

Intramolecular Condensation of Co-ordinated Acetonitrile in a Binuclear Complex of Cobalt(III). X-Ray Crystallographic Analysis of $\text{Na}[(\text{NH}_3)_3\text{Co}\{\mu\text{-OH}, \mu\text{-NH}_2, \mu\text{-MeC(NH)}_2\}\text{Co}(\text{NH}_3)_3](\text{S}_2\text{O}_6)_2 \cdot \text{H}_2\text{O}$

Lee Roecker, Alan M. Sargeson, and Anthony C. Willis

The Research School of Chemistry, Australian National University, G.P.O. Box 4, Canberra, A.C.T. 2601, Australia

The dimer complex $[(\text{NH}_3)_4\text{Co}(\mu\text{-OH}, \mu\text{-NH}_2)\text{Co}(\text{NH}_3)_4](\text{CF}_3\text{SO}_3)_4$ in acetonitrile generates an acetamidino complex which bridges both Co atoms, presumably as a result of substitution of acetonitrile and intramolecular attack by a co-ordinated amido ion.

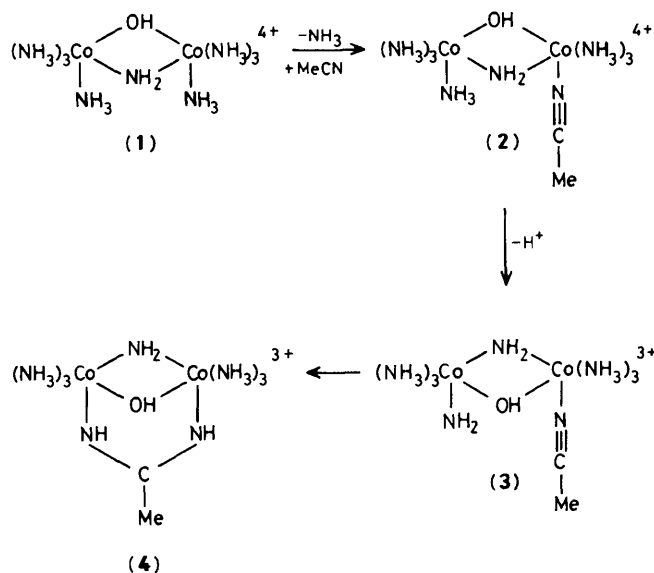
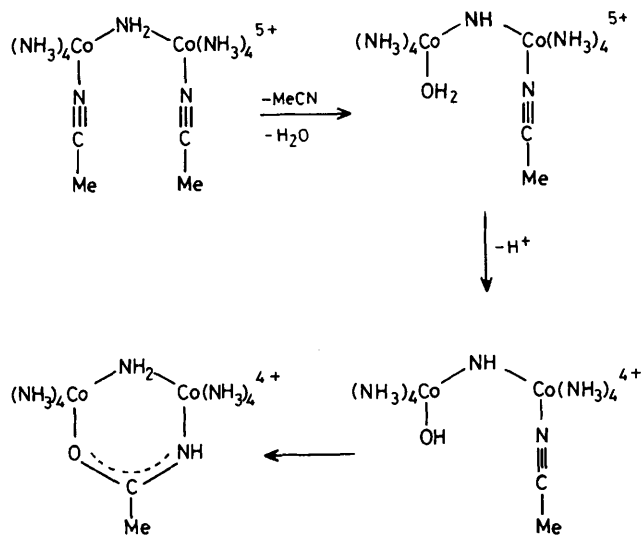
Recently we have been examining the roles of combinations of metal ions in catalysis of reactions of co-ordinated organic substrates. For example, it has been shown that the hydrolysis of $[(\text{NH}_3)_4(\text{MeCN})\text{Co}(\mu\text{-NH}_2)\text{Co}(\text{MeCN})(\text{NH}_3)_4]^{5+}$ results in the formation of a complex containing a bridging acetamide ligand.¹ The ligand reaction occurs as outlined in Scheme 1 after rate determining loss of acetonitrile. Extrapolation of the rate law for the process to pH 7 implied a rate enhancement of $\geq 10^{15}$ -fold due to the combined activation effect of having both a co-ordinated substrate (MeCN) and an intramolecular nucleophile (OH^-). In another example of these effects we have observed the formation of (4) (Scheme 2), presumably resulting from the intramolecular condensation of co-ordinated acetonitrile with co-ordinated ammonia in acetonitrile.

Complex (4) was synthesized by stirring $[(\text{NH}_3)_4\text{Co}(\mu\text{-NH}_2,$

$\mu\text{-OH})\text{Co}(\text{NH}_3)_4](\text{CF}_3\text{SO}_3)_4 \cdot \text{H}_2\text{O}$ in MeCN overnight at room temperature, filtering to remove unreacted starting material, and precipitating the orange complex with diethyl ether.[†] Although we do not have any detailed mechanistic evidence for the reaction pathway, given the nature of the starting material, knowledge of the product, and knowledge of the behaviour of co-ordinated acetonitrile, the simple pathway outlined in Scheme 2 is likely.

Complex (1) has been shown to decompose in aqueous solution with the initial loss of ammonia as a result of labilization imparted by both the bridging hydroxide² and amido ions *via* a $S_{\text{N}}1_{\text{cb}}$ path (Scheme 3). This process must

[†] Satisfactory elemental analyses were obtained for $(4) \cdot (\text{CF}_3\text{SO}_3)_3 \cdot 2\text{H}_2\text{O}$.



occur in MeCN to allow formation of (2). Intermediates (2) and (3) were not observed directly. Intramolecular involvement of co-ordinated amide ion is implied, however, since $[\text{MeCNC}(\text{NH}_3)_5]^{3+}$ does not react with NH_3 intermolecularly,³ but intramolecular reactions of co-ordinated nitriles with amido ion are known.⁴ Addition of H_2O to the MeCN results in a noticeable rate reduction possibly due to competition for the co-ordination site vacated by the lost ammonia. Reaction in a 1 : 1 mixture of MeCN- H_2O leads to decomposition of (1) with no formation of (4).

^1H and ^{13}C N.m.r., i.r., and elemental analysis of the product were consistent with the assignment of structure (4). N.m.r. data (D_2O) show the complex to be symmetrical with three broadened singlets at δ 1.77, 2.79, and 3.55 arising from the bound ammonia groups and the methyl group of the bridging ligand is observed as a sharp singlet at δ 2.50. ^{13}C N.m.r. (D_2O , 0.1 M- DClO_4) data are consistent with the

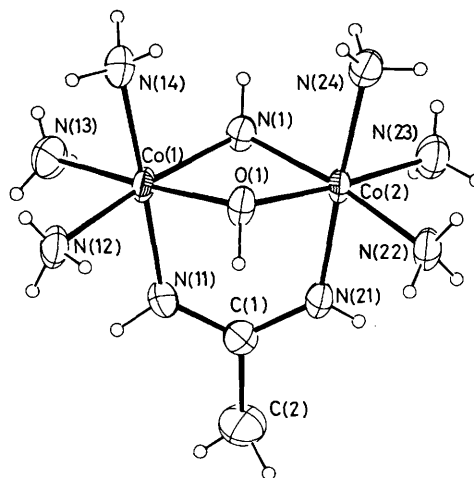
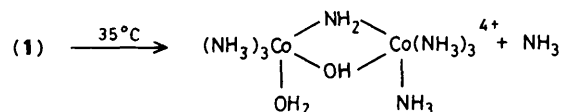


Figure 1. Structure of (4) showing the labelling of the non-hydrogen atoms. Thermal ellipsoids enclose 50% probability levels except for the hydrogen atoms which are drawn as circles of arbitrary radius. Selected bond distances (\AA) and angles ($^\circ$): $\text{Co}(1) \cdots \text{Co}(2)$ 2.867(1), $\text{Co}(1)-\text{O}(1)$ 1.920(3), $\text{Co}(2)-\text{O}(1)$ 1.916(3), $\text{Co}(1)-\text{N}(1)$ 1.919(3), $\text{Co}(2)-\text{N}(1)$ 1.923(3), $\text{Co}(1)-\text{N}(11)$ 1.907(4), $\text{Co}(2)-\text{N}(21)$ 1.895(3), $\text{C}(1)-\text{N}(11)$ 1.300(5), $\text{C}(1)-\text{N}(21)$ 1.318(5), $\text{C}(1)-\text{C}(2)$ 1.496(6); $\text{Co}(1)-\text{N}(1)-\text{Co}(2)$ 96.51(14), $\text{Co}(1)-\text{O}(1)-\text{Co}(2)$ 96.71(12), $\text{N}(14)-\text{Co}(1)-\text{N}(11)$ 178.44(14), $\text{N}(24)-\text{Co}(2)-\text{N}(21)$ 177.52(14), $\text{Co}(1)-\text{N}(11)-\text{C}(1)$ 128.1(3), $\text{Co}(2)-\text{N}(21)-\text{C}(1)$ 128.0(3), $\text{N}(11)-\text{C}(1)-\text{N}(21)$ 121.5(4), $\text{N}(11)-\text{C}(1)-\text{C}(2)$ 120.2(4), $\text{N}(21)-\text{C}(1)-\text{C}(2)$ 118.3(4).

incorporation of only two carbon atoms into the reactant [singlet signals at δ 106 (N=C) and -42 ($-\text{CH}_3$) vs. 1,4-dioxane (at δ 67.4 vs. SiMe_4)]. An i.r. (Nujol, KBr discs) spectrum of the product shows stretching frequencies at 1630 and 1580 cm^{-1} and no $\text{C}\equiv\text{N}$ stretching frequency. The identity of the amidine product was confirmed by X-ray crystallography.†

Crystals suitable for the X-ray diffraction experiment were grown at 4°C by dissolving a quantity of (4)· $(\text{CF}_3\text{SO}_3)_3\cdot 2\text{H}_2\text{O}$ in a minimum amount of saturated $\text{Na}_2\text{S}_2\text{O}_6$. After one week a crystalline precipitate was collected and air dried. Its u.v.-visible and ^1H n.m.r. spectra were identical to that of (4)· $(\text{CF}_3\text{SO}_3)_3\cdot 2\text{H}_2\text{O}$.§

† Crystal data for (4)· $\text{Na}(\text{S}_2\text{O}_6)_2\cdot 2\text{H}_2\text{O}$: $\text{C}_2\text{H}_{28}\text{Co}_2\text{N}_9\text{NaO}_{14}\text{S}_4$, $M = 671.39$, triclinic, space group $P\bar{1}$, $a = 14.655(2)$, $b = 10.113(1)$, $c = 7.803(2) \text{ \AA}$, $\alpha = 87.51(2)$, $\beta = 82.48(1)$, $\gamma = 88.53(1)^\circ$, $U = 1145.20 \text{ \AA}^3$, $D_c = 1.947 \text{ g cm}^{-3}$, $Z = 2$, Mo- K_α radiation, $\lambda = 0.70930 \text{ \AA}$, $\mu = 18.9 \text{ cm}^{-1}$. A Philips PW 1100/20 diffractometer was used to collect 3497 unique observed reflections, ($4 \leq 2\theta \leq 50^\circ$) with $I \geq 3\sigma(I)$. Structures were solved using MULTAN80 and subsequent Fourier difference syntheses and refined using full-matrix least-squares methods until all shift : error ratios were < 0.03 and final values of $R = 0.041$ and $R_w = 0.061$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ Satisfactory elemental analyses were obtained for (4)· $\text{Na}(\text{S}_2\text{O}_6)_2\cdot 2\text{H}_2\text{O}$: λ_{max} (0.01 M- $\text{CF}_3\text{SO}_3\text{H}$) 300 nm ($2140 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), 360(sh) (730), 500(200).

The geometry of the cation is depicted in Figure 1. Bond lengths and angles within the cation are consistent with those observed in similar structures.^{1,4-6} The amidine ligand is planar and there is one proton bound to each of the N atoms. Delocalisation is implied by the C-N bond lengths (1.30, 1.32 Å). The angle between the two equatorial planes about each cobalt centre linked by OH and NH₂ is 20.9°.

The chemistry described appears to be another example of dual activation effects from metal ions, one where the metal ion activates the substrate by co-ordination of the functional group and the other where the metal ion provides a proximal nucleophile poised to react with the co-ordinated functional group. However, in this example we have not been able to observe the intermediates and thereby quantify the activation effects. The reaction also implies a new route for synthesising

dimeric metal ion complexes which share a common octahedral face.

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References

- 1 N. J. Curtis, K. S. Hagen, and A. M. Sargeson, *J. Chem. Soc., Chem. Commun.*, 1984, 1571.
 - 2 R. S. Taylor and A. G. Sykes, *J. Chem. Soc. (A)*, 1971, 1426.
 - 3 R. F. Keene and A. M. Sargeson, unpublished work.
 - 4 I. I. Creaser, S. F. Dyke, A. M. Sargeson, and P. A. Tucker, *J. Chem. Soc., Chem. Commun.*, 1978, 289.
 - 5 M. R. Churchill, R. A. Lashewycz, K. Koshy, and T. P. Dasgupta, *Inorg. Chem.*, 1981, **20**, 376.
 - 6 G. S. Mandel, R. E. Marsh, W. P. Schaefer, N. S. Mandel, and B. C. Wang, *Acta Crystallogr., Sect. B.*, 1977, **33**, 3185.
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