

## ACID DISSOCIATION CONSTANTS OF SOME AQUO AMINE COBALT(III) COMPLEXES\*

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Apart from their intrinsic worth the acid dissociation constants of complexes are of importance in kinetic studies. Where the complex can react through either the acid form or the conjugate base the temperature dependence of the dissociation constant  $K_a$  may contribute significantly to the "apparent" activation energy of the latter path. For this reason accurate  $K_a$  values at different temperatures are required to determine the "real" kinetic parameters of the conjugate base reaction.

The  $pK_a$  values for the cobalt(III) triethylenetetramine (trien) complexes recorded in Table 1 were determined largely for this purpose and they may be compared with values for  $[\text{Coen}_2\text{OH}_2\text{X}]^{n+}$  complexes which have been reported previously<sup>1</sup> (Table 2). It can be seen that a temperature difference of 10° leads to a  $pK_a$  difference of 0.3–0.4 or a factor of 2–2.5 in the concentration of the conjugate base. When this was applied to the observed<sup>2</sup> rates of aquation of *cis*- $\alpha$  [ $\text{CotrienClOH}$ ]<sup>2+</sup>§ the "apparent"  $E_a$  of 33 kcal mole<sup>-1</sup> was reduced to 19 kcal mole<sup>-1</sup>. Thus the significance of accurate  $pK_a$  values is apparent and those values given in Table 1 will be used in subsequent publications on the kinetics, of aquation of *cis*  $\alpha$  and  $\beta$  [ $\text{CotrienClOH}_2$ ]<sup>2+</sup> and of racemization and isomerization of *cis*  $\alpha$  and  $\beta$  [ $\text{Cotrien}(\text{OH}_2)_2$ ]<sup>3+</sup> ions.

The determination of the  $K_a$  values was complicated by hydrolysis and isomerization of some of the compounds in neutral and alkaline solution. This problem was surmounted to some extent by dissolving the complex in acid and by partially neutralizing aliquots of the parent solution for each titration point. The pH was then determined over the period of mixing and subsequent reaction and reasonable values for the pH ( $\pm 0.02$  units) were obtained by extrapolating the hydrolysis curves back to complete mixing.

All the *trans* isomers listed in Table 2 are stronger acids than the *cis* except for the aquo nitro ions and it is tempting to rationalize the differences in the acidities of the complexes in terms of the inductive and conjugative effects of the *cis* and *trans* substituents.<sup>3</sup> However, a comparison between the  $pK_a$  differences for *cis*

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§  $\alpha$  and  $\beta$  refer to the mode of attachment of the trien quadridentate to the metal ion. The  $\alpha$  isomer has the ligand configuration where both secondary nitrogens have their normal tetrahedral angles unstrained.

<sup>1</sup> Tobe, M. L., *Sci. Progr.*, 1960, **48**, 483.

<sup>2</sup> Sargeson, A. M., and Searle, G. H., unpublished data.

<sup>3</sup> Ingold, C. K., Nyholm, R. S., and Tobe, M. L., *Nature*, 1960, **187**, 477.

$\alpha$  and  $\beta$  [CotrienClOH<sub>2</sub>]<sup>2+</sup> ions and *cis* and *trans* [Coen<sub>2</sub>ClOH<sub>2</sub>]<sup>2+</sup> is revealing. Clearly the geometrical arrangement of the substituents is not the only factor of major significance in determining the difference between the  $pK_a$  values.

The difference between the acidities of the  $\alpha$  and  $\beta$  [CotrienClOH<sub>2</sub>]<sup>2+</sup> ions was also evident in the relative importance of the aquo and hydroxo aquation paths for each ion. While the former was quite significant for the  $\alpha$  isomer practically all the

TABLE 1  
ACID DISSOCIATION CONSTANTS (MEAN  $\pm$  MAXIMUM DEVIATION)  
 $I = 0.1M$  (NaClO<sub>4</sub>)

Complex	10°		20°		Method
	$pK_{a,1}$	$pK_{a,2}$	$pK_{a,1}$	$pK_{a,2}$	
<i>cis</i> - $\alpha$ [Cotrien(H <sub>2</sub> O) <sub>2</sub> ] <sup>3+</sup>	5.8 $\pm$ 0.05	7.8 $\pm$ 0.1	5.4 $\pm$ 0.05	7.3 $\pm$ 0.1	A
<i>cis</i> - $\beta$ [Cotrien(H <sub>2</sub> O) <sub>2</sub> ] <sup>3+</sup>	5.6 $\pm$ 0.05	7.9 $\pm$ 0.1	5.3 $\pm$ 0.05	7.8 $\pm$ 0.1	A
<i>cis</i> - $\alpha$ [CotrienClH <sub>2</sub> O] <sup>2+</sup>	7.46 $\pm$ 0.02		7.11 $\pm$ 0.02		B
<i>cis</i> - $\beta$ [CotrienClH <sub>2</sub> O] <sup>2+</sup>	6.2 $\pm$ 0.1		5.8 $\pm$ 0.1		B
<i>cis</i> -[Coen <sub>2</sub> ClH <sub>2</sub> O] <sup>2+</sup>	7.47 $\pm$ 0.02		7.13 $\pm$ 0.04		C
<i>trans</i> -[Coen <sub>2</sub> ClH <sub>2</sub> O] <sup>2+</sup>	6.37 $\pm$ 0.03		6.11 $\pm$ 0.01		C
<i>cis</i> -[Co(NH <sub>3</sub> ) <sub>4</sub> ClH <sub>2</sub> O] <sup>2+</sup>			6.6 $\pm$ 0.2		C

TABLE 2  
DISSOCIATION CONSTANTS FROM TOBE<sup>1</sup>

<i>trans</i> Complex	$pK_a$	Temp.	<i>cis</i> Complex	$pK_a$	Temp.
[Coen <sub>2</sub> OH <sub>2</sub> OH] <sup>2+</sup>	7.9	25°	[Coen <sub>2</sub> OH <sub>2</sub> OH] <sup>2+</sup>	8.2	25°
[Coen <sub>2</sub> OH <sub>2</sub> Cl] <sup>2+</sup>	7.2	25°			
[Coen <sub>2</sub> OH <sub>2</sub> NCS] <sup>3+</sup>	6.3	20°	[Coen <sub>2</sub> OH <sub>2</sub> NCS] <sup>2+</sup>	6.8	20°
[Coen <sub>2</sub> OH <sub>2</sub> NH <sub>3</sub> ] <sup>3+</sup>	5.8	20°	[Coen <sub>2</sub> OH <sub>2</sub> NH <sub>3</sub> ] <sup>3+</sup>	6.1	20°
[Coen <sub>2</sub> OH <sub>2</sub> OH <sub>2</sub> ] <sup>3+</sup>	4.5	25°	[Coen <sub>2</sub> OH <sub>2</sub> OH <sub>2</sub> ] <sup>3+</sup>	6.1	25°
[Coen <sub>2</sub> OH <sub>2</sub> NO <sub>2</sub> ] <sup>2+</sup>	6.4	25°	[Coen <sub>2</sub> OH <sub>2</sub> NO <sub>2</sub> ] <sup>2+</sup>	6.3	25°

aquation occurred through the hydroxo path for the  $\beta$  isomer. Similarly the racemization of the  $\alpha$  and  $\beta$  [Cotrien(OH<sub>2</sub>)<sub>2</sub>]<sup>3+</sup> occurred largely through the conjugate base and to about the same extent in each isomer, which is consistent with the similarities in their  $pK_a$  values.<sup>2</sup>

### Experimental

The thermostated reaction cell (a cylindrical glass vessel, 100 ml capacity) was closed by a rubber stopper through which passed the electrodes, a gas-bubbler, and a fine-bore Polythene tube connected to a micrometer syringe. Solutions were stirred with a magnetic stirrer and kept free of carbon dioxide by bubbling through scrubbed nitrogen. All pH measurements were made by using a Vibron Electrometer Model 33B (Electronic Instruments Ltd.), which was fitted with an internally shielded glass electrode and a saturated calomel electrode and which could be read directly to 0.001 pH unit. The output of the pH meter was also applied directly to a Rectiriter recording milliammeter (Texas Instruments Inc.) and the pH was followed over the

time of mixing and subsequent hydrolysis. The pH of freshly prepared 0.05M potassium hydrogen phthalate was taken as 3.999 and 4.001 at 10° and 20°, respectively; as a secondary standard, 0.05M sodium borate, pH = 9.313 (10°) and 9.227 (20°) was used.

The acid dissociation constants, which were calculated by the complete Henderson-Hasselbalch equation, are concentration constants; the concentration of H<sup>+</sup> was obtained from pH measurements by using an activity coefficient determined from a titration of the inert medium (0.1M sodium perchlorate) with acid of known concentration. Overlapping pK<sub>a</sub> values were calculated using the method of Speakman.<sup>4</sup>

The complexes *trans*[Coen<sub>2</sub>ClOH<sub>2</sub>]<sub>2</sub>SO<sub>4</sub>,<sup>5</sup> *cis*[Coen<sub>2</sub>ClOH<sub>2</sub>]<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O,<sup>5</sup> α[CotrienCl<sub>2</sub>]<sub>2</sub>ClO<sub>4</sub>,<sup>2</sup> β[CotrienCl<sub>2</sub>]<sub>2</sub>ClO<sub>4</sub>,<sup>2</sup> α[Cotrien(OH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>(ClO<sub>4</sub>)<sub>3</sub>,<sup>2</sup> β[Cotrien(OH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>(ClO<sub>4</sub>)<sub>3</sub>,<sup>2</sup> and [Co(NH<sub>3</sub>)<sub>4</sub>ClOH<sub>2</sub>]<sub>2</sub>SO<sub>4</sub>,<sup>6</sup> were titrated by one of the following methods, depending on their lability.

*Method A.*—A solution of the complex ( $1.0 \times 10^{-3}$ M) in HClO<sub>4</sub> ( $1.0 \times 10^{-3}$ M) was titrated with carbonate-free NaOH using a micrometer syringe. After each addition of NaOH, the pH remained constant for the two complexes examined by this method (Table 1).

*Method B.*—The dichloro complex was dissolved in an acid solution and sufficient time was allowed for the formation of the optimum concentration of the chloro aquo complex (α, 98% after 10 hr at 20°; β, 94% after 50 min at 20°).

Sufficient alkali was added to three aliquots of each stock solution to neutralize the acid and one-fifth, two-fifths, and one-half of the complex respectively and the pH was measured in each instance. In calculating the acid dissociation constants, corrections were made for the presence of small amounts of the diaquo complex (2% α and 6% β at 20°). The pH readings were not constant with time, owing to the hydrolysis of the coordinated Cl<sup>-</sup> ion. The rise in pH due to mixing and the subsequent decay in pH due to hydrolysis were followed on the Rectiriter recorder and the pH was extrapolated back to the time of complete mixing. At 10° the rate of hydrolysis was slower and the maximum pH values remained constant for several minutes.

*Method C.*—Individual solutions of the *cis* and *trans* [Coen<sub>2</sub>ClOH<sub>2</sub>]<sub>2</sub>SO<sub>4</sub> complexes ( $1.0 \times 10^{-3}$ M) in acid ( $1.0 \times 10^{-3}$ M) were prepared and immediately partially neutralized as in B. For readings at 20° the change in pH with hydrolysis was extrapolated back to complete mixing but at 10° the maximum pH values were constant for at least 5 min. The *cis* chloro aquo tetramine cobalt (III) ion was also treated in this manner and was the most labile of all the complexes measured.

<sup>4</sup> Speakman, J. C., *J. Chem. Soc.*, 1940, 855.

<sup>5</sup> Dwyer, F. P., Sargeson, A. M., and Reid, I. K., *J. Amer. Chem. Soc.*, 1963, **85**, 1215.

<sup>6</sup> Kauffman, G. B., and Pinnell, R. P., *Inorg. Synth.*, 1960, **6**, 176.