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Base Hydrolysis Kinetics of Cobalt(III) Spiro-Octaamine Dimer

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The preparation and characterisation of a cobalt (III) complex of octaaza ligand, 5, 5'-bis(4-amino-2-azabutyl)-1,9-diamino-3,7-diazanonane (octaam) is described. The base hydrolysis kinetics of bis cobalt(III) of octaam has been studied spectrophotometrically by the stopped-flow technique. A consequent reaction is observed in the base hydrolysis of the spiro-octaamine with the fast reaction having $k_{OH} = 3.55\ M^{-1}s^{-1}$ and the slower reaction $k_{OH} = 0.72\ M^{-1}s^{-1}$ at 298 K with $\Delta H^{\#} = 89$ kJ/mol for the fast stage and $\Delta H^{\#} = 102$ kJ/mol for the slow stage ($I = 0.4$ M $NaClO_4$). The fast reaction is assigned to the hydrolysis of the *trans* diaqua and the slower to further hydrolysis of the remaining Cl ions. The reaction appears to proceed predominantly by a D_{CB} (dissociative conjugate base) mechanism.

Introduction

The chemistry of binuclear metal complexes is a continuously growing field because of their relevance to the function of many metalloenzymes. Many examples of multidentate ligands capable of simultaneously complexing two metal ions have been reported[1−6]. Metal complexes with these kinds of ligands have also been used in recent years to study molecular recognition[7], the catalytic process[8] and the formation of dioxygen complexes[9]. Although there is a great deal of information available about the stability of mono- and binuclear complexes formed with polyaza ligands[10], relatively little is known about the kinetics of formation, decomposition and hydrolysis.

Experimental

Physical methods

Electronic spectra were recorded using a Hitachi 150-20 spectrophotometer. The IR spectra of the compounds dispersed in KBr discs were obtained on a Bio-Rad FT-IR 7 spectrometer. The NMR spectra were recorded

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using a JOEL FX90Q Fourier transform spectrometer with TMS as internal standard. ES-MS spectra were recorded using a VG Autospec-oa-TOF tandem high-resolution mass spectrometer and a Shimadzu QP5000 mass spectrometer (Figure 1).

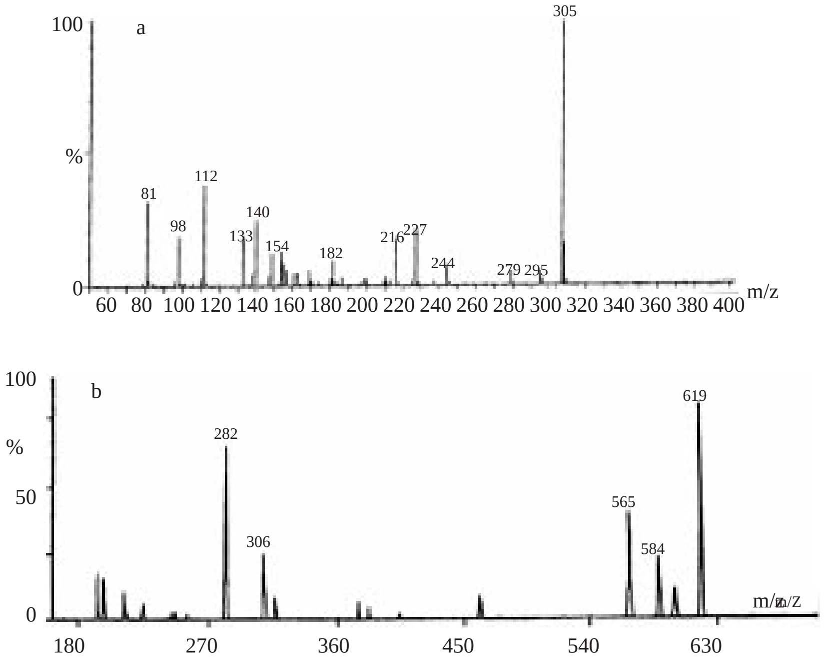


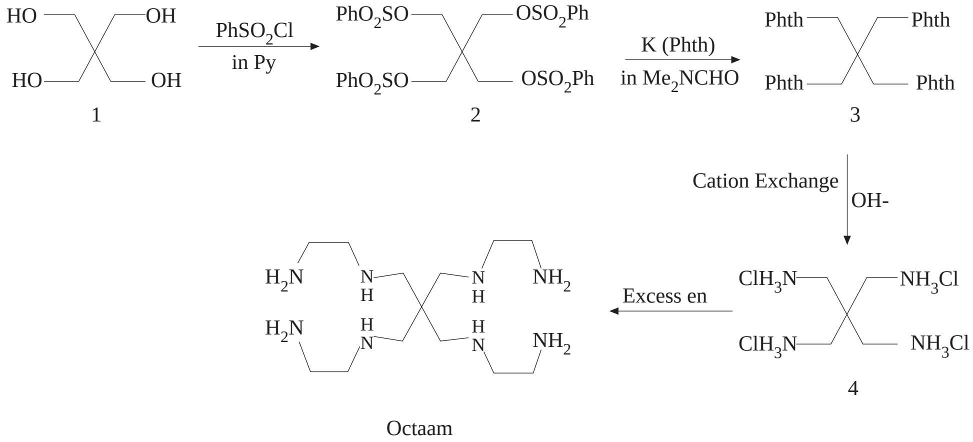
Figure 1. ES-MS spectra of the ligand (a) and complex (b)

Kinetics of base hydrolysis

Base hydrolysis kinetics were studied with an Applied Photophysics DX-17 stopped-flow spectrometer. The wavelength was selected from a preliminary spectral scanning experiment, 522 nm (peak appeared) and 617 nm (peak disappeared) and then at a number of wavelengths between 400 and 700 nm (multi wavelengths, step by step). Sodium hydroxide concentrations in the range 0.045-0.18 M were employed, with the ionic strength adjusted to 0.4 M with $NaClO_4$, and the complex concentration was 0.005 M. Temperature was controlled to within ± 0.1°C with a thermostatted circulating water-bath. Kinetic analysis employed the suit of programs provided with the instrument, including global analysis software developed for this machine. Rate constants of the base hydrolysis reactions were calculated by Glint global analysis software. Once the kinetic trace has been selected from one of the data buffers, it will be displayed on the screen and is ready for the analysis. Rate constants were calculated by non-linear curve fitting. The kinetics of base hydrolysis reactions were studied at four temperatures (20-35°C). Reported values of the rate constants correspond to the mean values for at least five values under each condition of base concentration and temperature. The deviation of observed rates between independent runs was always less than 5%. Data were analysed in terms of sequential reactions.

Preparation of octaam

The ligand, octaam was prepared by reacting benzenesulphonated pentaerythitrol[11] (prepared by the procedure of Herzog) and 1,2-diaminoethane (*en*) (Scheme). Benzene sulphonated pentaeryhirol (0.2 mol) and anhydrous 1,2-diaminoethane (4 mol) were dissolved in dry pyridine (500 mL) and heated under reflux for 48 h. Excess *en* was removed by rotary evaporation. The remaining yellow oil was diluted to 2 L with distilled water and acidified (pH 3, HCl), and sorbed onto a column (5 x 30 cm) of Dowex 50 W-X2 cation exchange resin (H^+ form). The column was washed with water, and then with 1 M HCl to remove diamine impurities. The octaam was eluted off with 4 M HCl. The octaam shows as a lighter-coloured band on the column. The collected eluent was evaporated to dryness on rotary evaporator. Solid octaam was redissolved in warm methanol and the product recrystallised. The white powder of octaam.8HCl was filtered off, washed with cold ether and dried under vacuum, yield 58%. Found(%): C, 25.66; H, 6.55; N, 18.91. $C_{13}H_{28}N_8 \cdot 8HCl$. Calc.(%): C, 25.55; H, 6.17; N,19.05. NMR and ES-MS data are given in Tables 3 and 4.



Scheme

Preparation of cobalt complex

Octaam.8HCl·3H_2O (0.01 mol) was dissolved in 200 mL water and to this solution $Co(ClO_4)_2 \cdot 6H_2O$ (0.02 mol) aqueous solution was added. The solution was aerated for 6 h. Some HCl and $NaClO_4$ were added to the solution and the solution turned green. This green solution was diluted to 1 L and sorbed onto a SP Sephedex C-25 cation exchange resin (Na^+ form). The green band was eluted with 0.25 M $NaClO_4$ and the eluate was reduced in volume by rotary evaporation. The dark green solution was left at room temperature for crystallisation. The green crystals were filtered off and washed with methanol and dried in a vacuum, yield 68%. Found: C, 19.17; H, 5.36; N, 13.65. $C_{13}H_{36}Cl_4N_8Co_2 \cdot 2ClO_4 . 3H_2O$ Calc: C, 19.11; H, 5.18; N, 13.88.

Results and Discussion

The UV-Vis data of the complex are summarised in Table 5. The spectra show two absorption maxima, which can be assigned to the transition $^1T_{1g} \leftarrow ^1A_{1g}$and $^1T_{2g} \leftarrow ^1A_{1g}$, commonly observed in Co(III) complexes of this type. The variation in the sixth ligand ($Cl^- \rightarrow OH^- \rightarrow H_2O$) causes a blue shift of maxima (λ_{max} 617 → 541 → 522 nm). Figure 2 shows the spectral changes following the stepwise aquation according to Equation 1. The kinetic of the base hydrolysis of Co (III) spiro-octaamine dimer can be described adequately and understood in terms of a SN1CB (conjugate base) mechanism with multi-dentate open-chain chelate ligands. The conjugate-base mechanism is described in detail by Tobe[12] and House[13]. The kinetics of the base hydrolysis of N_8-donor open-chain ligand with Cobalt(III) in water led to the two-stage reaction pattern. The initial fast second order intermediate formation is followed by product formation.

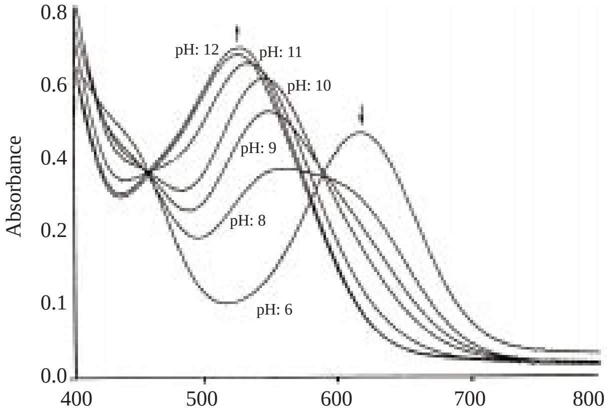


Figure 2. Spectral changes associated with the titration of the spiro-octaamine dimer Co(III) (5.0×10^{-3} M) with 0.090 M NaOH at 298 K and I = 0.4 M $NaClO_4$

$$\begin{array}{ccccc} & k_1(M^{-1}s^{-1}) & & k_2(M^{-1}s^{-1}) & \\ MLCl_4 + OH^- & \Leftrightarrow & [MLCl_2(H_2O)_2]int & \Leftrightarrow & ML(H_2O)_4 + 4Cl^-1 \\ & \text{fast (initial stage)} & & \text{slow (second stage)} & \end{array}$$

In each of the steps, a metal-bound chloride is successively replaced by a water molecule. In the first stage, the fast formation the of the *trans* aqua-chloride complex is preceded by a slow tetraaqua complex. After the fast stage the stereochemically and thermodynamically most stable *trans* complex formation probably plays a major role in the second slow stage. The magnitude of the rate constant k_1 was found to be three times faster than k_2 at 298 K (Table 1). Activation parameters of the base hydrolysis reaction have been determined for both fast and slow stages. The activation enthalpies and entropies are given in Table 2 for the fast and slow steps. As the base hydrolysis rate decreases for the second step activation enthalpy increases but activation entropy does not change. For both steps ΔS^* are large and positive. The latter effect is commonly observed for base hydrolysis reactions, which is appropriate for a dissociative-based isomerisation.

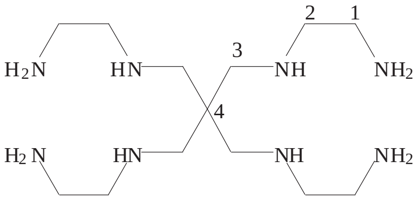
Table 1. Observed base hydrolysis rate constants for Co(III) spiro-octaamin dimer at 298 K.

[OH], M	0,045	0,090	0,18
k_1 ($M^{-1}s^{-1}$)	3.55	6.58	15.9
k_2 ($M^{-1}s^{-1}$)	0.72	2.06	4.42

Table 2. Activation parameters for the slow and fast base hydrolysis reactions of Co(III)-spiro-octaamin.

Slow reaction		Fast reaction	
$\Delta H^{\#}$ (kJ/mol)	102	$\Delta H^{\#}$(kJ/mol)	89
$\Delta S^{\#}$ (j/mol/K)	103	$\Delta S^{\#}$(j/mol.K)	72

Table 3. The ^{13}NMR data of octaam



δ (ppm)	Peak	Assignment
52.2	1	$-CH_2-NH_2$
46.8	2	$-NH-CH_2-$
44.8	3	$-CH_2-NH-$
38.5	4	Quart. C

Table 4. The ES-MS data of ligand and complex

Octaam: M^+: **305**		
$Co_2L|$: **564**.	$Co_2L.\ H(H_2O)|^+$: 583	$Co_2L.2H(H_2O)|^{+2}$: 292
$Co_2L.H|^+$: 565	$Co_2L.H(H_2O)_2|^+$: 601	$Co_2L.2H(H_2O)_2?^{+2}$: 301
$Co_2L.2H|^{+2}$: **282**	$Co_2L.H(H_2O)_3|^+$: **619**	$Co_2L.2H(H_2O)_3|^{+2}$: 310

Table 5. Visible absorption of the complex cation in aqueous solution at 298 K

Co_2LCl_4	617 (96) (λ_{max} nm, ε_{max} $M^{-1}cm^{-1}$)
$CoLCl_2$ $(H_2O)_2$	541 (81)
$CoL(H_2O)_4$	522 (130)

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