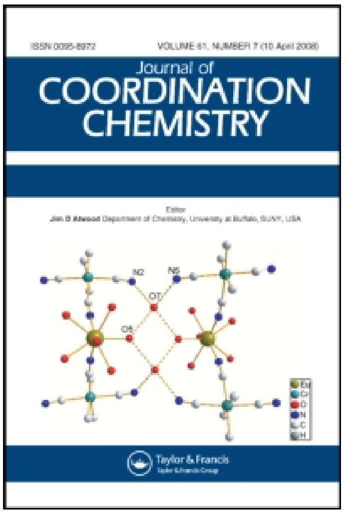

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Cobalt(III) complexes of tripod amines. Kinetics of aquation of dichloro[*N*-(2-aminoethyl)-*N*,*N*-*bis*-(3-aminopropyl)amine]cobalt(III) ion

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A new series of six-coordinate cobalt(III) complexes containing tripod tetradentate-N donors (N_4), $[Co(abap)Cl_2]ClO_4 \cdot H_2O$, $[Co(abap)(H_2O)Cl]Cl(ClO_4)$ and $[Co(N_4)X_2]ClO_4$ (N_4 = abap, $X = N_3$, NO_2; N_4 = TPA, X = Cl, NO_2) where abap = *N*-(2-aminoethyl)-*N*,*N*-*bis*(3-aminopropyl)amine and TPA = *tris*(2-pyridylmethyl)amine were synthesized and characterized by elemental analyses, UV–Vis, and IR. The kinetics of the primary aquation of the complex ion $[Co(abap)Cl_2]^+$ to $[Co(abap)(H_2O)Cl]^{2+}$ was followed spectrophotometrically in 50/50 (v/v) CH_3CN/aqueous $HClO_4$ (16–37°C and $I = 0.50$ M $NaClO_4$). Rate constants (k_1) evaluated under pseudo first-order conditions, were found to be independent of the $[H_3O^+]$ over the range of 0.10–0.50 M $HClO_4$ and of the initial complex concentration. At 25°C, the k_1 value was found to be $1.65 \times 10^{-3}\,s^{-1}$ indicating that this process is, unexpectedly, slightly slower than the corresponding reaction in $[Co(tren)Cl_2]^+$ ($k_1 = 2.96 \times 10^{-3}\,s^{-1}$). The activation parameters were calculated ($\Delta H_1^{\#} = 61.9 \pm 1.8\,kJ\,mol^{-1}$ and $\Delta S_1^{\#} = -91.0 \pm 6.1\,J\,K^{-1}mol^{-1}$), and the results are discussed in relation to other closely related systems with a dissociative I_d mechanism.

Keywords: Cobalt(III) complexes; Tripod amines; Kinetics; Acid hydrolysis; Aquation

1. Introduction

Tripod tetradentate amine-cobalt(III) complexes have been used to model the active sites in metalloenzymes and to efficiently hydrolyze phosphate esters and polyphosphates [1–7]. In cobalt(III) complexes containing these tripod amines, the stereochemistry imposed by these ligands enforces the formation of six-coordinate octahedral species with *cis*-geometry and therefore the complications associated with *cis*/*trans* isomerization are avoided [1, 2a, 8]. Although a number of these complexes were to be used in biological systems for different hydrolytic studies such as nucleotidyl transfer and non-oxidative hydrolysis of DNA [1, 6], some problems exist with these complexes [7]. One of these problems was addressed by Calafat and Marzilli who reported that attempts to hydrolyze the phosphate ester linkage in vitamin B_{12} and B_{12a}, resulted in reduction of $[Co(trpn)(H_2O)_2]^{3+}$ to Co(II) *via* oxidative N-dealkylation of the

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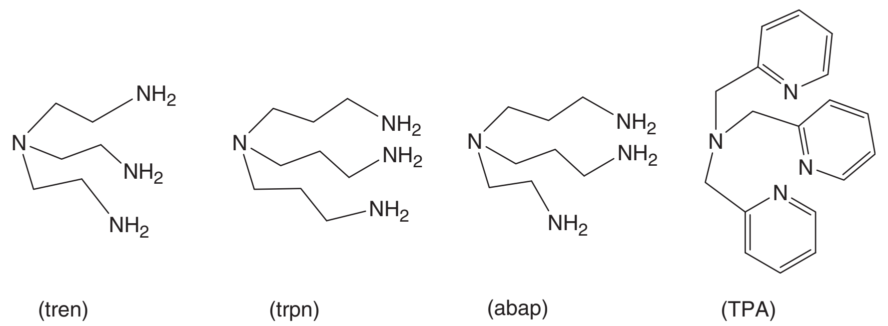

Scheme 1. Structure formulas for some tripod amines.

coordinated trpn ligand [7]. In contrast the analogous cobalt(III)-tren was found to be stable toward decomposition but exhibited low reactivity [7]. This result led us to design a new series of Co(III)-tripod tetraamine compounds to combine the effects of increasing stability and enhancing their catalytic lability and hoping to serve as *effective catalysts*.

In this article we report the synthesis of a new series of cobalt(III) complexes containing tripod amines. These amines were chosen to combine the ethyl and propyl arms in one ligand as in *N*-(2-aminoethyl)-*N*,*N*-*bis*(3-aminopropyl)amine (abap) and to contain heterocyclic rings in the ligand skeleton as in *tris*(2-pyridylmethyl)amine (TPA).[1] The structures of these ligands are illustrated in scheme 1. The variation in the structural skeleton of the tripod ligands surrounding the Co(III) center should have an influence on the reactivity of these complexes.

2. Experimental

2.1. *Materials and physical measurements*

2-Aminomethyl pyridine, 2-picolylchloride hydrochloride, N-(2-bromoethyl)phthalimide and 3,3′-diaminodipropylamine were purchased from Aldrich Chemical Company; phthalic anhydride and $Na_3[Co(NO_2)_6]$ were from Acros. All other materials were reagent grade quality.

Caution: Salts of perchlorate and azide as well as their metal complexes are potentially explosive and should be handled with great care and in small quantities.

Infrared spectra were recorded with a JASCO FT/IR-480 plus spectrometer as KBr pellets. Electronic spectra and kinetic data were recorded using Agilent 8453 HP diode UV–Vis spectrophotometer. Elemental analyses were performed by the Atlantic Microlaboratory, Norcross, Georgia USA.

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[1] Ligand abbreviations: abap = *N*-(2-aminoethyl)-*N*,*N*-*bis*(3-aminopropyl)amine; TPA = *tris*(2-pyridylmethyl)amine; trpn = *tris*(3-aminopropyl)amine; tren = *tris*(3-aminoethyl)amine; tn = 1,3-diamino-propane; trien = triethylene-tetraamine; 3,2,3-tet = 4,7-diaza-1,10-decanediamine; 2,3,2-tet = 3,7-diaza-1,9-nonanediamine; dpt = dipropylenetriamine; dien = diethylenetriamine; en = ethylenediamine; cyclam = 1,4,8,11-tetraazacyclotetradecane.

2.2. *Synthesis of the ligands*

abap · 4HCl · $3H_2O$: This ligand was prepared according to the literature method by fusing 3,3-diphthalimidodipropylamine with N-(2-bromoethyl)phthalimide followed by hydrolysis in 8 M HCl [2]. The ligand was sufficiently pure for use in the synthesis of the complexes.

TPA: The ligand was synthesized and characterized following the procedures described by Tyeklár *et al.* and Mukhopadhyay *et al.* [9, 10].

2.3. *Synthesis of the complexes*

2.3.1. [Co(abap)Cl_2]ClO_4 · H_2O. To a well stirred slurry of $Na_3[Co(CO_3)_3] \cdot 3H_2O$ [11] (3.60 g, 10 mmol) in H_2O (20 mL), the ligand abap · 4HCl · $3H_2O$ (3.75 g, 10 mmol dissolved in 20 mL H_2O) was added dropwise. The temperature of the solution was gradually increased to 75°C over a period of 1 h and stirring was continued at this temperature for 3 h. The resulting red solution was allowed to cool to room temperature, filtered through celite and evaporated under reduced pressure to ca 12 mL by rotavaporator. This was then treated with 1 mL 70% $HClO_4$, 50 mL absolute ethanol and left to crystallize in the refrigerator. The shiny blue crystalline compound, which separated was collected by filtration, washed with absolute ethanol and ether and air-dried (overall yield: 2.3 g, 55%). Characterization: Anal. Calcd for $CoC_8H_{24}N_4Cl_3O_5$: C, 22.79; H, 5.74; N, 13.29%. Found: C, 23.19; H, 5.45; N, 13.50%. UV–Vis in CH_3CN (λ_{max} in nm, ε in $M^{-1}\,cm^{-1}$): 640 nm (99 $M^{-1}\,cm^{-1}$) and 548 nm (sh). Selected IR bands (KBr, cm^{-1}): ν(O–H) (H_2O), 3435 (mb); ν(Cl–O) (ClO_4^-), 1143, 1120 and 1089 (vs); ν(N–H) stretching, 3300 (m) and 3253 (m) cm^{-1}.

2.3.2. [Co(abap)(H_2O)Cl]Cl(ClO_4). The complex [Co(abap)Cl_2]ClO_4 · H_2O (0.250 g) was dissolved in 2 M $HClO_4$ solution and the resulting mixture was heated on a steam bath for 15 min. Upon cooling and standing at room temperature for two days, the purple precipitate which separated out was collected, washed with absolute ethanol and ether and air dried (yield: 0.150 g, 60%). Characterization: Anal. Calcd for $CoC_8H_{24}N_4Cl_3O_5$: C, 22.79; H, 5.74; N, 13.29%. Found: C, 23.27; H, 5.41; N, 13.63%. UV–Vis in H_2O (λ_{max} in nm, ε in $M^{-1}\,cm^{-1}$): 550 nm (86 $M^{-1}\,cm^{-1}$) and 375 nm (sh). Selected IR bands (KBr, cm^{-1}): ν(O–H) (H_2O), 3434 (mb); ν(Cl–O) (ClO_4^-), centered at 1114 (vs); ν(N–H) stretching, 3309 (m) and 3258 (m) cm^{-1}.

2.3.3. [Co(abap)$(NO_2)_2$]ClO_4. To a hot aqueous solution of [Co(abap)Cl_2]ClO_4 · H_2O (0.211 g, 0.50 mmol) in 15 mL H_2O, two equivalents of $NaNO_2$ dissolved in 5 mL H_2O were added. This was then heated on a steam bath for 15 min, followed by addition of 1 mL of saturated $NaClO_4$ solution. The resulting solution was filtered and allowed to crystallize at room temperature. The golden yellow crystals, which separated were collected by filtration (yield: 0.170 g, 80%). Characterization: Anal. Calcd for $CoC_8H_{22}N_6ClO_8$: C, 22.63; H, 5.22; N, 19.79%. Found: C, 22.70; H, 5.34; N, 19.74%. UV–Vis in H_2O (λ_{max} in nm, ε in $M^{-1}\,cm^{-1}$): 474 nm (224 $M^{-1}\,cm^{-1}$). Selected IR bands (KBr, cm^{-1}): ν(N–O) (NO_2^-), 1431 (s), 1396 (s), 1312 (s) and 759 (m); ν(Cl–O) (ClO_4^-), 1120 (vs), 1054 (s); ν(N–H) stretching, 3237 (s) and 3159 (m) cm^{-1}.

2.3.4. [Co(abap)$(N_3)_2$]ClO_4. This crystalline compound, which has a wine-purple color, was prepared as essentially described above for the dinitrito species except for addition of NaN_3 instead of $NaNO_2$ (yield: 77%). Characterization: Anal. Calcd for $CoC_8H_{22}N_{10}ClO_4$: C, 23.06; H, 5.32; N, 33.61%. Found: C, 23.18; H, 5.43; N, 33.66%. UV–Vis in H_2O (λ_{max} in nm, ε in $M^{-1}cm^{-1}$): 552 nm ($333\,M^{-1}cm^{-1}$). Selected IR bands (KBr, cm^{-1}): $\nu(N_3)$, 2032 (vs); ν(Cl–O) (ClO_4^-), 1090 (vs); ν(N–H) stretching, 3248 (m) and 3159 (w) cm^{-1}.

2.3.5. [Co(TPA)Cl_2]ClO_4. To equimolar amounts of TPA (1.45 g, 5.0 mmol) and $CoCl_2 \cdot 6H_2O$ (1.20 g, 5.0 mmol) dissolved in methanol (50 mL), 2 mL of 30% H_2O_2 was added. Air was bubbled through the solution for 6 h and the resulting unidentified solid was filtered; the filtrate was evaporated on steam bath to ca 20 mL, followed by addition of 1 mL of 70% $HClO_4$ and allowing crystallization at room temperature. The crude solid which separated was fractionally crystallized from MeOH to give a green solution from which [Co(TPA)Cl]ClO_4 was separated and characterized [12]. The remaining undissolved compound was carefully washed with warm MeOH and air dried. The product was further re-crystallized from hot MeOH and allowed to stand in the refrigerator. After 1 week, the violet crystalline complex, which separated, was collected by filtration (yield: 0.55 g, 21%). Anal. Calcd for $CoC_{18}H_{18}N_4Cl_3O_4$: C, 41.60; H, 3.49; N, 10.78%. Found: C, 42.03; H, 3.86; N, 10.36%. UV–Vis in MeOH (λ_{max} in nm, ε in $M^{-1}cm^{-1}$): 554 nm ($136\,M^{-1}cm^{-1}$) and 376 nm ($723\,M^{-1}cm^{-1}$). Selected IR bands (KBr, cm^{-1}): ν(C–H), 3111, 3083, 2979, and 2929 (w); ν(Cl–O) (ClO_4^-), 1090 (vs) cm^{-1}.

2.3.6. [Co(TPA)$(NO_2)_2$]ClO_4. To a well stirred aqueous mixture containing TPA (0.145 g, 0.50 mmol in 10 mL H_2O) and 2 mL of 2 M $HClO_4$, an equimolar amount of $Na_3[Co(NO_2)_6]$ (0.202 g, 0.50 mmol) dissolved in H_2O (10 mL) was added dropwise. The solution was heated for 5 min during which a yellow precipitate formed, which was collected (yield: 0.240 g, 89%) and re-crystallized from hot water to give golden yellow needles. Anal. Calcd for $CoC_{18}H_{18}N_6ClO_8$: C, 39.98; H, 3.36; N, 15.54%. Found: C, 40.13; H, 3.27; N, 15.35%. UV–Vis in H_2O (λ_{max} in nm): 470 nm (saturated solution). Selected IR bands (KBr, cm^{-1}): ν(C–H), 3085 and 3083 (w); ν(Cl–O) (ClO_4^-), 1121, 1099 and 1084 (vs) cm^{-1}; ν(N–O) (NO_2^-), 1319 (s), 1287 (m) and 775 (m) cm^{-1}.

2.4. *Kinetic measurements*

The rate measurements for the primary aquation of $[Co(abap)Cl_2]^+$ ion were measured spectrophotometrically in thermostated matched cells over the temperature range (16–37) ± 0.1°C ($I = 0.50$ M $NaClO_4$). The decrease in absorbance at 640 nm, where a substantial difference in absorbance exists between $[Co(abap)Cl_2]^+$ and the product, $[Co(abap)(H_2O)Cl]^{2+}$ was monitored as a function of time. The acid hydrolysis was studied by dissolving a weighed sample of $[Co(abap)Cl_2]ClO_4 \cdot H_2O$ (in a 5.00 mL volumetric flask) in 2.50 mL of dry acetonitrile (stored over 4 Å molecular sieves). The solution in the flask was completed to the mark by adding $HClO_4$ (0.20–1.0 M), which was also pre-equilibrated at the same temperature, and a part of the contents was quickly transferred to a thermostated 1 cm cell. The concentration of the complex in these runs was 2.5–5.0 mM.

The rate constants were calculated by linear least squares of the first-order plots of ln $(A_t - A_\infty)$ *versus* time, where A_∞ is the final absorbance and was taken when no further changes were detected and A_t is the absorbance at time t. These plots were linear for at least four half-lives (~93%). Duplicate runs agreed within 5%.

3. Results and discussion

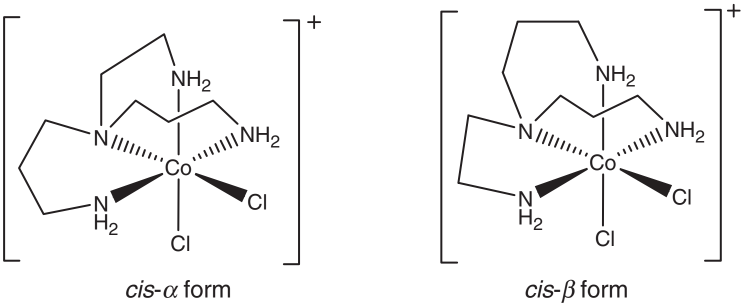
3.1. *Syntheses of the complexes*

The blue complex $[Co(abap)Cl_2]ClO_4 \cdot H_2O$ was synthesized by the reaction of *N*-(2-aminoethyl)-*N*,*N*-*bis*(3-aminopropyl)amine tetrahydrochloride trihydrate, abap · 4HCl · $3H_2O$ with $Na_3[Co(CO_3)_3] \cdot 3H_2O$, followed by addition of $HClO_4$ solution. No attempts were made to isolate the corresponding carbonato species. The chloride complex, $[Co(abap)Cl_2]Cl$ was previously synthesized *via* $[Co(abap)(O_2NO)](ClO_4)_2$ [2a]. In dilute $HClO_4$ solutions, the complex $[Co(abap)Cl_2]ClO_4 \cdot H_2O$ was found to undergo hydrolysis to the corresponding aquachloro species, $[Co(abap)(H_2O)Cl]Cl(ClO_4)$ which was separated and characterized. The dichloro complex also reacts with NaN_3 and $NaNO_2$ to yield $[Co(abap)(N_3)_2]ClO_4$ and $[Co(abap)(NO_2)_2]ClO_4$, respectively. The violet-purple $[Co(TPA)Cl_2]ClO_4$ was obtained in low yield by air oxidation of a methanolic solution containing TPA and $CoCl_2 \cdot 6H_2O$ in the presence of H_2O_2. The complex precipitated as perchlorate and a substantial amount of the green structurally characterized five-coordinate species $[Co(TPA)Cl]ClO_4$ was produced [12]. The dichloro complex $[Co(TPA)Cl_2]ClO_4$ is slightly soluble in H_2O and to a small extent in hot MeOH, limiting the possibility of performing further study. However, it should be noted that the complex hydrolyzes in aqueous $HClO_4$ solution, probably to $[Co(TPA)(H_2O)Cl]^{2+}$ at a rate which is much slower than that reported for the corresponding tren complex [12]. The $[Co(TPA)(H_2O)Cl](ClO_4)_2$ complex was previously isolated from the reaction of the parent dinitrito species with aqueous HCl solution [14]. The dinitro complex $[Co(TPA)(NO_2)_2]ClO_4$ was obtained by reaction of $Na_3[Co(NO_2)_6]$ with TPA in the presence of four equivalents of $HClO_4$.

3.2. *Characterization of the complexes*

The electronic spectra of the complexes under investigation, with the exception the dinitrito series and $[Co(abap)(N_3)_2]ClO_4$, display two bands over the wavelength range 640–360 nm. The high energy band in the TPA complexes is likely masked by intense charge transfer bands leading to the observation of one absorption band in the visible region for the dinitro and $[Co(abap)(N_3)_2]ClO_4$ compounds. The spectral features are consistent with octahedral *cis*-geometry and the bands arise from $^1T_{1g}(O_h) \leftarrow {}^1A_{1g}(O_h)$ and $^1T_{2g}(O_h) \leftarrow {}^1A_{1g}(O_h)$ transitions. Although the actual field is of lower symmetry (C_{4v}), this has a small effect upon the model and the $^1T_{1g}$ state is split into $^1E_{1g}$ and $^1A_{2g}$ (octahedral labels for simplicity) [15].

The infrared spectra of all complexes in this study exhibit strong absorption band(s) between 1140 to 1090 cm^{-1}, assigned to the ν(Cl–O) of the non-coordinated perchlorate



Scheme 2. The two isometric forms of $[Co(abap)Cl_2]+$ion.

ion which is known to give a strong absorption around 1090 cm^{-1}. The split of this band into two or three peaks indicates that the symmetry of the ClO_4^- ion is lowered from T_d to C_{3v} as observed for $[Co(abap)Cl_2]ClO_4 \cdot H_2O$ and $[Co(TPA)(NO_2)_2]ClO_4$. The complexes $[Co(N_4)(NO_2)_2]ClO_4$ display strong to medium bands at 1431(s) and 1396 (s) (split band), 1312 (s) and 759 (m) for $N_4 = $abap and at 1319, 1287 and 775 cm^{-1} for $N_4 = $TPA attributable to ν_a(N=O), ν_s(N–O) and δ(ONO) modes, respectively. The positions of these peaks are similar to those observed in *trans*-$[Co(3,2,3\text{-tet})(NO_2)Y]^+$ (Y = NO_2, SCN, Cl, Br) which display bands around 1420, 1310 and 820 cm^{-1} [16]; the N-bonded nature of the coordinated NO_2^- was demonstrated by the X-ray structure of *trans*-$[Co(3,2,3\text{-tet})(NO_2)_2]X$ (X = Cl and NO_3) [17]. This clearly confirms the nitro (NO_2–N) bond in the series $[Co(N_4)(NO_2)_2]ClO_4$ ($N_4 = $abap and TPA).

The IR spectrum of the diazido complex, $[Co(abap)(N_3)_2]ClO_4$ has a strong unresolved peak at 2032 cm^{-1}, attributable to the asymmetric stretching mode of the azido ligands, $\nu_a(N_3)$. In less symmetrical *cis*-diazido-cobalt(III) complexes, *cis*-$[Co(N_4)(N_3)_2]^+$ ($N_4 = $trien, tren, trpn, 2,3,2-tet), the $\nu_a(N_3)$ band is split whereas in the trans-diazido series only one band was detected [18]. A single unresolved $\nu_a(N_3)$ band in $[Co(abap)(N_3)_2]ClO_4$, is probably due to the relative broadness of the stretching frequency of the coordinated N_3^- group from overlap of two or more vibrational modes. Finally, the coordinated and lattice water in $[Co(abap)(H_2O)Cl]Cl(ClO_4)$ and $[Co(abap)Cl_2]ClO_4 \cdot H_2O$, show a broad band of medium intensity over the range 3430–3500 cm^{-1}, attributed to O–H stretching [19].

Due to the asymmetric nature of the tripod amine, abap in the dichloro complex $[Co(abap)Cl_2]^+$ two isomers may exist, depending on whether the Cl^- ions are opposite to the five- (*cis*-α form) or to the six-memebered ring (*cis*-β form) of the chelated abap ligand. The two forms are illustrated in scheme 2. In either isomer, one of the chloro ligands is located trans to the tertiary nitrogen; the two positions are chemically non-equivalent [20].

3.3. *Aquation of $[Co(abap)Cl_2]ClO_4 \cdot H_2O$*

The primary aquation of $[Co(abap)Cl_2]ClO_4 \cdot H_2O$ was conducted in a solution containing 50/50 by volume of CH_3CN and $HClO_4$. The blue complex ion $[Co(abap)Cl_2]^+$ undergoes the first acid hydrolysis step in aqueous perchloric acid solutions to form the purple aquachloro $[Co(abap)(H_2O)Cl]^{2+}$ ion. Since dissolution of $[Co(abap)Cl_2]ClO_4 \cdot H_2O$ in aqueous $HClO_4$ solutions is slow and accompanied with hydrolysis at the same time, dry CH_3CN was used as a solvent. The hydrolysis was followed spectrophotometrically by monitoring the absorbance decrease at 640 nm. The lowest energy d–d band maximum at $\lambda_{max} = 640$ nm ($\varepsilon = 99\,M^{-1}\,cm^{-1}$) shifted to lower wavelength, $\lambda_{max} = 550$ nm ($\varepsilon = 86\,M^{-1}\,cm^{-1}$). The spectral scans displayed two isosbestic points at 574 and 460 nm, which were maintained throughout the reaction. Thus, the hydrolysis of $[Co(abap)Cl_2]^+$ can be stoichiometrically represented by the following equation:

$$[Co(abap)Cl_2]^+ + H_2O \xrightarrow{k_1} [Co(abap)(H_2O)Cl]^{2+} + Cl^-$$

Evidence for the reaction stoichiometry include the following: (i) the final spectral scan for the hydrolysis product of the reaction, $[Co(abap)(H_2O)Cl]^{2+}$ was consistent with the isolated and characterized complex, $[Co(abap)(H_2O)Cl]Cl(ClO_4)$, (ii) the isosbestic points at 574 and 460 nm remained during the course of the reaction, (iii) the final spectral scans showed no appreciable change over a period of more than 3 h, and (iv) the kinetics were observed for at least 4 half-lives. The rate law for the release of the first chloride is given by

$$\frac{d[Co(abap)Cl_2^+]}{dt} = k_1[Co(abap)Cl_2^+]$$

The hydrolysis was followed in 0.10 M $HClO_4$ ($I = 0.50$ M $NaClO_4$), and some measurements were conducted at higher acid concentrations. First-order rate constants (k_1) calculated from the slopes of the linear plots of $\ln(A_t–A_\infty)$ *versus* t ($R = 0.937$–0.996) and measured at different temperatures are listed in table 1. The pseudo-first order rate constants (k_1) calculated at 640, 536 and 670 nm were in agreement within 5%, confirming the assumption that no other side reactions are complicating the study and were independent of the initial complex concentration. Also, rate measurements performed at 26°C and at various $[H_3O^+]$ were in agreement within 6% (table 1) which clearly indicates that the primary aquation of $[Co(abapCl_2]^+$ is acid-independent. The activation parameters ($\Delta H_1^{\#}$ and $\Delta S_1^{\#}$) were evaluated by least-squares analysis of Eyring plots ($\ln k_1/T$) *versus* $1/T$ (figure 1), $\Delta H_1^{\#} = 61.9 \pm 1.8\,kJ\,mol^{-1}$ and $\Delta S_1^{\#} = -91.0 \pm 6.1\,J\,K^{-1}\,mol^{-1}$ (the error limits quoted with the activation parameters are the standard deviations).

Table 1. Rate constants (k_1, s^{-1}) for the primary acid hydrolysis of $[Co(abap)Cl_2]^+$ ion in 50/50 by volume acetonitrile–$HClO_4$ mixture at different temperatures ($I = 0.50$ M $NaClO_4$).

T (°C)	$[H_3O^+]$ (M)	$10^3\ k_1\ (s^{-1})^a$
15.0	0.10	0.612 ± 0.018
20.0	0.10	0.986 ± 0.033
26.0	0.10	1.77 ± 0.043
	0.30	1.84 ± 0.030
	0.50	1.81 ± 0.032
32.0	0.10	2.84 ± 0.077
37.0	0.10	3.94 ± 0.044

[a] The error limits given correspond to the standard deviations (1σ).

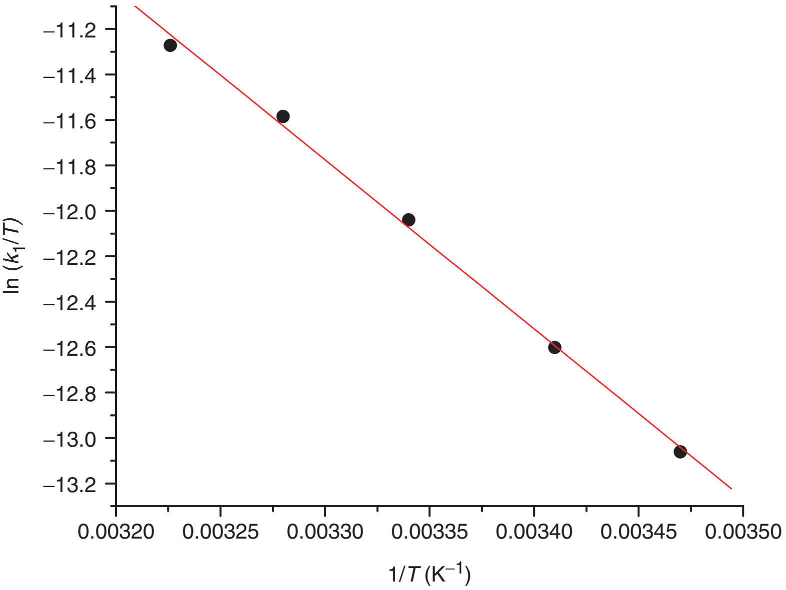


Figure 1. Erying plot for the primary aquation of $[Co(abap)Cl_2]^+$ in 50/50 by volume CH_3CN and 0.20 M $HClO_4$ ($I = 0.5$ M $NaClO_4$). The line represents the best fit for the points.

The two positions in the α- and β-isomers shown in scheme 2 are chemically and kinetically non-equivalent [20]; each isomer should produce two complex ions of the aqua-chloro species, $[Co(abap)(H_2O)Cl]^{2+}$ depending on whether the coordinated Cl^- and the H_2O ligands lie opposite to the chelated five-membered ring or to the six-membered ring, giving a total of four possible isomers. Based on the X-ray study of the *mer*-$[Co(dien)(NO_2)_2Cl]$ produced from the reaction of the corresponding trinitro species with HCl where the trans position to the NH group in the polyamine was found to be the most labile [21], it seems reasonable to consider the replacement of the chloride ion in each of the two $[Co(abap)Cl_2]^+$ isomeric forms trans to the tertiary nitrogen of abap. This is also cosistent with the fact that abap forms a polymeric 1-D chain bridging the Ni(II) centers in end-to-end bonding mode *via* azido ligands, $[Ni(abap)(\mu_{1,3}\text{-}N_3)]_n(ClO_4)_n$ where the bridged azide binds Ni^{2+} from the side that is trans to the tertiary nitrogen of the tetra-coordinated abap ligand [22].

The uncomplicated kinetics of the acid hydrolysis of $[Co(abapCl_2]^+$ shown by the agreement of the rate constants measured at three different wavelengths 640, 536 and 670 nm, the retention of the isosbestic points at 574 and 460 nm during the course of the reaction for at least $4\,t_{1/2}$, and by the stability of the final spectrum of the aqua-chloro product, indicates that there is only one isomeric species in solution; *cis*-α-$[Co(abap)(H_2O)Cl]^{2+}$ or *cis*-β-$[Co(abap)(H_2O)Cl]^{2+}$ (in both cases the H_2O ligand is trans to the tertiary nitrogen of abap). It is well established that reactivity of *cis*-dichlorotetraamine-cobalt(III) complex ions $[Co(N_4)Cl_2]^+$ towards acid hydrolysis in compounds containing only five-memered chelate rings (N_4 = tren: $k_1 = 2.96 \times 10^{-3}\,s^{-1}$; N_4 = trien, $k_1 = 1.5 \times 10^{-3}\,s^{-1}$; $(en)_2$: $k_1 = 2.5 \times 10^{-4}\,s^{-1}$) [13, 23, 24] is much smaller than those containing six-membered rings (N_4 = trpn, $(tn)_2$, where k_1 is very large and they hydrolyze almost instantaneously) [25, 26]. Based on these experimental facts and on the k_1 value estimated at 25°C ($1.65 \times 10^{-3}\,s^{-1}$) by the aid of the activation parameters for $[Co(abapCl_2]^+$, it is evident that this value is in the range reported for the primary aquation in five membered-chelate complexes. Thus, one can consider the chloro ligand trans to the tertiary nitrogen in the five-membered ring as the one undergoing hydrolysis, conversion of *cis*-α-$[Co(abap)Cl_2]^+$ to *cis*-α-$[Co(abap)(H_2O)Cl]^{2+}$ ion.

The acid-independent behavior observed here for the primary aquation of $[Co(abapCl_2]^+$ was compared to those reported in closely related systems of dihalotetraaminecobalt(III) ions, $[Co(N_4)X_2]^+$ ($X = Cl$, Br; $N_4 = (en)_2$, tren, trien, 2,3,2-tet, cyclam) [13, 24, 27–30] and to the solvolysis of $[Co(trpn)X_2]^+$ ($X = F$, Cl, Br) with acetonitrile [31]. An acid-dependent pathway was observed in the hydrolysis of aqua-halo species $[Co(N_4)(H_2O)X]^{2+}$ ($X = Cl$, Br; $N_4 =$ tren, trien) [32, 33] and $[Co(dpt)(H_2O)X_2]^+$ ($X = Cl$, Br) [34]. At 25°C, the rate constant for the primary aquation of *cis*-α-$[Co(abapCl_2]^+$ ($1.65 \times 10^{-3}\,s^{-1}$) was found to be smaller by about half of the corresponding value reported for $[Co(tren)Cl_2]^+$ ($2.96 \times 10^{-3}\,s^{-1}$) [13]. We expected the reactivity of this system to be somewhere between the extremely labile $[Co(trpn)Cl_2]^+$ [26, 31] where the coordinated trpn ligand has three propyl-amine arms and the corresponding tren complex with three ethyl-amine arms. This unpredictable result requires more work to understand how the stereochemistry of the chelate rings of the amine ligand in $[Co(abapCl_2]^+$ affect its reactivity.

The mechanism adapted for the acid hydrolysis and substitution reactions in cobalt(III) complexes is the dissociative I_d mechanism [13, 23–34]. The very negative entropy of activation observed here in the aquation of $[Co(abapCl_2]^+$ ($\Delta S_1^{\#} = -91.0 \pm 6.1\,J\,K^{-1}\,mol^{-1}$) does not reflect the dissocative nature of the reaction. However, this value can be understood in terms of the increase of electrostatic interaction between the solvent molecules and the complex ion in the transition state on going from $[Co(abap)Cl_2]^+$ to $[Co(abap)(H_2O)Cl]^{2+}$ and Cl^- ions where more charges are created. Therefore, we decided to examine the isokinetic correlation ($\Delta H^{\neq}$ *versus* $\Delta S^{\neq}$) for our system along with the available published kinetic data for six-coordinate

Table 2. Rate constants at 25°C and activation parameters for the acid-independent pathway for aquation and solvolysis with CH_3CN in Co(III)-amine complexes.[a]

No.	Co(III) complex ion	k (s^{-1})	$\Delta H^{\neq}$ ($kJ\,mol^{-1}$)	$\Delta S^{\neq}$ ($J\,K^{-1}mol^{-1}$)[b]	Ref.
1	$[Co(tren)Cl_2]^+$	2.96×10^{-3}	74.5	−43.5	13
2	*cis*-β-$[Co(trien)Cl_2]^+$	1.5×10^{-3}	84.9	−12.6	24
3	$[Co(abap)Cl_2]^+$	1.65×10^{-3}	61.9 ± 1.8	−91.0 ± 6.1	This work
4	*cis*- β-$[Co(2,3,2\text{-}tet)Cl_2]^+$	1.1×10^{-3}	93.3	8.4	27
5	$[Co(trpn)Cl_2]^{+\,c}$	1.66×10^{-3}	56.9 ± 2.5	−108 ± 7.5	31
6	*cis*-$[Co(cyclam)Cl_2]^{2+}$	1.6×10^{-2}	76.6	−25.1	30
7	$[Co(tren)Br_2]^+$	2.81×10^{-2}	63.2	−61.9	28
8	$[Co(trpn)Br_2]^{+\,c}$	1.87×10^{-2}	21.1 ± 3.3	−207 ± 10	31
9	*cis*-$[Co(en)_2Br_2]^{+\,d}$	1.04×10^{-3}	99.3 ± 1.3	31.6 ± 2.2	29
10	$[Co(trpn)F_2]^+$	1.28×10^{-3}	53.6 ± 2.1	−121 ± 6.3	26
11	$[Co(trpn)F_2]^{+\,c}$	7.8×10^{-4}	103 ± 2.5	45.2 ± 7.5	31
12	$[Co(trpn)(CH_3CN)_2]^{3+}$	1.91×10^{-2}	66.9 ± 8.4	−53.1 ± 2.5	26
13	*fac*-$[Co(dpt)(H_2O)Cl_2]^+$	1.70×10^{-4}	106 ± 0.4	40.2 ± 1.7	34
14	*fac*-$[Co(dpt)(H_2O)Br_2]^+$	5.25×10^{-4}	91.6 ± 0.4	0.4 ± 1.7	34

[a] Ionic strength in many of these reactions were not clearly stated.

[b] The error limits associated with some of the $\Delta S \neq$ values correspond to the standard deviations (1σ).

[c] Solvolysis in CH_3CN.

[d] The activation parameters were calculated from Eyring plot of ($\ln k_1/T$) *vs.* $1/T$ given in Ref. [29].

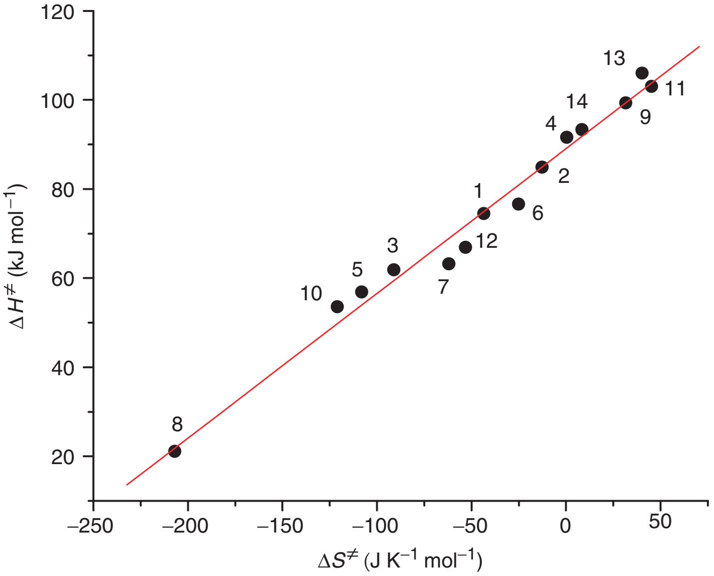


Figure 2. Isokinetic plot for the acid-independent pathway for the aquation and for the solvolysis with CH_3CN in Co(III)-amine complexes. For numbering of the complexes refer to table 2. The line represents the best fit for the points.

cobalt(III)-amine complexes with *cis* or *fac* geometry. These data are given in table 2 and the isokinetic plot is shown in figure 2. The data in table 2 reveal that $\Delta S^{\neq}$ values are both positive and negative, probably because of the variable nature of the complex solvent interactions. The parallel changes in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ lead only to small changes in $\Delta G^{\neq}$, and for such a closely related series a common mechanism is implied [31, 35, 36]. The slope of the linear plot of $\Delta H^{\neq}$ *versus* $\Delta S^{\neq}$ gives the isokinetic temperature, which is equal to 326 K. Below this temperature the reactions are controlled by $\Delta H^{\neq}$ values and above this temperature by $\Delta S^{\neq}$ values [35].

In conclusion, contrary to expectations, the primary aquation of *cis*-α-$[Co(abap)Cl_2]^+$ was found to be relatively slower than the corresponding process in $[Co(tren)Cl_2]^+$. Also, preliminary data indicated that $[Co(TPA)Cl_2]^+$ is even less reactive. This may minimize the possibility of using aqua derivatives of $[Co(abap)Cl_2]^+$ and $[Co(TPA)Cl_2]^+$ as efficient promoters in the hydrolysis reactions of biological molecules.

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References

[1] (a) F. Tafesse, S.S. Massoud, R.M. Milburn. *Inorg. Chem.*, **32**, 1864 (1993); (b) F. Tafesse, S.S. Massoud, R.M. Milburn. *Inorg. Chem.*, **24**, 2591 (1985); (c) S.S. Massoud. *J. Inorg. Biochem.*, **55**, 183 (1994); (d) S.S. Massoud, R.M. Milburn. *J. Inorg. Biochem.*, **39**, (1990) 337.

[2] (a) R.L. Fanshawe, A.G. Blackman. *Inorg. Chem.*, **34**, 421 (1995); (b) R.L. Fanshawe, A.G. Blackman, C.R. Clark. *Inorg. Chim. Acta*, **342**, 342 (2003).

[3] (a) N.H. Williams, B. Takasaki, A. Wall, J. Chin. *Acc. Chem. Res.*, **32**, 485 (1999); (b) N.H. Williams, W. Cheung, J. Chin. *J. Am. Chem. Soc.*, **120**, 8979 (1998); (c) J. Chin. *Acc. Chem. Res.*, **24**, 145 (1991); (d) J. Chin, M. Banaszczyk, V. Jubian. *J. Chem. Soc., Chem. Commun.*, 735 (1988).

[4] P. Hendry, A.M. Sargeson. *Progress Inorg. Chem.: Bioinorganic Chemistry*, S. J. Lippard (Ed.), Wiley & Sons, Inc., 38, 201 (1990) and references therein.

[5] (a) G.H. Rawaji, M. Yamada, N.F. Sadler, R.M. Milburn. *Inorg. Chim. Acta*, **303**, 168 (2000); (b) G.H. Rawaji, R.M. Milburn. *Inorg. Chim. Acta*, **150**, 227 (1988); (c) A. Connolly, M. Banaszczyk, R.C. Hynrs. J. Chin. *Inorg. Chem.*, **33**, 665 (1994); (d) J. Chin, M. Banaszczyk, V. Jubian, X. Zou. *J. Am. Chem. Soc.*, **111**, 186 (1989).

[6] (a) R. Hettich, H.-J. Schneider. *J. Am. Chem. Soc.*, **119**, 5638 (1997).

[7] (a) A.M. Calafat, L.G. Marzilli. *Inorg. Chem.*, **31**, 1719 (1992); (b) A. M. Calafat, L. G. Marzilli. *Inorg. Chem.*, **32**, 2906 (1993).

[8] (a) S.S. Massoud, R.M. Milburn. *Inorg. Chim. Acta*, **163**, 87 (1989); (b) S.S. Massoud, R.M. Milburn. *Polyhedron*, **8**, 2389 (1989).

[9] Z. Tyeklár, R.B. Jacobson, N. Wei, N.N. Murthy, J. Zubieta, K.D. Karlin. *J. Am. Chem. Soc.*, **115**, 2677 (1993).

[10] U. Mukhopadhyay, I. Bernal, S.S. Massoud, F.A. Mautner. *Inorg. Chim. Acta*, **357**, 3673 (2004).

[11] H.F. Bauer, W.C. Drinkards. *J. Am. Chem. Soc.*, **74**, 5031 (1960).

[12] S.S. Massoud, K.T. Brousrard, F.A. Mautner, R. Vicente, M.K. Saha, I. Bernal (Submitted for publication).

[13] S.K. Madan, W.M. Reiff, J.C. Bailar Jr. *Inorg. Chem.*, **4**, 1366 (1965).

[14] J.B. Mandel, C. Maricondi, B.E. Douglas. *Inorg. Chem.*, **27**, 2990 (1988).

[15] F. Basolo, C.J. Ballahausen, C.J. Bjerrum. *Acta Chim. Scand.*, **9**, 810 (1955).

[16] S.S. Massoud. *Polyhedron*, **13**, 1467 (1994).

[17] I. Bernal, J. Cetrullo, J. Cai, S.S. Massoud. *Struct. Chem.*, **6**, 99 (1995).

[18] S.S. Massoud. *Polyhedron*, **13**, 3127 (1994).

[19] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th Edn, Part A, John Wiley and Sons, New York (1997).

[20] E. Martins, P.S. Sheridan. *Inorg. Chem.*, **17**, 2822 (1978).

[21] A.V. Ablov, E.P. Popa. *Russ. J. Inorg. Chem.*, **8**, 161 (1963).

[22] S.S. Massoud, F.A. Mautner, R. Vicente, E. Ducasse and A. A. Gallo. *Eur. J. Inorg. Chem.*, 1091 (2007).

[23] S.C. Chan. *J. Chem. Soc.*, **5137** (1963).

[24] A.M. Sargeson, G.H. Searle. *Inorg. Chem.*, **6**, 2172 (1967).

[25] I.R. Jonasson, S.F. Lincoln, D.R. Stranks. *Aust. J. Chem.*, **23**, 2267 (1970).

[26] S.S. Massoud, R.M. Milburn. *Polyhedron*, **8**, 275 (1989).

[27] R. Niththyananthan, M.L. Tobe. *Inorg. Chem.*, **8**, 1589 (1969).

[28] S.K. Madan, J. Peone Jr. *Inorg. Chem.*, **6**, 463 (1967).

[29] W.F. Cain, J.A. Mclean Jr. *Inorg. Chem.*, **4**, 1416 (1965).

[30] C.K. Poon, M.L. Tobe. *Inog. Chem.*, **7**, 2398 (1968).

[31] S.S. Massoud, R.M. Milburn. *Polyhedron*, **8**, 415 (1989).

[32] (a) W.V. Miller, S.K. Madan. *Inorg. Chem.*, **10**, 1250 (1971); (b) W.V. Miller, S.K. Madan. *Inorg. Chem.*, **9**, 2362 (1970).

[33] A.M. Sargeson, G.H. Searle. *Nature (London)*, **200**, 356 (1963).

[34] S.S. Massoud, R.M. Milburn. *Inorg. Chim. Acta*, **148**, 233 (1988).

[35] R.G. Wilkins. *The Study and Mechanism of Reactions of Transition Metal Complexes*, p. 100, Allyn and Bacon, Boston (1974).

[36] S.S. Massoud, R.B. Jordan. *Inorg. Chim. Acta*, **221**, 9 (1994).