Novel Mixed Tris-complexes of Cobalt(III) with α- and β-Amino-acids: Isolation, Adsorption Chromatography, and Absorption Spectra

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Summary All eight possible geometrical isomers of the mixed cobalt(III) complexes containing 5-membered glycinato- and 6-membered β-alaninato-metal chelate rings, $[Co(\beta\text{-Ala})_x(Gly)_{3-x}]$ (I; $x = 1$ or 2), have been isolated by adsorption chromatography on a cation exchanger in the H^+-form owing to the difference in basicities of carbonyl groups hydrogen-bonded to the resin; surprising dissimilarities in absorption spectra of meridional isomers arise from the differences in Co–O π-interactions influenced by the conformations of the 6-membered rings.

WE report the synthesis, separation, and characterisation of all eight theoretically predicted geometrical isomers of the tris(bidentate) complexes of cobalt(III) containing both 5-membered glycinato (Gly) and 6-membered β-alaninato (β-Ala) metal chelate rings, $[Co(\beta\text{-Ala})_x(Gly)_{3-x}]$ (I; $x = 1$ or 2) (Figure 1), representing the first example of mixed tris(amino-acidato) complexes of any metal in which the chelates differ solely in the ring size.

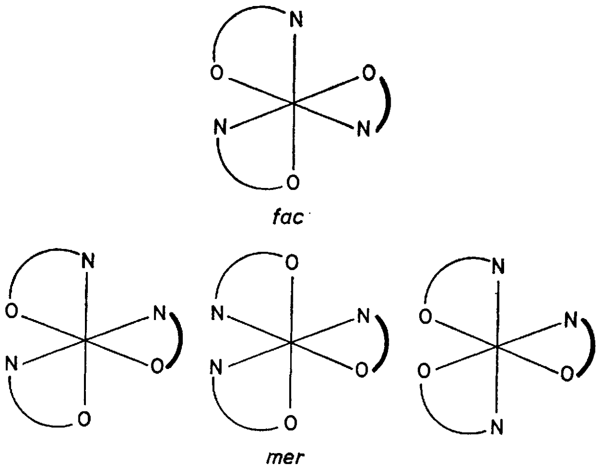
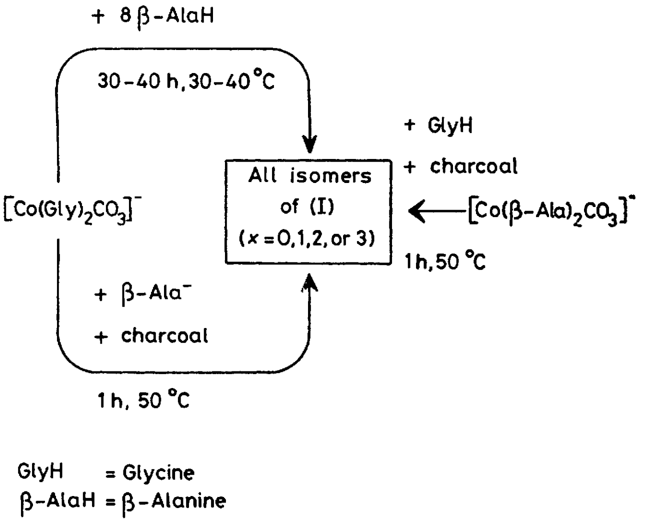


FIGURE 1. Possible geometrical isomers of (I; $x = 1$ or 2). The heavy line indicates a ligand different from the other two; when $x = 1$ it is β-Ala, when $x = 2$ it is Gly.

Syntheses, which are operative under a wide range of experimental conditions (see Scheme), involve treatment of carbonatobis(amino-acidato)cobaltate(III)[1] with the corresponding other amino-acid or its anion. Interestingly, from the single starting isomer twelve different species, *i.e.* all isomers of (I; $x = 0$, 1, 2, or 3), were isolated.



Scheme

The mixture of products was first chromatographed on a column of Dowex 50W-X8 (200—400 mesh) in Na$^+$-form with water as eluent utilizing the ion exclusion phenomenon.[2] By-products and the unchanged starting material were eluted first, followed by two bands, violet and red, consisting of meridional (*mer*) and facial (*fac*) isomers of (I; $x = 0$, 1, 2, or 3), respectively. The two solutions were then separately chromatographed on columns of the same cationite but this time in the H$^+$-form. Different complexes were eluted with water in the order of increasing x (from 0 to 3). Three *mer* isomers (see Figure 1) were separated for each of the two mixed complexes (I; $x = 1$ or 2).† Pure complexes‡ were obtained by evaporating the corresponding fractions to dryness *in vacuo*.

Complete separation of these neutral complexes on the H$^+$-cationite is feasible because of the difference in hydrogen-bonding capability of C=O groups in Gly and β-Ala chelate rings.§

Characteristic differences in the visible electronic spectra of *fac* and *mer* configurations of complexes of tris(amino-acidato)cobalt(III) with α-[3] or β-amino-acids[4] are also retained in the mixed complexes (I; $x = 1$ or 2). However, the first spin-allowed band shows a quite different splitting pattern (Figures 2 and 3) in the three *mer* forms in both series of mixed complexes, although they all have the same (C_{2v}) microsymmetry of the ligand field. We attribute these differences to the effects of Co–O π-interactions. Overlap between metal *t*- and oxygen *p*-orbitals depends on the conformation of the flexible 6-membered β-Ala ring, and may be quite different from that of the essentially planar 5-membered Gly ring. Therefore, in *mer* isomers of the mixed complexes (I; $x = 1$ or 2) the fact that each of the three intrinsically non-equivalent oxygen donors are part of a chelate ring different from the other two will

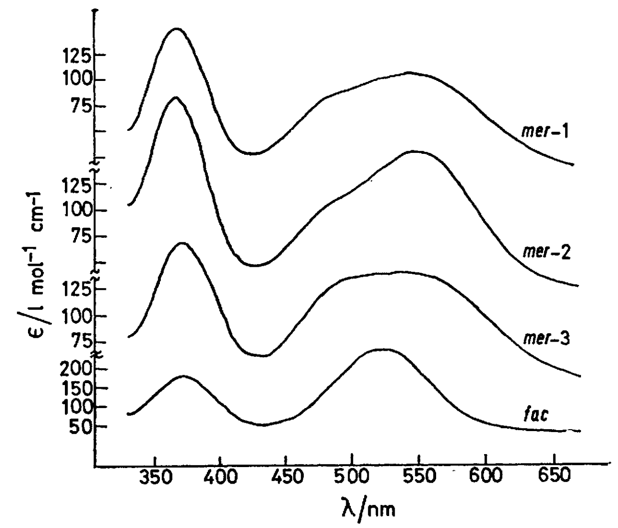


Figure 2. Absorption spectra of all isomers of (I; $x = 1$). The *mer* isomers are numbered in the elution order.

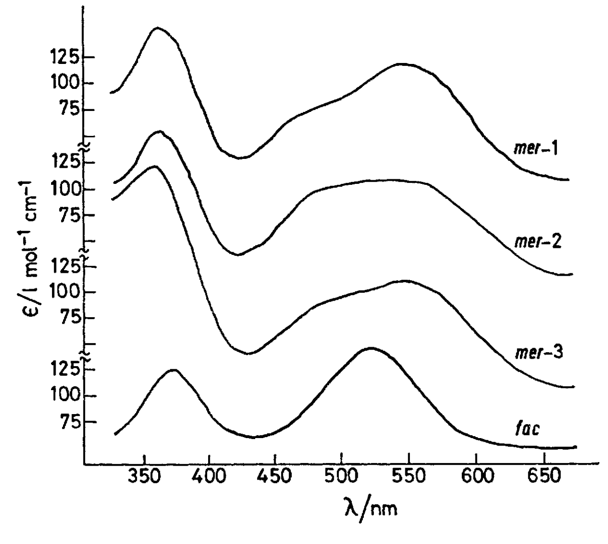


Figure 3. Absorption spectra of all isomers of (I; $x = 2$). The *mer* isomers are numbered in the elution order.

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† When a combined solution of all *fac* and all *mer* isomers of (I; $x = 0$, 1, 2, or 3) was chromatographed on the H$^+$-cationite, bypassing the prior separation on the Na$^+$-column, the elution followed the order of increasing x, the *fac* isomer being eluted after *mer* isomer(s) within each value of x. However, this procedure is prohibitively long and tedious for preparative application.

‡ Satisfactory elemental and amino-acid analyses were obtained for all compounds.

§ Full details of the pertinent electronic and steric factors, which enhance the basicity of β-Ala C=O group over that of Gly, will be given in a later publication.

result in slight but discernible changes in the energies of the low symmetry components of the ${}^1T_{1g}$ level, accounting for the observed patterns in electronic spectra (Figures 2 and 3).

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[1] C_1-*cis*(*N*)-K[Co(Gly)$_2$CO$_3$]·H$_2$O was prepared by the method of M. Shibata, H. Nishikawa, and Y. Nishida, *Inorg. Chem.*, 1968, **7**, 9; *trans*(*N*)-Na[Co(β-Ala)$_2$CO$_3$] was prepared by the method of K. Marković, B.Sc. Thesis, University of Beograd, 1972; this procedure is analogous to that described by Shibata *et al.*

[2] For a discussion of ion exclusion see, for example, 'Dowex Ion Exchange,' The Dow Chemical Company, 1964, p. 30.

[3] F. Basolo, C. J. Ballhausen, and J. Bjerrum, *Acta Chem. Scand.*, 1955, **9**, 810; Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, 1956, **29**, 311.

[4] M. B. Ćelap, S. R. Niketić, T. J. Janjić, and V. N. Nikolić, *Inorg. Chem.*, 1967, **6**, 2063.