

# Di- $\mu$ -hydroxo Bridge Cleavage Reactions between $[\text{Co}(\text{nta})(\mu\text{-OH})]_2^{2-}$ and various N,N-Bidentate Ligands

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## ABSTRACT

The cleavage of the di- $\mu$ -hydroxo bridges of  $[\text{Co}(\text{nta})(\mu\text{-OH})]_2^{2-}$  by en and *N,N*-Et<sub>2</sub>en (en = ethylenediamine and *N,N*-Et<sub>2</sub>en = *N,N*-diethylethylene-diamine) has been investigated.  $[\text{Co}(\text{nta})(\mu\text{-OH})]_2^{2-}$  equilibrates rapidly in aqueous basic solutions, yielding a mono- $\mu$ -hydroxo-bridged Co(III) complex [ $\text{pK}_{\text{OH}} = 3.3(1)$ ] and both these species react with the incoming ligand to form different ion associated species. These, in turn, react to form presumably a ligand-substituted, mono-bridged species,  $[(\text{nta})(\text{OH})\text{Co}-\mu\text{-OH}-\text{Co}(\text{nta})(\text{L-L})]^{2-}$ , which upon ring-closure rapidly form the products. Values for  $k_2$ , the preferred pathway for these reactions, vary between  $1.42(4) \times 10^{-2} \text{ s}^{-1}$  (en) and  $3.2(1) \times 10^{-3} \text{ s}^{-1}$  (*N,N*-Et<sub>2</sub>en) at 25.0°C,  $\mu = 0.2 \text{ M}$  (NaClO<sub>4</sub>).

## KEY WORDS

Bridge cleavage, cobalt(III), kinetics, mechanism, nitrilotriacetate.

## 1. Introduction

The aqueous chemistry of transition metals in the presence of ligands which contain hard donor groups that are likely to be important in natural systems, are instructive in many ways. Aluminium(III), for example, is a non-essential ion to living systems, but its bio-availability has increased over the last few decades because of the formation of soluble aluminium(III) complexes. The solution chemistry of many M(III) complexes (M = Co, Cr, Fe, Al etc.) is influenced by the formation of hydroxo ligand complexes, bridged and non-bridged. Very few kinetic studies on the cleavage of hydroxo-bridged species at high pH exist in the literature. Only a few reports on the cleavage of  $\mu$ -hydroxo bridges by CO<sub>2</sub> in weakly basic media to form dimeric Co(III) complexes where CO<sub>3</sub><sup>2-</sup> is the bridging ligand,<sup>1</sup> or to form monomeric complexes with CO<sub>3</sub><sup>2-</sup> acting as a bidentate ligand,<sup>2</sup> are available in the literature.

In an attempt to shed more light on these types of reactions, we investigated the bridge cleavage of cobalt(III)-nta (nta = nitrilotriacetate) complexes. Previous studies<sup>3-5</sup> indicated that  $[\text{Co}(\text{nta})(\mu\text{-OH})]_2^{2-}$  can successfully be used as starting material for the synthesis of monomeric Co(III)-nta complexes like  $[\text{Co}(\text{nta})(\text{L})_2]$  or  $[\text{Co}(\text{nta})(\text{L-L})]$  (L = dimethylaminopyridine (dmap)/ py; L-L = en/*N,N*-Et<sub>2</sub>en) at higher pH values. It was reported that  $[\text{Co}(\text{nta})(\mu\text{-OH})]_2^{2-}$  is stable in aqueous solution at pH 6.0–7.0, but react with ligands like dmap (dimethylaminopyridine) and *N,N*-Et<sub>2</sub>en (*N,N*-diethylenediamine) at high pH to give similar products to that isolated for the reactions of  $[\text{Co}(\text{nta})(\text{CO}_3)]^{2-}$  with the same ligands<sup>6</sup>.

The mechanism of the hydroxo bridge cleavage of  $[\text{Co}(\text{nta})(\mu\text{-OH})]_2^{2-}$  complexes in acidic medium has been investigated before.<sup>7,8</sup>  $[\text{M}(\text{nta})(\mu\text{-OH})]_2^{2-}$  complexes [M = Cr(III), Co(III)] undergo bridge cleavage in solution upon acidification<sup>1,3,7,9,10</sup> to form *cis*-[M(nta)(H<sub>2</sub>O)<sub>2</sub>]. The latter monomeric complexes undergo substitution by ligands such as NCS<sup>-3,9</sup> or redox reactions with ligands like I<sup>-7</sup>.

A recent study<sup>6</sup> reported the successive bridge cleavage of  $[\text{Co}_2(\text{nta})_2(\mu\text{-OH})]_2^{2-}$ , by two monodentate ligands, dimethyl-

aminopyridine (dmap) and pyridine (py) at pH 9.0–11.5. It was reported that the dimeric species equilibrates rapidly in solution with presumably a mono- $\mu$ -hydroxo-bridged cobalt(III) complex, and that both these species react with the incoming ligand to form different ion associated pairs, which in turn react in the subsequent rate determining steps to form presumably a ligand-substituted, mono-bridged complex,  $[(\text{nta})(\text{OH})\text{Co}-\mu\text{-OH}-\text{Co}(\text{nta})(\text{L})]^{2-}$  (L = py/dmap). The latter decomposes rapidly to form the products. The preferred pathway for these bridge cleavage seemed to be the reaction of the mono- $\mu$ -hydroxo-bridged cobalt(III) species with the entering ligand.

This paper deals with the di- $\mu$ -hydroxo bridge cleavage reactions of  $[\text{Co}(\text{nta})(\mu\text{-OH})]_2^{2-}$  and two bidentate ligands (en and *N,N*-Et<sub>2</sub>en) in order to expand on the study with monodentate ligands<sup>6</sup> and to try to further verify the mechanism proposed for these types of reactions. The possible effect of the two ethyl substituents on the *N,N*-Et<sub>2</sub>en ligand on the rate of the reaction is also of key interest.

## 2. Results and Discussion

The study of the bridge cleavage of  $[\text{Co}(\text{nta})(\mu\text{-OH})]_2^{2-}$  with bidentate ligands such as en and *N,N*-Et<sub>2</sub>en at high pH were undertaken to expand on the previous work<sup>6</sup> and to investigate the possible effect of the two ethyl groups on *N,N*-Et<sub>2</sub>en on the rate of the reaction. Both these ligands have similar nucleophilicities ( $\text{pK}_{\text{a}2}(\text{en}) = 9.96$  vs.  $\text{pK}_{\text{a}2}(\text{N,N-Et}_2\text{en}) = 10.46$ ) so any major differences in rate could be ascribed to the bulkiness of *N,N*-Et<sub>2</sub>en.<sup>12</sup>

The synthesis and characterization of  $[\text{Co}(\text{nta})(\text{en})]$  and  $[\text{Co}(\text{nta})(\text{N,N-Et}_2\text{en})]$  from  $[\text{Co}(\text{nta})(\mu\text{-OH})]_2^{2-}$  at high pH have been reported earlier.<sup>4,12</sup> Our previous study revealed that  $[\text{Co}(\text{nta})(\mu\text{-OH})]_2^{2-}$  is stable in solution up to pH  $\approx 11.5$ . At pH 12.0–14.0 a completely different change in UV/vis spectrum compared to that of the substitution reactions of  $[\text{Co}(\text{nta})(\mu\text{-OH})]_2^{2-}$  with the various ligands was observed. The formation of a brown-green precipitate, believed to be Co<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O, accompanied these shifts in spectra at high pH, which was confirmed with IR and <sup>1</sup>H NMR data.<sup>6</sup>

In a preliminary UV/vis study we found that the rates of

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the substitution reactions between  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  and the different ligands increased with an increase in  $[\text{OH}^-]$  up to pH 11.5. At pH >11.5 a totally different metal species as described before<sup>6</sup> is formed in solution, leading to a discontinuity of the kinetics.

From the evidence obtained above it was decided to study the  $\mu$ -hydroxo bridge cleavage of  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  with en and  $N,N\text{-Et}_2\text{en}$  between pH 9.0 and 11.5 in order to avoid the formation of a different Co species at higher pH.

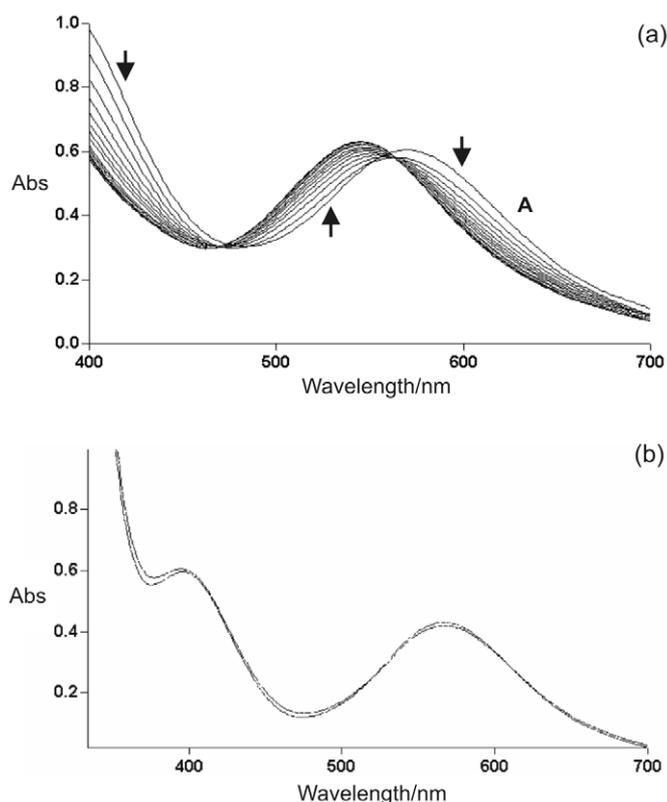
Initial tests also revealed that plots of  $k_{\text{obs}}$  vs. ligand concentration were non-linear. The final UV/vis spectra of the reaction solutions obtained, gave absorption maxima at 234 and 543 nm ( $N,N\text{-Et}_2\text{en}$ ) and 231 and 550 nm (en) (Fig. 1).  $^1\text{H}$  NMR. data obtained after drying the final reaction solutions were also in accordance with that found previously for  $[\text{Co}(\text{nta})(\text{en})]$  and  $[\text{Co}(\text{nta})(N,N\text{-Et}_2\text{en})]$ ,<sup>4,12</sup> indicating that the observed reactions were the formation of the final product and not an intermediate species.

Only one reaction was observed spectrophotometrically under the experimental conditions. On the basis of the experimental results, the mechanism in Scheme 1 is proposed. It is proposed that  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  equilibrates rapidly in aqueous basic solutions with a mono- $\mu$ -hydroxo-bridged species. Both these species then react with the incoming ligand to form different ion associated species which react in the rate determining steps ( $k_1$  and  $k_2$ ) to form presumably a ligand-substituted, mono-bridged species,  $[(\text{nta})(\text{OH})\text{Co}-\mu\text{-OH}-\text{Co}(\text{nta})(\text{L-L})]^{2-}$  followed by rapid ring-closure to yield the products.

Ethylenediamine and  $N,N\text{-Et}_2\text{en}$  both exist as two species ( $\text{p}K_{\text{a}2}(\text{en}) = 9.96$  and  $\text{p}K_{\text{a}2}(N,N\text{-Et}_2\text{en}) = 10.46$ )<sup>11</sup> in the pH range studied. Our initial studies indicated that neither of the two ligands used in this study reacted with  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  at pH < 9.0, well below their corresponding  $\text{p}K_{\text{a}2}$  values. This, together with the fact that it is generally accepted that N-type donor ligands do not react in the fully protonated form<sup>13,14</sup> enabled us to propose that the active coordinating species of en-type ligands is the fully deprotonated form.

This is similar to the mechanism proposed for the successive bridge cleavage by monodentate ligands.<sup>6</sup> The ring closure step in this study is very rapid and similar to the formation of the final product in the previous study where the coordination of the second ligand was not observed spectrophotometrically.

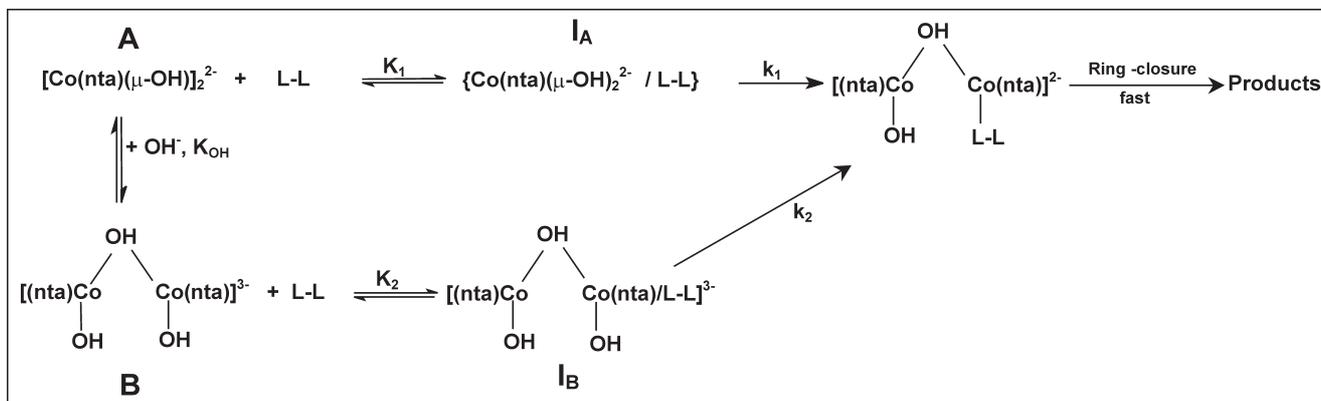
Support for the existence of intermediate  $\mu$ -hydroxo species similar to  $I_A$  and  $I_B$  in basic solutions exists in the literature.<sup>12</sup> The cleavage of tri- $\mu$ -hydroxo bridges by  $\text{CO}_2$  in weakly basic media suggested intermediates with at least one of the hydroxo bridges opened. On the other hand, the nucleophilic attack of  $\text{OH}^-$  on A



**Figure 1** UV/vis spectra of (a)  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  ( $1.5 \times 10^{-4}$  M) and en (0.2 M) at 25.0°C,  $\mu = 0.2$  M ( $\text{NaClO}_4$ ), pH = 10.7. (A) represents scan immediately after mixing. (b)  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  ( $2 \times 10^{-4}$  M) at pH (a) 7.55 and (b) 11.31, 25.0°C,  $\mu = 0.2$  M ( $\text{NaClO}_4$ ).

could result in a tri- $\mu$ -hydroxo species which, upon reacting with L, could form a di- $\mu$ -hydroxo species,  $[(\eta^3\text{-nta})(\text{OH})\text{Co}(\mu\text{-OH})_2\text{Co}(\eta^3\text{-nta})\text{L}]$ , as a product of the  $k_2$ -pathway. The decision whether bridge cleaving (leading to B) or bridge formation is operative in the  $K_{\text{OH}}$  equilibrium is a speculative one. However, the current results support the saturation kinetics for the subsequent reactions of A and B.

Spectral changes in further support of the existence of the intermediate species  $I_A$  and  $I_B$  were not pronounced enough at the low ligand concentrations at which our kinetic study was performed. This was solved by increasing the ligand concentration substantially.<sup>15</sup> The UV/vis spectrum for a typical reaction between en and  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  at pH = 10.5 is illustrated in Fig. 1a. In Fig. 1a, Spectrum A was obtained immediately after



L-L = neutral form of en/ $N,N\text{-Et}_2\text{en}$

Scheme 1.

mixing solutions of en and  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  at pH = 10.5. Subsequent scans clearly indicate isosbestic points which do not coincide with the first spectrum (A). This presumably points to the formation of a first intermediate species which then reacts to  $[\text{Co}(\text{nta})(\text{en})]$ , yielding additional evidence for the proposed mechanism. Formation of  $[\text{Co}(\text{nta})(\text{en})]$  is accompanied by well-defined isosbestic points at 471 and 522 nm, a decrease in absorption between 550 and 650 nm and the appearance of a small band at 490 nm.

In an attempt to confirm the existence of B in Scheme 1, a spectrum of a solution ( $100 \text{ cm}^3$ ;  $0.02 \text{ mol dm}^{-3}$ ) of  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  was recorded (a in Fig. 1b). The pH was then adjusted from 7.55 to 11.31 by transferring a minimum amount of concentrated aqueous NaOH to the dimeric solution by dipping a thin glass rod in both, to eliminate observed spectral changes by dilution. The spectrum at pH 11.31 was recorded (b in Fig. 1b), and a small increase in absorbance in the 375–390 nm and 560–590 nm regions were observed, pointing to the existence of an equilibrium between  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  and another species. Unfortunately it was impossible to determine this equilibrium spectrophotometrically because of the rapid decomposition of  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  at high hydroxide concentrations.

According to Scheme 1, considering the above-mentioned arguments, the overall rate can be described by Equation 1.

$$R = k_1[I_A] + k_2[I_B] \quad (1)$$

$[I_A]$  and  $[I_B]$  represent the concentration of intermediates  $I_A$  and  $I_B$  in Scheme 1. The total Co(III) concentration,  $[\text{Co}]_{\text{tot}}$ , is indicated by Equation 2, where  $[A]$  represents the concentration of  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  and  $[B]$  that of the mono- $\mu$ -hydroxo-bridged Co(III)-nta species (Scheme 1).

$$[\text{Co}]_{\text{tot}} = [A] + [B] + [I_A] + [I_B] \quad (2)$$

The expression describing  $K_{\text{OH}}$  in Scheme 1 is given by Equation 3.

$$K_{\text{OH}} = \frac{[B]}{[A][\text{OH}^-]} \quad (3)$$

The observed rate constant,  $k_{\text{obs}}$ , can be obtained from Equations 1–3 and the general definitions of  $K_{a2}$ ,  $K_1$  and  $K_2$ .

$$k_{\text{obs}} = \frac{(k_1 K_1 [\text{H}^+] / K_{a1} + k_2 K_2 K_{\text{OH}} [\text{OH}^-]) [\text{N} - \text{N}]_{\text{tot}}}{(1 + [\text{H}^+] / K_{a1} + K_{\text{OH}} [\text{OH}^-] [\text{H}^+] / K_{a1} + K_{\text{OH}} [\text{OH}^-]) + (K_1 [\text{H}^+] / K_{a1} + K_2 K_{\text{OH}} [\text{OH}^-]) [\text{N} - \text{N}]_{\text{tot}}} \quad (4)$$

Equation 4 can be simplified to Equation 5, assuming  $\text{p}K_{a2}(\text{en}) = 9.96$  vs.  $\text{p}K_{a2}(\text{N,N-Et}_2\text{en}) = 10.46$  and from the experimental conditions between pH = 9–11.5 ( $K_{\text{OH}}[\text{OH}^-][\text{H}^+]/K_{a2} < 1$ ).

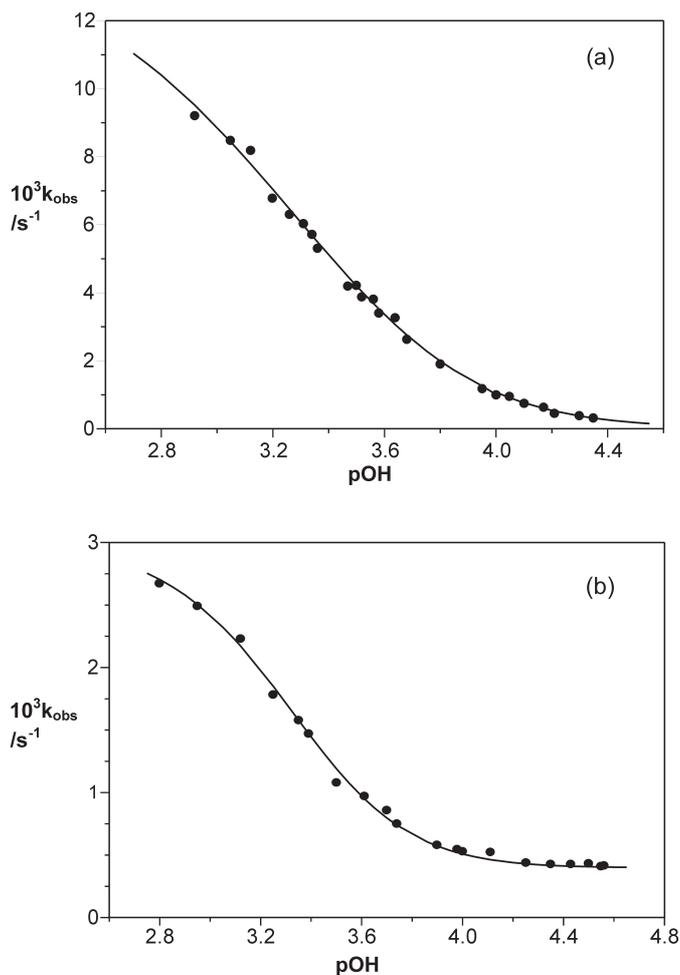
$$k_{\text{obs}} = \frac{(k_1 K_1 [\text{H}^+] / K_{a1} + k_2 K_2 K_{\text{OH}} [\text{OH}^-]) [\text{N} - \text{N}]_{\text{tot}}}{(1 + [\text{H}^+] / K_{a1} + K_{\text{OH}} [\text{OH}^-]) + (K_1 [\text{H}^+] / K_{a1} + K_2 K_{\text{OH}} [\text{OH}^-]) [\text{N} - \text{N}]_{\text{tot}}} \quad (5)$$

A simplified version of Equation 5 is illustrated in Equation 6.

$$k_{\text{obs}} = \frac{C_1 [\text{N} - \text{N}]_{\text{tot}}}{C_2 + C_3 [\text{N} - \text{N}]_{\text{tot}}} \quad (6)$$

Equation 6 predicts that a plot of  $k_{\text{obs}}$  vs.  $[\text{N} - \text{N}]_{\text{tot}}$  will be non-linear at any pH and will reach a plateau at high  $[\text{N} - \text{N}]_{\text{tot}}$ .

The reaction between  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  and L-L was investigated by performing two separate experiments. Firstly,  $k_{\text{obs}}$  was measured as a function of  $[\text{L} - \text{L}]$  at constant pH (Fig. 2a,b) and, secondly,  $k_{\text{obs}}$  was measured as a function of pH and constant  $[\text{L} - \text{L}]$  (Fig. 3a,b). The results clearly indicate a non-linear relation



**Figure 2** Plot of  $k_{\text{obs}}$  vs. pOH for the reaction between (a)  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  and en, and (b)  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  and  $N,N\text{-Et}_2\text{en}$ .  $T = 25.0^\circ\text{C}$ ,  $\mu = 0.2 \text{ M}$  ( $\text{NaClO}_4$ ),  $\lambda = 325 \text{ nm}$ ,  $[\text{dimer}] = 1.5 \times 10^{-4} \text{ M}$ .

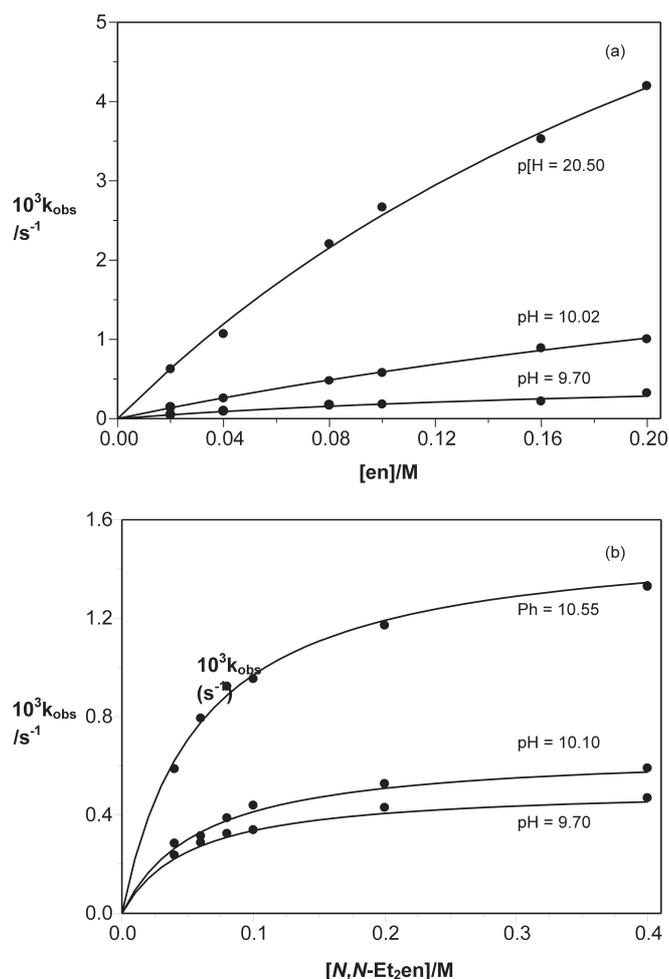
between  $k_{\text{obs}}$  and  $[\text{L} - \text{L}]$  that reaches a plateau at high  $[\text{L} - \text{L}]$ .

The values for  $k_1$ ,  $k_2$ ,  $K_1$ ,  $K_2$  and  $K_{\text{OH}}$  in Scheme 1 were calculated by fitting the data from these two experiments simultaneously into Equation 5 with the value of  $K_{a2}$  constant at 9.96 (en) or 10.46 ( $N,N\text{-Et}_2\text{en}$ ). These results are reported in Table 1.

It is clear from Table 1 and the preceding figures that the experimental data fits well into the proposed rate law.

The value obtained for  $k_1(\text{en})$  is  $8.7(7) \times 10^{-5} \text{ s}^{-1}$  and is 160 times smaller than  $k_2(\text{en})$  [ $1.42(4) \times 10^{-2} \text{ s}^{-1}$ ]. The rate constants for the reaction between  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  and  $N,N\text{-Et}_2\text{en}$  show similar trends. However, the value obtained for  $k_1$ ,  $7.2(7) \times 10^{-4} \text{ s}^{-1}$ , is only four times smaller than  $k_2$  [ $3.2(1) \times 10^{-3} \text{ s}^{-1}$ ]. This indicates a *ca.* factor of ten increase in  $k_1$  from en to  $N,N\text{-Et}_2\text{en}$ , but a corresponding *ca.* fivefold decrease in  $k_2$  from en to  $N,N\text{-Et}_2\text{en}$ . This cannot be completely explained with the current data in hand, and clearly points to additional future research. It is nevertheless evident from the above data that the nature of the bidentate ethylene diamine ligand does not substantially influence the rate of the reaction. The fact that  $k_1(N,N\text{-Et}_2\text{en})$  is higher than  $k_1(\text{en})$ , while the value obtained for  $k_2$  is smaller, indicates that steric hindrance is not the only factor that influences the rate of these reactions. This might be explained by examining the proposed mechanism.

It is possible that  $N,N\text{-Et}_2\text{en}$  first associates with its unsubstituted nitrogen atom in the rate determining step, after which the fast, ring-closure step takes place. The rate-determining step



**Figure 3** Plot of (a)  $k_{\text{obs}}$  vs.  $[\text{en}]$  and (b)  $N,N\text{-Et}_2\text{en}$ , for the reaction between  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  and en/ $N,N\text{-Et}_2\text{en}$  at different pH values, 25.0°C,  $\mu = 0.2 \text{ M}$  ( $\text{NaClO}_4$ ),  $\lambda = 325 \text{ nm}$ ,  $[\text{dimer}] = 1.5 \times 10^{-4} \text{ M}$ .

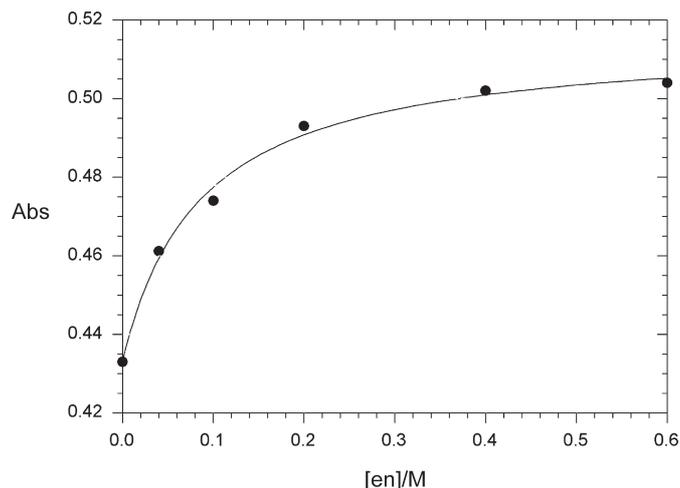
would then be basically the same for both ligands as was observed. The ring-closure step is so fast that it could not be detected spectrophotometrically, in spite of the substituents on the closing arm of the bidentate ligand in the case of  $N,N\text{-Et}_2\text{en}$ , that should influence this reaction step to some extent.

However, in both cases these results indicate, as with the reactions between the dimeric species and monodentate ligands,<sup>6</sup> that the mono-bridged species (B in Scheme 1) labilizes the Co(III)-hydroxo bond to such an extent that the  $k_2$  pathway is the preferred pathway for product formation. Additional important observations can be made from this and the earlier study with py and dmap.<sup>6</sup>

Firstly, it seems that the bridge cleavage of  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  at high pH is greatly influenced by the presence of  $\text{OH}^-$  ions. The existence of another species, supposedly a mono-bridged complex, at pH 10.0 and higher was proven kinetically by the

**Table 1** Summary of the rate constants for the reaction between  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$  and L-L (L-L = en/ $N,N\text{-Et}_2\text{en}$ ) at 25.0°C;  $\mu = 0.2 \text{ M}$  ( $\text{NaClO}_4$ ).

	en	$N,N\text{-Et}_2\text{en}$
$(10^5)k_1 (\text{s}^{-1})$	8.7(7)	72(7)
$K_1 (\text{M}^{-1})$	2.5(3)	15(3)
$(10^3)k_2 (\text{s}^{-1})$	1.42(4)	0.32(1)
$(10^{-3})K_2 (\text{M}^{-1})$	2.9(2)	4.6(6)
$\text{pK}_{\text{OH}}$	3.3(1)	3.3(1)



**Figure 4** Absorbance change at 522 nm upon addition of en to  $[\text{Co}(\text{nta})(\mu\text{-OH})_2]^{2-}$ , 25.0°C, pH = 10.5,  $\mu = 0.2 \text{ M}$  ( $\text{NaClO}_4$ ). The solid line represent a least-squares fit to Equation 7 and gives a value of  $K' = 11(1) \text{ M}^{-1}$ .

fact that  $\text{pK}_{\text{OH}}$  is the same for all four kinetic studies. Both the dimeric species and the mono-bridged complex react with the incoming ligand under the current experimental conditions.

Secondly, it seems that the mono-bridged species (B in Scheme 1) labilizes the Co(III)-hydroxo bond to such an extent that the  $k_2$  pathway seems to be the preferred pathway for product formation. This seems to be highly likely as the one extra  $\text{OH}^-$  ligand would further increase the electron density on the mono- $\mu$ -hydroxo-bridged Co(III) complex, thereby making it react more like a labile Co(II) species. In the case of en as incoming ligand the difference between  $k_1$  and  $k_2$  was two orders of magnitude, illustrating this point.

The stability constant  $K_1(\text{en})$  [ $2.5(3) \text{ M}^{-1}$ ] is three orders of magnitude smaller than  $K_2(\text{en})$ , which was determined as  $2.9(2) \times 10^3 \text{ M}^{-1}$ , while  $K_1(N,N\text{-Et}_2\text{en})$  [ $15(3) \text{ M}^{-1}$ ] is 300 times smaller than  $K_2(N,N\text{-Et}_2\text{en})$ , which was determined as  $4.6(6) \times 10^3 \text{ M}^{-1}$ . This indicates that the stability of the intermediate complexes  $I_B$  are similar and not that dependent on the entering bidentate ligand (not even a twofold difference in  $K_2$  values for en and  $N,N\text{-Et}_2\text{en}$ ). However, the stability of  $I_A$  is seemingly more dependent on the nature of the en-type ligand, showing a *ca.* fivefold difference. Again, this cannot be explained with the current data, and requires additional future research.

Determination of the stability constants,  $K_1$  and  $K_2$ , spectrophotometrically were precluded by the experimental conditions and chemical limitations. To measure  $K_2$ , one would ideally perform a titration at a pH where the influence of the  $k_1$  pathway can be ignored. This was of course impossible due to the limits set by secondary reactions at  $\text{pH} > 11.5$ . Similarly, at low pH ( $< 9.0$ ), spectral changes were not significant enough to successfully measure  $K_1$ . This does not subtract from the correctness of the proposed mechanism as these measurements were obtained to confirm the existence of an intermediate species. This was not done in the previous study.<sup>10</sup>

To determine the relative overall contributions of both  $K_1(\text{en})$  and  $K_2(\text{en})$  the increase in absorbance as a function of ligand concentration was monitored at 522 nm (isosbestic point) and  $\text{pH} = 10.5$ , where the intermediate species was best observed. The data were fitted to Equation 7 and the value obtained for  $K'$  was  $11(1) \text{ M}^{-1}$ , see Fig. 4. This value compares reasonably with that obtained for  $K_1$  from the kinetic data, possibly indicating that  $K'$  is more representative of the  $k_1$  pathway at  $\text{pH} = 10.5$ .

$$A = \frac{(A_M + A_{ML} K' [N - N]_{tot})}{1 + K' [N - N]_{tot}} \quad (7)$$

The overall conclusion from this study is that [Co(nta)( $\mu$ -OH)]<sub>2</sub><sup>2-</sup> equilibrates rapidly in aqueous basic solutions with a mono- $\mu$ -hydroxo-bridged Co(III) species and that both these species react with the entering ligand to form different intermediate species. The latter undergo ring-closure (bidentate ligands) or another substitution step (monodentate ligands), both rapid, to form the products.

### 3. Experimental Procedures

All reagents and chemicals were of analytical grade and double distilled water was used in all experiments. All pH measurements were performed on a Hannah model 8519 pH meter using standard buffer solutions for calibration. Kinetic measurements were done on a GBC 916 spectrophotometer. Temperature control of the reaction solutions was maintained to within  $\pm 0.1^\circ\text{C}$  by means of a circulating water bath system. The Scientist<sup>16</sup> program was used to fit the data to selected functions. All the kinetic runs were performed under pseudo first-order conditions with the ligand in excess in each case. The solid lines in the figures represent least-squares computer fits of data, while the experimentally determined values are represented by dots.

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