Intramolecular Hydrolysis of Co-ordinated Acetonitrile in a Binuclear μ-Amido-octa-amminedicobalt(III) Complex

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Intramolecular attack by co-ordinated hydroxide on one metal ion at acetonitrile bound to the other metal ion in binuclear μ-amido-octa-amminedicobalt(III) species is observed under acid conditions to give a chelated acetamide product, established by *X*-ray crystallographic analysis.

There are interesting roles for combinations of metal ions in catalysing the reactions of co-ordinated organic substrates. One possibility is that a bound metal ion may activate the substrate to attack by a nucleophile while another binds a functional group and assists it to leave the substrate in a synchronous process. Another possibility is that one metal activates the substrate while the other provides an intramolecular co-ordinated nucleophile, such as OH^- to effect efficient hydrolysis. Both mechanisms are possible and could be relevant to the role of the two Ni^{2+} ions in Jack Bean urease[1] or the two Zn^{2+} ions in *Escherichia coli* alkaline phosphatase.[2] The use of binuclear complexes to assess the efficacy of the metals in these two roles is an obvious step to take and this paper reports some preliminary observations on a system which appears to be of the latter kind, involving the hydrolysis of a nitrile bound to a metal ion.

A binuclear dicobalt(III) dinitrile complex, (**1**), was synthesised from the μ-hydroxo-μ-amido dimer,[3] (**5**), *via* the μ-amido ditriflate,[4] (**6**), and acetonitrile† as outlined in Scheme 1. In acid conditions, pH 0—4, one of the nitriles was hydrolysed to acetamide after the rate determining loss of the first nitrile. The evidence we have indicates the intermediacy of an aquo nitrile dimer complex (**2**) leading to the formation of acetamide. When (**1**) was dissolved in 0.1 M $DClO_4$ (in D_2O) at 20 °C, the ^1H n.m.r. spectrum showed the loss of co-ordinated acetonitrile (δ 2.69) and the growth of sharp signals at δ 2.26 and 2.03 (free MeCN). The product (δ 2.26) was isolated‡ and its ^1H n.m.r. spectrum (five NH_3 signals) indicated an unsymmetrical binuclear complex. It also showed i.r. frequencies at 1630 and 1570 cm^{-1} and no C≡N stretching frequency. These results implied the presence of an amide and that was established by *X*-ray crystallographic analysis on the dithionate salt§ which showed the product to be the chelate μ-acetamido-μ-amido-octa-amminedicobalt(III), species (**4**), see Figure 1. Moreover the visible spectra of the product at pH 1 and 9 were the same which implies that the chelate remains intact and no water molecule is bound to Co^{III} in these aqueous conditions. By analogy with the general Co^{III} amine chemistry, deprotonation of co-ordinated water (pK_a 6—7) and an appreciable spectral change would be expected going from pH 1 to 9.

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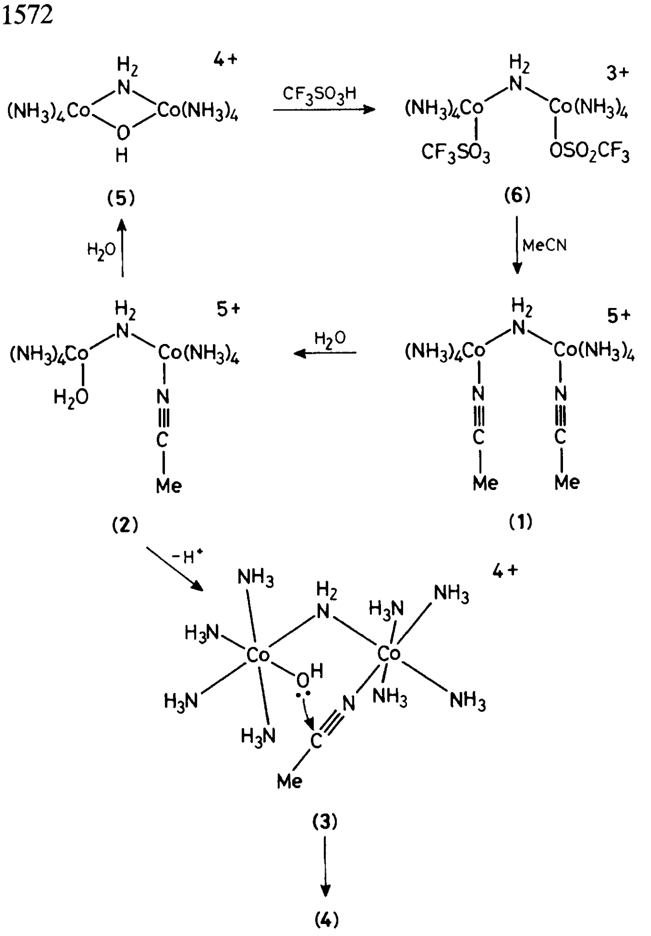
† Heated at 80 °C for 1 h, cooled, 1 volume of diethyl ether added and the orange-pink powder collected (89% yield). Satisfactory elemental analyses were obtained for (**1**)·$(CF_3SO_3)_5 \cdot 3H_2O$. I.r.(KBr) $\nu_{C\equiv N}$ 2300, 2330 cm^{-1}. ^1H N.m.r. (0.1 M $DClO_4$) δ 2.70 (s, 6H), 3.53, 3.74 (s) and 3.93 (s) (together 26H). $\lambda_{max.}$ (MeCN) 353 (ε 815 $dm^3\ mol^{-1}\ cm^{-1}$), 496 nm (421).

‡ Isolated as the triflate salt. Satisfactory elemental analyses were obtained for (**4**)·$(CF_3SO_3)_4$. ^1H n.m.r. (0.1 M $DClO_4$) δ 2.27 (s, 3H), 2.56 (s, 6H), 2.76 (s, 2H), 3.03 (s, 9H), 3.48 (s, 3H), 3.56 (s, 3H), 3.93 (s, 3H), 6.36 (s, 1H). $\lambda_{max.}$ (0.1 M $HClO_4$, 0.9 M $NaClO_4$) 357 (ε 572 $dm^3\ mol^{-1}\ cm^{-1}$), 498 nm (274).

§ Satisfactory elemental analyses were obtained for (**4**)·$(S_2O_6)_2 \cdot 4H_2O$.



Scheme 1

The structure is very similar to that of the μ-amido-μ-sulphato-bis[bis(ethylenediamine)cobalt(III)]^5 ion in that the acetamido ligand is skewed at an angle of 24° to the coplanar atoms Co(A), Co(B), N(6), and C(1), with O(1) and N(1) 0.49 below and 0.40 Å above the plane, respectively. Delocalisation of the acetamido group^6 is implied by the short bond lengths for C–O and C–N relative to single bonded species.

From pH 1 to 3.8 the hydrolysis followed a single first order rate,¶ with $k = 3.0 \pm 0.1 \times 10^{-4}\ s^{-1}$ at 25 °C. In 1 M $HClO_4$ consecutive reactions were seen, with the slower process having the same time constant as that seen at pH 1 and the other with $k = 8 \pm 0.5 \times 10^{-4}\ s^{-1}$. The ratios of products of the reactions in 0.01 M $HOSO_2CF_3$/0.99 M $NaOSO_2CF_3$, 0.1 M $HOSO_2CF_3$/0.9 M $NaOSO_2CF_3$, and 1 M $HOSO_2CF_3$ were analysed crudely by ^1H n.m.r. spectroscopy of the reaction mixtures in equivalent $DClO_4$ solutions and of the evaporated reaction mixtures in D_2O. Peaks due to both (**4**) and (**5**) were observed. With increasing pH, the proportion of (**4**) increased and at pH 2, only a little of (**5**) was evident. These results demonstrate the loss of one MeCN as a rate determining step up to high acid concentration at which point the nitrile hydrolysis to the amide and loss of the second nitrile was observed. The results indicate that nitrile hydrolysis occurs by a path inversely dependent on $[H^+]$ which implicates co-ordinated OH^- as the nucleophile. They also indicate loss of the second MeCN as a pH independent process in acid which leads on to the μ-hydroxo-μ-amido product, (**5**). The intramolecular nucleophilic path is also implied by the chelated acetamido product and its stability to ring opening.

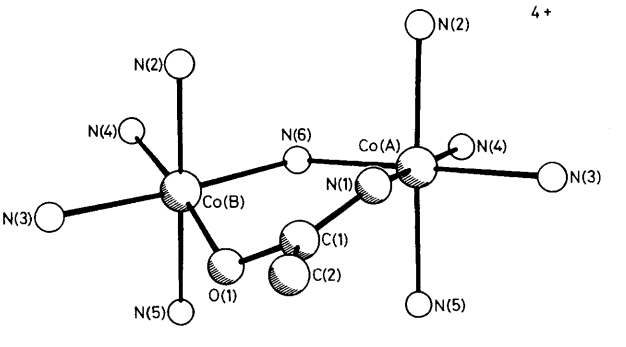


Figure 1. Structure of (**4**). Selected distances (Å) and angles (°): Co ··· Co 3.492(4), Co(A)–N(1) 1.92(2), Co(B)–O(1) 1.93(1), C(1)–O(1) 1.29(3), C(1)–N(1) 1.31(3), C(1)–C(2) 1.53(3), Co(A)–N(6) 1.97(2), Co(B)–N(6) 1.97(2), N(6)–Co(B)–O(1) 97.5(6), N(1)–Co(A)–N(6) 94.6(6), Co(A)–N(6)–Co(B) 124.4(8), O(1)–C(1)–N(1) 124(2). *Crystal data* for (**4**)·$(S_2O_6)_2 \cdot 4H_2O$: $C_2H_{34}Co_2N_{10}O_{15}S_4$, monoclinic, space group $P2_1/c$, a = 12.553(2), b = 15.699(1), c = 12.917(2) Å, β = 93.40(1)°, U = 2544(1) Å^3, D_c = 1.88 g cm^{-3}, Z = 4. The intensities of 1090 reflections ($F \geq 3\sigma F$, $3° < 2\theta < 36°$) were collected at ambient temperature on a Nicolet R3m diffractometer and corrected analytically for absorption (μ = 16.5 cm^{-1}). The structure was solved by the Patterson technique and refined to R = 6.9% with anisotropic refinement on only the Co and S atoms. H atoms have not been included. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The hydrolysis rate is $>10^{-4}\ s^{-1}$ at pH 0 and given the pK_a of co-ordinated water in (**2**) is 6—7, the extrapolated first order rate constant for the hydrolysis to acetamide is $>10^2\ s^{-1}$. This is a handsome increase relative to the same reaction in the absence of metal complex, under the same conditions. The rate of external attack of MeCN by OH^- is enhanced some 10^6 times on co-ordination to penta-amminecobalt(III)^7 and there is no evidence for attack by a water molecule. A large rate enhancement of *ca.* 10^{12} fold at pH 7 was seen for intramolecular attack by co-ordinated hydroxide on a pendent non-co-ordinating nitrile in *cis*-$[en_2Co(OH)NH_2CH_2CN]^{2+}$ (en = ethylenediamine), compared with the unco-ordinated case.^{8} The current example shows a rate enhancement of $\geqslant 10^{15}$ fold arising from both types of path given the rate law extrapolated to pH 7. The additional enhancement arising from the combination of electrophile activating the nitrile and the intramolecular nucleophile is therefore not surprising. It has also been observed in the Ag^+ and Hg^{2+} catalysed paths for the *cis*-$[en_2Co(OH)NH_2CH_2CN]^{2+}$ cyclisation.

The stereochemistry for the cyclisation of intermediate (**3**) is implied by the conformation of the product. It readily meets the supposed directional requirements for attack of a nucleophile at a nitrile carbon centre and for a 6-endocyclic ring closure.^{9} The process is efficient despite the rotational degrees of freedom for the molecule as a whole. In this respect, two of the four possible rotamers about Co(B)–NH_2- in the orientation shown in (**3**) are productive and the reaction is also assisted by the cylindrical symmetry of the electrophile.

¶ Monitored at 490 or 510 nm, in triplicate, 25.0 ± 0.1 °C, I = 1.0 M (ClO_4^-). pH 0, $k_1 = 8.0 \pm 0.5 \times 10^{-4}\ s^{-1}$, $k_2 = 3.0 \pm 0.1 \times 10^{-4}\ s^{-1}$; pH 1, $k = 2.93 \pm 0.02 \times 10^{-4}\ s^{-1}$; pH 2, $k = 3.01 \pm 0.01 \times 10^{-4}\ s^{-1}$; pH 3.78, $k = 3.12 \pm 0.06 \times 10^{-4}\ s^{-1}$.

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