

Inter- and Intra-molecular Condensations of CN^- and NH_2^- with Co-ordinated Acetonitrile: an Amino Acid Synthesis. X-Ray Crystal Structure of $[(\text{NH}_3)_3\text{Co}\{(\text{Me})\text{C}(\text{NH}_2)(\text{NH}=\text{CNH}_2)_2\}]\text{Br}_3 \cdot \frac{2}{3}\text{H}_2\text{O}$

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Summary $[(\text{NH}_3)_3\text{CoN}\equiv\text{CMe}]^{3+}$ is attacked by CN^- at the nitrile C atom and addition of another CN^- with two intramolecular condensations involving bound amide ions yields a tridentate bis(amidine)aminomethyl malonate chelate complex $[(\text{NH}_3)_3\text{Co}\{(\text{Me})\text{C}(\text{NH}_2)(\text{NH}=\text{CNH}_2)_2\}]\text{Br}_3 \cdot \frac{2}{3}\text{H}_2\text{O}$ whose structure is reported.

SEVERAL publications have appeared recently concerned with the reactivity of co-ordinated nitriles. Some of these have displayed the enhanced susceptibility of the nitrile carbon atoms to attack by nucleophiles.¹ In addition, intramolecular cyclisations of unco-ordinated nitriles with co-ordinated nucleophiles have been observed where both bound OH^- and NH_2^- have been seen to be especially reactive.^{2,3} Using CN^- as the nucleophile, a combination of both types of activity was envisaged and this paper describes the result of the attack of CN^- on co-ordinated acetonitrile in the ion $[(\text{NH}_3)_3\text{CoN}\equiv\text{C-Me}]^{3+}$ under basic conditions.

The complex ion was treated with a NaCN-HCN buffer (pH 10, 1 mol l^{-1}) in the presence of 1 mol of disodium ethylenediaminetetra-acetic acid for 20 min at 25 °C. After sorbing the reaction mixture on a cation exchange resin and removing the excess reagents, a cobalt(III) complex was eluted and crystallised as the bromide in 40% yield, the structure of which has been determined by X-ray crystallography.

Crystal data: Crystals of the tribromide- $\frac{2}{3}$ hydrate, $\text{C}_4\text{H}_{20}\text{Br}_3\text{CoN}_8 \cdot \frac{2}{3}\text{H}_2\text{O}$, are hexagonal, space group $P6_3/m$, with $a = 14.455(1)$, $c = 13.300(1)$ Å, $Z = 6$. Intensities were measured on a Picker FACS-I diffractometer using Mo-K_α radiation and were corrected for absorption. Full-matrix least-squares refinement including the hydrogen atom positional and isotropic thermal parameters converged with $R = 0.036$ for the 1661 unique reflections with $I > 3\sigma(I)$

and $\theta < 30^\circ$. The cation has a crystallographic mirror plane through N(1), Co, C(1), C(2), and N(3).†

Two molecules of HCN condense with the nitrile species and two bound ammonia molecules to give a tridentate cap to the Co atom. The geometry of the cation is depicted in the Figure with details of the structure determination. The

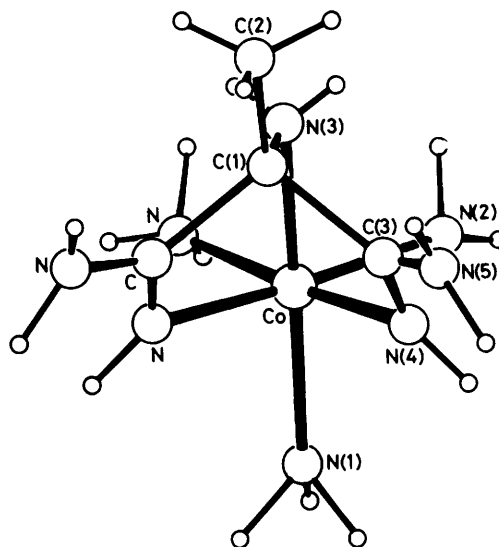
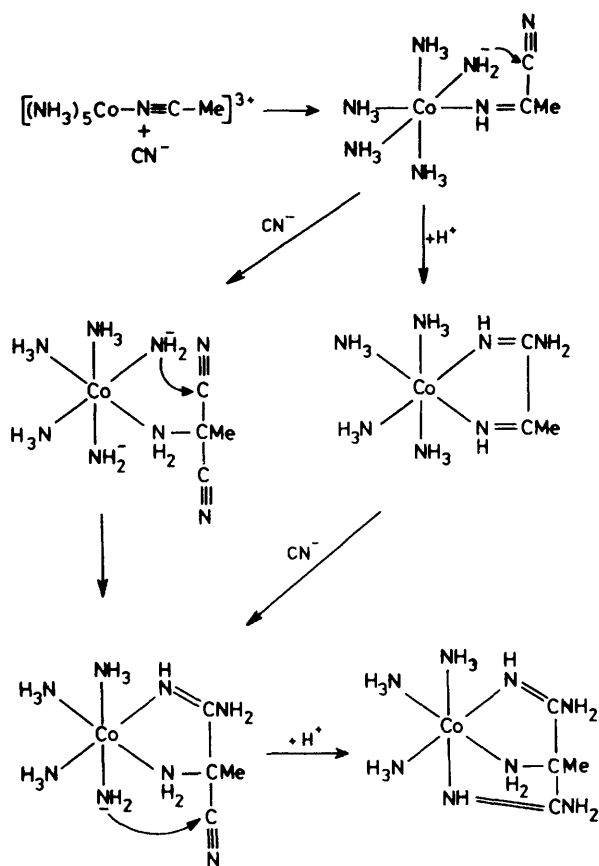


FIGURE. Molecular geometry of the cation. Selected bond lengths and angles are Co-N(1), 1.960; Co-N(2), 1.963; Co-N(3), 1.930; Co-N(4), 1.919; N(4)-C(3), 1.295; C(3)-N(5), 1.334; C(1)-N(3), 1.472; C(1)-C(3), 1.531; and C(1)-C(2), 1.515 Å; $\angle \text{N(4)-Co-N'(4)}$, 80.6; $\angle \text{Co-N(4)-C(3)}$, 113.6; $\angle \text{N(4)-C(3)-C(1)}$, 112.0; $\angle \text{C(3)-C(1)-N(3)}$, 103.0; $\angle \text{C(3)-C(1)-C'(3)}$, 103.2, and $\angle \text{C(1)-N(3)-Co}$, 102.0°, with e.s.d.'s of not more than 0.006 Å in a length or 0.4° in an angle.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



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co-ordination about N(4), C(3), and N(5) is approximately planar and the torsion angles about N(4)-C(3) and C(3)-N(5) are small ($<11^\circ$) in keeping with the substantial delocalisation over the N(4)-C(3)-N(5) fragments [C(3)-N(4) 1.295 Å and C(3)-N(5) 1.334 Å]. The internal angles of the tridentate ligand are indicative of considerable strain, each being smaller than the 'expected' tetrahedral or trigonal values.

Intramolecular involvement of co-ordinated amide ion is implied since the bound ammonia is co-ordinatively saturated. The rate constants for proton exchange with these ions are large (*ca.* $10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ at 25°C) in basic media and the $\text{p}K_{\text{a}}$ is *ca.* 14-16. These properties allow for rapid proton transfer in the routes for the condensation depicted in the Scheme. Initially CN^- attacks the nitrile C atom to give a co-ordinated imine. The reaction proceeds either by attack of another CN^- on the co-ordinated imine followed by an intramolecular addition of *cis* amide ion or by intramolecular attack of amide, to produce a chelated amidine, followed by addition of further CN^- . A second intramolecular amide addition results in the tridentate bis(amidine)aminomethyl malonate. By either route the appropriate imine species will be more susceptible to attack by CN^- than the original nitrile.³

Reduction of the Co^{III} ion to Co^{II} and removal of the ligand with acid led to the isolation of aminomethylmalonic acid which readily decarboxylated to alanine. The reaction therefore introduces the possibility of a general amino acid synthesis from nitriles and a means of labelling the carboxy group.

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² D. A. Buckingham, A. M. Sargeson, and A. Zanella, *J. Amer. Chem. Soc.*, 1972, **94**, 8246.

³ J. Springborg and J. M. Harrowfield, unpublished work.