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Base Hydrolysis of *cis*-Chloro(1-methylimidazole)bis(1,2-diaminoethane)-cobalt(III) and Related Complex Cations

MARIA C. GOMEZ-VAAMONDE and KEVIN B. NOLAN*

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

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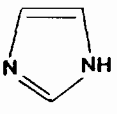
Abstract

The second order rate constant for base hydrolysis of the complex *cis*-$[Co(en)_2(1\text{-Meim})Cl]^{2+}$ (1-Meim = 1-methylimidazole) is 25.1 ± 2.1 $dm^3\ mol^{-1}\ s^{-1}$ at 298 K, $I = 0.1$ mol dm^{-3} $NaClO_4$. This is similar to the value of 28.0 ± 1.5 $dm^3\ mol^{-1}\ s^{-1}$ measured for the imidazole (imH) complex *cis*-$[Co(en)_2(imH)Cl]^{2+}$ under the same conditions. Both of these complexes are much less reactive than the benzimidazole (bzimH) complex *cis*-$[Co(en)_2(bzimH)Cl]^{2+}$ for which k_2 = 240 ± 12 $dm^3\ mol^{-1}\ s^{-1}$ also at 298 K, I = 0.1 mol dm^{-3}. Unlike the 1-Meim complex the imH and bzimH complexes undergo acid dissociation in the pH range of investigations and pK_a values of 10.25 ± 0.03 and 8.67 ± 0.03 respectively have been obtained for these complexes both at 298 K, I = 0.1 mol dm^{-3} $NaClO_4$. Rate constants have also been measured for base hydrolysis of the conjugate bases of these complexes and the relative reactivities of the various species are discussed in terms of electronic and steric effects.

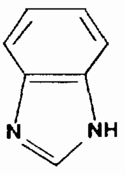
Introduction

The facile reaction between *trans*-$[Co(en)_2Cl_2]^+$ (en = 1,2-diaminoethane) and primary amines, RNH_2, to give products of the type *cis*-$[Co(en)_2(RNH_2)Cl]^{2+}$ [1] has led to the accumulation of a wealth of kinetic data for the hydrolysis of such complexes [2] and structural effects on rates are by now well understood. Rate constants for base hydrolysis of straight chain alkylamine complexes lie in the range 7–13 $dm^3\ mol^{-1}\ s^{-1}$ while the introduction of substituents at the α-position can lead to rate acceleration due either to steric effects in the case of branched substituents (increased k_{cb} in the generally observed base hydrolysis rate expression, rate = Kk_{cb}[complex] $[OH^-]$ [3]) or electronic effects in the case of electron-withdrawing substituents (increased K) [4].

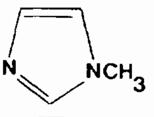
Kinetic studies on base hydrolysis of the complexes *cis*-$[Co(en)_2(imH)Cl]^{2+}$ and *cis*-$[Co(en)_2(bzimH)Cl]^{2+}$ (imH = imidazole, bzimH = benzimidazole) have recently been carried out [5–7]. While the free imidazoles (**I**, **II**) are very weak acids (pK_a for imidazole is 14.2 [8] and for benzimidazole is 12.8 [9], both at 298 K) complexation of a metal ion at the 'pyridinium' nitrogen causes enhanced acidity of the 'pyrrole' NH and pK_a values ranging from 7.2 in $[Ru(NH_3)_5(bzimH)]^{3+}$ [10] to 12.5 in $[Co(imH)_4]^{2+}$ [11] both at 298 K have been reported for these ligands.



I



II



III

Accordingly pH–rate profiles for base hydrolysis of the cobalt(III) complexes are consistent with ionization of an acidic group, presumably the pyrrole N–H [5, 6]. In this paper we report results of our studies on the base hydrolysis of *cis*-$[Co(en)_2(1\text{-Meim})Cl]^{2+}$ (1-Meim = 1-methylimidazole, **III**) which does not contain an acidic imidazolyl NH group and compare these with rates of base hydrolysis of *cis*-$[Co(en)_2(imH)Cl]^{2+}$ and *cis*-$[Co(en)_2(bzimH)Cl]^{2+}$, which were investigated under the same conditions.

Experimental

The complexes *cis*-$[Co(en)_2(imH)Cl]Cl_2$, *cis*-$[Co(en)_2(bzimH)Cl]Cl_2$ and [*cis*-$Co(en)_2(1\text{-Meim})Cl]Cl_2$ were prepared by literature methods [12]. The last complex was obtained as a crystalline perchlorate by the addition of an aqueous solution of sodium perchlorate to a concentrated solution of the chloride salt in water followed by cooling.

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*Author to whom correspondence should be addressed.

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Anal. Calcd. for $[Co(en)_2(imH)Cl]Cl_2 \cdot \frac{1}{2}H_2O$(%): C, 23.2; H, 5.85; N, 23.2. Found: C, 23.2; H, 5.79; N, 22.9. Calcd. for $[Co(en)_2(bzimH)Cl]Cl_2 \cdot H_2O$: C, 31.3; H, 5.74; N, 19.9. Found: C, 31.3; H, 5.88; N, 19.7. Calcd., for $[Co(en)_2(1\text{-}Meim)Cl](ClO_4)_2$: C, 19.4; H, 4.48; N, 16.95. Found: C, 19.5; H, 4.54; N, 16.91.

Near UV-visible spectra of the complexes were recorded on a Pye-Unicam SP 8-100 spectrophotometer. Kinetics of base hydrolysis were followed at 298 K by the pH-stat method using a Radiometer pH Meter 26, linked to a Titrator II with alkali (0.1 mol dm^{-3}) being added from an ABU 2 autoburette and monitored against time on a Titrigraph. Complex concentrations were typically 5 × 10^{-3} mol dm^{-3} (25.0 cm^3) and each solution had an ionic strength of 0.1 mol dm^{-3} ($NaClO_4$). The pK_a values of the imidazole and benzimidazole complexes at 298 K, and I = 0.1 were measured directly using the aforementioned potentiometric assembly with the same concentrations of complex and base. Values of $[OH^-]$ were calculated from pH using a pK_n value of 14.0 and an activity coefficient of 0.772.

Results and Discussion

The UV-visible spectra of the complexes in aqueous solution each display two absorption bands, the positions and molar absorption coefficients of which imply *cis* configurations [1]. For *cis*-$[Co(en)_2(imH)Cl]Cl_2$ these bands, with molar absorption coefficients (dm^3 mol^{-1} cm^{-1}) in parentheses, are centred at 524 (78.4) and 363 (93.4) nm; for *cis*-$[Co(en)_2(bzimH)Cl]Cl_2$ at 524 (82.9) and 375 (116.7) nm; for *cis*-$[Co(en)_2(1\text{-}Meim)Cl](ClO_4)_2$ at 522 (79.0) and 364 (75.5) nm.

In basic solutions *cis*-$[Co(en)_2(1\text{-}Meim)Cl]^{2+}$ undergoes base hydrolysis and follows a steric course which has been shown [13] to yield 19% *trans*- and 81% *cis*-$[Co(en)_2(1\text{-}Meim)OH]^{2+}$. The rate constants for this reaction, determined by the pH-stat method, are presented in Table I. In the pH range investigated the values of k_2, the second order rate constant for base hydrolysis (= $k_{obs}/[OH^-]$), are virtually constant (23–27 dm^3 mol^{-1} s^{-1}) and do not differ sufficiently from the corresponding rate constants for reactions of similar alkylamine complexes to suggest any special labilising properties associated with the 1-methylimidazole ligand.

TABLE I. Rate Data for Base Hydrolysis of *cis*-$[Co(en)_2(1\text{-}Meim)Cl]^{2+}$ at 298 K and I = 0.1 mol dm^{-3} ($NaClO_4$).

pH	k_{obs}/s^{-1}	$k_{obs}/[OH^-]/dm^3\ mol^{-1}\ s^{-1}$
9.55	1.11×10^{-3}	24.2
9.98	2.83×10^{-3}	22.9
10.31	6.67×10^{-3}	24.9
10.63	1.54×10^{-2}	27.0
10.96	3.16×10^{-2}	26.7

TABLE II. Rate Data for Base Hydrolysis of (a) *cis*-$[Co(en)_2(imH)Cl]^{2+}$ and (b) *cis*-$[Co(en)_2(bzimH)Cl]^{2+}$ at 298 K, I = 0.1 mol dm^{-3} ($NaClO_4$).

(a) pH	k_{obs}/s^{-1}	$k_{obs}/[OH^-]/dm^3\ mol^{-1}\ s^{-1}$
9.03	3.45×10^{-4}	24.8
9.39	8.07×10^{-4}	25.4
9.69	1.51×10^{-3}	23.8
9.98	2.59×10^{-3}	21.0
10.29	4.26×10^{-3}	16.9
10.57	6.56×10^{-3}	13.6
10.98	1.04×10^{-2}	8.4
(b) pH	k_{obs}/s^{-1}	$k_{obs}[OH^-]/dm^3\ mol^{-1}\ s^{-1}$
7.99	3.17×10^{-4}	250
8.25	5.26×10^{-4}	228
8.49	7.76×10^{-4}	194
8.67	9.40×10^{-4}	155
8.99	1.58×10^{-3}	125
9.35	2.11×10^{-3}	72.8
9.69	3.26×10^{-3}	51.3
9.98	5.15×10^{-3}	41.6
10.24	7.21×10^{-3}	32.0
10.47	1.15×10^{-2}	30.1
10.67	1.75×10^{-2}	28.9
10.82	2.27×10^{-2}	26.3
11.02	3.34×10^{-2}	24.6

Base hydrolysis of the complexes *cis*-$[Co(en)_2(imH)Cl]^{2+}$ and *cis*-$[Co(en)_2(bzimH)Cl]^{2+}$ were carried out under the same conditions (I = 0.1 mol dm^{-3}, T = 298 K). Both complexes behave as weak monobasic acids in aqueous solution. In a potentiometric titration against standard base pK_a values of 10.25 ± 0.03 and 8.76 ± 0.03 respectively were obtained for these complexes. In each case the pK_a value represents an average of values calculated from the pH of the solution after the addition of 0.1 equivalent aliquots of base* (above 0.8 equivalents of added base interference from hydrolysis was observed and the calculations were discontinued at this point). Hence coordination of imidazole and benzimidazole to $Co(en)_2Cl^{2+}$ results in a 10^4-fold increase in the acidity of these species. The pK_a values agree favourably with those reported for other complexes. Hence Hay *et al.* determined pK_a values of 8.84 ± 0.06 for

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*The pK_a values reported are mixed constants as defined in this ref. 14.

TABLE III. Second Order Rate Constants for Base Hydrolysis of Various Complexes at 298 K, $I = 0.1$ mol dm^3.

Complex	k_2/dm^3 mol^{-1} s^{-1}
cis-$[Co(en)_2(1\text{-}Meim)Cl]^{2+}$	25.1 ± 2.1
cis-$[Co(en)_2(imH)Cl]^{2+}$	28.0 ± 1.5
cis-$[Co(en)_2(im)Cl]^+$	4.0 ± 0.2
cis-$[Co(en)_2(bzimH)Cl]^{2+}$	257 ± 12
cis-$[Co(en)_2(bzim)Cl]^+$	21.6 ± 1.5

coordinated benzimidazole in *cis*-$[Co(en)_2(bzimH)OH]^{2+}$ [6] and 10.52 ± 0.05 for coordinated imidazole in *cis*-$[Co(en)_2(imH)OH]^{2+}$ [5] both at 298 K and $I = 0.1$ mol dm^{-3}. In other but not so similar examples (different metal and/or charges) pK_a values of 8.9 and 10.02 have been determined for the imidazole ligand in $[Ru(NH_3)_5(ImH)]^{3+}$ [10] and $[Co(NH_3)_5(imH)]^{3+}$ [15] respectively, while a pK_a value of 7.2 ($I = 0.003$ mol dm^{-3}, T = 298 K) was reported for ionization of benzimidazole in $[Ru(NH_3)_5(bzimH)]^{3+}$ [10].

Rate constants for the base hydrolysis of the complexes *cis*-$[Co(en)_2(imH)Cl]^{2+}$ and *cis*-$[Co(en)_2(bzimH)Cl]^{2+}$ at 298 K and $I = 0.1$ mol dm^{-3} are presented in Table II. In both cases values of $k_{obs}/[OH^-]$ decrease with increasing pH although for the benzimidazole complex a constant value is approached in the higher pH range investigated. This pattern of reactivity is in accordance with a base hydrolysis scheme, illustrated as follows for the imidazole complex:

$$\begin{tikzcd}
cis\text{-}[Co(en)_2(imH)Cl]^{2+} \arrow[r, shift left, "K_a"] \arrow[d, "OH^-,\ k_{imH}"] & cis\text{-}[Co(en)_2(im)Cl]^+ + H^+ \arrow[l, shift left] \arrow[d, "+OH^-,\ k_{im}"] \\
cis\text{-}[Co(en)_2(imH)OH]^{2+} \arrow[r, shift left] & cis\text{-}[Co(en)_2(im)OH]^+ + H^+ \arrow[l, shift left]
\end{tikzcd}$$

Scheme 1.

For such a scheme it can be shown that:

$$(k_{obs}/[OH^-])\{[H^+] + K_a\} = k_{imH}[H^+] + k_{im}K_a$$

where k_{obs} is the pseudo first order rate constant of reaction followed at constant $[OH^-]$. Hence it follows that a plot of $(k_{obs}/[OH^-])([H^+] + K_a)$ *vs.* $[H^+]$ should be linear with slope k_{imH} and intercept $k_{im}K_a$.

Excellent linear plots were found for both imidazole complexes under investigation. The second order rate constants for base hydrolysis of the various species thus obtained are presented in Table III, together with the value for the 1-methylimidazole complex for comparative purposes. Base hydrolysis of the imidazole complex has previously been shown to proceed along a pathway which results in 21% *trans*-, 79% *cis*-hydroxo products while the benzimidazole complex gives 6% *trans*- and 94% *cis*-products [13].

The similar reactivities of the 1-methylimidazole and imidazole complexes is to be expected since methyl substitution at the N-site remote from the reaction centre should have little effect on reactivity in base hydrolysis. The benzimidazole complex *cis*-$[Co(en)_2(bzimH)Cl]^{2+}$ is some nine-fold more reactive than its imidazole analogue and the enhanced reactivity probably results from transmission of the electronwithdrawing effect of the phenyl ring to the amine ligand undergoing deprotonation (hence increased K in the base hydrolysis rate expression rate = Kk_{cb}[complex] $[OH^-]$) rather than from any extra steric compression which would promote loss of Cl^- from the amido conjugate base (increased k_{cb}). In concordance with this view the complex *cis*-$[Co(en)_2(py)Cl]^{2+}$ (py = pyridine), which would reasonably be expected to contain amine (en) protons of greater acidity than *cis*-$[Co(en)_2(bzimH)Cl]^{2+}$* and which if anything should be less sterically compressed than the latter complex, undergoes more rapid base hydrolysis (k_2 = 332 dm^3 mol^{-1} s^{-1}, 298 K, $I = 0.1$ mol dm^{-3}) [17]. In addition it is difficult to see from the crystal structure of *cis*-$[Co(en)_2(imH)Cl]Cl_2$ [18] how the introduction of the phenyl ring could to any appreciable extent increase the steric strain at the reaction site. The activating effect of the phenyl ring is also evident in the relative reactivities of the unipositively charged benzimidazolate and imidazolate complexes, both of which, as expected, undergo base hydrolysis at slower rates than their conjugate acids.

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*A pyridine ligand should be more electron withdrawing than a benzimidazole ligand adjudged from the relative acidities of the pyridinium (pK = 5.31, 298 K, $I = 0.1$ mol dm^{-3}) and benzimidazolium (pK = 5.66, 298 K, $I = 0.05$ mol dm^{-3}) cations. If the effect is transmitted to a 1,2-diaminoethane ligand through the metal, then amine ligands in the pyridine complex would be more acidic. For the pK values above see ref. 16.

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