

SYNTHESIS OF  $\Delta$ -(C<sub>3</sub>)-*mer*-Co[(S)-(-)-TYROSINATE]<sub>3</sub>

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Tris[(S)-(-)-tyrosinato]cobalt(III) was prepared by the reaction of [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> with (S)-(-)-tyrosine in the presence of charcoal. The courses of the electronic absorption spectrum (region of *d*-*d* transitions) and the IR spectrum correspond to a *mer* isomer. Its absolute configuration, inferred from rotatory dispersion, corresponds to a right-handed arrangement of the chelate rings about the C<sub>3</sub> axis, *i.e.*  $\Delta$ -(C<sub>3</sub>).

The complexes of cobalt(III) with  $\alpha$ -amino acids, of the type Co(AB)<sub>3</sub>, which may exist in four stereoisomeric forms, were studied mainly in the case of aliphatic amino acids<sup>1-5</sup>. Denning and Piper<sup>6</sup> have pointed to the possible steric interactions preventing the existence of some of the isomers. It was also established that the mutual ratio of the isomers formed depended on the reaction time, steric factors, and also on the method of preparation used<sup>7,8</sup>. Generally, starting from Co(OH)<sub>3</sub>, [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> and using a direct oxidation of cobaltous salts in the presence of a corresponding amino acid, a mixture of facial (*fac*) and meridional (*mer*) isomers may be obtained, while from K<sub>3</sub>[Co(CO<sub>3</sub>)<sub>3</sub>] *mer* isomers<sup>9</sup> are formed predominantly.

In this paper the preparation of a cobalt(III) complex with (S)-(-)-tyrosine is described. Although this complex may exist in the following isomeric forms (in view of the character of the donor atoms and the chiral arrangement on the  $\alpha$ -carbon atom):  $\Lambda$ -(C<sub>3</sub>)-*fac*,  $\Delta$ -(C<sub>3</sub>)-*fac*,  $\Lambda$ -(C<sub>3</sub>)-*mer*,  $\Delta$ -(C<sub>3</sub>)-*mer* (according to Piper<sup>10</sup>  $\Lambda$ -(C<sub>3</sub>) and  $\Delta$ -(C<sub>3</sub>) mean absolute configuration of the complex in relation to the threefold axis of rotation), the formation of only the  $\Delta$ -(C<sub>3</sub>)-*mer* isomer was observed (Fig. 1). It was possible to prepare this isomer only by a modified substitution method, starting from [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub>, under the catalytic effect of charcoal. The reaction yield is dependent on the reaction time<sup>11</sup>: with increasing time the yield decreases because the reaction is complicated by the oxidation of tyrosine. The reaction mixture always contained a substance with a positive charge (demonstrated by electrophoresis, probably an intermediate of the substitution reaction). Other methods gave negative results (the electrophoresis of the reaction mixture always indicated the presence of predominantly cobaltous ions<sup>11</sup>).

Electronic absorption spectrum of cobalt(III) tris-(S)-tyrosinate shows a maximum at 545 nm and an inflexion at 370 nm, and by its course it corresponds to the spectra of the complexes of amino acids with trivalent cobalt with a meridional arrangement of the ligands (rhombic symmetry, splitting of the absorption band in the T<sub>1g</sub>

transition region). The infrared spectrum also shows a maximum characteristic of the coordination of the COO<sup>(-)</sup> group at 1600 cm<sup>-1</sup>, while the region of the NH<sub>2</sub> group absorption is covered by a broad absorption band of the OH vibration of water.

The synthesis of a *mer* isomer exclusively indicates weaker interactions in the transition intermediate of the substitution in comparison with the *fac* arrangement. Generally, all amino acids with a sterically bulky non-polar chain give higher yields of the *mer* isomers<sup>7,8,12</sup>. The equilibration of the *mer* isomer in the presence of charcoal (methanolic solution) causes the decomposition of the complex (proved electrochemically).

The absolute configuration of *mer*-tris[(S)-(-)-tyrosinato]cobalt(III) was determined on the basis of an optical rotatory dispersion curve (Fig. 2), utilizing the rule<sup>13</sup> according to which the isomer with the negative Cotton effect in the T<sub>1g</sub> transition region has a  $\Delta$  configuration, *i.e.* one in which the disposition of chelate rings corresponds to right-handed chirality (Fig. 1). The heating of the methanolic solution of the  $\Delta$ -(C<sub>3</sub>)-*mer* isomer in the presence of charcoal for 5 hours led to the decrease in the values of molar rotation; simultaneously Co<sup>2+</sup> ions appeared in the solution, indicating that this decrease in the [M] value is probably caused by a partial decomposition of the complex.

## EXPERIMENTAL

**Chemicals used:** (S)-(-)-tyrosine ([ $\alpha$ ]<sub>D</sub> -10° in 1M-HCl) was a product of Reanal, Budapest. [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> was prepared according to literature<sup>14</sup>.

**Apparatus:** electronic absorption spectrum was measured with an Optica-Milano apparatus, the infrared spectra on a Perkin-Elmer spectrophotometer, using the KBr technique. For the measurement of the optical rotation an Opton (GFR) apparatus was employed. The electrophoresis was carried out on a Tatrachema apparatus (Czechoslovakia). Paper Whatman No 1 and 0.05M-NaClO<sub>4</sub> were used.

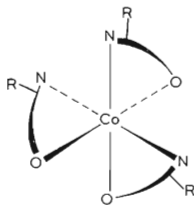


FIG. 1

Configuration of  $\Delta$ -(C<sub>3</sub>)-*mer*-Co[(S)-(-)-tyrosine]<sub>3</sub>

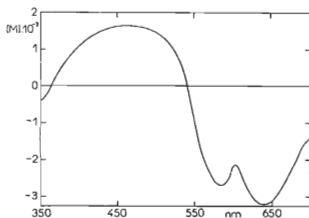


FIG. 2

Optical Rotatory Dispersion Curve of  $\Delta$ -(C<sub>3</sub>)-*mer*-Co-[(S)-(-)-tyrosine]<sub>3</sub>

*Preparation of the complex:* To a solution of 0.03 mol of (S)-(-)-tyrosine dissolved in 50 ml of hot water 0.01 mol of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  and 0.2 g of charcoal were added. The reaction mixture was stirred and heated at 60°C for 15 minutes. After cooling, it was chromatographed on a column of Dowex 50 W  $\times$  8 (in  $\text{H}^+$  cycle). The obtained eluate was evaporated to dryness *in vacuo*. The isolated complex is soluble in ethanol. For  $\text{C}_{27}\text{H}_{30}\text{CoN}_3\text{O}_9 \cdot 4\text{H}_2\text{O}$  (671.5) calculated: 48.25% C, 5.70% H, 6.25% N; found: 48.12% C, 5.77% H, 5.91% N.

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