Conjugate Bases of Tris(ethylenediamine)cobalt(III) and Nitropenta-ammine-cobalt(III) in Aqueous Hydroxide–Dimethyl Sulphoxide Mixtures

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Summary The conjugate bases of tris(ethylenediamine)-cobalt(III) and nitropenta-amminecobalt(III) are characterized in aqueous hydroxide–dimethylsulphoxide mixtures, pK_a values being determined using an acidity function derived from the solvent dependence of the rate of base hydrolysis of chloropenta-amminecobalt(III).

AQUEOUS hydroxide–dimethyl sulphoxide mixtures have previously been used in the study of weak organic acids with pK_a values in the range 14—26.[1] We have now studied spectrophotometrically the neutralization of $[Coen_3]^{3+}$ by tetramethylammonium hydroxide in Me_2SO–H_2O mixtures containing up to 86·4 mol % Me_2SO. In the most strongly basic solutions, absorbance increases linearly with added base until a 1 : 1 ratio of complex : OH^- is reached, and remains constant for further additions of base. Figure 1 shows the visible–u.v. spectrum of $[Coen_2(en\text{-}H)]^{2+}$. The logarithm of the ratio of conjugate base and acid forms of $[Coen_3]^{3+}$ is given in Figure 2 as a function of solvent composition for the range where measurements were possible, 14—44 mol % Me_2SO.

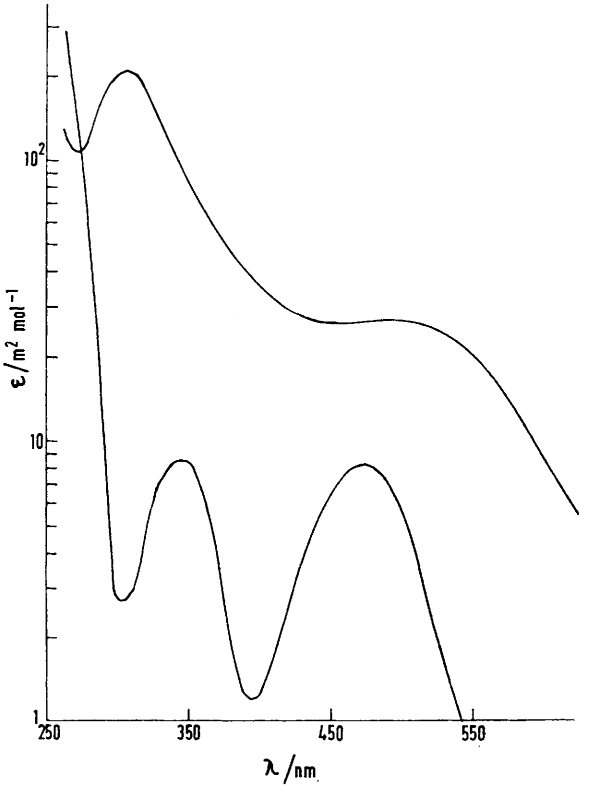

FIGURE 1. Spectra of tris(ethylenediamine)cobalt(III) (lower curve) and its conjugate base, measured in 86·4 mol % Me_2SO–H_2O.

Figure 2 reports second-order rate constants for the base hydrolysis reactions of two acidopenta-ammine-cobalt(III) complexes in aqueous hydroxide–dimethyl sulphoxide mixtures. The hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ was followed over the range 0—75 mol % Me_2SO, spectrophotometric monitoring of the reaction at high basicity requiring a stopped-flow apparatus. Methods described by Lalor and Lang[2] were adapted to follow the base hydrolysis of $[Co(NH_3)_5NO_2]^{2+}$ over the range 40—80 mol % Me_2SO.

All three reactions studied show the same dependence on solvent basicity. Plots of log $k_{OH^-}^{nitro}$ and log ($[Coen_2(en\text{-}H)]/[Coen_3]$) *vs.* log $k_{OH^-}^{chloro}$ are linear, with slopes 1·00 ± 0·02 and 1·05 ± 0·04 respectively. These correlations and the increase of $k_{OH^-}^{chloro}$ by five orders of magnitude over the composition range studied accord with the S_N1cb reaction scheme,[3] shown in equations (1) and (2).

$$HA^{2+} \overset{K_a}{\rightleftharpoons} H^+ + A^+ \qquad (1)$$

$$A^+ \xrightarrow{k} \text{products} \qquad (2)$$

We deduce that the ionization behaviour of the reactive ammines and of $[Coen_3]^{3+}$ vary in the same way with solvent basicity, that the rate constant k for the dissociative step (2) can change only slightly over the range 15—40 mol % Me_2SO, and that any variations in k over the range 40—70 mol % Me_2SO are the same for both $[Co(NH_3)_5Cl]^{2+}$ and $[Co(NH_3)_5NO_2]^{2+}$. These conclusions are compatible with the lack of marked solvent dependence on the rates of aquation of Co^{III} complexes.[4]

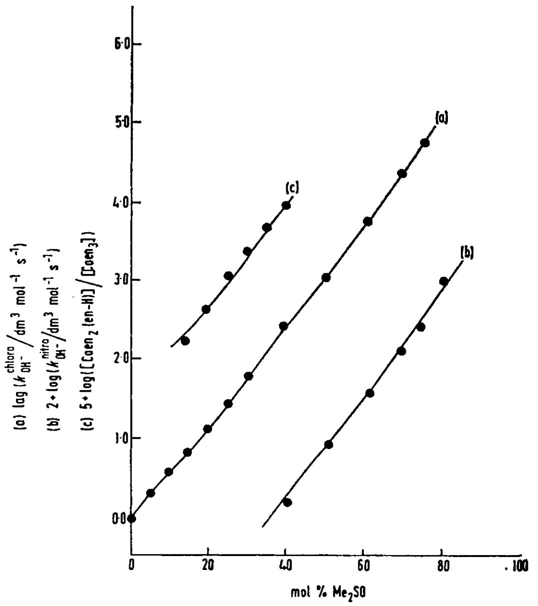

FIGURE 2. Solvent effects on base-hydrolysis rate constants for (a) chloro- and (b) nitro-penta-amminecobalt(III); (c) ratio of conjugate base and acid forms of tris(ethylenediamine)cobalt(III). For (a) and (b), $[OH^-] = I = 1{\cdot}1 \times 10^{-2}$ mol dm^{-3}. For (c), $[OH^-] = 3{\cdot}8 \times 10^{-3}$ mol dm^{-3}, $I = 3{\cdot}1 \times 10^{-2}$ mol dm^{-3}.

An H_+ acidity function for Co^{III} complexes was derived from the kinetic data for $[Co(NH_3)_5Cl]^{2+}$, with the assumption that k is independent of solvent composition. Data points in plots (b) and (c) of Figure 2 are accordingly fitted to lines drawn parallel to plot (a). Extrapolation of plot (c) to 0 mol % Me_2SO permits evaluation of the pK_a of $[Coen_3]^{3+}$ in the aqueous standard state, giving pK_a = 15·2 at ionic strength $3{\cdot}1 \times 10^{-2}$ mol dm^{-3}, and the calculated thermodynamic pK_a = 14·9 at $I = 0$. The characteristic red colour of the deprotonated $[Coen_3]^{3+}$ species noted in this study and previously by Watt *et al.*[5] cannot be detected in aqueous hydroxide solutions,[6,7] and we feel that data by Navon *et al.*[6] to deduce a pK_a of 14·3 should be re-interpreted in terms of ion pairing.[7]

$[Co(NH_3)_5NO_2]^{2+}$, like $[Coen_3]^{3+}$, shows an instantaneous and reversible increase of absorbance when mixed with OH^- in solutions with a high Me_2SO content. A spectrophotometric titration of $[Co(NH_3)_5NO_2]^{2+}$ gives $pK_a = 16{\cdot}8$ on the H_+ scale defined earlier. We believe that this is the first direct characterization of a conjugate base of a reactive ammine complex. At $H_+ = pK_a$, the S_N1cb scheme requires that $k_{OH^-}^{nitro} = \frac{1}{2}k$. The expected turnover in the kinetic plot is not observed, and in 80 mol % Me_2SO $k_{OH^-}^{nitro}$ is four times its value in 75 mol % Me_2SO, where $H_+ = pK_a$. This behaviour can be accounted for by a second deprotonation yielding $[Co(NH_3)_3(NH_2)_2NO_2]^0$, if the ratio of ligand loss from this and the singly-deprotonated complex equals the ratio of the first and second acid dissociation constants, $K_{HA^{2+}}/K_{A^+}$.

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