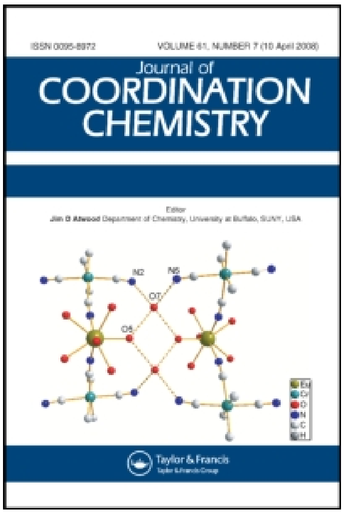

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MONO- AND DINUCLEAR COBALT(III) COMPLEXES WITH *S*-TYROSINE

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In a direct synthesis, by oxidation of cobalt(II) to cobalt(III) by oxygen in the presence of the lithium salt of *S*-tyrosine, the following isomers of the *tris(S*-tyrosinato)cobalt(III) complex were obtained: Δ-$(-)_{589}$-*facial*, Λ-$(+)_{589}$- and Δ-$(-)_{589}$-*meridional*, and $(-)_{589}$-*anti(N)*-Δ-*cis(N), cis(O)*-Λ-*cis(N), cis(O)*-di-μ-hydroxo-*tetrakis(S*-tyrosinato)dicobalt(III). Their composition was established by microanalysis, and their structure by electronic absorption, CD and ^{13}C NMR spectra. Finally, it was found that Δ-*mer-tris(S*-tyrosinato)cobalt(III) described earlier is a mixture of Δ and Λ diastereomers of the complex.

Keywords: *S*-tyrosine; cobalt(III); synthesis; configuration; CD spectra; ^{13}C NMR spectra

INTRODUCTION

Tris(aminocarboxylato)cobalt(III) complexes with aliphatic aminoacids have been mainly described so far. On the contrary, corresponding cobalt(III) complexes with aromatic aminoacids have been studied to a minor extent. On the basis of this fact it could be assumed that these complexes are hard to prepare compared to those containing aliphatic aminocarboxylato ligands. This assumption is in accordance with the nature of phenyl group, which is very voluminous and exhibits a negative inductive effect that should decrease the coordination ability of the ligands. Therefore, we wished to examine the synthesis of *tris(S*-

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tyrosinato)cobalt(III) isomers in view of the fact that corresponding *tris(S*-alaninato)cobalt(III) isomers have already been described [1-3].

EXPERIMENTAL

The Synthesis of *tris(S*-tyrosinato)cobalt(III) Isomers and $(-)_{589}$-*anti(N)*-Δ-*cis(N), cis(O)*-Λ-*cis(N), cis(O)*-di-μ-hydroxo-*tetrakis(S*-tyrosinato)dicobalt(III)

In a 250 cm^3 flask was placed 1.20 g (6.62 mmol) of *S*-tyrosine, 0.18 g (7.36 mmol) of LiOH and 70 cm^3 of ethanol and water mixture (1:1). The flask was heated on a water bath at 60°C for as long as necessary for the substances to dissolve, then a solution of 0.58 g (2.0 mmol) of $Co(NO_3)_2 6H_2O$ in 10 cm^3 of the mentioned solvent was added. The reaction mixture was heated for 15 minutes and a stream of air passed through it during 3 hours (the stream was previously passed through a wash-bottle containing a saturated solution of KOH). After 90 minutes, 10 cm^3 more ethanol was added. After the oxidation was complete the suspension was acidified with glacial CH_3COOH to pH 5 and small quantities of a violet precipitate and unreacted amino acid were filtered off.

The filtrate was left in the fridge during the night and the violet $[Co_2(OH)_2(S\text{-}tyr)_4]$ complex separated was filtered off, washed with water and ethanol and dried in air (0.18 g; 38.6%).

The filtrate was poured onto a CM Sephadex C-25 column in the sodium form and eluted with water when two zones were formed, a large violet, and a small red one. The eluates were concentrated to small volume (about 10 cm^3) on a rotatory evaporator at 30°C.

The concentrated eluate of the second (red) zone was left in the fridge during the night. The red Δ-$(-)_{589}$-*facial* isomer of *tris(S*-tyrosinato)cobalt(III) complex obtained (0.021 g; 3.5%) was filtered off, washed with water, dried in air and then for one hour in a drying oven at 110°C.

The concentrated eluate of the first zone was poured onto a Dowex 50W-X4 column in the hydrogen form (200-400 mesh) and eluted with water, whereby the violet zone separated into two violet zones with opposite signs of optical rotation at 589 nm. Both eluates were evaporated to dryness on a rotatory evaporator at 30°C, and then the violet *meridional* diastereomers of *tris(S*-tyrosinato)cobalt(III) complex obtained were kept first in a desiccator over anhydrous $CaCl_2$ for one day and then in a drying oven for an hour at 110°C. From the first zone 0.070 g (11.7%) of the Λ-$(+)_{589}$ isomer and from the second 0.044 g (7.3%) of the Δ-$(-)_{589}$ isomer were obtained. The results of the analyses of the complexes obtained are given in Table I.

TABLE I Microanalyses of the complexes obtained.

	%C	%H	%N
mer-(+)$_{589}$-[Co(*S*-tyr)$_3$]·H_2O, Calcd.	52.51	5.23	6.81
Found	52.38	5.46	6.50
mer-(−)$_{589}$-[Co(*S*-tyr)$_3$]·4H_2O, Calcd	48.28	5.71	6.25
Found	48.34	5.57	5.91
fac(−)$_{589}$-[Co(*S*-tyr)$_3$]·3H_2O, Calcd	49.61	5.56	6.43
Found	49.58	5.45	6.41
[$Co_2(OH)_2$(S-tyr)$_4$]·2H_2O, Calcd	47.58	5.12	6.16
Found	47.71	5.31	6.20

Measurements

Electronic spectra were recorded with a GBC UV/VIS 911 A spectrophotometer. CD spectra were recorded using a Jasco 500 automatic spectropolarimeter. ^{13}C NMR spectra were recorded with a Bruker AM 600 spectrospin spectrometer.

RESULTS AND DISCUSSION

Synthesis

As seen from the Experimental Section, we succeeded in preparing three of the four theoretically possible isomers of the tris(*S*-tyrosinato)cobalt(III) complex as follows: Δ-(−)$_{589}$-*facial* isomer and Λ-(+)$_{589}$- and Δ-(−)$_{589}$-*meridional* isomers, as well as a dinuclear complex (−)$_{589}$-*anti*(N)-Δ-*cis*(N), *cis*(O)-Λ-*cis*(N), *cis*(O)-di-*μ*-hydroxo-*tetrakis*(*S*-tyrosinato)dicobalt-(III). They were formed by passing a stream of air through an ethanol solution of cobalt(II) in the presence of the lithium salt of *S*-tyrosine. Dinuclear complex was obtained from the precipitate formed in the mother liquor and the other mentioned complexes were isolated from the filtrate by chromatography. Among the obtained isomers, in the literature [4] only the Δ-*mer-tris(S*-tyrosinato)cobalt(III) species has been reported, obtained by reaction of cobalt(III) hydroxide with *S*-tyrosine. However, as seen in Figure 1, the obtained product was a mixture of both diastereomers of *meridional* isomers.

Determination of Configurations

Geometrical configuration of the tris(S-tyrosinato)-cobalt(III) diastereomers

Geometrical configurations of the isolated isomers of the *tris(S*-tyrosinato)cobalt(III) complex were determined by means of electronic and ^{13}C NMR spectroscopy. In the first instance assignment was achieved by the Basolo, Ballhausen and Bjerrum rule [5], according to which *meridional* isomers of *tris(S*-aminocarboxylato)cobalt(III) complexes have an asymmetrical first absorption band, due to a rhombic chromophore, in contrast to *facial* isomers which possess a cubic chromophore causing a symmetrical band. Therefore, to the violet isomers, which were first eluted and have an asymmetric first absorption band (Figure 2), we also ascribe *meridional* configuration, and to the red isomer, of which the first absorption band was symmetric (Figure 3), we ascribe *facial* configuration.

The *facial* isomer in the ^{13}C NMR spectrum exhibits only one peak for the carboxylate carbon atom at 179.94 ppm and one peak for the α-carbon atom at 58.85 ppm (Figure 4). It shows that all three coordinated *S*-tyrosinato ligands are equivalent, thus proving the assumed *facial* configuration. On the contrary, *meridional* isomers have inequivalent chelate rings, and therefore three peaks are expected in their ^{13}C NMR spectra both for carboxylic and for α-carbon atoms. In Figure 5 it is seen that the *meridional* Λ-$(+)_{589}$ isomer exhibits the mentioned peaks at about 180.5 and about 58.5 ppm, respectively, which proves its assumed

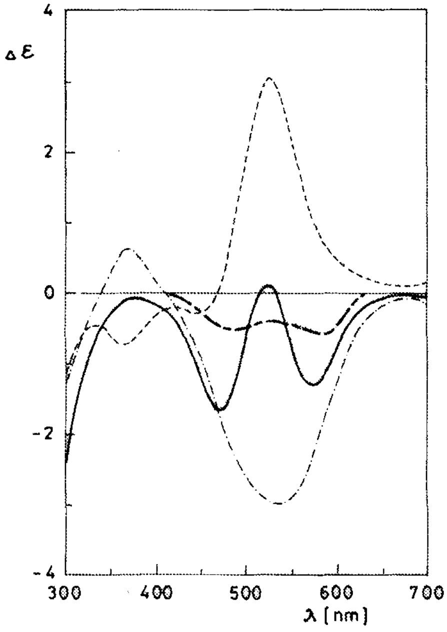

FIGURE 1 CD spectra of *meridional* Λ-$(+)_{589}$ (- - -) and Δ-$(-)_{589}$ (- · · · -) diastereomers of [Co(*S*-tyr)$_3$] complexes, the CD spectrum of their mixture (—) and the CD spectrum of the [Co(*S*-tyr)$_3$] complex described earlier[4] (- · · · -).

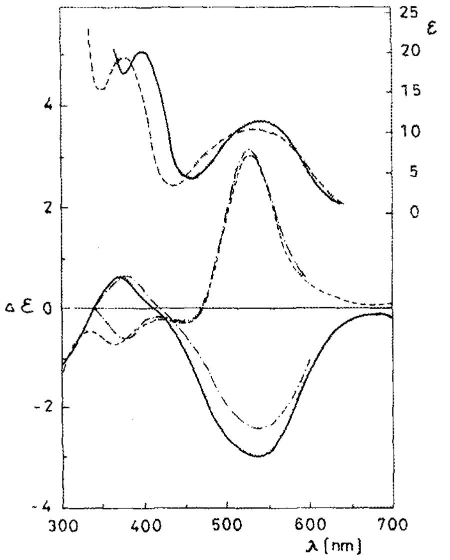

FIGURE 2 Electronic absorption and CD spectra of the *meridional* Λ-$(+)_{589}$(- - -) and Δ-$(-)_{589}$(—) [Co(*S*-tyr)$_3$] diastereomers as well as the CD spectra of the corresponding *S*-alanine complexes (- · - · -).

configuration. In addition, in the same Figure it is seen that the signals of two of the carbon atoms, both of carboxylate and α-carbon atoms, are very close to each other and the third differs in its chemical shift, thus proving that in *meridional* isomers one chelate ring differs from the other two; namely, it shows their asymmetric arrangement.

Absolute configuration of the tris(S-tyrosinato)-cobalt(III) diastereomers

CD spectra of the diastereomers are given in Figures 2 and 3, together with CD spectra of the *tris(S*-alaninato)cobalt(III) diastereomers, of which the absolute configurations were determined by Denning and Piper [3] by means of their CD and ^{1}H NMR spectra. In addition, absolute configurations of the Λ-$(+)_{589}$- and Δ-$(-)_{589}$-*meridional S*-alanine isomers were proved by means of X-ray analysis by Drew *et al.* [6] and Herak *et al.* [7], respectively.

Since all these complexes have analogous composition and structure and the same Co(III)N_3O_3 chromophore, giving rise to almost identical CD spectra for the same geometrical isomers, we compared their spectra and concluded that our *mer*-$(+)_{589}$ diastereomer has Λ, *mer*-$(-)_{589}$ diastereomer Δ and *fac*-$(-)_{589}$ diastereomer Δ absolute configurations.

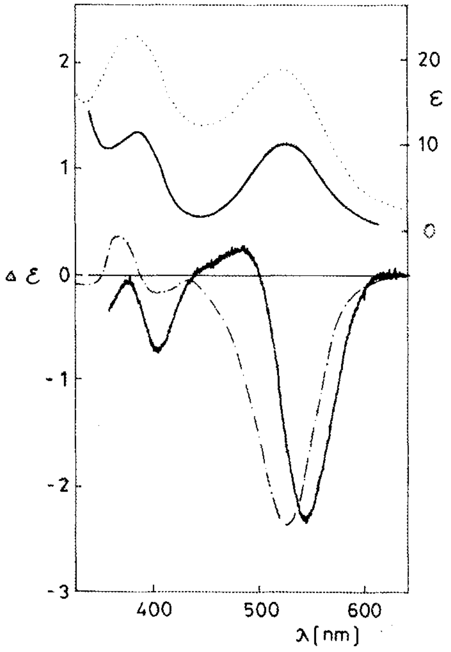

FIGURE 3 Electronic absorption and CD spectra of the Δ-$(-)_{589}$*fac*-[Co(*S*-tyr)$_3$] diastereomer (—), the CD spectrum of the corresponding *S*-alanine complex (- · · · -) and the electronic absorption spectrum of the Δ-$(-)_{589}$-*fac*-[Co(*S*-argH)$_3$]$^{3+}$ complex (......).

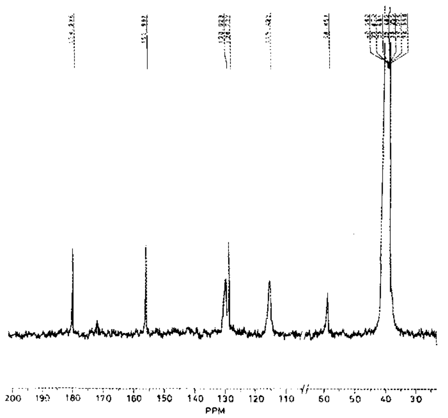

FIGURE 4 ^{13}C NMR spectrum of the Δ-$(-)_{589}$-*fac*-[Co(*S*-tyr)$_3$]diastereomer.

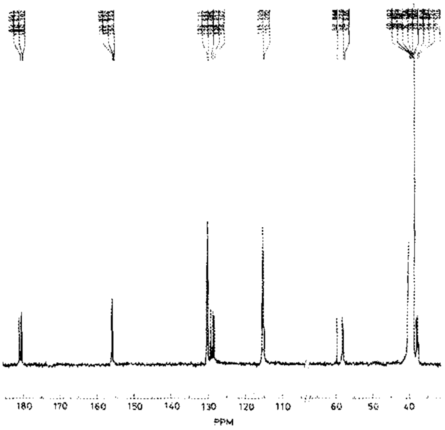

FIGURE 5 ^{13}C NMR spectrum of the Λ-(+)$_{589}$-*mer*-[Co(*S*-tyr)$_3$] diastereomer.

Configuration of the dinuclear complex

Di-μ-hydroxo-*tetrakis(S*-tyrosinato)dicobalt(III) could theoretically occur in the form of seven geometrical isomers, and if the chirality around each cobalt ion is taken into account, 24 isomers altogether are theoretically possible. The substance isolated has CD and electronic absorption spectra very similar to the spectra of the analogous dinuclear complex with *S*-arginine, the structure of which was determined by X-ray analysis [8], except that its first absorption maximum was shifted to longer wavelengths by 10 nm (Figure 6). This is in accordance with the above assumed weaker ligand field of the *S*-tyrosinato ligand in relation to *S*-arginine, as well as with the data obtained by comparison of *tris(S*-arginine)cobalt(III) spectra with the corresponding *S*-tyrosinato complex spectrum, Figure 3. On this basis, it was assumed that the dinuclear complex obtained in this work has an analogous configuration to the arginine complex, namely that it is *anti*(N)-Δ-*cis*(N), *cis*(O)-Λ-*cis*(N), *cis*(O)-di-μ-hydroxo-*tetrakis(S*-tyrosinato)dicobalt(III). This is also in accordance with its ^{13}C NMR spectrum (Figure 7). It is seen in the spectrum that for the carboxylic carbon atoms four peaks are obtained (at about 181 ppm), as in the case for the α-carbon atoms (at about 59 ppm); consequently it could be concluded that the symmetry around cobalt atoms is similar to the symmetry of the corresponding arginine complex, which also exhibits four peaks for carboxyl and α-carbon atoms, and which are in the same regions as for the *S*-tyrosinato complex [8].

On this basis we assume that the dimer represents one of the isomers where both cobalt atoms have *cis*(N), *cis*(O) configuration and it is likely that the absolute configurations around cobalt atoms are of opposite sign, whereby the

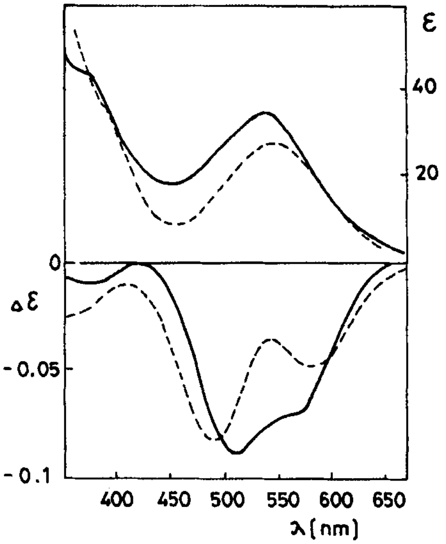

FIGURE 6 Electronic absorption and CD spectra of *anti*(N)-Δ-*cis*(N),*cis*(O)-Λ-*cis*(N),*cis*(O)-di-μ-hydroxo-*tetrakis*(*S*-tyrosinato)dicobalt(III) complex (- - -) and the corresponding electronic absorption and CD spectra of the dinuclear *S*-arginine complex (—).

negative sign prevails. The final complex configuration can be determined only by means of X-ray analysis.

As it is seen from the presented work, we suceeded in obtaining three of four theoretically possible isomers of *tris*(*S*-tyrosinato)cobalt(III), in contrast to the *tris*(*S*-alaninato)cobalt(III), for which all four isomers are described [1-3]. Based on this it could be assumed that the discrepancy is due to weaker coordination ability of the *S*-tyrosinato ligand. It is not likely that it is due to steric effects,

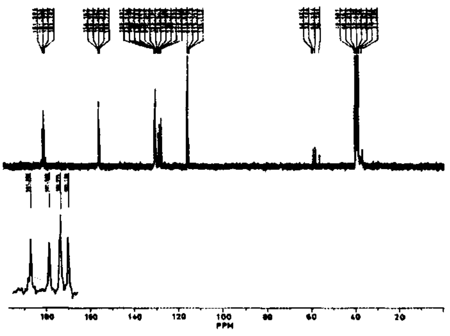

FIGURE 7 ^{13}C NMR spectrum of the dinuclear *S*-tyrosine complex.

because of molecular models, and is in contrast with the results obtained by Denning and Piper [3], who for the analogous *S*-proline diastereomers with very pronounced steric effects obtained the Λ-$(+)_{589}$-*facial*, and not the Λ-$(+)_{589}$-*meridional* isomer.

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