Organic Synthesis at Co-ordinated Ligands: Synthesis and Stabilisation of a Pyrroline Ring System and *X*-Ray Structure of (Tetra-ammine)-4,5-dihydroxy-4,5-dimethyl-Δ^1-pyrroline-2-carboxylatocobalt(III) Perchlorate Hydrate

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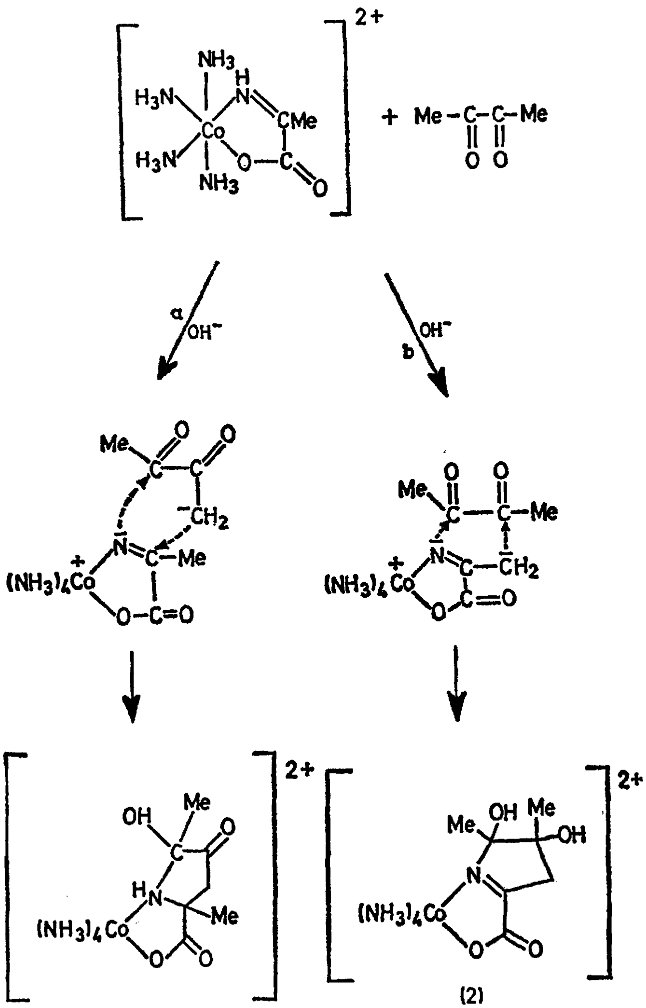
Summary The rapid stereospecific synthesis and stabilisation of a pyrroline carboxylate using co-ordinated nitrogen and carbanion nucleophiles, and the *X*-ray structure of (tetra-ammine)-4,5-dihydroxy-4,5-dimethyl-Δ^1-pyrroline-2-carboxylatocobalt(III) perchlorate hydrate, is described.

PREVIOUS articles[1–3] have shown the potential of intramolecular reactions of co-ordinated amide ions in directing the formation and stabilisation of imine chelates. Subsequent observation of the high nitrogen and α-carbon acidity of these imine species raised the prospect of intermolecular reactions with bifunctional organic molecules to produce heterocycles.



(1) (2)

When the imine complex (1)[1] was mixed with OH^- (1 mol. equiv.) and an excess of biacetyl a rapid reaction occurred (complete in < 30 s, pH 12). After quenching with acid, an orange crystalline perchlorate salt was obtained (50%). The ^1H n.m.r. spectrum indicated four NH_3 groups, two saturated CMe groups (singlets at δ 1·54 and 1·58 from sodium 3-trimethylsilylpropanesulphonate) and non-equivalent methylene protons (AB doublet pair at δ3·30). However, the results were reconcilable with either path (a) or (b) and the pyrroline structure (2) was established by 3-dimensional *X*-ray structural analysis (Figure).

Crystals of (*SS* + *RR*) (tetra-ammine)-4,5-dihydroxy-4,5-dimethyl-Δ^1-pyrroline-2-carboxylatocobalt(III) perchlorate hydrate $[C_7H_{22}CoN_5O_4(ClO_4)_2,H_2O]$ were monoclinic, space group $P2_1/c$, with $a = 11·984(5)$, $b = 8·836(4)$, $c = 19·609(7)$ Å, $\beta = 110·58(2)°$, $Z = 4$. Reflection data were collected on a Picker FACS-I diffractometer using graphite crystal monochromated Cu-K_α radiation [1616 independent reflections, with $I/\sigma(I) \geqslant 3·0$]. Data have been corrected for absorption effects, and the structure has been fully refined (block-diagonal least-squares methods, anisotropic thermal parameters for Co, Cl, O, N, and C atoms) to a conventional *R*-factor of 0·063. Hydrogen atoms cannot be located, and their contributions have not been included in the refinement; one perchlorate is disordered, and has been included with 8 half oxygen atoms.

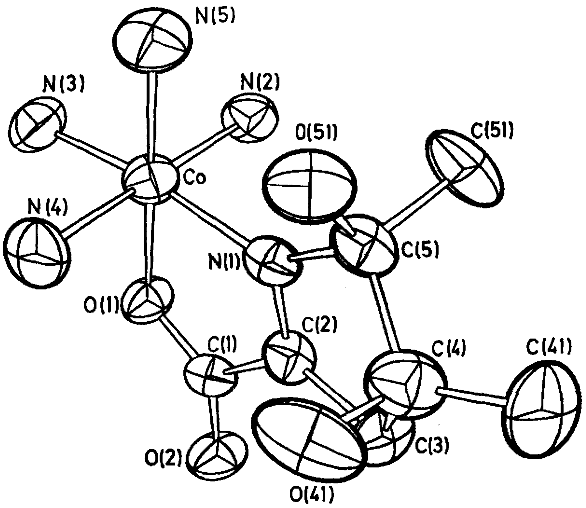


FIGURE. Overall stereochemistry of the complex cation. Bond lengths (e.s.d.'s are given in parentheses): Co–O(1), 1·909(4); Co–N(1), 1·933(7); Co–N(2), 1·968(7); Co–N(3), 1·968(8); Co–N(4), 1·973(8); Co–N(5), 1·977(6); C(1)–O(1), 1·276(9); C(1)–O(2), 1·228(7); C(1)–C(2), 1·52(1); C(2)–N(1), 1·292(8); C(2)–C(3), 1·49(1); C(3)–C(4), 1·57(1); C(4)–C(5), 1·57(1); C(4)–O(41), 1·45(1); C(4)–C(41), 1·49(1); C(5)–N(1), 1·50(1); C(5)–O(51), 1·41(1); C(5)–C(51), 1·51(1) Å.

The essentially octahedral cation shows the expected bond distances (see Figure). The following structural features are of special interest. (i) The hydroxy-groups [O(41) and O(51)] are *cis*, and the short O–O distance [O(41)–O(51), 2·583(8) Å] indicates that there may be a bent hydrogen bond of the type *O*–H · · · O. (ii) The distance C(2)–N(1) [1·292(8) Å] is consistent with that expected for a C=N bond, and is only slightly longer than the C=N (imine) distance of 1·252(7) Å found for $[Co(NH_3)_3\{NH_2{\cdot}C(Me)[CH_2C(Me)=NH]{\cdot}CO_2\}]S_2O_6$.[3]

Addition of the deprotonated imine nitrogen centre to a carbonyl centre is preferred as the initial step because proton exchange on the imine methyl is slow when the imine N centre is deprotonated ($t_{\frac{1}{2}}$ *ca.* 10 h, pH 10, 32 °C). However, in the *N*-methylated imine complex, $(NH_3)_4\overline{CoOC(:O)C(Me)=N}Me^{2+}$, the C-methyl proton exchange is much faster ($t_{\frac{1}{2}}$ *ca.* 5 min, pH 10, 30 °C).[4] Clearly the latter behaviour is only consistent with alkylation of the N centre as the first step which then allows the ready deprotonation of the imine methyl to generate the carbanion to complete the cyclisation. Moreover this methyl must be sufficiently acidic and reactive to compete with deprotonation of an adjacent co-ordinated ammonia (pK_a *ca.* 16) and attack of that amide ion at the carbonyl centre to generate a tridentate complex.[3]

Apart from the speed of synthesis of the pyrroline ring system, an interesting feature of the reaction is the stereospecificity of the orientation of the methyl and hydroxy-substituents in the product. A preference would have been expected for a *trans* arrangement of the methyl groups since this would minimise non-bonded interactions between the methyl protons. Clearly this was not observed and there was no evidence for the presence of such an isomer. An explanation for the *cis* configuration of the substituents may be inferred from the structural analysis. The surprisingly short O–O distance implies bridging *via* a hydrogen bond. If the H-bond were initiated before addition at the second carbonyl centre then a specific direction could be imposed on that step to yield the two carbinol units with a catoptric relationship.

The reaction demonstrates an easy synthesis and stabilisation of a pyrroline ring system and the aptitude which co-ordinated nucleophiles have to organise and control such syntheses. Another potentially useful aspect is the ease of generation of a carbanion at the imine methyl centre once the imine nitrogen is alkylated.

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[3] B. T. Golding, J. MacB. Harrowfield, G. B. Robertson, A. M. Sargeson, and P. O. Whimp, *J. Amer. Chem. Soc.*, **1974**, **96**, **3691**.
[4] J. MacB. Harrowfield, unpublished work.