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Determination of the Acid Dissociation Constants of Coordinated Water in *cis*-$[Cotn_2(H_2O)_2]^{3+}$ Ion

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Experimental

Materials

Reagent grade chemicals were used in all procedures. The 1,3-diaminopropane (tn) was purchased from Aldrich Chemical Co. NaOH (0.10 M) solutions were prepared by diluting 'J. Baker concentrated NaOH' with CO_2-free deionized water.

The elemental analyses of the isolated diaqua complex were performed at Galbraith Chemical Laboratories, Knoxville, Tenn., U.S.A.

Synthesis of the Complexes

$[Cotn_2CO_3]ClO_4$

This complex was prepared via $Na_3[Co(CO_3)_3]\cdot 3H_2O$ [1] by the earlier method described in the literature [2]. The purity was checked by comparing its electronic spectrum with that reported elsewhere [3].

cis-$[Cotn_2(H_2O)_2](ClO_4)_3\cdot H_2O$

The diaqua complex was prepared by treating $[Cotn_2CO_3]ClO_4$ (1 g) with 3 ml of 6 M $HClO_4$ at room temperature. The resulting red solution was heated for 5 min at 70 °C to expel CO_2, then stored in a vacuum desiccator over P_4O_{10}. After two days, a red crystalline complex separated out. It was collected by filtration, washed with cold absolute ethanol and ether, and air dried (yield 80%). *Anal.* Calc. for $[Co(C_3H_{10}N_2)_2(H_2O)_2](ClO_4)_3\cdot H_2O$: C, 12.88; H, 4.64; N, 10.01. Found: C, 12.82; H, 4.57; N, 9.69%.

Measurements of the Acid Dissociation Constants

The values of the first and second acid dissociation constants K_1 and K_2 for the complex *cis*-$[Cotn_2(H_2O)_2]^{3+}$ ion were measured at 25 °C and $\mu = 0.5$ M ($NaClO_4$). The pH measurements were carried out using a Radiometer pH meter PHM 62, equipped with a glass electrode type GK 2421 C, and a saturated calomel electrode as a reference. These were used in conjunction with an autoburette (ABU 12) and a titration assembly (TTA 66).

Due to the rapid isomerization [4] of the $[Cotn_2(H_2O)_2]^{3+}$ system, a definite volume of 0.10 NaOH was added in one shot to a definite volume of a thermostated stirred solution of the diaqua complex (5 ml of 6.984×10^{-3} M) in a jacketed reaction vessel. In this way, it was possible to take the first reading about 10 s (time taken for the glass electrode to adjust to the new pH) after the addition of the base. The pH was recorded as a function of time.

Results and Discussion

The visible spectra of $[Cotn_2(H_2O)_2]^{3+}$ ion, in 0.1 M $HClO_4$, showed only two absorption bands at 506 and 362 nm with molar absorptivities equal to 53.5 and 65.4 M^{-1} cm^{-1}, respectively. Such spectral behaviour is similar to that observed in *cis*-$[Cotren(H_2O)_2]^{3+}$ [5] and *cis*-$[Coen_2(H_2O)_2]^{3+}$ [6] complexes (tren = 2,2′,2″-triaminotriethylamine and en = 1,2-diaminoethane). Therefore, the two coordinated water molecules in $[Cotn_2(H_2O)_2]^{3+}$ must have the *cis* geometry [7].

It has been pointed out that *trans*-$[Cotn_2(H_2O)_2]^{3+}$ isomerizes rapidly to the *cis* isomer in acidic medium (at 25 °C, $t_{1/2} = 70$ s), while in the buffer pH range the isomerization rate is even greater [8]. Consequently, in order to minimize the complications due to the high rate of *cis–trans* isomerization, an experiment of the type used by Rasmussen and Bjerrum was performed [6], where definite volumes of NaOH were added in 'one-shot' and the pH change was recorded as a function of time. The plots of pH *versus* time are shown in Fig. 1. The extrapolated lines obtained from these plots gave pH_0 (at time $t = 0$), *i.e.* the pH of pure *cis*-$[Cotn_2(H_2O)_2]^{3+}$, upon the addition of NaOH. From the titration curve (pH_0 *versus* volume of NaOH added), the acid dissociation constants K_1 and K_2 for the coordinated water molecules in *cis*-$[Cotn_2(H_2O)_2]^{3+}$ ion were evaluated [9]. Such dissociations can be represented by the following equations

$$cis\text{-}[Cotn_2(H_2O)_2]^{3+} + H_2O \overset{K_1}{\rightleftharpoons} cis\text{-}[Cotn_2(OH)(H_2O)]^{2+} + H_3O^+ \quad (1)$$

$$cis\text{-}[Cotn_2(OH)(H_2O)]^{2+} + H_2O \overset{K_2}{\rightleftharpoons} cis\text{-}[Cotn_2(OH)_2]^{+} + H_3O^+ \quad (2)$$

However, when the *cis–trans* isomerization has been established and the values of pH_∞ are plotted *versus* the added volume of NaOH, the p*K*s obtained

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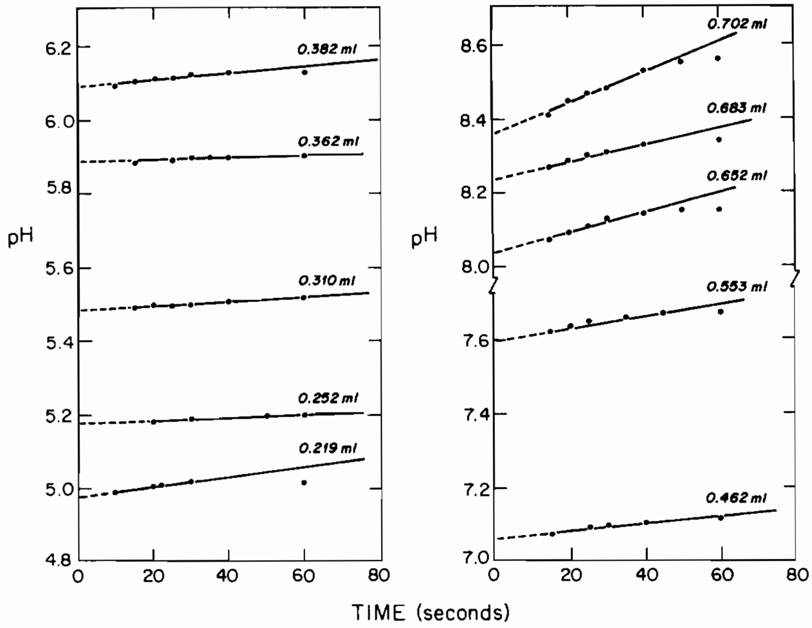

Fig. 1. The pH change as a function of time during the titration of *cis*-$[Cotn_2(H_2O)_2]^{3+}$ (6.984×10^{-3} M, 5 ml) with 0.10 N NaOH (upon the addition of definite volumes of NaOH) at 25.0 °C and $\mu = 0.5$ M.

TABLE I. The Acid Dissociation Constants of Coordinated Water Molecules in the $[Cotn_2(H_2O)_2]^{3+}$ Ion

Complex ion	pK_1	pK_2	Temperature (°C)	μ
cis-$[Cotn_2(H_2O)_2]^{3+}$	4.98	6.92	25	0.5
$[Cotn_2(H_2O)_2]^{3+a}$	4.78	7.22	25	0.5
$[Cotn_2(H_2O)_2]^{3+a,b}$	4.75	7.45	22	1.0

[a]An average pair of acidity constants. [b]Data taken from ref. 8.

can be considered as an average pair of acidity constants. The values of p*K*s of water molecules coordinated to $[Cotn_2(H_2O)_2]^{3+}$ are given in Table I. At 25 °C and $\mu = 0.5$ M, the *cis*-$[Cotn_2(H_2O)_2]^{3+}$ ion has $pK_1 = 4.98$ and $pK_2 = 6.92$, while the corresponding values at equilibrium are 4.78 and 7.22, respectively. The latter values are very close to those obtained by Stranks and Fowless [8] (Table I). It is evident, from these data, that for the first dissociation the *cis* isomer is less acidic than the *trans* isomer, while for the second dissociation the situation is inverted.

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