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Kinetics & Mechanism of Hydrolysis of *cis*-(Bromo)bis(ethylenediamine)(2-aminothiazole)cobalt(III) Cation

A. C. DASH*
Department of Chemistry, Utkal University, Bhubaneswar 751004
and
S. K. MOHAPATRA
Department of Chemistry, Regional College of Education, Bhubaneswar 751006

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The kinetics of aquation of *cis*-(bromo)(2-aminothiazole)bis(ethylenediamine)cobalt(III) cation have been investigated at 30-50° in $HClO_4$ and acetate buffer media of $I = 0{\cdot}3$ mol dm^{-3}. The rate of aquation obeys the rate law $-d \ln [\text{Complex}]_T/dt = k_1 + k_2 K_{NH}/[H^+] + k'_3 [MeCO_2^-]$ where k_1 and k_2 are the rate constant for *cis*-$[CoBr(NH_2tz)(en)_2]^{2+}$ and its amido conjugate base respectively; K_{NH} is the dissociation constant of the amine proton (believed to be that of coordinated NH_2tz) and k'_3 is a constant characterizing the acetate ion catalysed path. The values of k_1, k_2K_{NH} and k'_3 at 45° are $(2{\cdot}95 \pm 0{\cdot}04) \times 10^{-4}$ sec^{-1}, $(5{\cdot}18 \pm 0{\cdot}15) \times 10^{-9}$ mol dm^{-3} sec^{-1} and $(4{\cdot}75 \pm 0{\cdot}25) \times 10^{-4}$ dm^3 mol^{-1} sec^{-1} respectively. Solvent assistance is invoked in the k_1 path. The activation parameters indicate that the mechanism is essentially dissociative for all the three paths. From the activation entropy data, the transition states in the k_1 and k'_3 paths are believed to be tetragonal in nature. Trigonal bipyramidal transition state appears to be more likely in the k_2 path.

EXTENSIVE investigations have been carried out on the kinetics of substitution reactions of octahedral cobalt(III) complexes of the type *cis*-$[CoXL(en)_2]^{2+}$ where en represents ethylenediamine, L is a monodentate non-replaceable amine ligand and X stands for Cl or Br[1]. We have been interested in the study of the kinetics and mechanism of substitution reactions of the complexes of the type mentioned above with L as a weakly basic amine ligand. Our aim is to (i) examine the acid ionization of the NH group of the coordinated amine, and (ii) assess the factors governing the rates and mechanism of substitution reactions of such complexes as well as their conjugate bases. We report in this paper the synthesis and kinetics of hydrolysis of *cis*-(bromo)bis(ethylenediamine)(NH_2tz)cobalt(III) ion (NH_2tz = 2-aminothiazole). The results obtained have been compared with similar data for certain other weakly basic amine complexes of the type *cis*-$[CoBr(\text{amine})(en)_2]^{2+}$.

Materials and Methods

The bromo-bis(ethylenediamine)(2-aminothiazole)-cobalt(III) bromide was prepared by the method of Bailar and Clapp[2]. The complex was recrystallized at 0° as the perchlorate salt from aqueous solution acidified with perchloric acid using saturated sodium perchlorate solution as the precipitant. The complex was washed successively with ice-cold water, ethanol, diethyl ether and then stored over fused calcium chloride in a desiccator painted black {Found: Co, 10·26; Br, 14·45 $[CoBr(C_3N_2SH_4)(en)_2](ClO_4)_2$ requires Co, 10·55; Br, 14·32%}. The corresponding chloro complex could not be prepared with high degree of purity by this method.

2-Aminothiazole (Koch Light) was used without further purification. Sodium perchlorate used for ionic strength adjustment was Riedel's reagent grade sample. All other chemicals were Analar grade. Copper(II) and mercury(II) perchlorate solutions were prepared by dissolving the metal(II) oxides in excess of perchloric acid. Copper(II) was estimated iodometrically and mercury(II) by EDTA titration. Back titration procedure using standard Zn(II) solution and Erio T indicator was adopted for Hg(II) estimation[3]. The free acid contents of the metal perchlorate solutions were estimated by a combined procedure involving cation exchange and acidimetry. The alkali was standardized against potassium hydrogen phthalate. All ion-exchange experiments were performed with Dowex 50-WX-8 resin in acid form. All solutions were prepared in freshly distilled water.

Infrared spectra (nujol) were recorded with a Perkin-Elmer 337 spectrophotometer. The electronic spectra were obtained with a Beckman DU2 spectrophotometer using 1 cm quartz cells. All numerical calculations were performed on an IBM 1130 computer.

Kinetic measurements — Rate measurements were made at 35-50° in perchlorate medium of $I = 0{\cdot}3$ mol dm^{-3}. The concentration of the complex was $(2\text{-}3) \times 10^{-3}$ mol dm^{-3}. The reaction mixtures of appropriate composition (see Tables 1 and 2) were prepared in 50 ml measuring flasks and thermostated to ±0·1°. The reaction mixture (5 ml) was withdrawn at convenient time intervals; the aquo product and the unreacted bromo complex were removed by Dowex 50-WX8 resin in acid form and then the liberated bromide estimated potentiometrically using silver nitrate (0·01 mol dm^{-3}). The pseudo-first-order rate constants (k_{obs}) were calculated from the gradients of the least squares best line plots of ln ($V_\infty - V_t$) against time where V_t and V_∞ stand for the titre values at time t and infinity (i.e. for complete release of bromide) respectively. k_{obs} was weighted inversely as its variance while calculating its average from replicate runs.

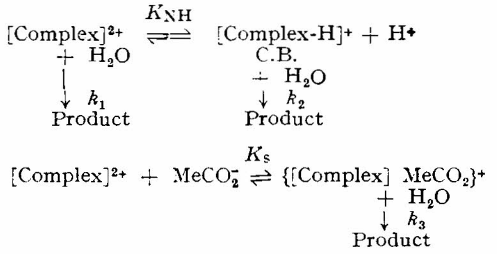
Results

[CoBr(NH$_2$tz)(en)$_2$]$^{2+}$ has the absorption maximum at 525 nm with molar absorption coefficient of 93·0 dm^3 mol^{-1} cm^{-1} in 0·1 mol dm^{-3} HClO$_4$ medium which compares satisfactorily with the position and intensity of $1A_{1g} \rightarrow 1T_{1g}$ transition of several *cis*-halo-(amine)-bis(ethylenediamine)cobalt(III) complexes[4]. The second ligand field band due to $^1A_1 \rightarrow {}^1T_{2g}$ transition is, however, masked by the charge transfer spectrum of the bromo complex at 300-400 nm. The UV spectra [λ_{max}, nm (ϵ_1 dm^3 mol^{-1}cm^{-1}): 250 (15530) in 0·1 mol dm^{-3} HClO$_4$ medium] indicate the coordinated 2-aminothiazole[5]. Recently House *et al.*[6] have shown that the chloro(amine)-bis(ethylenediamine)cobalt(III) complexes obtained from Bailer and Clapp's preparations have the *cis*-configuration. Considering the method of preparation and the visible spectral data it is reasonable to assign *cis*-configuration to [CoBr(NH$_2$tz)(en)$_2$]$^{2+}$. Singh and Shukla[7] from the consideration of the lowering of the asymmetric νNH of NH$_2$tz from 3400 to 3310 cm^{-1} concluded that 2-aminothiazole coordinates to Sn(IV) through the primary amino group. The IR spectrum of [CoBr(NH$_2$ tz)(en)$_2$]$^{2+}$ exhibits bands at 3360, 3275 and 3240 cm^{-1} indicating lowering of asymmetric νNH of 2-aminothiazole on coordination to cobalt(III). Bands at 1600, 1560 and 1525 with shoulders at 1555, 1480 and 1350 cm^{-1} are observed. Apparently the asymmetric νNH$_2$ is lowered and the stretching frequency of the thiazole ring is not raised up as NH$_2$tz coordinates to cobalt(III). It is, therefore, most likely that the NH$_2$tz is bound to cobalt(III) by the primary amine function[8].

We attempted to study the protonation of the ring nitrogen of the coordinated NH$_2$tz spectrophotometrically at 25° and $I = 0·3$ mol dm^{-3}. The UV spectrum of *cis*-[CoBr(NH$_2$tz)(en)$_2$]$^{2+}$ (240-260 nm) was found to be virtually acid independent in the range of [H$^+$] = 0·001-0·3 mol dm^{-3} suggesting thereby that the complex does not undergo protonation to detectable extent in the range of [H$^+$] investigated.

Aquation — Both the ligand field bands are observed for the [Co(NH$_2$tz)(en)$_2$(OH$_2$)]$^{3+}$ generated by the spontaneous aquation of the bromo complex in 0·1 mol dm^{-3} HClO$_4$ medium at 60° [λ_{max}, nm (ϵ_{max}, dm^3 mol^{-1} cm^{-1}): 486 (77·0); 338 (148)]. Our attempt to generate the aquo complex by Hg(II)-catalysed aquation of the bromo complex and check its spectral data quoted above was unsuccessful as a pale yellow precipitate gradually developed on adding Hg(ClO$_4$)$_2$ to the solution of the bromo complex. The observed spectral shift due to the aquation of the bromo complex is in accordance with the spectrochemical order of OH$_2$ and Br[9].

Table 1 presents the rate data at 45° for the aquation of *cis*-[CoBr(NH$_2$tz)(en)$_2$]$^{2+}$ studied in HClO$_4$ and acetate buffer media of $I = 0·3$ mol dm^{-3}. It is evident that the pseudo-first-order rate constant (k_{obs}) virtually levels off to a constant value at [H$^+$] = 0·001 mol dm^{-3}. The plots of k_{obs} against [H$^+$]$^{-1}$ at constant [MeCO$_2^-$] and k_{obs}, against [MeCO$_2^-$] at constant [H$^+$] are linear with positive gradients. The inverse acid dependence of k_{obs} is reconciled with the formation of a reactive conjugate base (C.B.) presumably [CoBr(NHtz)(en)$_2$]$^+$. Catalysis of aquation of the bromo complex by acetate ion may be attributed to the formation of a reactive ion-pair, {[CoBr(NH$_2$tz)(en)$_2$]MeCO$_2$)}$^+$. The various steps involved in the aquation may be delineated as shown in Scheme 1.



$$\begin{array}{ccc} [\text{Complex}]^{2+} & \overset{K_{NH}}{\rightleftharpoons} & [\text{Complex-H}]^{+} + \text{H}^{+} \\ + \text{H}_2\text{O} & & \text{C.B.} \\ & & + \text{H}_2\text{O} \\ \downarrow k_1 & & \downarrow k_2 \\ \text{Product} & & \text{Product} \end{array}$$

$$\begin{array}{c} [\text{Complex}]^{2+} + \text{MeCO}_2^- \overset{K_s}{\rightleftharpoons} \{[\text{Complex}]\ \text{MeCO}_2\}^{+} \\ + \text{H}_2\text{O} \\ \downarrow k_3 \\ \text{Product} \end{array}$$

Scheme 1

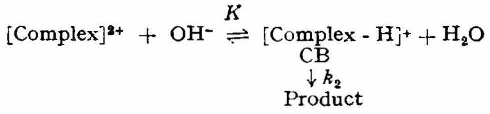
Consistent with this mechanism, the rate law of aquation takes the form (1)

$$-d\ \ln[\text{Complex}]_{T/dt} = k_{obs} = \frac{k_1 + k_2K_{NH}/[\text{H}^+] + k_3K_s[\text{MeCO}_2^-]}{1 + K_{NH}/[\text{H}^+] + K_s[\text{MeCO}_2^-]} \quad \ldots(1)$$

where k_1, k_2, k_3 stand for the rate constant for *cis*-[CoBr(NH$_2$tz)(en)$_2$]$^{2+}$, its conjugate base and its acetate ion pair respectively; K_{NH} is the N-H dissociation constant of the complex and K_s is the formation constant of its acetate ion-pair. Eq. (1) reduces to Eq. (2) if $K_{NH}/[\text{H}^+] + K_s[\text{MeCO}_2^-] \ll 1$ and k_3K_s is taken to be k_3'

$$k_{obs} = k_1 + k_2K_{NH}/[\text{H}^+] + k_3'[\text{MeCO}_2^-] \quad \ldots(2)$$

Eq. (2) is in accord with the observed dependence of k_{obs} on [H$^+$]$^{-1}$ and [MeCO$_2^-$] as mentioned earlier. An alternative interpretation may also be given to the conjugate base path as shown in Scheme 2



$$\begin{array}{c} [\text{Complex}]^{2+} + \text{OH}^- \overset{K}{\rightleftharpoons} [\text{Complex - H}]^{+} + \text{H}_2\text{O} \\ \text{CB} \\ \downarrow k_2 \\ \text{Product} \end{array}$$

Scheme 2

where K stands for the equilibrium constant of formation of the conjugate base as stated above. But this is kinetically equivalent to the proton dissociation scheme mentioned earlier as it can be shown that $K_{NH} = KK_w$ where K_w is the ionic product of water. Apparently the mode of representation of the conjugate base equilibrium is ambiguous. This is however, of little importance in the present context due to the kinetic equivalence of both the schemes and as we are concerned with the rate of aquation and equilibrium constant of formation of the conjugate base.

The rate data in Table 1 were fitted to Eq. (2) by means of a computer programme which

TABLE 1 — RATE DATA FOR AQUATION OF *cis*-$[CoBr(NH_2tz)(en)_2]^{2+}$ IN PERCHLORIC ACID AND ACETATE BUFFER MEDIA OF $I = 0{\cdot}3$ mol dm^{-3} AT 45°C

$[HClO_4]$ mol dm^{-3}	10^4kobs.* sec^{-1}	$[MeCO_2^-]$ mol dm^{-3}	$10^5[H^+]$ mol dm^{-3}	10^4kobs.* sec^{-1}
0·001	3·20 ± 0·10	0·01	30·1	3·32 ± 0·24
0·002	3·09 ± 0·11	0·08	7·52	4·13 ± 0·06
0·005	2·81 ± 0·12	0·05	6·02	4·21 ± 0·08
0·01	2·79 ± 0·09	0·10	6·02	4·50 ± 0·15
0·02	2·92 ± 0·04	0·10	4·51	4·58 ± 0·09
0·05	3·01 ± 0·10	0·15	4·01	5·31 ± 0·23
0·10	2·82 ± 0·07	0·01	3·01	5·17 ± 0·11
0·20	2·79 ± 0·07	0·02	3·01	5·24 ± 0·21
0·30	2·81 ± 0·08	0·05	3·01	5·22 ± 0·18
		0·10	3·01	5·32 ± 0·25
		0·15	3·01	5·49 ± 0·25
		0·25	3·01	5·86 ± 0·10
		0·10	1·50	6·71 ± 0·22
		0·25	1·20	8·31 ± 0·08
		0·15	1·00	8·57 ± 0·23
		0·25	0·602	12·9 ± 0·2
		0·10	0·301	19·3 ± 0·6

*Average of at least duplicate runs.

floated the values of k_1, k_2K_{NH}, k'_3 and minimized $\sum_{i=1}^{n} w_i(k_{cal\,i}-k_{obs\,i})^2$. The reciprocal of the variance of k_{obs} was taken to be the weighting factor. The values of k_1, k_2K_{NH}, and k'_3 used as inputs were obtained from the graphical plots mentioned earlier. The least squares best values of these parameters at different temperatures are given in Table 2.

The effect of Cu(II) on the rate of aquation of the complex was examined at 35° and $I = 0{\cdot}3$ mol dm^{-3}. With $[H^+]_T = 0{\cdot}01$ and $[Cu^{2+}] = 0{\cdot}02$, 0·04, 0·06 mol dm^{-3}, we obtained $k_{obs} = (0{\cdot}86 \pm 0{\cdot}01) \times 10^{-4}$ sec^{-1} which agree satisfactorily with the value of k_{obs} at $[Cu^{2+}] = 0$, $[H^+]_T = 0{\cdot}01$ mol dm^{-3} (see Table 2). Thus evidence for the association of Cu^{2+} with the thiazole ring leading to metal ion catalysed aquation of $[CoBr(NH_2tz)(en)_2]^{2+}$ is lacking.

TABLE 2 — PARAMETERS OF EQ. (2)

Temp. °C	$10^4\,k_1$ Sec^{-1}	$10^9\,k_2K_{NH}$ mol dm^{-3} sec^{-1}	$10^4\,k'_3$ dm^3 mol^{-1} sec^{-1}
35	0·89 ± 0·01	0·74 ± 0·02	1·4 ± 0·1
40	1·68 ± 0·02	2·1 ± 0·1	2·8 ± 0·2
45	2·95 ± 0·04	5·2 ± 0·2	4·8 ± 0·3
50	4·79 ± 0·10		

Discussion

Table 3 presents the kinetic data for the aquation of several *cis*-bromo-(amine)-bis(ethylenediamine)-cobalt(III) complexes derived from weakly basic amines[10,11]. The kinetic patterns of such complexes are alike. Differences in their substitutional labilities, which are controlled by both enthalpy and entropy of activation, are evident. The acid independent rate constants at 50° (see Table 3) indicate that the 2-aminothiazole complex is 9 and 15 times more reactive than its imidazole and aniline counterparts respectively. This reactivity difference cannot be rationalized in terms of the steric influence of the vicinal amine ligand on the departing bromide. $\Delta S^\ddagger$ values being either low positive or negative the transition state of the k_1 path of aquation of aniline, imidazole and 2-aminothiazole complexes appears to be essentially dissociative in nature involving a tetragonal pyramidal configuration[12]. The dissociative activation for the 2-aminothiazole complex is also supported by the observed acetate ion catalysis; strikingly the temperature dependence of k'_3 gave $\Delta H^\ddagger = 95{\cdot}7 \pm 7{\cdot}4$ kJ mol^{-1} and $\Delta S^\ddagger = -8{\cdot}1 \pm 23$ JK^{-1} mol^{-1} which are close to the values of the analogous parameters for the k_1 path. The kinetic parameters of spontaneous aquation of the complexes listed in Table 3 remaining essentially the same, the observed reactivity order might be indicative of the preferential solvation of the 2-aminothiazole complex due to the cooperative hydrogen bonding effect (structure-I) which is not available to its aniline and imidazole counterparts.

We attempted to study the base hydrolysis of *cis*-$[CoBr(NH_2tz)(en)_2]^{2+}$ at 25° in diethanolamine buffer of *p*H 8·6-9·2. But the reaction was too fast to be studied. This precluded independent assessment of k_2 and K_{NH}. The values of K_{NH} not being known it is not possible to accurately predict the reactivities of the conjugate bases of NH_2tz and aniline complexes. Disregarding the minor effect of ionic strength, it is, however, important to note that the value of $(k_2K_{NH})_{C_6H_5NH_2}/(k_2K_{NH})_{tzNH_2}$ is 26 at 50° (Table 3). The acid disso-

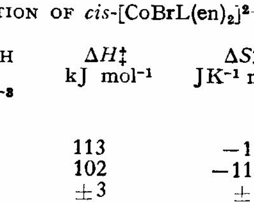


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TABLE 3 — RATE AND ACTIVATION PARAMETERS OF THE AQUATION OF *cis*-$[CoBrL(en)_2]^{2+}$

L	I mol dm^{-3}	10^4k_1 (50°) sec^{-1}	$\Delta H^\ddagger$ kJ mol^{-1}	$\Delta S^\ddagger$ JK^{-1}mol^{-1}	$10^9k_2K_{NH}$ (50°) mol dm^{-3} sec^{-1}	$\Delta H^\ddagger$ kJ mol^{-1}	$\Delta S^\ddagger$ JK^{-1} mol^{-1}	Ref.
Aniline	0·06	0·31	110	+7	420	113	−12	(10)
Imidazole	0·3	0·55	94·5	−34	0·33	102	−113	(11)
		±0·01	±0·3	±1	±0·01	±3	±8	
2-Aminothiazole	0·3	4·79	92·1	−23·7	15·0[a]	157	88	(This work)
		±0·10	±3·0	±9·8		+4	±12	

a, extrapolated value.

ciation constant of benzimidazole (bzimH) in *cis*-$[CoBr(bzimH)(en)_2]^{2+}$ has been found to be ~10 times higher than that of imidazole (imH) in *cis*-$[CoBr(imH)(en)_2]^{2+}$ under comparable condition[11,13]. On this basis and considering the conjugative interaction of the lone pair of the amido nitrogen with the tertiary nitrogen of the thiazole ring, the amine proton of the coordinated NH_2tz is expected to be more acidic than that of coordinated aniline. This would then mean that the reactivity of *cis*-$[CoBr(NHC_6H_5)(en)_2]^+$ is ~26 times higher than that of *cis*-$[CoBr(NHtz)(en)_2]^+$. Strikingly the conjugate base, *cis*-$[CoBr(bzim)(en)_2]^+$, has been found to be less reactive than the *cis*-$[CoBr(im)(en)_2]^+$(ref. 11,13). These results point to the fact that the depletion of electron density from the amido nitrogen bonded to cobalt(III) reduces its labilizing action on the Co-X bond.

A near constancy in the values of ΔH and ΔS for the dissociation of N-H proton from coordinated aniline, imidazole, benzimidazole and 2-aminothiazole is most likely. For the *cis*-$[CoX(bzimH)(en)_2]^{2+}$ we obtained ΔH (K_{NH}) = 41 kJ mol^{-1} and ΔS (K_{NH}) = −23 JK^{-1} mol^{-1} (ref. 13). Thermodynamic data for other *cis*-$[CoX(amine)(en)_2]^{2+}$ (X = Cl or Br) complexes are not available. Therefore, with ΔH (K_{NH}) and ΔS (K_{NH}) data for the benzimidazole complex as the guide we are led to believe from the observed high positive values of the overall activation parameter data ($\Delta S^\ddagger$ in particular) for the NH_2tz complex (acid dependent path) that the conjugate base undergoes considerable rearrangement and passes through the trigonal bipyramidal transition state[4,12,14] for which there may arise considerable gain in entropy.

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