X-Ray Structure and Stereoselective Intramolecular Synthesis of a Novel Quadridentate Complex

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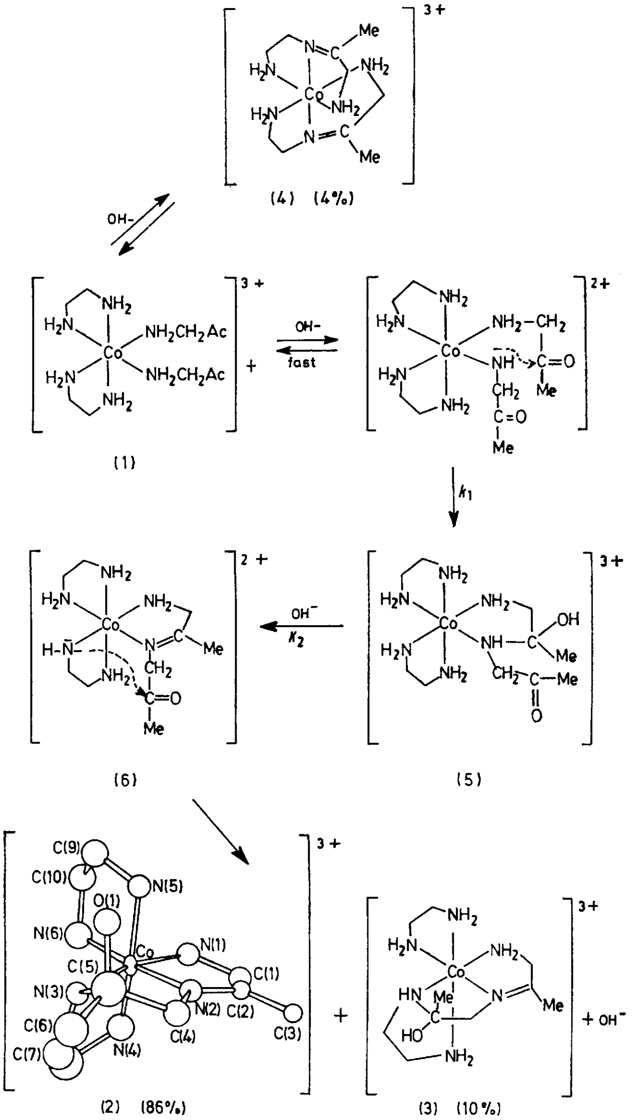
Summary The stereoselective synthesis and structure of a metal-stabilised carbinolamine: racemic ($\Lambda SR + \Lambda RS$)-[(1,8-diamino-2,5-dimethyl-5-hydroxy-3,6-diazaoct-2-ene)(1,2-diaminoethane)cobalt(III)]hexachlorothallate(III), $2H_2O$ are described.

During a study of stereoselective syntheses of polyamine complexes[1,2] in which intramolecular condensations of *N*-co-ordinated aminoacetaldehyde or aminoacetone with another amine centre are utilised, a cobalt(III) complex **(2)** containing the novel ligand (*RS*)-1,8-diamino-2,5-dimethyl-5-hydroxy-3,6-diaza-oct-2-ene was isolated. This complex is the major product (86%) from the base-catalysed condensation of ligands in *cis*-bis(aminoacetone)bis-(1,2-diaminoethane)cobalt(III) ion (**1**). It is accompanied by complexes (**3**) (10%) and (**4**) (4%) which were separated from (**2**) chromatographically. The structure of complex (**2**) was defined by *X*-ray crystallography[‡] and a reduced ORTEP drawing of one catoptric form is shown inset in the Figure. The structures of (**3**), a diastereoisomer of (**2**), and (**4**) follow from their spectroscopic and analytical data. Complex (**2**) has the larger substituent (methyl) at C-5 pseudo-equatorial and is therefore more stable than (**3**). Since this difference is likely felt at the transition states for formation of these complexes, (**2**) is produced with high stereoselectivity.

Numerous products are possible from (**1**), depending on whether the aminoacetones react with themselves and/or the ethylenediamines and whether the derived carbinolamine groups are dehydrated or not. Since the conjugate acid of aminoacetone is more acidic than that of ethylenediamine (*cf.* pK_a values 7·87 and 10·0 respectively at 25° and μ = 0·01), it is likely that the first step of the major course of the reaction is the condensation of the carbonyl group of one aminoacetone with the deprotonated amino group of another (*cf.* Figure). A preliminary kinetic study has revealed two consecutive processes in the formation of (**2**) and (**3**) from (**1**): generation of a carbinolamine intermediate (**5**) (k_{obs} *ca.* 10^8[OH$^-$] s^{-1} at 25°, μ = 1M NaClO$_4$) followed by dehydration to the imine (**6**) and second cyclisation (combined k_{obs} *ca.* 10^7[OH$^-$] s^{-1}). Presumably the C=N in (**6**), by preferring co-planarity for its attached atoms, directs the second cyclisation in the same plane as the first, rather than at apical amino centre. It is remarkable that the condensation is arrested at the carbinolamines (**2**) and (**3**). Further dehydration to a bis-imine would be expected to occur readily with the free ligand or, if this ligand could act as a tetradentate ligand, to four co-planar co-ordination sites of a metal. However, formation of the bis-imine from (**2**) would lead to a situation wherein the preference for planarity about the imino functions would be incompatible with the four predestined (non-coplanar) co-ordination sites at cobalt.

The reaction described demonstrates the facility which metal ions have to effect and control complex condensations of their organic ligands. The ligands never leave the cobalt ion and at pH 7 the process is complete in a few seconds. Indeed, the formation of (**2**)—(**4**) is only slightly slower than proton exchange at the amino centres,[1] which demonstrates the efficiency of capture of the carbonyl groups and the potential for such reactions in inorganic and organic syntheses.



Figure

Reaction scheme for the formation of products in the base-catalysed condensation of bis(aminoacetone)bis(ethylenediamine)-cobalt(III) ion.

(*Received, 3rd September* 1974; *Com.* 1123.)

[‡] The yellow rhombic crystals of racemic Λ*SR* + Λ*RS*-[(1,8-diamino-2,5-dimethyl-5-hydroxy-3,6-diaza-oct-2-ene)(1,2-diaminoethane)cobalt(III)] hexachlorothallate (III), 2H$_2$O were monoclinic, a = 8·15, b = 17·62, c = 18·14 Å, β = 106·1°, D_m = 2·04 ± 0·03, D_c = 2·02 g cm^{-3}, Z = 4, space group $P2_1/c$. The observed independent reflections (1640 > 3σ) were recorded with zirconium-filtered Mo-K_α radiation using a four-circle diffractometer and corrected for absorption (μ 83·9 cm^{-1}). Two thallium atoms (0,0,0;½,½,0) on sites of $\bar{1}$ symmetry were located from a three-dimensional Patterson synthesis. The remainder of the structure was solved by conventional methods. The structure has been refined to a residual (observed reflections) of 0·107 using full-matrix least squares calculations with anisotropic temperature factors assigned to thallium, cobalt and chlorine stoms and isotropic temperature factors to the remainder. Refinement is continuing and the water molecules remain to be located.

[1] A. R. Gainsford, unpublished work.
[2] B. T. Golding, J. MacB. Harrowfield, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1974, **96**, 3003.