Pergamon

0277–5387(95)00163–6

Polyhedron Vol. 14, No. 23–24, pp. 3611–3616, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0277-5387/95 $9.50+0.00

SYNTHESIS AND KINETICS OF THE ACID HYDROLYSIS OF THE MONOTHIOOXALATO-*S,O*-BIS(ETHYLENEDIAMINE)CHROMIUM(III) COMPLEX

ZHONG CHEN, YI-JIAN ZHANG, YANG GUNG and YIFAN WU

Department of Chemistry, Teacher's College, Yangzhou University,
Yangzhou 225002, China

and

RUHULLAH MASSOUDI*

Department of Physical Sciences, South Carolina State University, Orangeburg,
SC 29117, U.S.A.

(*Received* 17 *January* 1995; *accepted* 10 *April* 1995)

Abstract—*Cis*-[Cr(en)$_2$(SC$_2$O$_3$)]Cl·H$_2$O has been synthesized by a new method involving the reaction of *cis*-[Cr(en)$_2$Cl$_2$]Cl with K$_2$SC$_2$O$_3$ at 60°C and the kinetics of the acidic aquation of this complex have been studied. The complex has been characterized by IR and electronic spectroscopic techniques. The aquation of the purified product was carried out at 30, 40 and 50°C in acidic media at constant ionic strength. The experimental result indicates a pH-dependent aquation of the compound in HCl solutions to yield H$_2$S and ethylenediamine. The plot of the rate of the reaction versus the square of the proton concentration, [H$^+$]^2, produces a straight line giving the pseudo-first-order rate constant, k_{obs}. Activation energies were found to be proportional with the entropies in various acidic solutions. The "isokinetic temperature" of 285 K and the free energy of activation, $\Delta G\ddagger = 94.7$ kJ mol^{-1}, were determined from the linear relationship. The results of experiments for the aquation of this compound suggest a mechanism through formation of a conjugate acid of an asymmetric atom, and the Cr—S bond cleavage is considered as the rate determining step.

Chromium(III) complexes of the type Cr(en)$_2$X$_2$$^+$ have been the subject of extensive photochemical investigation, where en represents ethylenediamine, and X denotes F,[1] Cl,[2] Br,[3] I,[3] SCN,[3] H$_2$O,[4] N$_3$, OH[3,5] and C$_2$O$_4$.[6] Kirk *et al.*[6] reported that the thermal aquation of [Cr(en)$_2$C$_2$O$_4$]$^+$ takes place by loss of ethylenediamine in acidic solution. The photolysis of this ion occurs in the pH range of 1–3, yielding a monodentate protonated ethylenediamine complex which in turn undergoes further thermal aquation with a loss of ethylenediamine ligand.

The present work concerns the kinetics and photochemistry of a Cr(en)$_2$X$_2$$^+$ type complex ion containing a monothiooxalate ligand; apparently, this kind of work on Cr^{III} complexes containing chelating sulphur and oxygen to Cr^{III} have rarely been reported. The kinetics of the Cr^{III} complex in our work containing a Cr—S bond could be compared to the work on [Cr(en)$_2$C$_2$O$_4$]$^+$.

Weschler *et al.*[7] have reported the oxidation of *O,S*-mercaptoacetato bis(ethylenediamine)chromium(III) by the oxidants Np^{VI} and Ce^{IV} to the Cr^{III} monothiooxalato complex and considered it as a possible pattern for the aldehyde dehydrogenase reaction; the details of the synthesis work, however, were not reported.[7] In our work, the complex was

---

* Author to whom correspondence should be addressed.

prepared by the reaction of *cis*-$[Cr(en)_2Cl_2]^+$ with $K_2SC_2O_3$ at 60°C, and was then characterized by IR and electronic spectroscopy. We also report the kinetics of thermal aquation of the above complex in HCl solution at constant ionic strength of 6.0 mol dm^{-3} in HCl solution with a concentration range of 0.01–6 mol dm^{-3}.

EXPERIMENTAL

Preparation of the complex

Reagent grade chemicals were used to synthesize the complex. Published literature procedures were used to prepare *cis*-$[Cr(en)_2Cl_2]Cl$[8] and $K_2SC_2O_3$.[9] To synthesize *cis*-$[Cr(en)_2(SC_2O_3)]Cl \cdot H_2O$, a 1.0 g sample of *cis*-$[Cr(en)_2Cl_2]Cl$ was dissolved in 6 cm^3 of water at 60°C producing a purple–red solution; a 0.5 g sample of $K_2SC_2O_3$ was added to the purple–red solution, the mixture was stirred to dissolve and was promptly filtered. The filtrate was stirred for several minutes before a reddish precipitate formed, which was then washed with ethanol and ether, then air dried. The yield of product salt was determined to be 0.70 g (60%). The crude product was further purified by dissolving in a small amount of water at 60°C, then filtered and recrystallized on cooling. These crystals were washed with methanol and ether, then air dried. The purified crystal weighed 0.2 g (29%). Found: Cr, 15.6; C, 22.6; H, 5.0; N, 16.2; S, 9.3. Calc.: Cr, 15.8%; C, 21.9; H, 5.5; N, 17.0; S, 9.7%.

Analytical procedures

Chromium(III) in the complex was oxidized with hydrogen peroxide in alkaline solution to form Cr^{VI}; it was then quantified spectrometrically at 372 nm ($\varepsilon = 4815$ mol^{-1} dm^3 cm^{-1}). The $C_2O_4^{2-}$ ion was analysed by the method described by Buriel-Marti *et al.*[10] Lead acetate test paper was used to determine the amount of H_2S produced in the acidic aquation of the complex. The analyses of carbon, hydrogen, nitrogen and sulphur were performed by the Shandong Chemical Institute. Finally, the water of hydration was determined from the weight loss from the complex, by baking it at 104°C for 4 h.

Kinetic studies

The thermal aquation rate of *cis*-$[Cr(en)_2(SC_2O_3)]^+$ was studied in HCl solutions with a concentration range of 0.01–6.0 mol dm^{-3}, which was adjusted to an ionic strength of 6.0 mol dm^{-3} by the addition of an appropriate amount of potassium chloride. The concentration of the complex was chosen as 1.5×10^{-3} mol dm^{-3}, and the pH of the solution essentially remained constant during the reaction. The progress of the reaction was followed by monitoring the absorbance, A, at 375 nm, the wavelength of maximum absorbance. An HP Model 8451A spectrometer was used for these measurements. A measured volume of the acidic solution was placed in a rectangular 1 cm cell and then placed in a thermostatic chamber within the HP89054A, with a controlling temperature of ±0.1°C. After the desired temperature was attained, a required amount of solid complex was added and shaken vigorously, then the system was ready to carry out measurements. It was possible to record absorbance against time in about 10 s after the addition of the complex.

Absorbance measurements for aquation of the complex were recorded for 3–4 half-life periods. Absorbance value at infinite time, A_∞, was taken to be the value reached at 10–15 half-lives. The reported values of the pseudo-first-order rate constant, k_{obs}, were determined by the least squares method, even though the plots of ln $(A_t - A_\infty)$ against time were reasonably linear.

RESULTS AND DISCUSSION

The Cl^- ion is a relatively good leaving ligand, therefore an aqueous solution of *cis*-$[Cr(en)_2Cl_2]^+$ was chosen to react with $K_2SC_2O_3$ to synthesize the complex *cis*-$[Cr(en)_2(SC_2O_3)]Cl \cdot H_2O$. The displacement reaction of Cl^- in *cis*-$[Cr(en)_2Cl_2]^+$ by $SC_2O_3^{2-}$ is a fast one, and the decomposition of a small amount of $K_2SC_2O_3$ was observed at the start of the reaction, necessitating prompt filtration after mixing the reactants.

The $SC_2O_3^{2-}$ ion in $[Cr(en)_2(SC_2O_3)]^+$ is apparently a bidentate ligand which can form only a *cis* structure. The two chelating sites could be chosen from among four potential donor atoms of sulphur–oxygen (S,O) or oxygen–oxygen (O,O). The IR spectrum of the monothiooxalato complex consists of absorption bands in the carbonyl region, which can be attributed to the C=O, S—C=O and C—O vibrations.[9,11] Three carbonyl-related IR bands for the monothiooxalato complex, regardless of the type of chelation, were observed. The corresponding energies of these vibrations, however, are different from each other, providing an excellent criterion to determine the kind of chelation adopted by the complex. The monothiooxalato complex exhibits three intense bands in the C=O stretching region (1680, 1590 and 1400 cm^{-1}), while the IR spectra of the complex shows two high-energy frequencies associated with O,O coordination and one low-energy, C—O related, stretching frequency

Table 1. Absorption features of *cis*-$[Cr(en)_2(SC_2O_3)]^+$ in aqueous solution

Feature		
λ (nm)	ε ($mol^{-1}\ dm^3\ cm^{-1}$)	Assignment[a]
494 (max)	108.33	${}^4B_{1g} \rightarrow {}^4B_{2g}({}^4T_{2g})$
434 (min)	59.42	
378 (max)	180.35	${}^4B_{1g} \rightarrow {}^4E_g({}^4T_{1g})$

[a] Octahedral parent states are given in parentheses.

indicative of an O,S chelation for the complex. The IR spectrum of *cis*-$[Cr(en)_2(SC_2O_3)]Cl \cdot H_2O$ exhibits two other intense bands, one at 1053 cm^{-1} attributed to C—C and the other at 853 cm^{-1} associated with C—S stretching frequencies. Also, there are three weak bands at 3200, 1464 and 1224 cm^{-1} that are associated with N—H, C—H and C—N stretching, respectively. There is also a broad band around 3400 cm^{-1} that corresponds to OH stretching of the water of crystallization. Appropriate assignments for the transitions and exact wavenumbers of the peaks are tabulated in Table 1.[12]

The kinetics of acidic aquation

Representative spectra for acidic aquation of *cis*-$[Cr(en)_2(SC_2O_3)]^+$ are shown in Fig. 1. At the beginning of the reaction, the spectrum shows distinct isokinetic points, whereas, as the reaction proceeds, the isokinetic points gradually disappear, indicating the possibility that some secondary processes could occur in the reaction. The spectrum of *cis*-$[Cr(en)_2(SC_2O_3)]^+$ in acidic solution at the end of the reaction agrees closely with that of acidic aquation of *cis*-$[Cr(en)_2C_2O_4]^+$, which was prepared separately. The H_2S produced from the aquation of the complex in acidic solution was identified by lead acetate test paper. The pH of the solutions, shown in Fig. 2, is apparently increasing with time, suggesting that the acidic aquation of the complex is accompanied by the production of H_2S and the loss of ethylenediamine.

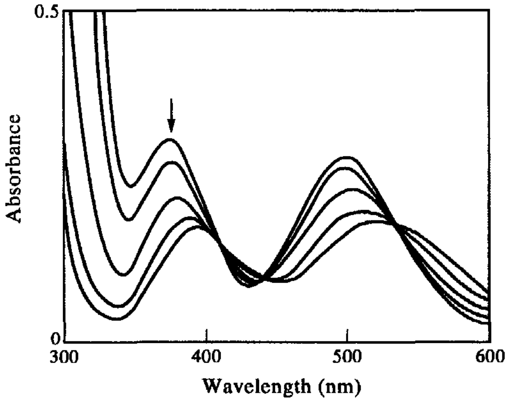

Fig. 1. Spectral changes during aquation of 1.5×10^{-3} mol dm^{-3} *cis*-$[Cr(en)_2SC_2O_3]^+$ in 4 mol dm^{-3} HCl and 0.5 mol dm^{-3} ionic strength (KCl) at 50°C. Upper to lower spectra are at successive times of 0, 5, 15, 30 and 50 min.

The pseudo-first-order rate constants at three temperatures for the acidic aquation of *cis*-$[Cr(en)_2(SC_2O_3)]^+$ are tabulated in Table 2. The graphs of rate constants, k_{obs}, against $[H^+]$ illustrated in Fig. 3 are non-linear, whereas they become quite linear with positive slopes when k_{obs} values are plotted *versus* squares of the proton concentration, $[H^+]^2$, as can be seen in Fig. 4. The experimental results indicate that the pseudo-first-order rate constants become independent of ionic strength at ionic strengths below 1.5 mol dm^{-3} (KCl).

The enthalpy and entropy of activation values for the reaction were determined from the Eyring relationship, $k_{obs} = (kT/h)\exp(\Delta S\ddagger/R)\exp(-\Delta H\ddagger/RT)$. A plot of $\ln(k_{obs}h/kT)$ against $1/T$ produces a straight line, enabling us to determine $\Delta S\ddagger$ from the intercept and $\Delta H\ddagger$ from the slope values; however, we have calculated $\Delta H\ddagger$ values by the use of least squares analyses. We observe that when $\Delta H\ddagger$ and $\Delta S\ddagger$ values are plotted against $[H^+]$, the result is a straight line, as shown in Fig. 5.

Figure 6 shows an excellent linear relationship between the enthalpies and entropies of activation for the entire range of data for acidic aquation of the complex. It is clear that the changes in the values of $\Delta H\ddagger$ are proportional to the changes of $\Delta S\ddagger$, which would cause only a small change in $\Delta G\ddagger$ values; therefore, a common mechanism would apply for our system. The values of isokinetic temperature and $\Delta G\ddagger$ can be determined from the slope and the intercepts of the line, respectively.[13]

The results of the present investigation can best be explained by a mechanism representing the following equations:

$$[\mathrm{Cr(en)_2SC_2O_3}]^+ + [\mathrm{H^+}] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Cr(en)_2HSC_2O_3}]^{2+} \quad (1)$$

$$[\mathrm{Cr(en)_2HSC_2O_3}]^{2+} + 2\mathrm{H_2O} \xrightarrow{k_2} [\mathrm{Cr(en)(enH)(H_2O)C_2O_4}]^{2+} + \mathrm{H_2S} \quad (2)$$

$$[\mathrm{Cr(en)_2HSC_2O_3}]^{2+} + \mathrm{H^+} + 3\mathrm{H_2O} \xrightarrow{k_3} [\mathrm{Cr(en)(H_2O)_2C_2O_4}]^{+} + \mathrm{H_2S} + \mathrm{enH_2^{2+}} \quad (3)$$

$$[\mathrm{Cr(en)_2HSC_2O_3}]^{2+} + 2\mathrm{H^+} + 4\mathrm{H_2O} \xrightarrow{k_4} [\mathrm{Cr(en)(H_2O)_3C_2O_4}]^{2+} + \mathrm{H_2S} + \mathrm{enH_2^{2+}}. \quad (4)$$

The rate expression for the scheme is given by

$$-\mathrm{d}\ln[\mathrm{Cr^{III}}]/\mathrm{d}t = k_{\mathrm{obs}} = \frac{k_1k_2[\mathrm{H^+}] + k_1k_3[\mathrm{H^+}]^2 + k_1k_4[\mathrm{H^+}]^3}{k_{-1} + k_2 + k_3[\mathrm{H^+}] + k_4[\mathrm{H^+}]^2}. \quad (5)$$

Considering the contribution of $k_{-1} + k_2$ to be negligible in acidic aquation and dividing the numerator and denominator by $[\mathrm{H^+}]$, eq. (5) reduces to:

$$k_{\mathrm{obs}} = \frac{k_1k_2 + k_1k_3[\mathrm{H^+}] + k_1k_4[\mathrm{H^+}]^2}{k_3 + k_4[\mathrm{H^+}]}. \quad (6)$$

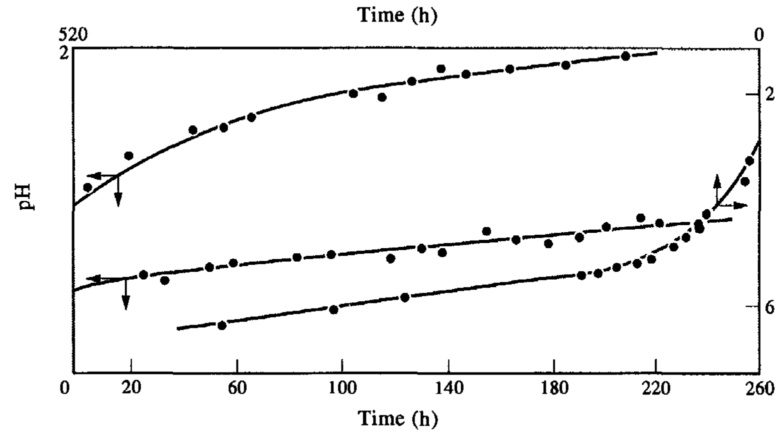

Fig. 2. The pH changes of solutions for acidic aquation of 1.0×10^{-2} mol dm^{-3} *cis*-$[\mathrm{Cr(en)_2SC_2O_3}]^+$ with time in HCl solution at room temperature. The concentration of $\mathrm{H^+}$ ion equals 0.05 mol dm^{-3} for the upper line, 0.1 mol dm^{-3} for the middle line and 0.01 mol dm^{-3} for the lower line.

Table 2. Pseudo-first-order rate constants for the aquation of *cis*-$[\mathrm{Cr(en)_2(SC_2O_3)}]^+$ at an ionic strength of 0.5 mol dm^{-3} (KCl)

$[\mathrm{H^+}]$ (mol dm^{-3})	10^4 k$_{\mathrm{obs}}$ (s^{-1})[a]		
	30°C	40°C	50°C
0.01	0.57±0.005	0.82±0.005	1.42±0.02
0.1	0.69±0.01	1.04±0.01	1.49±0.02
0.5	0.71±0.15	1.10±0.04	1.57±0.03
1.00	0.75±0.08	1.17±0.04	1.92±0.02
2.00	0.77±0.001	1.36±0.01	2.37±0.14
3.00	0.86±0.03	1.62±0.02	3.05±0.22
4.00	1.07±0.21	2.36±0.26	4.23±0.01
6.00	1.64±0.05	4.20±0.29	7.98±0.54

[a] The average of two or more independent runs.

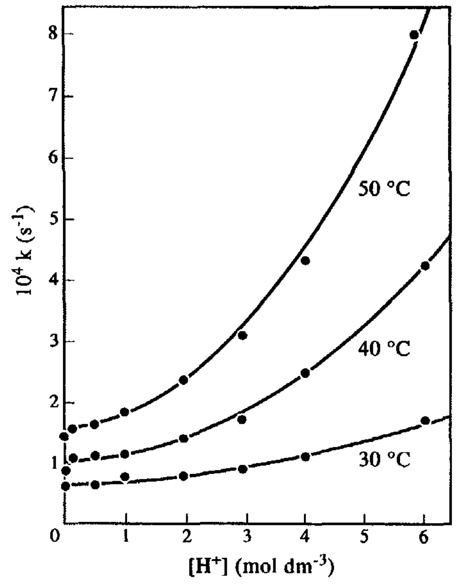

Fig. 3. Plots of k_{obs} vs [H^+] for *cis*-[$Cr(en)_2SC_2O_3$]$^+$.

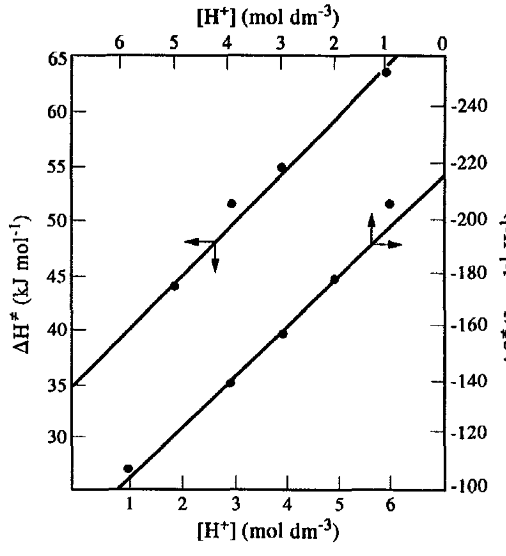

Fig. 5. Plots of ΔH‡ and ΔS‡ vs [H^+] for *cis*-[$Cr(en)_2$ SC_2O_3]$^+$.

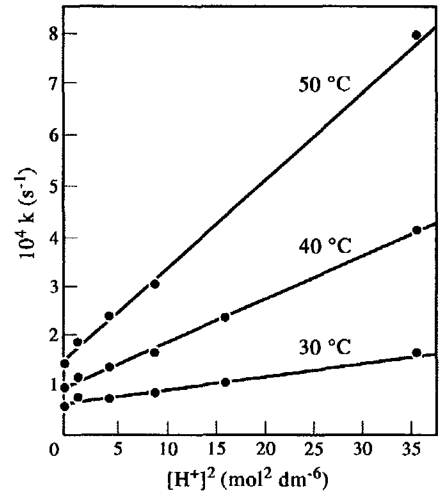

Fig. 4. Plots of k_{obs} vs [H^+]2 for *cis*-[$Cr(en)_2SC_2O_3$]$^+$.

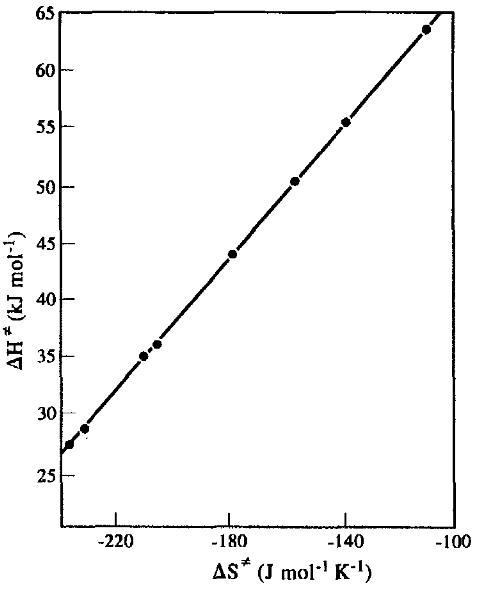

Fig. 6. Isokinetic plots for the acidic aquation of *cis*-[$Cr(en)_2SC_2O_3$]$^+$.

Assuming that $k_4[H^+] \ll k_3$, eq. (6) would further simplify to:

$$k_{obs} = k_1k_2/k_3 + k_1[H^+] + k_1k_4[H^+]^2/k_3. \quad (7)$$

Since k_{obs} bears a linear relationship to $[H^+]^2$, the contribution of the $k_1[H^+]$ term in eq. (7) is insignificant and our experimental data can best fit into the relationship:

$$k_{obs} = k_1k_2/k_3 + k_1k_4[H^+]^2/k_3. \quad (8)$$

The intercepts of the lines at 30, 40 and 50°C were 0.07×10^{-4}, 1.05×10^{-4} and 1.66×10^{-4} s^{-1}, respectively, and the corresponding slopes yielded 2.18×10^{-6}, 7.77×10^{-6} and 1.63×10^{-5} s^{-1} mol^{-2} dm^6. The values of the activation parameters at $[H^+] = 0$, $k_{obs} = k_1k_2/k_3$, would be $\Delta H‡ = 35.4 \pm 0.2$ kJ mol^{-1} and $\Delta S‡ = 208 \pm 0.6$ J mol^{-1} K^{-1}. The present values of these parameters are similar to those found for the acid-catalysed dissociation of asymmetrical chelate complexes,[14] in which the rupture of the metal chelate bond is important to the transitional state. There was no free oxalate ion observed in solution at the end of the reaction for the formation of the conjugate acid of the asymmetrical coordinated atom. There is a strong bond between Cr^{III} and a bidentate oxalate ion during the time that the rupture of the Cr—S bond is in the transitional state. These $\Delta S\ddagger$ values are large and negative, the magnitude being higher in the more acidic solutions. The $\Delta S\ddagger$ values indicate that the dissociation of one end of the chelate in the transitional state is a slow step corresponding to a highly ordered arrangement of the structure.[15] The acidified product from the transitional state would undergo further thermal aquation with loss of ethylenediamine and with an IR spectrum identical to that of the acidic aquation of *cis*-$[Cr(en)_2C_2O_4]^+$; therefore, this last product is considered to be *cis*-$[Cr(H_2O)_4C_2O_4]^+$.

Acknowledgements—The authors thank the National Science Foundation of China for their support. The authors also wish to express their gratitude to Professor Arthur W. Adamson, Department of Chemistry, University of Southern California, Los Angeles, for his constructive advice.

REFERENCES

1. S. C. Pyke and R. G. Linck, *J. Am. Chem. Soc.* 1971, **93**, 5281.
2. A. D. Kirk, K. C. Moss and J. G. Valentin, *Can. J. Chem.* 1971, **49**, 1524.
3. W. A. Baker Jr and M. G. Phillips, *Inorg. Chem.* 1966, **5**, 1042.
4. K. Woldbye, *Acta Chem. Scand.* 1958, **12**, 1079.
5. A. W. Adamson, *Adv. Chem.* 1965, **49**, 237.
6. A. D. Kirk, K. C. Moss and J. G. Valentin, *Can. J. Chem.* 1971, **49**, 375.
7. C. J. Weschler, J. C. Sullivan and E. Deutsch, *J. Am. Chem. Soc.* 1973, **95**, 2720.
8. E. Pedersen, *Acta Chem. Scand.* 1970, **24**, 3367.
9. M. Leitheiser and D. Coucouvanis, *J. Inorg. Nucl. Chem.* 1977, **39**, 811.
10. F. Buriel-Marti, J. Ramirez-Munoz and R. Fernandez-Caldas, *Analyt. Chem.* 1953, **25**, 583.
11. R. N. Figgis, *Introduction to Ligand Fields.* Wiley Interscience, New York (1966).
12. P. Riccieri and E. Zinato, *Inorg. Chem.* 1980, **19**, 853.
13. Ralph G. Wilkins, *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes.* Allyn & Bacon, Boston (1974).
14. B. Chakravarty, U. Kumar and I. Ghosh, *Indian J. Chem.* 1985, **24A**, 103.
15. B. E. Douglas, D. H. McDaniel and J. J. Alexander, *Concepts and Models of Inorganic Chemistry*, p. 363. John Wiley, New York (1983).