

KINETIC STUDIES ON THIOCYANATE SUBSTITUTION IN DIMERIC HALO SCHIFF BASE CHROMIUM (III) COMPLEXES — A CORRELATION OF RATES AND STRAIN ENERGIES

S.C. PAL AND M.T.H. TARAFDER

Department of Chemistry, Rajshahi University, Rajshahi 6205, Bangladesh

(Received June 12, 1995; revised April 22, 1997)

The kinetics and mechanism of thiocyanate substitution in dimeric chromium (III) complexes, $\text{Cr}_2\text{L}_2^{\text{I}}\text{Cl}_2$ and $\text{Cr}_2\text{L}_2^{\text{II}}\text{Cl}_2$ where $\text{L}^{\text{I}} = \text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_2$ (deprotonated Schiff base derived from diethylenetriamine and salicylaldehyde) and $\text{L}^{\text{II}} = \text{C}_{21}\text{H}_{26}\text{N}_4\text{O}_2$ (deprotonated Schiff base derived from N, N Bis (2-aminoethyl) 1, 3 propanediamine and salicylaldehyde) have been studied spectrophotometrically at 20°C in ammonium thiocyanate medium in the concentration range 0.2-1.0 mol dm⁻³. The values of K_{obs} show a nonlinear dependence on square of NCS⁻ concentration for both the complexes. These have been found to increase with the increase in derived strain energies of the metal-ligand rings in the complexes.

Key words: Kinetic studies, Cr(III) complexes, Thiocyanate substitution.

Introduction

In recent years a great deal of interest has been focussed on the kinetic and equilibrium studies of ligand substitution reactions of transition metal complexes containing macrocyclic ligands [1-10]. Solvent extraction and hydrometallurgy, now-a-days, find the use of tetraaza macrocycles where a rapid complexation and dissociation rates of appropriate metal complexes are to be ensured [8]. In addition this type of kinetic study is of considerable interest in developing macrocyclic ligand commercially for metal detoxification [6]. Some Cr(III) complexes have potential use as inner sphere reductant for the identification of binding sites in electron transfer reactions in metalloproteins [4].

The literature survey reveals some interesting reports on this type of study. Hay and Banerjee [3] studied the kinetics and mechanism of the base hydrolysis of Bis (ethylcysteinato) palladium(II) and proposed a two-step reaction mechanism involving two different rate constants. Hay and Pujari [8] reported the acid dissociation kinetics of copper(II) complex containing a 18-membered tetraaza macrocycle and nickel(II) complex containing a 17-membered tetraaza macrocycle. Massoud *et al.* [7] investigated the kinetics and mechanism of aquation of dihaloacetonitrile and dibromoacetonitrile-(3,3',3''-triaminotripropylamine) cobalt(III) perchlorate in aqueous perchloric acid solution. Hung *et al.* [2] reported the kinetics of aquation of dichlorotetramine complexes of Co(II) containing tetraazamacrocyclic ligands of varying ring size and correlated the rates of first aquation with the ring size. Richens *et al.* [5] reported the kinetic and equilibrium studies on reactions of the diaqua chromium(III) complex containing a saturated tetradentate tetraaza 15-membered macrocyclic ligand. They used thiocyanate as the complexing agent and

explored the substitution properties of the chromium(III) complexes. Ranganathan and co-workers [11] have studied the kinetics of hydrogen peroxide reaction of diperoxo (amine) chromium(IV) complexes.

In one of our previous reports we investigated [12] the kinetics and mechanism of aquation of some haloamine chromium(III) complexes and suggested a two-step mechanism for the reaction in which chelate effect and metal-ligand ring size were correlated with the rates of aquation. We thus thought it interesting to examine the kinetics of thiocyanate substitution in two dimeric chromium(III) complexes, $\text{Cr}_2\text{L}_2^{\text{I}}\text{Cl}_2$ and $\text{Cr}_2\text{L}_2^{\text{II}}\text{Cl}_2$ containing two different Schiff bases, L^{I} and L^{II} derived from salicylaldehyde and diethylenetriamine and N, N' Bis (2-aminoethyl) 1,3 propanediamine since thiocyanate has strong nucleophilic properties (Fig. 1).

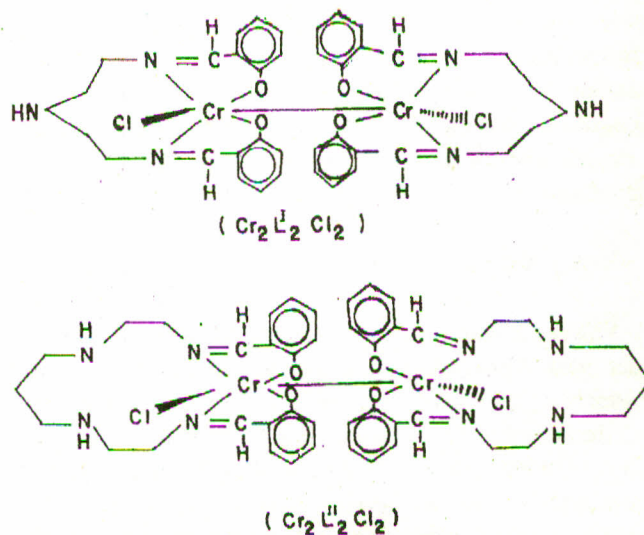


Fig. 1. Dimeric chromium (III) complexes.

Experimental

Reagent. Ammonium thiocyanate was used as supplied by E. Merck.

Kinetic studies. The Schiff bases and Cr(III) complexes (Fig. 1) used here for kinetic studies were synthesised by the reported procedure [13]. $[\text{Cr}_2\text{L}_2^{\text{I}}\text{Cl}_2]$, diamagnetic, (Found: C, 54.4; H, 4.8; N, 10.4% Calcd. for: C, 54.5; H, 4.8; N, 10.5%; ν_{max} 1575 (C=N) ($\sim 30\text{cm}^{-1}$ shift towards lower frequency compared to free ligand value), 520 (Cr-N), 1150 (C-O), 450 (Cr-O), OH band of free ligand disappeared, 230cm^{-1} (Cr-Cr). $[\text{Cr}_2\text{L}_2^{\text{II}}\text{Cl}_2]$, diamagnetic, (Found: C, 55.6; H, 5.6; N, 12.4%, Calcd. for: C, 55.6; H, 5.8; N, 12.3%); ν_{max} 1580 (C=N), ($\sim 30\text{cm}^{-1}$ shift towards lower frequency compared to free ligand value), 520 (Cr-N), 1150 (C-O), 415 (Cr-O), 260cm^{-1} (Cr-Cr).

Kinetic studies were carried out using ammonium thiocyanate solutions of concentrations in the range 0.2-1.0 mol dm^{-3} . All the rate measurements were made spectrophotometrically at 20°C with a LKB Biochrom Ultrospec 4053 UV-visible spectrophotometer at 381 nm and 392 nm where a large difference between molar absorbances for the chloro and thiocyanato complexes was observed. In each kinetic run, a weighed quantity (10^{-5} mol) of each of the complexes was suspended quickly in the thiocyanate solutions (10cm^3) and the clear portion of the solutions was transferred into a quartz cell, where the rate of anation was monitored with time by recording molar absorbances. Molar absorbances were found to decrease with time during the reaction period. Rate constants were calculated from pseudofirst-order plots.

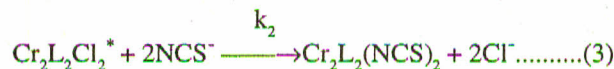
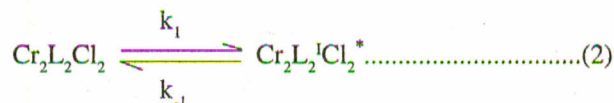
Results and Discussion

The kinetics of anation of two chloro Schiff base Cr(III) complexes, $[\text{Cr}_2\text{L}_2^{\text{I}}\text{Cl}_2]$ and $[\text{Cr}_2\text{L}_2^{\text{II}}\text{Cl}_2]$ (L^{I} and L^{II} are deprotonated Schiff bases, $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_2$ and $\text{C}_{21}\text{H}_{26}\text{N}_4\text{O}_2$ respectively) were studied at 20°C using ammonium thiocyanate solutions in the concentration range 0.2-1.0 mol dm^{-3} . The rate constants, k_{obs} (Table 1) have been calculated from the linear pseudofirst-order plots of $\ln(A_t - A_\infty)$ versus time (t), where A_t is the absorbance at time t and A_∞ is the final absorbance according to the following equation.

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - kt \dots \dots \dots (1)$$

Figures 2 and 3 show two representative pseudofirst-order plots. Again a nonlinear dependence of observed rate constants k_{obs} on square of the NCS^- concentration in case of both the complexes is observed (Fig. 4), showing an increase of k_{obs} with the increase in square of NCS^- concentration. These observations are indicative of a reaction path that involves a rate-determining pre-equilibrium between the

dominant form (cis or trans) of the complex and its activated or reactive form (Eq. 2) followed by a rapid 2:2 replacement of chlorides by thiocyanate ions (Eq. 3).



Where L stands for L^{I} and L^{II} ; k_1 and k_{-1} are the rate constants for activation and deactivation respectively and k_2 is the rate constant for thiocyanate substitution.

TABLE 1. OBSERVED RATE CONSTANTS (k_{obs}) OF ANATION IN DIMERIC Cr(III) COMPLEXES, $[\text{Cr}_2\text{L}_2\text{Cl}_2]$ ($\text{L} = \text{L}^{\text{I}}$ OR L^{II}) AT 20°C .

$[\text{Cr}_2\text{L}_2^{\text{I}}\text{Cl}_2]$, $\lambda = 392\text{ nm}$		$[\text{Cr}_2\text{L}_2^{\text{II}}\text{Cl}_2]$, $\lambda = 381\text{ nm}$	
Concentration of thiocyanate (mol dm^{-3})	$10^3 k_{\text{obs}}$ (s^{-1})	Concentration of thiocyanate (mol dm^{-3})	$10^3 k_{\text{obs}}$ (s^{-1})
0.20	4.44	0.20	3.47
0.40	5.67	0.40	4.04
0.60	6.83	0.60	5.56
0.80	7.85	0.80	6.43
1.00	8.82	1.00	7.67

Applying steady state approximation for $\text{Cr}_2\text{L}_2\text{Cl}_2^*$ in the reaction scheme, equation (4) can be readily derived.

$$\text{Rate} = \frac{-d[\text{Cr}_2\text{L}_2\text{Cl}_2]}{dt} = \frac{k_1 k_2 [\text{Cr}_2\text{L}_2\text{Cl}_2] [\text{NCS}^-]^2}{k_{-1} + k_2 [\text{NCS}^-]^2} \dots \dots \dots (4)$$

Rearranging equation (4) we get,

$$\frac{-d[\text{Cr}_2\text{L}_2\text{Cl}_2]}{dt} / [\text{Cr}_2\text{L}_2\text{Cl}_2] = k_{\text{obs}} = \frac{k_1 k_2 [\text{NCS}^-]^2}{k_{-1} + k_2 [\text{NCS}^-]^2} \dots \dots \dots (5)$$

Further rearrangement of equation (5) yields equation (6).

$$1/k_{\text{obs}} = \frac{k_{-1}}{k_1 k_2 [\text{NCS}^-]^2} + \frac{1}{k_2} = \frac{k'}{[\text{NCS}^-]^2} + \frac{1}{k_2} \dots \dots \dots (6)$$

$$\text{Where } k' = \frac{k_{-1}}{k_1 k_2}$$

According to equation (6), plot of $1/k_{\text{obs}}$ versus $1/[\text{NCS}^-]^2$ should be a straight line yielding k' and k_1 from the slope and the intercept respectively. The experimental plots (Fig. 5) were linear conforming equation 6 and proposed the mechanism of the reactions of interest. The plots yielded slopes with k' values 15.69 and 23.33, for the complexes with L^I and L^{II} respectively and the intercepts are 92 and 114 respectively for them. The value of k_1 for the complex with L^I was $1.09 \times 10^{-2} \text{ s}^{-1}$ and that for the complex with L^{II} was $0.88 \times 10^{-2} \text{ s}^{-1}$ at 20°C . The difference in the k_1 and k_{obs} values is explained in terms of deactivation process that occurs in the primary equilibrium situation.

The replacement of chlorides by NCS^- ions from the coordination sphere is evident from the comparative UV-visible spectra of the chloro and thiocyanato species under investigation (Figs. 6 and 7).

An examination of the observed rate constant values (k_{obs}) presented in Table 1 shows that these values are higher for anation in $\text{Cr}_2\text{L}_2^I\text{Cl}_2$ than those for anation in $\text{Cr}_2\text{L}_2^{II}\text{Cl}_2$ in each identical concentration of thiocyanate. The results can be rationalised by considering the strain energy involved in the metal-ligand rings of the complexes, although there is no

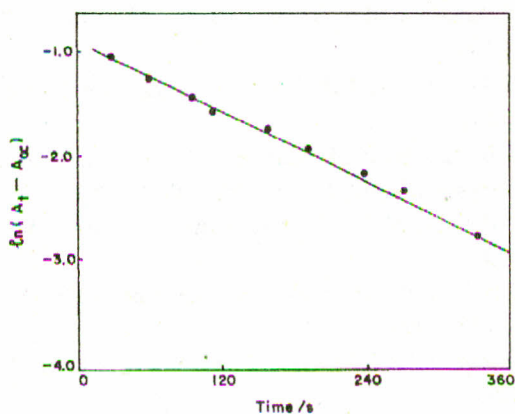


Fig. 2. Plot of $\ln(A_1 - A_\infty)$ versus time for the thiocyanate substitution in $\text{Cr}_2\text{L}_2^I\text{Cl}_2$ in 0.2 mol dm^{-3} NCS^- concentration and at 20°C , $\lambda = 392 \text{ nm}$.

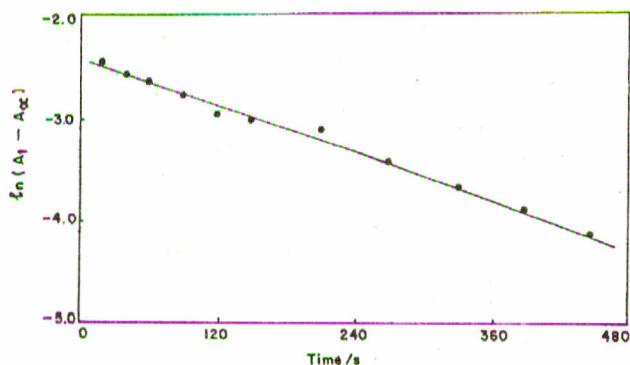


Fig. 3. Plot of the $\ln(A_1 - A_\infty)$ versus time for the thiocyanate substitution in $\text{Cr}_2\text{L}_2^{II}\text{Cl}_2$ in 0.2 mol dm^{-3} NCS^- concentration and at 20°C , $\lambda = 381 \text{ nm}$.

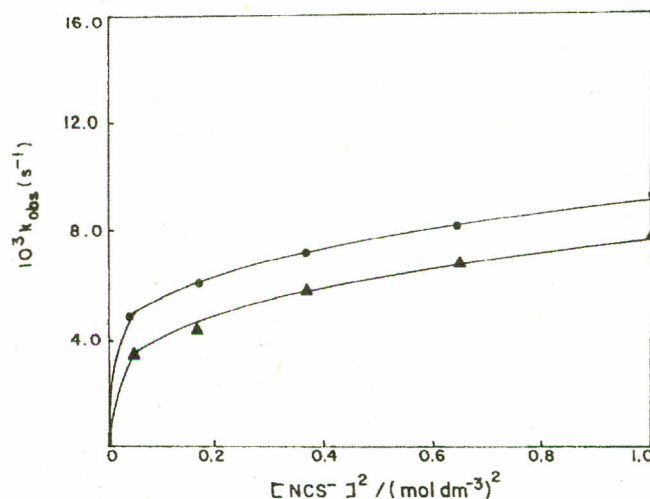


Fig. 4. Dependence of k_{obs} on square of NCS^- concentration for the anation in the complexes, $\text{Cr}_2\text{L}_2^I\text{Cl}_2$ (●) and $\text{Cr}_2\text{L}_2^{II}\text{Cl}_2$ (▲).

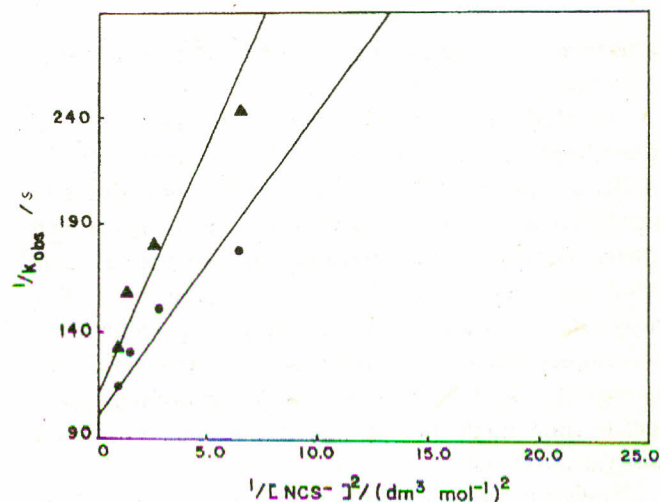


Fig. 5. Double reciprocal plots of $1/k_{\text{obs}}$ versus $1/(\text{NCS}^-)^2$ for the anation in the complexes, $\text{Cr}_2\text{L}_2^I\text{Cl}_2$ (●) and $\text{Cr}_2\text{L}_2^{II}\text{Cl}_2$ (▲).

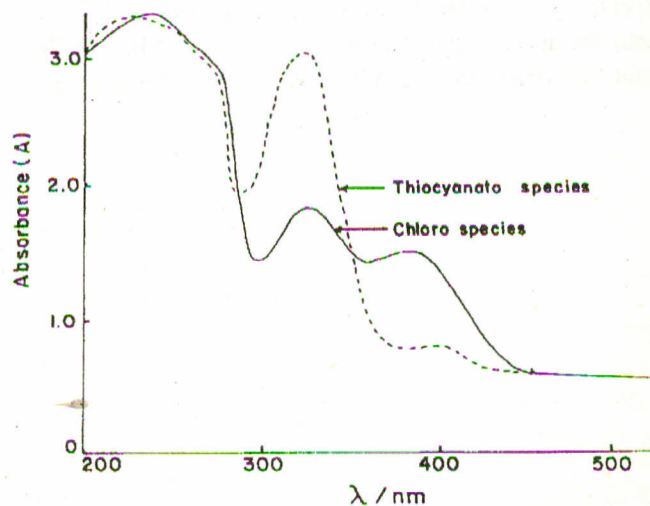


Fig. 6. UV-visible spectra of chloro and thiocyanato species of complexes with L^I .

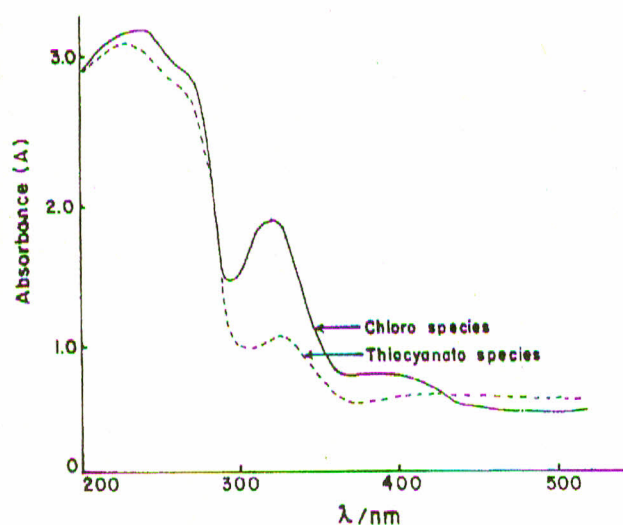


Fig. 7. UV-visible spectra of chloro and thiocyanato species of complex with L^{II} .

difference in the chelate effect or donor capacity of ligands under investigation.

The flexibility of the metal-chelate rings [12] is believed to be related in part to the reactivity of these chloro Schiff base Cr(III) complexes. Complex with L^I contains four six-membered and two eight-membered metal-chelate rings whereas complex with the ligand L^{II} contains four six-membered and two twelve-membered metal-chelate rings. Obviously, complex with L^I possesses a greater strain compared to the complex with L^{II} . This difference in strain is reflected in the respective k_{obs} values. The strain or flexibility of the metal-chelate rings might play a vital role in the formation of thiocyanato anation product.

Torsional deformation and bond angle stretching [2] are the sources of strain energies of the starting complexes and are unambiguously related to rates of anation. The electronic effects play a vital role in modifying the rates of anation as the metal-chelate ring size changes. Complex involving smaller metal-ligand ring size is identified with greater rates of anation

and that with greater metal-ligand ring size yields smaller rates of anation. The present results are quite consistent with the standard mechanism [14-15].

References

1. G. Sammuels and J.H. Espenson, *Inorg. Chem.*, **18**, 2588 (1979).
2. Yann Hung and Daryl H. Busch, *J. Am. Chem. Soc.*, **99** (15), 4977 (1977).
3. R.W. Hay and P. Banerjee, *Inorganica Chimica Acta*, **44**, 1205 (1980).
4. I.K. Adzamali, R.A. Henderson, H. Ong and A.G. Sykes, *Biochem. Biophys. Res. Commun.*, **105**, 1582 (1982).
5. D.T. Richens, I.K. Adzamali, Peter Leupin and A. Geoffrey Sykes, *Inorg. Chem.*, **23**, 3065 (1984).
6. R.W. Hay, M.P. Pujari, W.T. Moodie, S. Craig, D.T. Richens, A. Perotti and L. Urganetti, *J. Chem. Soc. Dalton Trans.*, 2065 (1987).
7. Salah S. Massoud and Ronald M. Milburn, *Polyhedron*, **8** (3), 275 (1989).
8. R.W. Hay and Mahesh P. Pujari, *Trans. Met. Chem.*, **11**, 261 (1986).
9. M. E. Sosa and M. L. Tobe, *J. Chem. Soc. Dalton Trans.*, 427 (1986).
10. R.W. Hay and M.T.H. Tarafder, *Trans. Met. Chem.*, **18**, 604 (1993).
11. C.K. Ranganathan, T. Ramaswami, D. Ramaswami and M. Santappa, *Inorg. Chem.*, **28**, 1306 (1989).
12. S.C. Pal and M.T.H. Tarafder, *Ind. J. Chem.*, **34A**, 38 (1995).
13. M.T.H. Tarafder and S.C. Pal, *J. Bangladesh Chem. Soc.*, **7**(2), 126 (1994).
14. F. Basolo and R.G. Peterson, *Prog. Inorg. Chem.*, **4**, 447 (1962).
15. D.H. Bush, *Helv. Chim. Acta.*, Warner commemoration volume, 174 (1967).