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Kinetics of Complex Formation Between Cobalt(II) and the Polyamine Me_2Octaen

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The kinetics and the equilibria of complex formation between Co(II) and the linear polyamine 1,25-dimethyl-1,4,7,10,13,16,19,22,25-nonaazapentacosane (Me_2Octaen) have been investigated in aqueous solution under anaerobic conditions by the stopped-flow and potentiometric method. Static titrations and kinetic experiments indicate that below pH 5.6 the binding of Co(II) to the ligand gives rise to several 1 : 1 complexes differing for their degree of protonation, whereas above pH 5.6 binuclear complexes are formed as well. The analysis of the kinetic data reveals that the mostly reactive form of the ligand (denoted in its fully protonated form as H_9L^{9+}) is H_6L^{6+}. The species H_5L^{5+} and H_4L^{4+} yield only a minor contribution to the overall process of complex formation. Measurements at different ionic strengths have shown positive salt effects, as expected for reactive processes involving particles with charges of the same sign. The analysis of the results shows that Co^{2+} and H_6L^{6+} react according to the internal conjugate base mechanism.

Keywords: Me_2Octaen; Polyamines; Cobalt(II); Kinetics; Equilibria; ICB mechanism

INTRODUCTION

Synthetic Co(II) complexes able to bind and to activate molecular dioxygen have been thoroughly studied [1] and, during the last years, a particular attention has been devoted to Co(II) complexes with binucleating ligands [2]. The latter contain a number of oxygen and/or nitrogen atoms sufficient to coordinate more than one Co^{2+} ion, thus they can act as biomimetic models of natural non-heme respiratory proteins. Among the binucleating ligands, the large polyamines containing from 9 to 11 nitrogen donor atoms, synthesised by Paoletti [3] and coworkers, turn out to be rather interesting. In collaboration with this group, we have previously performed a careful kinetic and thermodynamic investigation on the formation of oxygenated complexes of these polyamines with cobalt(II) [4]. Furthermore we have studied the binding mechanism of Ni(II) to the linear polyamine 1,25-dimethyl-1,4,7,10,13,16,19,22,25-nonaazapentacosane (Me_2Octaen) [5]. Me_2Octaen is a linear polyamine made by the union of eight *en* units bearing two methyl residues at the ends of the chain. Most of the kinetic investigations on the binding of polyamines to divalent heavy metal ions are confined

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to Ni(II) and Cu(II) [6], whereas studies involving Co(II) are quite scarce [7], probably due to the difficulties of making the apparatuses for the study of fast reactions completely oxygen free. We present in this paper some results on complex formation of Co(II) with the linear polyamine Me$_2$Octaen obtained under conditions where the oxygen interference could be avoided.

RESULTS

At constant pH the reacting system is conveniently described by the apparent reactions

$$M_f + L_f \rightleftharpoons ML_T \qquad (1)$$

$$2M_f + L_f \rightleftharpoons M_2L_T \qquad (2)$$

where M_f and L_f indicate the free reactants, whereas ML_T and M_2L_T indicate the total mononuclear and binuclear species respectively.

Owing to the complexity of the system, we have concentrate our attention on the results obtained at pH values between 4.6 and 5.6, where only the mononuclear complex is present. Below pH 4.6 no sensible complex formation can be seen, whereas above pH 5.6 the formation of both mono- and binuclear complexes occurs.

The kinetic experiments were carried out under pseudo first-order conditions. In the pH range studied the kinetic curves are fitted by single exponential functions. Figure 1 shows the metal ion concentration dependence of the observed time constant, $1/\tau$, measured at pH 5.0 where only reaction 1 does contribute to the kinetic behaviour of the system at ionic strength 0.1 M (Fig. 1A) and 0.3M (Fig. 1B). For $C_M \gg C_L$ the observed time constant is expressed by Eq. (3)

$$\frac{1}{\tau} = k_f C_M + k_d \qquad (3)$$

where k_f and k_d are respectively the formation and dissociation rate constants of reaction 1 and could be evaluated from slope and intercept of the straight line fitting to the experimental data. It can be observed that, contrary to the expected behaviour, the points of Figure 1A deviate from linearity for cobalt concentrations larger than 5×10^{-3} M. We got evidence that this effect is due to the presence of traces of oxygen. Despite the solutions in the reagent reservoirs were carefully deareated, it was impossible to prevent any penetration of traces of air into the apparatus. Owing to the extremely high absorbance of the oxygenated complex at the working wavelength, traces of this complex largely affect the kinetic response. A solution to this problem has

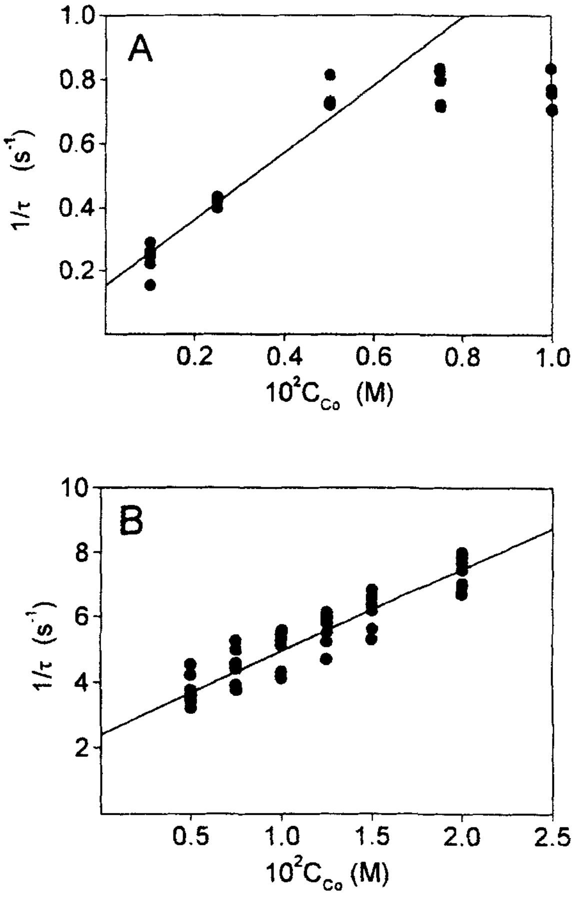


FIGURE 1 Dependence of the pseudo first-order rate constant, $1/\tau$, on the metal concentration for the Co(II)-Me$_2$Octaen system at pH = 5.0 and T = 298.1 K. (A) I = 0.10 M, (B) I = 0.30 M.

been found by increasing the ionic strength to the value of 0.3 M. In such a way the complex formation reaction (involving highly charged species of like sign) is strongly accelerated, and can be thus separated from the subsequent process of oxygen uptake, as shown by the linearity of the plot of Figure 1B.

Under these circumstances the equilibrium constant of reaction 1, denoted as K_{1app}, could be evaluated as the ratio between k_f and k_d.

The best representation of the dependence of K_{1app} on the hydrogen ion concentration is provided by the equation

$$K_{1app} = \left(\frac{A}{[H^+]} + B + C \cdot [H^+]\right)\alpha_{H_5L} \qquad (4)$$

where $\alpha_{H_5L} = [H_5L]/C_L$ has been evaluated for any $[H^+]$ by using the protonation constants at $I = 0.3\,M$ reported in Table I.

A plot of K_{1app}/α_{H_5L} *vs.* $[H^+]$ is shown in Figure 2. The equilibrium parameters A, B and C were obtained by a non-linear least-square fitting to Eq. (4). Models requiring replacements of α_{H_5L} by α_{H_4L} or by α_{H_6L} gave definite deviations from the experimental trend. These findings enable us to state that the prevailing species between pH 4.6 and 5.6 at $I = 0.3\,M$ are MH_4L^{6+}, MH_5L^{7+} and MH_6L^{8+}. The values of the parameters are $A = 5 \times 10^{-4}$, $B = 7 \times 10^2\,M^{-1}$ and $C = 5 \times 10^7\,M^{-2}$. The formation constants for the above mentioned bound forms can be derived from the parameters of Eq. (4) as $K_4 = AK_{A5}$, $K_5 = B$, $K_6 = C/K_{A6}$. Note that the equilibrium constants of the individual steps are defined as $K_i = [MH_iL]/[M]\,[H_iL]$, $K_{Ai} = [H]\,[H_{i-1}L]/[H_iL]$, $K_{Ci} = [H]\,[MH_{i-1}L]/[MH_iL]$. Their values are given in logarithmic form in Table I. In the same table the observed basicity

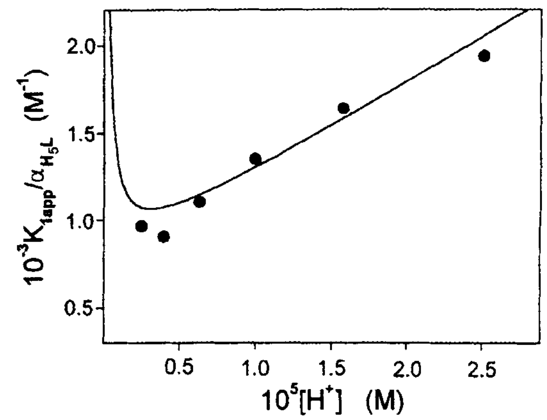


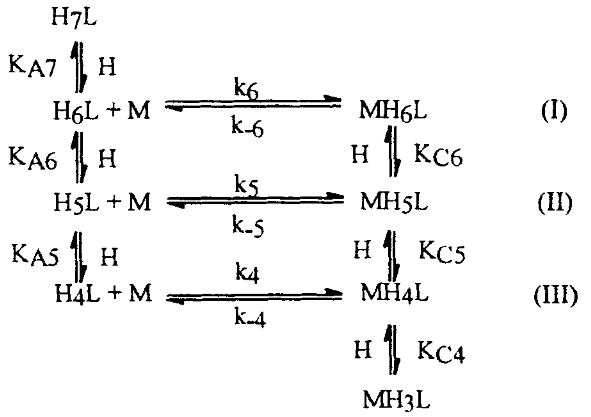
FIGURE 2 Plot of K_{1app}/α_{H_5L} *vs.* the hydrogen ion concentration for the Co(II)-Me$_2$Octaen system at $I = 0.3\,M$ and $T = 298.1\,K$.

TABLE I Logarithms of the protonation constants of Me$_2$Octaen and of its complex formation constants with Cobalt(II) at $T = 298.1\,K$ and $I = 0.3\,M$ (NaClO$_4$)

Reaction	Potentiometry	Kinetics
$L + H^+ = LH^+$	11.35	
$LH^+ + H^+ = LH_2^{2+}$	9.77	
$LH_2^{2+} + H^+ = LH_3^{3+}$	9.83	
$LH_3^{3+} + H^+ = LH_4^{4+}$	8.83	
$LH_4^{4+} + H^+ = LH_5^{5+}$	8.57	
$LH_5^{5+} + H^+ = LH_6^{6+}$	6.04	
$LH_6^{6+} + H^+ = LH_7^{7+}$	4.13	
$LH_7^{7+} + H^+ = LH_8^{8+}$	3.55	
$LH_8^{8+} + H^+ = LH_9^{9+}$	2.30	
$Co^{2+} + LH^+ = CoLH^{3+}$	14.50	
$Co^{2+} + LH_2^{2+} = CoLH_2^{4+}$	12.72	
$Co^{2+} + LH_3^{3+} = CoLH_3^{5+}$	9.34	
$Co^{2+} + LH_4^{4+} = CoLH_4^{6+}$	5.85	5.27
$Co^{2+} + LH_5^{5+} = CoLH_5^{7+}$		2.87
$Co^{2+} + LH_6^{6+} = CoLH_6^{8+}$		1.02
$2Co^{2+} + L = Co_2L^{4+}$	22.68	

constants for Me$_2$Octaen, and the complexation stability constants with Co(II) are also reported.

Concerning the kinetic measurements, we note that both k_f and k_d change with $[H^+]$. This observation not only confirms the existence of several acid-base equilibria between the differently protonated forms of the ligand and between the differently protonated forms of the mononuclear complex, but could also indicate which forms are able to bind the metal ion. In the investigated range of pH the species H_3L^{3+}, H_2L^{2+}, HL^+ and L could not make any contribution to the reaction rate, owing to their extremely low concentrations. All the remaining species, in principle, should be considered as possible candidates to participate in the binding process. The model which, among the tested ones, provides the best representation of the kinetic behaviour is that depicted below (charges have been omitted for the sake of simplicity):



According to the above reaction scheme the dependence of k_f and k_d on the hydrogen ion concentration is provided by the relationships:

$$\frac{k_f}{\alpha_{H_5L}} = \frac{k_4}{K_{A5}[H^+]} + k_5 + k_6K_{A6}[H^+] \qquad (5)$$

$$\frac{k_d}{\alpha_{MH_5L}} = \frac{k_{-4}}{K_{C5}[H^+]} + k_{-5} + k_{-6}K_{C6}[H^+] \qquad (6)$$

where $\alpha_{MH_5L} = [MH_5L]/C_L$.

Figure 3 shows the dependence of k_f/α_{H_5L} on $[H^+]$ whereas the dependence of k_d/α_{MH_5L} on $[H^+]$ is shown in Figure 4. The experimental trend of Figure 3 is in agreement with Eq. (5), but, unfortunately, the terms $k_4/K_{A5}[H^+]$ and k_5 are too small to be evaluated. The value of the individual rate constant of step (I) in the forward direction, k_6, has been obtained by the slope of the plot of Figure 3, where only the highest hydrogen ion concentrations data points have been considered. The value of k_6 is 5.1×10^2 $M^{-1}s^{-1}$. The dependence of k_d/α_{MH_5L} on acidity, shown in Figure 4, is more illuminating. The

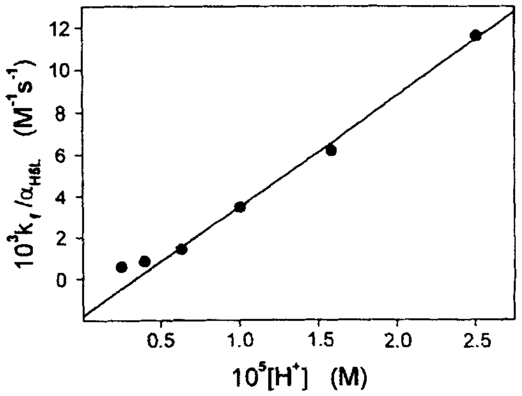


FIGURE 3 Plot of k_f/α_{H_5L} *vs.* the hydrogen ion concentration for the Co(II)-Me$_2$Octaen system at I = 0.3 M and T = 298.1 K.

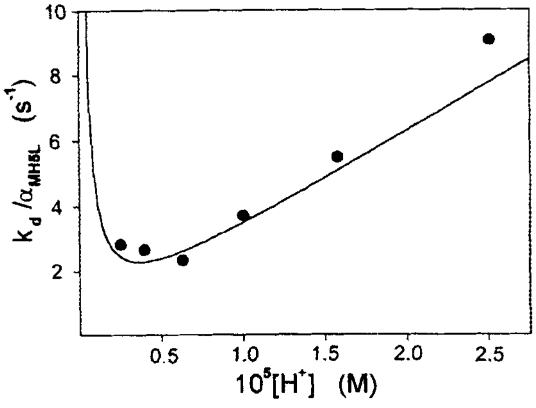


FIGURE 4 Plot of k_d/α_{MH_5L} *vs.* the hydrogen ion concentration for the Co(II)-Me$_2$Octaen system at I = 0.3 M and T = 298.1 K.

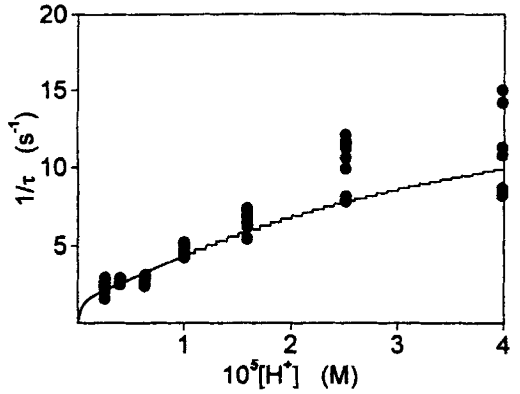


FIGURE 5 Dependence of the pseudo first-order rate constant, $1/\tau$, on the hydrogen ion concentration for the Co(II)-Me_2Octaen system at $C_M = 1 \times 10^{-2}$M, I = 0.3 M and T = 298.1 K. The calculated trend is based on Eq. (7).

occurrence of a minimum is in keep with the reaction scheme (I – III). The rate constants of the individual steps are $k_{-4} = 1.6\,s^{-1}$, $k_{-5} = 0.1\,s^{-1}$, $k_{-6} = 19\,s^{-1}$. To confirm the validity of the proposed reaction scheme, the experimental values of $1/\tau$ have been compared with those calculated according to Eq. (7) where k_d and K_{1app} have been calculated with the help of Eqs. (6) and (4) respectively.

$$\frac{1}{\tau} = k_d(1 + K_{1app}C_M) \qquad (7)$$

Figure 5 shows the experimental points for $C_M = 1 \times 10^{-2}$ M and the corresponding calculated trend.

DISCUSSION

It should be noted that the potentiometric method does not enable us to detect the species MH_5L and MH_6L whereas the kinetic method is insensitive to the presence of MH_3L. The species MH_4L has been detected by both methods and the agreement between the values of K_4 obtained by potentiometry and kinetics should be considered satisfactory in view of the different grounds on which the two methods are based. A comparison between the equilibrium constants measured in this work (I = 0.3 M) with those measured at I = 0.15 M [3b,8] shows a remarkable increase of these constants with the ionic strength, in agreement with the electrostatic theory of the electrolytes. This change amounts to half LogK unit for the protonation constants and to about one LogK unit for the complex formation constants.

Concerning the kinetic aspects of this work, it has been noted above that the reaction is rather sensitive to the ionic strength. The ratio between k_6 at I = 0.3 M and k_6 at I = 0.1 M has been experimentally found to be 1.7. This value coincides with the value calculated with the equation $\text{Log } k = \text{Log } k° + Z_M Z_L \times 1.01[\sqrt{I}/(1 + \sqrt{I}) - BI]$ [9], where $Z_M Z_L = 12$ is the charge product and the empirical parameter B is set equal to 0.45. The value of B is somewhat higher than the usual value of 0.3 but it is reasonable in view of the high charges of the reaction partners [10].

The complexation of Co^{2+} by Me_2Octaen should present the ICB effect [11], according to which the reactivity of a metal ion toward polyamines should be higher than that calculated according to the Eigen criterion [12], that applies to systems reacting by the Id mechanism. We could evaluate the ICB effect displayed by the Co(II)-Me_2Octaen system by comparing the first-order rate constant, $k^*_{H_6L}$, for the conversion of the outer-sphere $Co(H_2O)_6H_6L^{8+}$ complex into the inner-sphere complex with the corresponding constant, $k^*_{NH_3}$, for the Co(II)-NH_3 system. Following the Diebler and Eigen argument [13], the second-order rate constant for the binding of Co^{2+} ion to H_6L^{6+} should be given by the relationship $k_6 = K_{os}k^*_{H_6L}$, where K_{os} is the stability constant of the outer sphere complex. By using the Eigen-Fuoss equation [14,15] one could estimate $K_{os} = 3.86 \times 10^{-5}\,M^{-1}$ for a distance between the charge centres of 5×10^{-8} cm. This leads to $k^*_{H_6L} = 1.35 \times 10^7\,s^{-1}$, whereas the value of $k^*_{NH_3}$ for the Co(II)-NH_3 system [16] is $3.7 \times 10^5\,s^{-1}$. Thus the observed

ICB effect is

$$k^{*}_{H_6L}/k^{*}_{NH_3} = 37 \qquad (8)$$

Note that this value does constitute a lower limit since it should be multiplied by a factor larger than unity which accounts for steric and statistical effects [17]. The ICB effect for the Ni(II)-Me_2Octaen system is 56 [5]. The closeness of this result to that of the present system suggests that both metals bind to Me_2Octaen with the same mechanism, a mechanism where the formation of the first M—N < bond is rate determining [5, 11].

MATERIALS AND METHODS

Materials

Me_2Octaen prepared according to the procedure described in Ref. [3d], was kindly furnished by Prof. P. Paoletti as hydrochloride salt. Its purity was checked by elemental, mass spectroscopy and NMR analysis. Cobalt perchlorate (Fluka, purum p.a.) was dissolved into doubly distilled water. The obtained stock solution was standardised using the cationic resin DOWEX50: the eluate solution was added to sodium carbonate in slight excess and the excess was titrated using HCl and bromocresol green as an indicator. All other chemicals were reagent-grade products and were used without further purification. Doubly distilled water was used to prepare the solutions and as a reaction medium.

Methods

All measurements have been performed at 298.1K. The course of the complex formation reaction was monitored at 230 nm using a stopped-flow apparatus devised and assembled in our laboratory. A Hi-Tech SF-61 mixing unit was coupled to a spectrophotometric line through two optical guides. The ultraviolet radiation produced by a 75 Watt Hg-Xe Hamamatsu "quiet" lamp was passed through a Bausch and Lomb 338875 high intensity monochromator and then split in two beams. The reference beam was sent directly to a 1P28 photomultiplier. The measuring beam was sent through an optical quartz guide to the observation chamber and then, through a second optical guide, to the measuring photomultiplier, also 1P28.

In order to prevent every possible effect of molecular oxygen on the signal, the reagent reservoirs were very carefully deareated, by flushing N_2 into them for more than 15 minutes. Because of the possibility of a little oxygen permeation into the apparatus in time, such a procedure has been repeated before every measurement.

The outputs of the two photomultipliers were balanced before each shot and the signal revealing the course of the reaction was sent to a Tektronix 2212 digital oscilloscope with a maximum sampling rate of 4000 data points in 200 microseconds and a minimum sampling rate of 4000 data points in 500 seconds. Finally, the acquired signal was transferred to a personal computer *via* a GPIB interface and analysed by a non-linear least square procedure expressly devised to fit multiexponential functions [18]. The time constants used in this work have been averaged over nine repeated experiments.

Current pH measurements were performed with a PHM 84 research pH-meter (Radiometer Copenhagen). A suitable calibration procedure [19] enabled us to convert the pH-meter output into hydrogen ion concentration.

The equilibrium protonation constants of Me_2Octaen and the stability constants for the complexation reactions with cobalt(II), at ionic strength 0.3 M $NaClO_4$, were determined by potentiometric measurements, by using a Crison Micro TT 2050 automatic titrating system equipped with a combined glass electrode. The reference electrode was an Ag/AgCl electrode in saturated NaCl solution. The glass electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with

CO_2-free NaOH solutions and determining the equivalent point by the Gran's method [20] which allows to determine the standard potential E°, and the ionic product of water ($pK_w = 13.73$ at 298.1 K in 0.3 M $NaClO_4$). Ligand concentrations [L] ranged from 0.4×10^{-3} M to 1.2×10^{-3} M and metal ion concentration [M] from 1×10^{-2} M to 0.7×10^{-3} M. The titration experiments were carried out in argon atmosphere. To evaluate the protonation constants three potentiometric titrations (about 100 data points each) performed in the pH range 2.5–10.5. The complexation stability constants were determined by six potentiometric titrations (about 50 data points each) carried out in the pH range 2.5–8 where the ligand to metal concentration ratio ranged from 1 to 0.2. The computer program HYPERQUAD [21] was used to calculate equilibrium constants from e.m.f. data. The titrations were processed either separately or after accumulation of the data points, without significant variation in the values of the equilibrium constants. The standard deviations of the logarithms of the equilibrium constants ranged between 0.01 and 0.08.

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