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The pK_a Value and Volume Change for the Neutralization of [Co(edda)($H_2NCH_2CH_2OH$)]$^+$

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Synopsis. The pK_a value of [Co(edda) ($H_2NCH_2CH_2OH$)]$^+$at 25 °C has been determined spectrophotometrically to be 5.01±0.05. The volume change for the equilibrium: [Co(edda)($H_2NCH_2CH_2OH$)]$^+$+OH^-=[Co(edda)($H_2NCH_2CH_2O$)]^0+H_2O has been found to be 16.9±0.7 cm^3/mol at 25 °C at an ionic strength of *ca.* 5 mM (1 mM $=10^{-3}$ mol dm^{-3}).

The volume change (ΔV) for the neutralization equilibrium of a complex ion is essential for the interpretation of the activation volume for a reaction of a complex ion, proceeding *via* the S_N1 CB mechanism.[1,2] Values of ΔV for three such equilibria of trivalent complex ions are known:

$$[Co(NH_3)_5H_2O]^{3+} + OH^- = [Co(NH_3)_5OH]^{2+} + H_2O \quad (1)$$

ΔV_1=20.6 cm^3/mol at 30 °C;[3]

$$[Cr(H_2O)_6]^{3+} + OH^- = [Cr(H_2O)_5OH]^{2+} + H_2O \quad (2)$$

ΔV_2=18.3 cm^3/mol at 25 °C;[4]

$$[Fe(H_2O)_6]^{3+} + OH^- = [Fe(H_2O)_5OH]^{2+} + H_2O \quad (3)$$

ΔV_3=20.9 cm^3/mol.[5]

A value of ΔV for the analogous equilibrium of a univalent complex ion is however not known and is of interest with respect to the charge effect on the magnitude of ΔV.

α-*cis*-Ethylenediamine-*N*,*N'*-diacetato(2-aminoethanol)cobalt(III) perchlorate, α-*cis*-[Co(edda)(Hame)]ClO_4 was obtained by Kuroda.[6] The aqueous solution of this complex gives a low pH value (3.94 in a 2.5 mM solution) and the indication is that in water there exists an acid dissociation equilibrium:[6]

$$[Co(edda)(Hame)]^+ = [Co(edda)(ame)]^0 + H^+, \quad (4)$$

where Hame=$H_2NCH_2CH_2OH$ and ame=$H_2NCH_2CH_2O^-$.

The determination of the pK_a value of 4 is significant *per se*, since the pK_a values of Co(III) complex ions are known only for ones with the aqua ligand so far.[7] The volume change (ΔV_5) for the equilibrium:

$$[Co(edda)(Hame)]^+ + OH^- = [Co(edda)(ame)]^0 + H_2O \quad (5)$$

has been measured in relation to the interpretation of the activation volume for the base hydrolysis reactions of α-, β-*cis*-[Co(edda)$(NH_3)_2$]$^+$.[8]

Experimental

α-*cis*-[Co(edda)(Hame)]ClO_4 was obtained by the standard method and identified by the visible absorption spectrum of a 5 mM aqueous solution.[6] The λ_{max} (ε_{max}) values were 536 nm(89.2), 380 nm(84.4) which compare to the values reported by Kuroda of 535 nm(90.3), 377 nm(85.1) respectively. A Hitachi-Horiba M-5 pH meter was used and a Carlsberg dilatometer for the measurement of the volume change. The procedures were essentially the same as those described by Spiro *et al.*[3] Two liquids separated by kerosene were mixed and the volume change obtained from the change of the kerosene level in the capillary. 10 min was required for the establishment of the thermal equilibrium. In some experiments slow linearly time-dependent variations of the kerosene level were observed before and after mixing. The dilatometer readings were extrapolated to the time of mixing. The radius of the capillary was calibrated with mercury (0.0202±0.0003 cm) and the kerosene level read by a cathetometer. The thermostat was maintained at 25.02±0.02 °C with a variation of less than 0.002 °C. Boiled out water was used. The kerosene was purified.

Results and Discussion

The color of a solution of [Co(edda)(Hame)]ClO_4 in 0.01 M HCl is reddish pink and in 0.01 M KOH it is pale blue violet (1 M=1 mol dm^{-3}). The color changes instantaneously and reversibly by the addition of an acid or an alkali, which indicates that the color change is caused by a shift of the chemical equilibrium. The absorption spectrum is illustrated in Fig. 1. The absorption maxima (*ca.* 570 and 384 nm) of [Co(edda)(ame)]^0 (in 0.01 M KOH) lie at longer wavelengths relative to those (536 and 380 nm) of [Co(edda)(Hame)]$^+$ (in 0.01 M HCl). This tendency is analogous to the relative position of bands of the complexes with a hydroxo ligand to those of the corresponding complexes with an aqua ligand. In pure water the spectrum is similar to that in 0.01 M HCl and the complex exists mostly in the acid form, [Co(edda)(Hame)]$^+$.

The pK_a value was determined from the optical densities (OD) at 300 nm in a 1 mM solution of the complex in acetate buffers (Table 1). The absorption coefficients at 300 nm of [Co(edda)(Hame)]$^+$ and [Co-

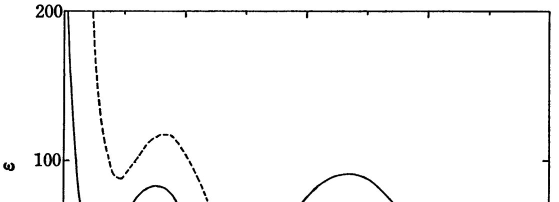

Fig. 1. Visible absorption spectra of 5 mM-[Co(edda)(Hame)]ClO_4. ——: in 0.01 M HCl, ----: in 0.01 M KOH.

Table 1. Spectrophotometric determination of the pK_a value at 25 °C

Solvent$^{a)}$	pH$^{b)}$	OD$^{b)}$	pK_a
5.5/54.5	5.60	0.701	5.06
8.0/52.0	5.42	0.660	5.03
12.0/48.0	5.26	0.613	5.03
16.7/43.3	5.05	0.563	4.99
23.1/36.9	4.86	0.505	4.99
30.0/30.0	4.67	0.457	4.96
0.008 M HCl	2.18	0.290	
0.008 M KOH	11.75	0.842	

a) CH_3COOH(mM)/CH_3COONa(mM). b) Measured at 25 °C.

(edda)(ame)]^0 are 290 and 842 l mol^{-1} cm^{-1}, respectively. The activity coefficients of H^+ may be estimated according to the method of Davies.$^{9)}$ The magnitude of pK_a 5.01±0.05 is small compared with those of a Co(III) complex with an aqua ligand.$^{7)}$

An aqueous solution of [Co(edda)(Hame)]ClO_4 (25 cm^3) was mixed with 0.035 M KOH (10 cm^3). Values of the volume change were [given as the initial concentration of the complex/mM, volume change/μl]: 5.21, 2.31; 5.13, 2.10; 5.20, 2.25; and 5.14, 2.18. Heat was evolved in the mixing. As a blank test, water (25 cm^3) was mixed with 0.035 M KOH (10 cm^3) and the volume change found to be negligibly small (0.00±0.11 μl, average for five runs). Thus, a value of 17.1±0.7 cm^3/mol is obtained for $\alpha\Delta V(H_2O)+(1-\alpha)\Delta V_5$, where $\Delta V(H_2O)$ is the volume change (22.07 cm^3/mol at 25 °C) for the equilibrium, $H^+ + OH^- = H_2O$ and α is the degree of dissociation (0.04) of [Co(edda)(Hame)]$^+$ in the 5.2 mM solution.$^{10)}$ Thus, ΔV_5 at 25 °C is evaluated as 16.9±0.7 cm^3/mol. The magnitude of ΔV_5 is comparable to those of ΔV_1, ΔV_2, and ΔV_3, which indicates that the difference between the molar volume of water and the partial molar volume of OH^- (*ca.* 1.4 cm^3/mol) is the major contribution for the volume changes.$^{11)}$ The intrinsic volumes of the complex ions would be little affected by protonation and hence the somewhat smaller magnitude of ΔV_5 compared to those of ΔV_1, ΔV_2, and ΔV_3 may be qualitatively explained by the smaller contribution of the electrostrictive volume change (ΔV_{el}) of the complex in Equilibrium 5. To a first approximation, neglecting the compressibility of the complex ion$^{5)}$ and the dielectric saturation of water,$^{12)}$ the electrostrictive volume (V_{el}) for an ion of radius r and charge Ze in water is given by; $V_{el} = -(NZ^2e^2)(\mathrm{d}D/\mathrm{d}P)/(2rD^2)$, where N and D represent Avogadro's number and the bulk dielectric constant for water, respectively.$^{5)}$ Hence, ΔV_{el} in Equilibria 1, 2, and 3 ($\Delta Z^2 = -5$) is larger than that in Equilibrium 5 ($\Delta Z^2 = -1$). This difference in ΔV_{el} is evaluated as 5.5 cm^3/mol for $r=3$ Å, using the value of $(1/D^2)(\mathrm{d}D/\mathrm{d}P)$ at 1 bar (6.0×10^{-7} bar^{-1}).$^{13)}$ The water molecules around the ion however are under high pressure due to the electrostriction and this pressure is higher for ions of higher valency.$^{5)}$ Thus, values of $(1/D^2)(\mathrm{d}D/\mathrm{d}P)$ at high pressures must be used. Since, $(1/D^2)(\mathrm{d}D/\mathrm{d}P)$ decreases with increase in pressure, the difference in ΔV_{el} would be smaller than as simply estimated above.$^{13)}$

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