TABLE IV Rate constants for the dissociation of $\mathrm{Ni(EDDA)(bpy)}^{2+}$

pH	*[Ni(EDDA)]* (μM)	*[2,2′-bipyridine]* (μM)	$10^4 k$ (s^{-1})
4.84	10	300	1.96
4.86	10	500	2.72
4.98	30	300	2.47
5.17	10	300	1.31
5.27	10	300	1.01
5.50	20	300	0.822
5.55	20	100	0.236
5.69	10	100	0.226
6.01	10	500	1.17
6.39	30	500	0.835
6.95	10	300	0.459

DISCUSSION

The rate laws indicate that the rate is independent of bipyridine concentration for trien ligand exchange but is first order with respect to bipyridine for EDDA ligand exchange, implying that the mechanisms for these two ligand exchanges must be different.

Mechanisms

The proposed mechanisms for ligand exchange reactions in this study involve dissociation, through an unwrapping process, of the original ligand from the Ni center. The acid catalyzes this unwrapping by protonating the ligand's basic sites, thereby preventing reattachment to the metal center.

Proposed Ni(trien) Unwrapping

The rate equation for Ni(trien) exchange with bipyridine was found to be:

$$\text{Rate} = k[\text{Ni(trien)(bpy)}] \tag{12}$$

The rate-determining step does not involve coordination of bipyridine to nickel but does involve the dissociation of trien from the metal ion.

Figure 2 presents a proposed mechanism for the Ni(trien)–bipyridine exchange. In Step 1, a ternary complex of Ni(trien)(bpy) is formed. The next four steps (Steps 2–5) involve dissociation of successive nitrogen arms from the Ni center. The last step (Step 6) involves addition of two bipyridines to the Ni ion. This mechanism is consistent with the zero-order dependence of the rate on bipyridine. The rate-determining step does not involve coordination of bipyridine to the nickel, but involves dissociation of trien from the metal ion. The rate-determining step is proposed to occur after the first two Ni–nitrogen bonds have been broken [9]. The slow step is proposed to involve rupture of the third or fourth nitrogen bond given by Step 4 or 5. The exact location cannot be determined from our kinetic experiments. The mechanism also displays a significant steric effect, as the bulky trien prevents the addition of bipyridine until all four sites are available for coordination.

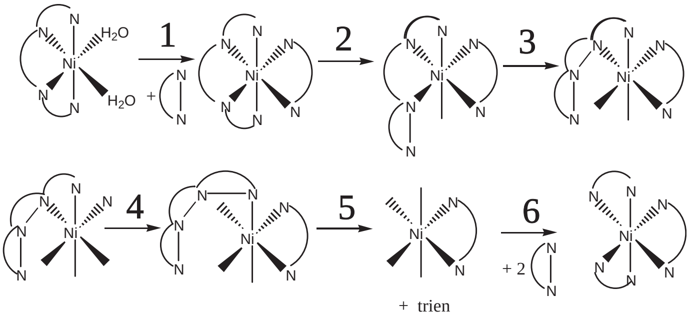

FIGURE 2 Proposed reaction mechanism of the exchange of bipyridine with trien in Ni complexes. The rate-determining step is proposed to be step 4 or 5 based on the kinetic data.

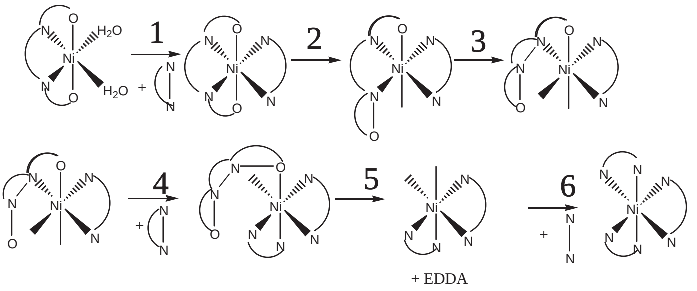

FIGURE 3 Proposed reaction mechanism of the exchange of bipyridine with trien in EDDA complexes. Based on the kinetic data the rate-determining step is proposed to be step 5, which involves either the breaking of a Ni–N or Ni–O bond.

Acid catalyzes this dissociation by attaching to the amine portions of the trien, consequently preventing rebinding of the dissociated ligand to the metal. The proton dependence for this reaction could not be proved conclusively, but earlier studies on the dissociation of trien from Ni have proposed a two-proton dependence [14].

Proposed Ni(EDDA) Unwrapping

The rate equation for Ni(EDDA) exchange with bipyridine was found to be:

$$\text{Rate} = k[\text{Ni(EDDA)(bpy)}][\text{bpy}]. \tag{13}$$

Unlike the Ni(trien) unwrapping, this rate involves the bipyridine concentration.

Figure 3 presents a proposed mechanism for the Ni(EDDA)–bipyridine exchange. In Step 1, a ternary complex of Ni(EDDA)(bipyridine) is formed. Steps (2–5) involve the unwrapping of the EDDA ligand from the metal ion. Since acetate groups are more labile than amine groups it is proposed that the Ni–O bond breaks before the Ni–N bond. The less bulky EDDA ligand allows bipyridine to attach to the nickel after two coordination sites are unwrapped. This is followed by two more steps of bond-breaking between Ni and EDDA, which occur before the third bipyridine attaches. The rate-determining step is proposed to occur after dissociation of the acetate and amine groups of EDDA from the nickel center. Because of the first-order dependence on bipyridine it must occur after the addition of the second bipyridine molecule. Thus it is proposed that the slow step of this ligand exchange reaction occurs with the breaking of the second segment of the nickel–acetate or nickel–amine bond. The best estimation would be the nickel–amine bond because of its greater bond strength but the precise location of the rate-determining step cannot be determined from our data.

Acid catalyzes the dissociation by preventing recoordination of EDDA to the metal. The dependence on the H^+ ion can be fit to a one-proton dependent term by writing the rate constant as:

$$k = k_{\text{bpy}}^{\text{Ni(EDDA)(bpy)}}[\text{bpy}] + k_{\text{H,bpy}}^{\text{Ni(EDDA)(bpy)}}[\text{H}^+][\text{bpy}], \tag{14}$$

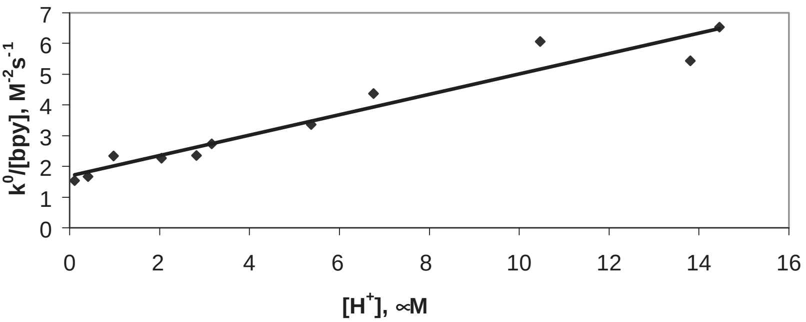

FIGURE 4 Dependence of rate constant on pH for Ni(EDDA) exchange with bipyridine. This shows the rate constants of proton independent and one-proton assisted kinetic dissociation of EDDA.

TABLE V Comparison of rate constants for various dissociation systems

Compound	*Unassisted proton rate constant* ($M^{-1}\,s^{-1}$)	*Proton-assisted rate constant* (s^{-1})
Ni(EDDA)phen	7.84×10^{-2}	5.17×10^{3}
Ni(EDDA)bpy	1.69	3.32×10^{5}

where $k_{\mathrm{bpy}}^{\mathrm{Ni(EDDA)(bpy)}}$ represents the unassisted proton rate constant and $k_{\mathrm{H,bpy}}^{\mathrm{Ni(EDDA)(bpy)}}$ represents the proton-assisted rate constant. The linearity of a graph of k/[bpy] *vs.* [H^+], illustrated in Fig. 4, clearly proves the first-order dependence of the reaction on bipyridine for the pH range of this study. The plot of k/[bpy] *vs.* [H^+] provides the rate constants of $k_{\mathrm{bpy}}^{\mathrm{Ni(EDDA)(bpy)}} = 1.69\,\mathrm{M}^{-2}\,\mathrm{s}^{-1}$ and $k_{\mathrm{H,bpy}}^{\mathrm{Ni(EDDA)(bpy)}} = 3.32 \times 10^{5}\,\mathrm{s}^{-1}$. These rate constants are compared to the phenanthroline kinetic studies of ligand exchange with Ni(EDDA) in Table V [3]. The rate constants are an order of magnitude greater for bipyridine than for phenanthroline, indicating that some ligand interaction effects, probably electronic in nature, are present in the dissociation. It has been proposed that the difference is due to the fact the spectator ligands with better acceptor properties decrease the rate of ligand dissociation by lowering the electron density on the metal ion, making the bond dissociation of Ni–N less likely [15]. Further investigations must be made to prove this statement's validity.

CONCLUSIONS

The proposed mechanisms of reaction show significant steric and electronic effects for ligand exchange processes in tetradentate nickel complexes. Results for the ligand exchange kinetics display a steric effect due to the bulky nature of trien that do not allow ligand replacement of bipyridine until all four amine sites of the trien are dissociated from the Ni metal center. The bipyridine ligand accelerates the rate of dissociation of the trien and EDDA ligand most likely through electronic effects. Acid catalyzes the dissociation of the ligand from the metal center by preventing recoordination of the free ligand. Future studies of phosphorus and sulfur ring analogs of bipyridine may confirm the electronic ligand effect.

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References

[1] W.W. Bedsworth and D.L. Sedlak, *Environ. Sci. Technol.* **33**, 926 (1999).
[2] J.M. Lyon and E. Gunther, *J. Coord. Chem.* **34**, 13 (1995).
[3] R.K. Steinhaus, *Inorg. Chim. Acta.* **63**, 1 (1982).
[4] R.K. Steinhaus and J.A. Boersma, *Inorg. Chem.* **11**, 1505 (1972).
[5] T.J.J. Kinnunen, M. Haukka, T.T. Pakkanen and T.A. Pakkanen, *J. Organomet. Chem.* **613**, 257 (2000).
[6] P.G. Daniele, G. Ostacoli and P.A. Caldoro, *Ann. Chim.* **66**, 127 (1976).
[7] F.P. Hinz and D.W. Margerum, *Inorg. Chem.* **13**, 2941 (1974).
[8] G. Degischer and G.N. Nancollas, *Inorg. Chem.* **9**, 1259 (1970).
[9] F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry (John Wiley & Sons, New York, 1988).
[10] R.E. Weber, *J. Appl. Physics* **72**, 1611 (1992).
[11] R.K. Steinhaus and B.I. Lee, *Inorg. Chem.* **21**, 1829 (1982).
[12] A.K. Das, *Int. J. Chem. Kin.* **28**, 275 (1996).
[13] A.K. Steinhaus and L.H. Kolopajlo, *Inorg. Chem.* **24**, 1845 (1985).
[14] D.W. Margerum, D.B. Rorabacher and J.F.G. Clarke, Jr., *Inorg. Chem.* **2**, 667 (1963).
[15] A.M. Funston, W.D. McFadyen and P.A. Tregloan, *J. Chem. Soc. Dalton Trans.* **9**, 2053 (2002).