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Aminosulphonic Acid Complexes of Cobalt(III). Preparation and Base Hydrolysis of *cis*-chlorobis(1,2-diaminoethane)-amino-alkylsulphonatecobalt(III) Chlorides and a Comparison with the Hydrolysis Behaviour of Analogous Aminoalkylcarboxylate Complexes

PETER D. FORD and KEVIN B. NOLAN*

Department of Chemistry, University of Surrey, Guildford GU2 5XH, Surrey, U.K.

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The aminosulphonic acid complexes cis-$[Co(en)_2\{NH_2(CH_2)_n SO_3^-\}Cl]Cl$ *(n = 1, 2), have been prepared and their hydrolysis in basic solution have been investigated. The aminomethylsulphonate complex* (k_2 = *2053 ± 50* $dm^3\ mol^{-1}\ s^{-1}$, $\Delta H^{\ddagger}$ = *99 ± 2 kJ* mol^{-1}, $\Delta S^{\ddagger}$ = *151 ± 8 J* K^{-1} mol^{-1} *at 298.2 K) is 200-fold more reactive towards base hydrolysis than analogous complexes containing unsubstituted alkylamine or aminocarboxylic acid ligands, a result which has been interpreted in terms of the relative ease of formation of the aminomethylsulphonate conjugate base complex. The sulphonate groups in both cases are ineffective in competing with water for the vacant coordination site in the five coordinate conjugate base intermediate* $[Co(en)_2\{NH(CH_2)_n SO_3^-\}]^+$. *This situation contrasts with that of the carboxylate group in the analogous glycinate complex which in base hydrolysis at pH > 10 yields a product mixture 46% of which is the chelated glycinate complex* $[Co(en)_2NH_2CH_2CO_2]^{2+}$. *Competition by carboxylate is negligible in the longer chain aminocarboxylate complexes.*

Introduction

The reaction between *trans*-$[Co(en)_2Cl_2]^+$ (en = 1,2-diaminoethane) and primary amines [1], provides a convenient route to the products *cis*-$[Co(en)_2(RNH_2)Cl]^{2+}$. As a result a wealth of kinetic data has accumulated for hydrolysis of such complexes [2]. Rate constants for base hydrolysis of straight chain alkylamine complexes are generally around 7–13 $dm^3\ mol^{-1}\ s^{-1}$ (298.2 K) while branching at the α position causes rate enhancement (R = $-CH(CH_3)_2$, k_2 = 52 $dm^3\ mol^{-1}\ s^{-1}$) due to steric acceleration [3], (in the analogous bromo complex where steric effects should be even more pronounced a 9-fold rate enhancement is observed as a result of chain branching [4]).

In the case of aromatic primary amine complexes rate constants for base hydrolysis are much larger and lie in the range 2.6×10^4 (R = $-C_6H_5$)–6.6×10^4 (R = p-$CH_3C_6H_4-$) at 298.2 K [5]. The enhanced reactivity of these species is due to the presence of the relatively acidic aniline or aniline-derived ligands and the consequent relative ease of formation of analido (compared to aliphatic amido) conjugate bases (large K_a in the base hydrolysis rate expression, rate = $K_a k_{cb}$[complex][OH^-] [6]). For a similar reason the chloropentamine species *cis*-$[Co(en)_2(NH_2CH_2SO_3^-)Cl]^+$ should be much more reactive in base hydrolysis than unsubstituted aliphatic chloropentamine complexes in view of the expected increase in acidity of the monodentate amine ligand containing the sulphonate group. We have prepared this complex and its aminoethylsulphonate analogue and have studied the kinetics of base hydrolysis of both complexes to see if the predicted rate enhancement occurs. We have also compared the product distribution resulting from these reactions with those formed in base hydrolysis of the corresponding aminocarboxylate complexes.

Experimental

The complexes *cis*-$[Co(en)_2\{NH_2(CH_2)_n SO_3^-\}Cl]^+$ (n = 1, 2) were prepared as follows. An aqueous paste containing equimolar amounts (0.01 mol) of *trans*-$[Co(en)_2Cl_2]Cl$ and the appropriate aminoalkylsulphonic acid (Aldrich Ltd.) was treated dropwise with diethylamine (0.01 mol) whereupon a colour change from green to purple occurred. The resulting paste was treated with methanol and the precipitate thereby obtained was recrystallised from a minimum volume of dilute HCl. *Anal.* Calcd. for the aminomethylsulphonate complex $CoC_5H_{20}N_5Cl_2O_3S$: C, 16.7; H, 5.6; N, 19.4%. Found: C, 16.5; H, 5.7;

*Author to whom correspondence should be addressed.

TABLE I. Electronic Solution Spectra for: (a) the Complexes *cis*-$[Co(en)_2\{NH_2(CH_2)_nSO_3^-\}Cl]^+$, (b) the Hydroxo Products of Base Hydrolysis and (c) the Aqua Complexes resulting from Acidification of (b).

	n	λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})			
(a)	1	521	(80.5)	369	(85.2)
	2	526	(77.5)	368	(84.8)
(b)	1	503	(89.3)	361	(114.4)
	2	503	(89.8)	370	(83.2)
(c)	1	490	(73.1)	352	(74.6)
	2	490	(69.7)	352	(69.1)

N, 18.8%. *Anal.* Calcd. for the aminoethylsulphonate complex $CoC_6H_{22}N_5Cl_2O_3S$ (+1.0 H_2O): C, 18.4; H, 6.2; N, 17.9%. Found: C, 18.5; H, 6.1; N, 17.8%. Near UV–visible spectra of the complexes were recorded on Pye Unicam SP 8-100 and 3000 (molar absorption coefficients) spectrophotometers. Kinetics of base hydrolysis of the complex *cis*-$[Co(en)_2(NH_2CH_2SO_3^-)Cl]^+$ were investigated spectrophotometrically on the former instrument. Kinetics of base hydrolysis of the aminoethylsulphonate complex were followed by the pH-stat method using a Radiometer pH Meter 26, linked to a Titrator 11, with alkali being added from an ABU 12 autoburette and monitored against time on a Titrigraph.

Results and Discussion

Although the reaction between *trans*-$[Co(en)_2Cl_2]^+$ and primary amines almost invariably yields *cis*-$[Co(en)_2(RNH_2)Cl]^{2+}$ products, the existence of other nucleophilic groups in the amine molecule offers the possibility of alternative reactions. Thus with aminocarboxylic acids under near neutral conditions ($^+NH_3$–$(CH_2)_n$–CO_2^-) the carboxylate group is the entering nucleophile while at higher pH (NH_2–$(CH_2)_n$–CO_2^-) a reaction typical of ordinary primary amines occurs [7]. A similar scheme leading to O-bonded or N-bonded products is possible for the reaction between *trans*-$[Co(en)_2Cl_2]^+$ and aminosulphonic acids. Previous reports on aminosulphonic acid complexes are mainly concerned with those of the sulphamadate ligand, $NH_2SO_3^-$. The N-bonded complex $[Co(NH_3)_5NH_2SO_3]^{2+}$ was found to equilibrate with its O-bonded linkage isomer $[Co(NH_3)_5NH_2SO_3]^{2+}$ prior to hydrolysis [8]. Linkage isomers of this ligand with Cu^{II} have been isolated [9], while sulphamadate complexes of the platinum metals appear to be exclusively N-bonded [10]. The only report on aminoethylsulphonate complexes deals with the determination of their formation constants in aqueous solution [11], while only Cu^{II} and Cr^{III} complexes of aminomethylsulphonate have so far been reported [9].

In our investigations we observed no reaction between the sulphamadate ion ($NH_2SO_3^-$) and *trans*-$[Co(en)_2Cl_2]^+$, presumably because the nucleophilicity of the amino group towards this substrate is lowered excessively by the SO_3^- substituent (the basicity of $NH_2SO_3^-$ is lowered 10^9 fold relative to NH_3 [12]).

In contrast to the behaviour of the corresponding aminocarboxylic acids we found that the sulphonate groups of aminoalkylsulphonic acids are non nucleophilic towards *trans*-$[Co(en)_2Cl_2]^+$ (no reaction between $^+NH_3$–$(CH_2)_n$–SO_3^- and the complex in near neutral media), although this is not entirely surprising in view of the much weaker basicity of the sulphonate group relative to the carboxylate group (*e.g.* $^+NH_3(CH_2)_2SO_3H$, pK_{a1} = 1.5; $^+NH_3(CH_2)_2CO_2H$, pK_{a1} = 3.61 [13]).

The purple products obtained after the addition of diethylamine to the *trans*-$[Co(en)_2Cl_2]^+$–aminoalkylsulphonic acid mixtures have all the characteristics expected for the pentamines *cis*-$[Co(en)_2\{NH_2(CH_2)_nSO_3^-\}Cl]^+$. The near UV visible spectra of the complexes (Table I) exhibit two bands, the lower energy one of which in each case has a λ_{max} typical of $Co^{III}N_5Cl$ chromophores [1]. The molar absorption coefficients of these bands are indicative of *cis* configurations.

In aqueous alkaline solution the complexes undergo base hydrolysis with Cl^- as the leaving group. The products of base hydrolysis are the corresponding hydroxopentamines and in neither case was the chelated aminoalkylsulphonate complex observed. To test for chelation a solution of each complex was allowed to undergo complete base hydrolysis at constant pH on a pH-stat instrument (n = 1, pH 8.60; n = 2, pH 9.60). In both cases exactly one mole of base per mole of complex was consumed (a chelation reaction would not involve base consumption) and the product-containing solutions in a titration with acid consumed one mole of titrant per mole of complex around pH 6 (the expected pK_a of an aquo ligand in a $Co^{III}N_5OH_2$ complex). For the aquoaminomethylsulphonate complex the mixed pK_a value [14] is 5.96 ± 0.03 while for the aquo-aminoethylsulphonate complex pK_a = 6.02 ± 0.03, both at 298.2 K, ionic strength 0.1 mol dm^{-3} ($NaClO_4$). Spectral data for the products of base hydrolysis and their aquoconjugate acids are given in Table I. The spectra suggest that the products of base hydrolysis are mainly *cis*-hydroxo complexes [1]. Despite using a variety of column chromatographic techniques and eluting agents we were unable to separate and estimate the contribution, if any, of *trans*-hydroxo complexes to the base hydrolysis mixtures (or *trans*-aquo complexes to acidified base hydrolysis mixtures).

TABLE II. Rate Data for Base Hydrolysis of the Complexes *cis*-$[Co(en)_2\{NH_2-(CH_2)_n-SO_3^-\}Cl]^+$ at Various Temperatures and Ionic Strength 0.1 mol dm^{-3} ($NaClO_4$).

n	T/K	pH (k_2/dm^3 mol^{-1} s^{-1})	
1	288.2	7.165(494)	7.500(488)
		7.860(510)	8.230(504)
	298.2	7.150(2026)	7.550(2004)
		7.830(2079)	8.250(2101)
	308.2	7.160(8065)	7.500(7686)
		7.850(7981)	8.230(7629)
2	298.2	9.155(30.3)	9.415(314)
		9.650(29.7)	
	308.2	8.400(112)	8.885(105)
		9.405(108)	
	318.2	7.925(361)	8.290(348)
		8.795(352)	

We have examined the extent of chelation in base hydrolysis of a series of aminocarboxylate complexes *cis*-$[Co(en)_2Cl\{NH_2-(CH_2)_n-CO_2^-\}]^+$also by monitoring volumes of alkali consumed at constant pH, for comparative purposes. For n = 1 the product mixture is 46% chelated glycinate $[Co(en)_2NH_2-CH_2-CO_2]^{2+}$, 54% hydroxoglycinate complexes $[Co(en)_2(NH_2-CH_2-CO_2^-)OH]^+$ (pH > 10). Base hydrolysis of the β-alaninate (n = 2), γ-aminobutyrate (n = 3) and ε-aminohexanoate (n = 5) complexes above pH 10 proceed without chelation. These results demonstrate the ability of the carboxylate group (in the glycinate complex) relative to the sulphonate group to compete with H_2O for the vacant coordination site of the five coordinate intermediate produced in base hydrolysis of Co^{III} complexes. The contrasting behaviour of glycinate and the other aminocarboxylate ligands is a consequence of the greater ease of formation of five over larger membered rings.

The kinetics of base hydrolysis of the aminoethylsulphonate complex was followed by the pH-stat method over the temperature range 298.2–318.2 K, and the pH range 7.925–9.650 at ionic strength 0.1 mol dm^{-3} $NaClO_4$. Complex concentrations were 5×10^{-3} mol dm^{-3} (40 cm^3) in all experiments and the titrant (NaOH) concentration was 0.1 mol dm^{-3}. The complex *cis*-$[Co(en)_2(NH_2CH_2SO_3^-)Cl]^+$ was not soluble at this concentration and we found that its base hydrolysis was more conveniently followed spectrophotometrically. Microlitre quantities of a stock solution of complex was added to a solution of 'HEPES' (N-2-hydroxyethylpiperazine-N'-2-ethanesulphonic acid, pK_a = 7.55 at 20 °C [15]) buffer contained in a 4 cm cell and equilibrated to the reaction temperature in the thermostatted cell compartment of the spectrophotometer. The solution also contained $NaClO_4$ (0.1 mol dm^{-3}) to ensure constant ionic strength during the reaction. Before the addition of complex the pH of the solution had been adjusted to the desired value by the addition of NaOH or $HClO_4$ solution as required. The total concentration of acidic and basic forms of the buffer was 0.01 mol dm^{-3}, the final concentration of complex in the reaction solution was about 0.001 mol dm^{-3} and the reaction was followed by monitoring the absorbance increase at 500 nm on the 0–0.05 scale (backed off) of an SP8-100 spectrophotometer. The pH of the solutions were measured before and after base hydrolysis and in no case was a pH drop greater than 0.02 observed. Reactions were investigated over the temperature range 288.2–308.2 K and the pH range 7.165–8.250.

Values of k_2 (k_{obs})/[OH^-]) at each pH and temperature investigated are listed in Table II. For the aminomethylsulphonate complex at 298.2 K, k_2 = 2053 ± 50 dm^3 mol^{-1} s^{-1}, $\Delta H^{\ddagger}$ = 99 ± 2 kJ mol^{-1}, $\Delta S^{\ddagger}$ = 151 ± 8 J K^{-1} mol^{-1}. For the aminoethylsulphonate complex at the same temperature k_2 = 30.4 ± 1.0 dm^3 mol^{-1} s^{-1}, $\Delta H^{\ddagger}$ = 94 ± 2 kJ mol^{-1}, $\Delta S^{\ddagger}$ = 99 ± 8 J K^{-1} mol^{-1}. The former complex is some 200 fold more reactive than unsubstituted alkylamine complexes towards base hydrolysis, while the latter complex exhibits only twice the normal reactivity. These results may be explained in terms of the S_NICB mechanism for base hydrolysis.

Since the acid $^+NH_3-CH_2-SO_3^-$ is some 10^5 fold more acidic than unsubstituted aliphatic ammonium ions (*e.g.* $^+NH_3CH_3$) [13] it may be assumed that $NH_2-CH_2-SO_3^-$ coordinated to Co^{III} would be more acidic by the same order of magnitude than similarly coordinated unsubstituted aliphatic amines. This results in higher equilibrium labile amido conjugate base concentrations (increased K_a in the rate expression rate = K_{cb}[complex][OH^-]). With chain lengthening the influence of the SO_3^- group on the acidity of the amine ligand is diminished and this is reflected in a decreased reactivity towards base hydrolysis. A similar reasoning has been used to explain the high reactivity towards base hydrolysis of cobalt(III) complexes containing aniline ligands.

Second order rate constants and activation parameters for the base hydrolysis of the aminocarboxylate complexes (also determined by the pH-stat method) are presented in Table III. In view of the much weaker acidity of $^+NH_3-(CH_2)-CO_2^-$ and its higher homologues relative to $^+NH_3-CH_2-SO_3^-$ [13] a similar reasoning may be applied to explain the more rapid base hydrolysis of the aminosulphonate complexes over the analogous aminocarboxylate complexes.

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TABLE III. Rate Data and Activation Parameters for Base Hydrolysis of *cis*-$[Co(en)_2\{NH_2-(CH_2)_n-CO_2^-\}Cl]^+$ Complexes* at Various Temperatures and Ionic Strength 0.1 mol dm^{-3} ($NaClO_4$).

n	T/K	pH, (k_2/dm^3 mol^{-1} s^{-1})		
1	298.2	9.78(14.7),	10.27(14.6),	10.76(14.3)
	308.2	9.35(53.9),	10.18(53.0),	9.95(52.9)
	318.2	8.64(192),	9.44(198),	9.51(194)
$\Delta H^{\ddagger}_{298.2}$ = 100 ± 2 kJ mol^{-1}, $\Delta S^{\ddagger}_{298.2}$ = 113 ± 8 J K^{-1} mol^{-1}				
2	298.2	9.82(10.8),	10.26(11.0),	10.76(10.6)
	308.2	9.42(38.3),	9.92(37.7),	10.23(39.2)
	318.2	9.19(135),	9.64(141),	9.80(143)
$\Delta H^{\ddagger}_{298.2}$ = 98.3 ± 2.2 kJ mol^{-1}, $\Delta S^{\ddagger}_{298.2}$ = 105 ± 8 J K^{-1} mol^{-1}				
3	298.2	9.75(9.06),	10.25(8.07),	10.74(10.0)
	308.2	9.24(32.0),	9.98(34.3),	10.25(30.0)
	318.2	9.25(110),	9.75(117),	
$\Delta H^{\ddagger}_{298.2}$ = 97.3 ± 2.2 kJ mol^{-1}, $\Delta H^{\ddagger}_{298.2}$ = 100 ± 8 J K^{-1} mol^{-1}				
5	298.2	9.98(7.56),	10.35(8.16),	10.75(7.93)
	308.2	9.64(28.7),	10.05(27.7),	10.44(27.9)
	318.2	9.04(103),	9.34(97.2),	10.05(100)
$\Delta H^{\ddagger}_{298.2}$ = 97.6 ± 2.2 kJ mol^{-1}, $\Delta S^{\ddagger}_{298.2}$ = 102 ± 8 J K^{-1} mol^{-1}				

*Analytically pure samples of these complexes were prepared by the method of Alexander and Busch [16].

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