

Kinetics and Mechanism of the Cobalt(Ⅲ) Tetraammine Complex-Promoted Hydrolysis of 4-Nitrophenyl Glycinate

Alka Anant Phulambrikar and Chinmay Chatterjee*

Department of Chemistry, Indian Institute of Technology, Powai Mumbai 400 076, India

(Received August 6, 2001)

The kinetics of the hydrolysis of 4-nitrophenyl glycine ester (PNPG) catalysed by $[Co(OH)(trien)(OH_2)]^{2+}$, $[Co(OH)(tren)(OH_2)]^{2+}$ and $[Co(OH)(en)_2(OH_2)]^{2+}$ complexes has been studied spectrophotometrically in weakly basic aqueous media (pH = 6.5 to 7.4). Kinetic experiments were carried out as a function of the pH, complex concentration and temperature. The rate of hydrolysis increases linearly with the complex concentration with a trend to wards rate saturation, suggesting the formation of associative species in a pre-equilibrium step. The pseudo-first order rate constant, k_{obs}, increases rapidly with a decrease in the hydrogen-ion concentration. The complexes promote the hydrolysis of 4-nitrophenyl glycinate significantly, and the acceleration rate is about 400–600. An attack of external OH^- on the chelated ester is suggested as a probable mechanism for the hydrolysis. The lower rate enhancements observed in the present study could probably be ascribed to a weaker cobalt(Ⅲ) alkoxy carbonyl interaction in the chelate, owing to a decreased nucleophilicity of the carbonyl oxygen in the *p*-nitrophenyl ester. The activation parameters for all three complex-promoted reactions are found to be comparable, thus suggesting a common mechanism operative in all complex catalysed reactions.

The metal ion-promoted hydrolysis of α-amino acid esters has attracted considerable attention due to the relevance of these systems to the reactions of a variety of metalloenzymes.[1–4] Studies have dealt with catalysis by labile metal ions, such as Cu(II)[5–11] and Ni(II)[12–14] as well as with non-labile ones, like Pd(II)[15–17] and Co(Ⅲ).[18–21] A major problem in studying the hydrolysis of α-amino acid esters in the presence of labile metal ions has been determining the actual binding site of ligands and the identification of the catalytically active species in the solution. The different pathways involved in the hydrolysis reactions have been deduced from studies involving kinetically robust complexes, predominantly of cobalt(Ⅲ). These studies have almost exclusively involved the use of alkyl esters (methyl or ethyl) which provide a poor leaving group. It is normally necessary to monitor these reactions by the pH stat technique, and is often not possible to greatly vary the metal-to-ligand ratio. On the other hand, the use of *p*-nitrophenyl esters which provide a good leaving group, present a number of advantages. For instance, the reaction can be monitored spectrophotometrically. Also in view of the fact that a low ester concentration is required, it is possible to study the kinetics of hydrolysis reactions over a varying range of metal-to-ligand ratios. The hydrolysis of *p*-nitrophenyl phosphate esters promoted by the tetraammineaqua hydroxocobalt(Ⅲ) complex has been the subject of several investigations.[9–12] The results of such studies reveal that the activity of the cobalt complex is sensitive to a tetraammine ligand structure. In marked contrast, the metal ion or complex-promoted hydrolysis of p-nitrophenyl amino acid esters has scarcely been reported. The reported investigations have dealt with the hydrolysis of these esters promoted by aromatic aldehydes[22] and Cu(II) ions.[23–24] The cobalt(Ⅲ)-promoted hydrolysis of *p*-nitrophenyl amino acid esters has not yet been reported. The present paper describes the kinetics of the hydrolysis of the 4-nitrophenyl glycinate (PNPG) catalysed by cis-hydroxoaquatetraammine cobalt(Ⅲ) complexes. The tetraammine ligands were used to block four coordination sites on Co(Ⅲ) and leave two sites for interactions with the ester. In order to examine the effect of the tetraammine ligand structure on the reactivity of complexes, the hydroxoaqua the complexes of bis(didentate), en; linear tetramine, trien, and tripodal tetramine, tren were employed for the study.

Materials and Method

Preparation of 4-Nitrophenyl Glycinate (PNPG) Hydrobromide: The ester hydrobromide was prepared by reacting *N*-benzyloxy-carbonyl ester with a saturated solution of HBr in glacial acetic acid by a method of Bem-Ishai and Berger.[25] Carbondioxide was evolved and the reaction was completed within a few minutes. When the evolution of carbon dioxide had ceased, dry ether was added to precipitate the ester hydrobromide, which was filtered off after keeping in a refrigerator for 4 hours; it was then washed with ether and dried over sodium hydroxide pellets. The crude 4-nitrophenyl glycinate ester hydrobromide was recrystallised from absolute ethanol by the addition of anhydrous ether. The purity of the sample was ascertained by an elemental analysis. The melting point (213 °C) of the compound matched well with the reported value (213 °C).[24]

The complexes trans-$[CoCl_2(en)_2]Cl$,[26] α-*cis*-$[CoCl_2(trien)]Cl$[27] and $[CoCl_2(tren)]Cl$[28] were prepared following methods described in the literature. An equimolar concentration (2.0×10^{-3} mol dm^{-3}) of $[Co(OH)(tren)(OH_2)]^{2+}$ and PNPG at pH 7.0 was heated at 40 °C for 3 hrs., whereupon the lowest ener-

gy d–d band shifted from 520 nm, characteristic of the $[Co(OH)(tren)(OH_2)]^{2+}$ ion,[29] to 500 nm, corresponding to the absorption maximum of the red isomer of the $[Co(gly)(tren)]^{2+}$ chelate,[28] in which the tertiary amine nitrogen of tren is trans to the amino group of glycine. A similar behaviour of shifting of the absorption maximum to a shorter wavelength was observed for other cobalt(III) complexes used in the study.

Kinetic Measurements: Kinetic measurements were carried out on a Shimadzu UV-2100 spectrophotometer equipped with a Julabo SC-12 constant-temperature water bath. The temperature of the cuvette was maintained within ±0.1 °C by circulating thermostated water through the cell compartments of the spectrophotometer. The pH measurements were made on a Metrohm 654 digital pH meter (with ±0.02 pH unit accuracy). The hydrolysis of 4-nitrophenyl glycinate was monitored following an increase in the absorbance at the p-nitrophenolate absorption maximum (400 nm). The reactions were carried out under pseudo-first order conditions, with a large excess of the complex over the ester. The pseudo-first order rate constants for the reactions were calculated from the slope of plots of $-\ln(A_\infty - A_t)$ against time using a standard software program for a least-squres regression analysis. The A_∞ values were recorded after ten half lives. The reported rate constants (k_{obs}) are an average of three kinetic runs with an error estimation of less than 5%. The ester stock solutions were prepared in dry methanol and the complex solutions in freshly boiled carbon dioxide-free double-distilled water. Because carbon dioxide is known to catalyse the hydrolysis of aryl esters of α-amino acids,[15] care was taken to prevent any CO_2 contamination of the solutions.

Results and Discussion

In typical kinetic measurements, a stock solution of cis-$[Co(OH)N_4(OH_2)]^{2+}$ (where N_4= $(en)_2$, trien or tren) was prepared by adding 1.5 equivalents of NaOH solution to the dichlorocomplex. After 20 minutes (1 hour for the tren complex) the solution pH was adjusted to the desired value. Hydrolysis of the ester was initiated by adding 5.0×10^{-6} mol dm^{-3} of a 0.015 mol dm^3 ester stock solution to 2.50 cm^3 of a freshly prepared complex solution equilibriated at the experimental temperature The ionic strength of the reaction mixtures was maintained at 0.1 mol dm^{-3} with the help of NaCl. The pH of the reaction solution did not change appreciably (±0.1) during the course of the reaction, due to a buffering effect of the cobalt complex solution.[18] The hydroxide-ion concentrations were evaluated from the appropriate molar activity coefficients and the values of [pK_w: 13.833 (30 °C); 13.68 (35 °C) and 13.535 (40 °C)] reported in the literature.[30] The hydrolysis reactions have been studied as a function of the complex concentration, pH and temperature. The pseudo first-order rate constants (k_{obs}) under different experimental conditions are summarized in Tables 1 to 3. The rate of hydrolysis increases linearly with the complex concentration with a trend towards rate saturation, as shown in Fig. 1. The rate of hydrolysis also increases with an increase in the pH of the medium, as shown in Fig. 2. The uncatalyzed rate constant (k_o) at different pH values takes the following values: at a pH of 6.5, $k_o = 0.80 \times 10^{-3}$/s; at a pH of 6.95, $k_o = 1.48 \times 10^{-3}$/s, and at a pH of 7.35, $k_o = 2.00 \times 10^{-3}$/s. The complex-promoted reactions can be explained in terms of Eqs. 1 and 2, involving the rapid formation of associated species with the coordination of glycine ester in a pre-equilibrium process, followed by a slow rate-determining base hydrolysis step:

$$HL^+ \leftrightarrows H^+ + L$$
$$M + L \overset{K_M}{\leftrightarrows} [ML] \quad (1)$$

$$[ML] + OH^- \xrightarrow{k_{MOH}} \text{Product}$$
$$L + OH^- \text{ or } H_2O \xrightarrow{k_o} \text{Product} \quad (2)$$

The complex is represented as M and the unprotonated ester species as L. A plot of k_{obs} versus the complex concentration (Fig. 1) indicates that the reaction follows a two-term rate law of the type

$$k_{obs} = k_o + \frac{k_{MOH}[OH^-]K_M[M]}{1 + K_M[M]} \quad (3)$$

where k_{obs}. is the observed first-order rate constant at constant pH, k_o is the rate constant due to the background hydrolysis reaction of L in the absence of the cobalt(III) complex ion, K_M is the association constant and k_{MOH} is the rate constant for a

Table 1. Pseudo First Order Rate Constants (k_{obs}) for Hydrolysis of PNPG Ester Promoted by $[Co(OH)(trien)(H_2O)]^{2+}$ at Different pH and Temperatures.[a)]

10^3[complex]/mol dm^{-3}	$10^3\ k_{obs}/s^{-1}$				
	pH = 6.95 ± 0.05			pH = 6.50 ± 0.05	pH = 7.35 ± 0.05
	303.3[b)]	308.3[b)]	313.3[b)]	308.3[b)]	308.3[b)]
2.5	1.65	2.35	3.20	1.27	3.42
5.0	2.40	3.50	4.65	1.70	4.85
7.5	3.10	4.55	5.87	2.18	6.26
10.0	4.25	5.55	6.98	2.70	7.57
12.5	5.20	6.65	8.50	3.20	9.07
15.0	6.10	7.75	9.82	—	—
17.5	6.75	8.60	10.91	—	—
20.0	7.20	9.45	11.78	—	—
22.5	—	10.10	—	—	—

a) [Ester] = 3×10^{-5} mol dm^{-3}, I = 0.1 mol dm^{-3} b) T/k.

Table 2. Pseudo First Order Rate Constants (k_{obs}) for Hydrolysis of PNPG Ester Promoted by $[Co(OH)(en)_2(OH_2)]^{2+}$ at Different pH and Temperatures[a)]

10^3[complex]/mol dm^{-3}	$10^3\ k_{obs}/s^{-1}$				
	pH = 6.95 ± 0.05			pH = 6.50 ± 0.05	pH = 7.35 ± 0.05
	303.3[b)]	308.3[b)]	313.3[b)]	308.3[b)]	308.3[b)]
2.5	1.58	2.20	2.85	1.25	3.01
5.0	2.10	2.95	3.90	1.65	3.96
7.5	2.58	3.70	4.55	2.05	3.96
10.0	3.07	4.44	5.31	2.40	5.80
12.5	3.70	5.04	6.20	2.75	6.75
15.0	4.25	5.65	6.86	—	7.55
17.5	4.65	6.36	7.85	—	—
20.0	5.05	6.75	8.60	—	—
22.5	5.45	7.33	9.41	—	—
25.0	5.85	7.72	10.10	—	—

a) [Ester] = 3×10^{-5} mol dm^{-3}, I=0.1 mol dm^{-3} b) T/k.

Table 3. Pseudo First Order Rate Constants (k_{obs}) for Hydrolysis of PNPG Ester Promoted by $[Co(OH)(tren)(OH_2)]^{2+}$ at Different pH and Temperatures[a)]

10^3[complex]/mol dm^{-3}	$10^3\ k_{obs}/s^{-1}$				
	pH = 6.95 + 0.05			pH = 6.50 + 0.05	pH = 7.35 + 0.05
	303.3	308.3	313.3	308.3	308.3
2.5	1.65	2.35	3.08	1.25	3.10
5.0	2.30	3.05	3.90	1.70	4.30
7.5	3.10	3.90	5.15	2.15	5.30
10.0	3.75	4.75	5.92	2.55	6.25
12.5	4.40	5.50	7.13	3.00	7.05
15.0	5.10	6.30	8.06	—	—
17.5	5.60	7.10	8.50	—	—
20.0	6.15	7.80	9.25	—	—
22.5	6.40	8.20	9.84	—	—
25.0	6.90	8.85	—	—	—

a) [Ester]=3×10^{-5} mol dm^{-3}, I=0.1 mol dm^{-3} b) T/k.

complex-promoted reaction. Rearranging Eq. 3 gives Eq. 4 :

$$1/(k_{obs} - k_o) = 1/k_{MOH}\,[OH^-]\,K_M[M] + 1/k_{MOH}\,[OH^-]. \quad (4)$$

The double reciprocal plot of $1/(k_{obs} - k_o)$ versus 1/[M] is found to be linear, indicating the validity of Eq. 3. The values of K_M and k_{MOH} calculated from the intercept by the slope (= K_M), and substituting the values of [OH$^-$] in the slope of the plots using a linear regression analysis, are tabulated in Table 4. The complex-promoted reactions were studied at three different temperatures (30, 35, and 40 °C) at pH 6.95. The magnitude of the rate constants (k_{MOH}) along with the activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, evaluated using the transition state equation, $k = (RT/Nh)\exp\left(-\Delta H^{\neq}/RT + \Delta S^{\neq}/R\right)$, are summarised in Table 4. The complex ion-catalysed hydrolysis of p-nitrophenyl glycinate has been studied in the pH range of 6.5 to 7.4, which is close to the physiological pH range. The pK_{a1} and pK_{a2} values of tetraamminediaqua cobalt(III) complexes are about 5.6 and 8.1, respectively,[18] and hence in the experimental pH range the hydroxo aqua form of the complex is the predominant species. The first step in the hydrolysis reaction involves a substitution of the aqua group of the complex by the amine group of the ester, resulting in the formation of the associated species, [ML]. The labilisation of the aqua for substitution can be ascribed to the cis effect[31] of the coordinated hydroxo group. A cis-libilisation effect of a coordinated hydroxide ion on a aqua ligand for substitution will not be present in the dihydroxo species, because the latter can not provide a good leaving group for the first act of substitution by the ester, and thus the major reaction pathway would involve predominant aqua hydroxo species. Thus, the increase in the rate with increasing complex concentration at a fixed temperature and pH can be attributed to the higher concentration of the ML species, which subsequently hydrolyses in a rate determining step. The trend towards rate saturation is observed only at high ML ratios, indicating that the K_M values are not very high. For all of these complexes used during the present study, it is observed that at a fixed complex concentration and temperature, the rate increases with the pH. In the pH range of 6.5 to 7.4, although the concentration of the hydroxoaqua form of the complex increases marginally, that of the ester changes appreciably. The pK_a of the 4-nitrophenyl glycinate hydrobromide (HL) is reported to be 7.1. Thus, the concentration of the unprotonated form of the ester L species is 18, 42 and 64% at pH values of 6.45, 6.95 and 7.35 respectively. Therefore, as the concentration of L increases, the forward reaction, as shown in

Table 4. Values of K_M, k_o and k_{MOH} at Different Temperatures for Hydrolysis of PNPG Ester (pH = 6.95 ± 0.05 [PNPG] = 3.0×10^{-5} mol dm^{-3}, I=0.1 mol dm^{-3})

T/K	10^7[OH$^-$]/ mol dm^{-3}	[Co(OH)(trien)(H$_2$O)]$^{2+}$			[Co(OH)(trien)(H$_2$O)]$^{2+}$			[Co(OH)(trien)(H$_2$O)]$^{2+}$		
		K_M	$10^3\,k_o$/s^{-1}	$10^{-4}\,k_{MOH}$/ mol dm^{-3} s^{-1}	K_M	$10^3\,k_o$/s^{-1}	$10^{-4}k_{MOH}$/ mol dm^{-3} s^{-1}	K_M	$10^3\,k_o$/s^{-1}	$10^{-4}\,k_{MOH}$/ mol dm^{-3} s^{-1}
303.3	1.91	27	1.0 ± 0.1	9.89	23	1.0 ± 0.1	8.74	36	1.0±0.1	8.17
308.3	2.72	20	1.5 ± 0.2	10.22	17	1.5 ± 0.2	9.19	31	1.5 ± 0.2	8.35
313.3	3.80	14	2.0 ± 0.2	11.97	11	2.0 ± 0.2	10.53	23	2.0 ± 0.2	9.39
$\Delta H^{\neq}$ kJ mol^{-1}			51.7 ± 3.2	22.7 ± 3.0		51.7 ± 3.2	20.3 ± 3.5		51.7 ± 3.2	18.2 ± 3.0
$\Delta S^{\neq}$ JK^{-1} mol^{-1}			31.7 ± 6.5	−75.6 ± 5.0		31.7 ± 6.5	−84.3 ± 4.5		31.7 ± 6.5	−92.0 ± 5.0

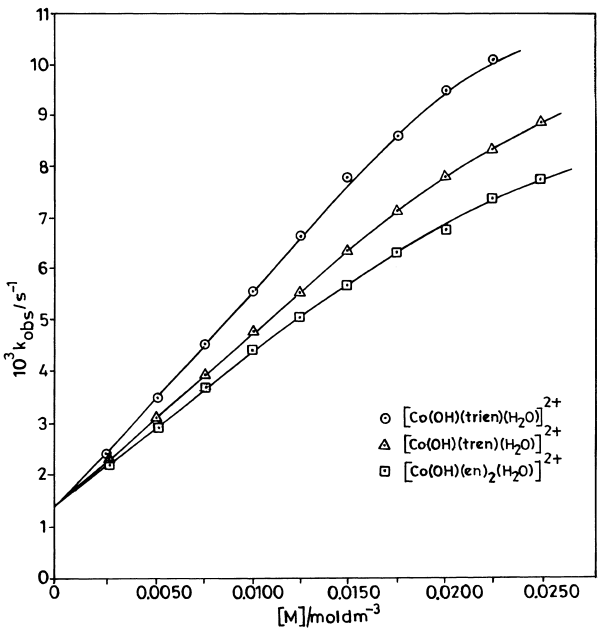


Fig. 1. Variation of Rate Constants (k_{obs}) with Complex Concentration for PNPG Ester at pH = 6.95 ± 0.05 and temp = 35.1 ± 0.1 °C.

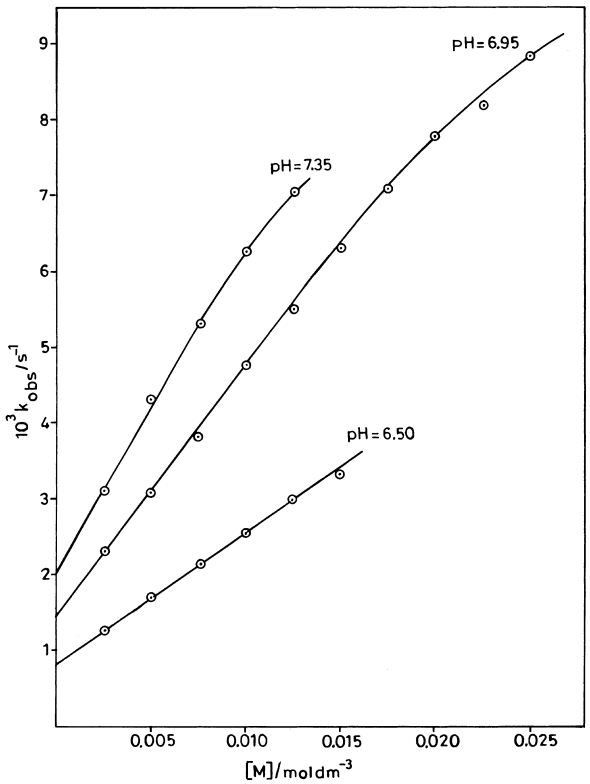


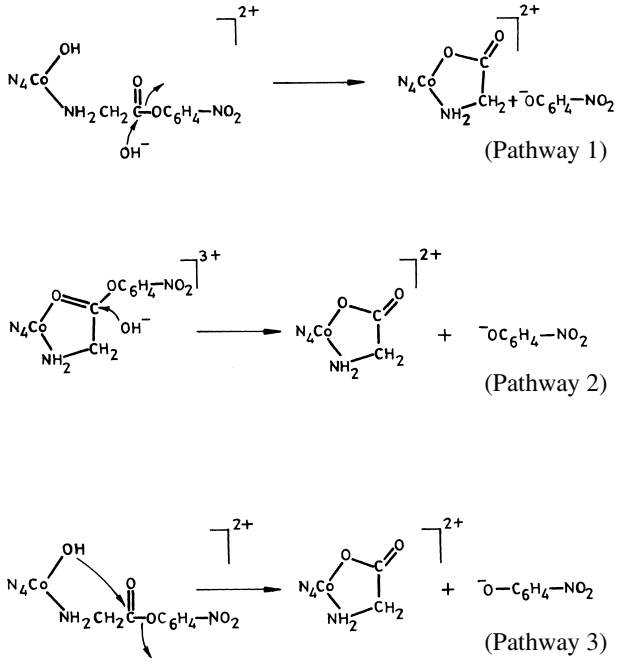
Fig. 2. Variation of Rate Constants (k_{obs}) with Complex Concentration [Co (OH) (tren) (OH$_2$)]$^{2+}$ for PNPG Ester at pH (temp = 35.1 ± 0.1 °C.)

Eq. 1, is favoured. This results in a higher a concentration of ML, leading to an increase in the rate.

The N-bound monodentate ester species thus formed can undergo base hydrolysis via any one of the three possible pathways (Pathways 1 to 3), as shown in Scheme 1.

It has been demonstrated that the observed rate accelerations can be correlated with the mechanism operative in the system.[2] The rate accelerations observed for a reaction proceeding via an external hydroxide ion attack on the N-bound monodentate ester (Pathways 1) are very low (< 100), while for reactions involving chelate ester species (Pathways 2) they are of the order of 10^3–10^5. The intramolecular pathway (Pathways 3) leads to a very large rate enhancement, $\sim 10^9$–10^{11}. The second-order rate constant (k_{MOH}), obtained for the metal-promoted pathway for trien, tren and $(en)_2$ complexes, are found to be of the order of 10^5 (Table 4). The value of k_{OH} for the base hydrolysis of L is reported to be 2.3×10^2 dm^3 mol^{-1} s^{-1}.[24] A comparison of the values of k_{MOH}/k_{OH} gives ~400–600. Thus, the mechanism involving the monodentate ester species (Pathways 1) and the intramolecular pathway (Pathways 3) can be ruled out based on the observed rate accelerations. An attack of external OH$^-$ on the chelated ester species, therefore, seems to be the most probable mechanism for the hydrolysis of 4-nitrophenyl glycinate.

Concerning the base hydrolysis of *β-cis*[CoCl(trien)-(glyOEt)]$^{2+}$, an ^{18}O tracer study has indicated that only 16% of *β-cis*[CoCl(trien)(gly)]$^+$ is formed via the intramolecular step, and that primarily the reaction proceeds via chelate formation.[32] The hydrolysis reaction in *β-cis*-[Co(OH) (trien) (gly gly OR)]$^{2+}$ is believed to occur via the chelated intermediate species.[33] The formation of the chelate demands the substitution of bound hydroxide. This was thought to be likely, as in a study of *β-cis*[Co(OH)(trien)(NH$_3$)]$^{2+}$, where it was observed that the exchange between coordinated hydroxide and the solvent was very fast at 25 °C and a pH of 7–8.[34] The chelate ester species in [Co(OH)(trien) (gly gly OR)]$^{2+}$ could thus be formed via a competition between the solvent water and carbonyl oxygen during the hydroxide exchange. A similar mechanism leading to the formation of the chelate ester species is



Scheme 1.

likely to be operative in the *cis*-[Co(OH) (trien) (NH_2 CH_2 $COOC_6H_4NO_2$)]$^{2+}$complex.

The activation parameters, ($\Delta H^{\neq}$ and $\Delta S^{\neq}$ (Table 4) for the trien, tren and $(en)_2$ complex-promoted reactions, have been found to be similar. This suggest that a common mechanism, involving an attack of external OH^- on the chelate ester species, is operative in all three complex-promoted reactions. The rate enhancements (~400–600) observed in the present study were slightly lower in comparison to those (10^3–10^5) observed for typical bidentate coordination esters. This could probably be ascribed to the weaker alkoxy carbonyl interaction in the chelate, owing to the decreased nucleophilicity of the carbonyl oxygen in the p-nitrophenyl amino acid ester.

References

1 P. A. Sutton and D. A. Buckingham, *Acc. Chem. Res.*, **20**, 357 (1987).

2 R. W. Hay, "Comprehensive Coordination Chemistry," Vol. 6, ed by G. Wilkinson, Pergamon Press (1987).

3 D. A. Buckingham, "Biological Aspects of Inorganic Chemistry," ed by A. W. Addison, W. R. Cullin, D. Dolphin and B. R. James, Wiley, New York (1976).

4 N. E. Dixon and A. M. Sargeson, "Zinc Enzymes," ed by T. G. Spiro, Wiley, New York (1983).

5 B. E. Leach and R. J. Angelici, *Inorg. Chem.*, **8**, 907 (1969).

6 R. D. Wood, R. Nakon, and R. J. Angelici, *Inorg. Chem.*, **17**, 1088 (1978).

7 R. Nakon, P. R. Rechani, and R. J. Angelici, *J. Am. Chem. Soc.*, **96**, 2117 (1974).

8 R. W. Hay and P. Banerjee, *J. Chem. Soc., Dalton Trans.*, **1980**, 2452, and references therein.

9 H. Chakrabarty and M. L. Rahman, *Trans. Met. Chem.*, **18**, 545 (1993).

10 H. Chakrabarty, N. Paul, and M. L. Rahman, *Transition. Met. Chem. London*, **19**, 524 (1994).

11 R. W. Hay and R. B. Nolan, *J. Chem. Soc., Dalton, Trans.*, **1974**, 2452.

12 M. M. Shonkry, W. M. Hosny, and M. M. Khalil, *Transition. Met. Chem.*, **20**, 252 (1995).

13 D. E. Newlin, M.A. Pellack, and R. Nakon, *J. Am. Chem. Soc.*, **99**, 1078 (1977).

14 N. Ahmad, M. A. Haque, and M. M. Ali, *Ind. J. Chem. Sect. A*, **36**, 228 (1997).

15 R. W. Hay and A. K. Basak, *J. Chem. Soc., Dalton Trans.*, **1982**, 1819, and references therein.

16 R. W. Hay and M. P. Pujari, *Inorg. Chim. Acta*, **123**, 175 (1986).

17 H. Chakrabarty and M. L. Rahman, *Transition. Met. Chem. London*, **19**, 481 (1990).

18 R. A. Kenley, R. H. Fleming, R. M. Laine, D. S. Tse, and J. S. Winterle, *Inorg. Chem.*, **23**, 1870 (1984).

19 J. Chin and X. Zou, *J. Am.Chem. Soc.*, **110**, 223 (1988).

20 J. Chin, M. Banaszczyk, V. Jubian and X. Zou, *J. Am. Chem. Soc.*, **111**, 186 (1989).

21 G. H. Rawji and R. M. Milburn, *Inorg. Chim. Acta*, **150**, 227 (1988).

22 R. W. Hay and L. Main, *Aust. J. Chem.*, **21**, 155 (1968).

23 R. W. Hay and A. K. Basak, *Inorg. Chim. Acta*, **123**, 237 (1986).

24 R. W. Hay and A. K. Basak, *J. Chem. Soc., Dalton Trans.*, **1986**, 39.

25 D. Ben-Ishai and A. Berger, *J. Org. Chem.*, **17**, 1564 (1952).

26 M. Krishnamurthy, *J. Inorg. Nucl. Chem.*, **34**, 3915 (1972).

27 A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967).

28 E. Kimura, S. Young, and J. P. Collman, *Inorg. Chem.*, **9**, 1183 (1970).

29 T. P. Dasgupta and G. M. Harris, *J. Am. Chem. Soc.*, **97**, 1733 (1975).

30 R. W. Hay, A. K. Basak and M. P. Pujari, *Transition. Met. Chem. London*, **11**, 27 (1986).

31 F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," 2nd ed, Wiley, New York, 1967.

32 D. A. Buckingham, D. M. Foster, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **9**, 11 (1970).

33 D. A. Buckingham, C. F. Davis, D. M. Foster, and A. M. Sargeson, *J. Am. Chem. Soc.*, **92**, 5571 (1970).

34 D. A. Buckingham, C. E. Davis, D. M. Foster, and A. M. Sargeson, *J. Am. Chem. Soc.*, **92**, 5571 (1970).