

THE SYNTHESIS AND PARTIAL RESOLUTIONS OF TRIS(α -AMINOISOBUTYRATO(1-)-O,N)COBALT(III)

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On reaction of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $\text{K}_3[\text{Co}(\text{CO}_3)_3]$ and $\text{Co}(\text{OH})_3$ with α -aminoisobutyric acid or on oxidation of CoSO_4 in its presence the isomers of tris(α -aminoisobutyrate(1-)-O,N)cobalt(III) have been prepared. The first two reactions afforded predominantly *fac* isomers, while the other two gave *mer* isomers. Under the configurational effect the geometric isomers are enantiomeric on the cobalt atom. Chromatography on a starch column gave *A-fac*, *A-fac*, *A-mer* and *A-mer* isomers which were identified by physico-chemical methods.

Amino acids form with cobalt(III) octahedral tris-bidentate complexes, which in view of different donor atoms (N and O) can form facial and meridional isomers¹. The arrangement of the chelate rings itself has the formation of a chirality center on the cobalt atom as a consequence. The ratio of geometric isomers of complexes of the type $\text{Co}(\text{AB})_3$ (where AB is amino acid anion) is dependent both on the method of preparation of the complexes and on the type of amino acid². An increase in the steric volume of the aliphatic chain on the α -carbon atom increases the yield of *mer* isomers. The ratio of the optical isomers obtained also depends on sterical factors. In the case of tris(glycinato(1-)-O,N)cobalt(III) a mixture of geometric isomers in the 1:1 ratio is usually obtained³. Substitution on the α -carbon atom (α -alanine) increases the yield of *fac* isomers⁴ in the substitution reaction and as this amino acid contains a center of chirality the relation of optical isomers is also different (*A-fac* isomer prevails). Another homologous amino acid the complexes with cobalt(III) of which were investigated is (S)-(+)-valine that, however, in a substitution reaction did not afford any *fac* isomer⁵. α -Aminoisobutyric acid represents an intermediary step between the mentioned amino acids, and in its cobalt(III) complexes this character should be manifest. In this paper the results obtained in this direction are described.

Tris(α -aminoisobutyrate(1-)-O,N)cobalt(III) was prepared by all known methods which were suitable for the preparation of complexes of amino acids with cobalt(III). From Table I it is evident that the substitution methods lead predominantly to *fac* isomers. In this respect the behaviour of α -aminoisobutyric acid is analogous to that of (S)-(+)-alanine and quite different from that of (S)-(+)-valine with which the substitution reaction does not give any *fac* isomer. At the same time it is important

to consider mainly the sterical relations in the transition intermediate of the substitution, which are close to those of (*S*)-(+)- α -alanine. The substituents on the α -carbon atom of α -alanine and of α -aminoisobutyric acid are not sterically comparable with the isopropyl chain of valine where the possible interactions prevent a *mer* \rightarrow *fac* isomerisation. The increased yield of *fac* isomer in the case of a reaction catalysed with charcoal (see Table I) is a consequence of a *mer* \rightarrow *fac* isomerisation which was also observed in the case of tris(α -alaninato(1-)-O,N)cobalt(III) (ref.⁴). As follows from Table II the yield of *mer* isomer increases with the reaction time. Hence, it is a substitution reaction accompanied by isomerisation.

The prepared complexes are very poorly soluble in water (especially *fac* isomers), but they dissolved in salt solutions (for example KCl) or in H_2SO_4 . The identification of geometric isomers was carried out on the basis of spectral analysis. The differences in symmetry of both geometric isomers become evident in ultraviolet spectra in the region of ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transitions. In the *mer* isomer (λ_{max} 370 and 520 nm) the band corresponding to the mentioned transition is split in view of the C_1 symmetry, while in the case of the *fac* isomer (λ_{max} 377 and 523 nm), with a C_2 symmetry, the mentioned band is symmetrical. Another proof of geometric isomerism follows from the infrared spectrum⁶, where the band due to the $\nu(COO^-)_{as}$ vibration is in the case of the *fac* isomer split (1660 and 1610 cm^{-1}), while the *mer* isomer displays in this region only a single maximum at 1660 cm^{-1} . The difference in symmetry is also evident from the fact that the IR spectrum of the *mer* isomer is much more complex than that of the *fac* isomer.

We attempted to resolve the geometrical isomers obtained into optical antipodes. Their electroneutral character limited the possibility of resolving them to chromatography on a chiral sorbent. Applying column chromatography on starch and elution with water both *fac* and *mer* isomers could be separated to optical antipodes. In agree-

TABLE I
Yields (%) of the Isomers of Tris(α -aminoisobutyrate(1-)-O,N)cobalt(III) Obtained by Various Synthetic Routes

Method	Total yield	<i>fac</i>	<i>mer</i>
$[Co(NH_3)_6]Cl_3$	41.1	86.6	13.4
$[Co(NH_3)_6]Cl_3^a$	54.8	95.0	5.0
$K_3[Co(CO_3)_3]$	62.7	96.1	3.9
$CoSO_4 + H_2O_2$	41.1	0	100.0
$Co(OH)_3$	2.7	0	100.0

^a Reaction carried out in the presence of activated charcoal, without adjusting pH.

TABLE II
Yields (%) of the Isomers of Tris(α -aminoisobutyrate(1-)-O,N)cobalt(III) Obtained from $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ in Dependence on the Reaction Time

Time, h	Total yield	<i>fac</i>	<i>mer</i>
1.0	41.1	86.6	13.4
4.5	49.0	83.8	16.2
24.0	50.7	72.9	27.1

TABLE III
Specific Rotation $[\alpha]$ of Selected Fractions of *fac* and *mer* Isomers at Various Wave-Lengths λ (nm)

Isomer	578	546	436	405	365
<i>A-fac</i>	+41.70°	0.00°	-27.80°	-27.80°	-56.60°
Δ - <i>fac</i>	-10.90°	0.00°	+65.20°	+97.80°	+130.40°
<i>A-mer</i>	+15.15°	+9.09°	-6.67°	-3.34°	-12.14°
Δ - <i>mer</i>	-26.66°	-22.22°	+13.33°	+17.78°	+22.22°

ment with other cases, in both cases the isomer with the pseudoaxial arrangement of the side chain was eluted first. Proper collection of fractions or their rechromatography gave the following substances of undefined optical purity: *A-fac*, Δ -*fac*, *A-mer*, Δ -*mer* (for symbols see⁷). The assignment of the absolute configuration of optical isomers was carried out on the basis of the application of an empirical rule^{8,9}, according to which the isomer with the positive Cotton effect in the ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$ transition region has the *A* configuration. The course of the optical rotatory dispersion for single isomers, given in Table III, corresponds to that of the corresponding isomers of tris(α -alaninato(1-)-O,N)cobalt(III) the absolute configuration of which is known⁴.

EXPERIMENTAL

Chemicals and Apparatus

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $\text{K}_3[\text{Co}(\text{CO}_3)_3]$ were prepared according to literature^{10,11}. Potato starch was washed with water prior to use. Electronic absorption spectra were measured on an Optica-Milano apparatus, infrared spectra on a Perkin-Elmer spectrograph, using the KBr technique. For the measurement of optical rotation polarimeter Opton was used.

Tris(α -aminoisobutyrate(1-)-ON)cobalt(III) was prepared according to procedures starting with $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (ref.^{2,6}), $\text{K}_3[\text{Co}(\text{CO}_3)_3]$ (ref.¹⁰), $\text{Co}(\text{OH})_3$ (ref.¹²) and direct oxidation of

CoSO₄ in the presence of α -aminoisobutyric acid⁵. The geometrical isomers were separated on the basis of their different solubility in water. Optical isomers were obtained by chromatography of 30 ml of a saturated complex solution on a starch column (500 g, 70 \times 3.5 cm column), using water for elution.

For C₁₂H₂₄N₃O₆ (365.2) calculated: 39.42% C, 6.59% H, 11.50% N; found for *fac*-isomer: 39.00% C, 6.63% H, 11.47% N; for *mer*-isomer: 38.85% C, 6.70% H, 11.36% N.

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