

Synthesis of *trans*-Tris(*s*-leucinato)cobalt(III)

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Received June 18, 1969

Oxidation of CoSO_4 in the presence of *s*-leucine using PbO_2 as oxidizing agent in the presence of activated charcoal leads to the synthesis of *trans*- Δ, Δ - $\text{Co}(s\text{-leucinate})_3$ and only a small amount of Δ, Δ -*cis* isomer. Without catalysis a mixture of *trans*- Δ, Δ and Δ -*cis* isomers were obtained. Reaction yields are discussed in terms of different isomer stabilities. Thermal gravimetric analysis of *trans* isomers showed, that dehydration occurs at 40–160°C.

Metal amino acid complexes exist in four isomeric forms. Using different synthetic procedures, different ratios of isomers is obtained. Thus the reaction of amino acids with cobalt(III) hydroxide leads to a mixture of *cis* and *trans* isomers [1], similarly as the reaction with $\text{K}_3[\text{Co}(\text{CO}_3)_3]$ [2]. On the other hand, a method using $[\text{Co}(\text{NH}_3)_6]^{3+}$ as precursor of Co^{3+} ions is according to the literature [2, 3] suitable for the preparation of *cis* isomers. However, the results of our present studies, indicate that in this reaction *trans* isomers are also formed [4].

In our previous work [5] we studied oxidation of Co^{2+} ions in the presence of glycine using different oxidizing agents. It was found that the oxidation gives a 1 : 1 mixture of *cis* and *trans* isomers of triglycinatocobalt(III) regardless the oxidizing agent. When using for the oxidation either air or H_2O_2 , a compound of anionic nature was detected, suggesting that the reaction proceeds *via* a polynuclear intermediate. The oxidation in the presence of activated charcoal led to higher yields of *trans* isomer. The synthesis of the 1 : 1 mixture of geometrical isomers is explained on the basis of equal stabilities of both these enantiomers. For this reason we were interested in the study of direct synthesis of cobalt(III) complexes containing optically active amino acids. These complexes are diastereoisomers and differences in stabilities between them may arise. In the present paper the synthesis of tris(*s*-leucinato)cobalt(III) with the regard to the isomers formed is described.

Experimental

s-Leucine, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and PbO_2 were obtained from Lachema (Brno). Electronic absorption spectra were recorded on the Optica-Milano apparatus. Infrared spectra were measured by using KBr technique on the UR-10 spectrophotometer. Optical rotatory dispersion were measured on the Jasco optical rotatory dispersion recorder Model-5.

Procedure

2.87 g (0.01 mole) of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and 3.93 g (0.03 mole) of *s*-leucine were dissolved in 100 ml of hot distilled water and refluxed with about 5 g of PbO_2 for about 30 minutes.

After cooling to the room temperature, all insoluble material was filtered off. This material was extracted with hot methanol, further with conc. HCl and thereafter with 50% H₂SO₄.

Both filtrate and methanolic solution containing *trans* isomers were evaporated to dryness in vacuo. The solid residue was dissolved in 85% ethanol and chromatographed on an alumina column. Both HCl and H₂SO₄ extracts were further treated according to Denning and Piper [6].

Analysis

trans-Λ,Λ-Co(*s*-leucinate)₃ · 3H₂O. For CoC₁₈H₄₂N₃O₉ (495.46) calculated: 43.00% C, 8.42% H, 8.39% N; found: 42.68% C, 8.65% H, 8.23% N.

cis-Λ-Co(*s*-leucinate)₃ · 3H₂O. For CoC₁₈H₄₂N₃O₉ (495.46) calculated: 43.00% C, 8.42% H, 8.39% N; found: 43.28% C, 8.56% H, 8.27% N.

cis-Δ-Co(*s*-leucinate)₃ · 2H₂O. For CoC₁₈H₄₀N₃O₈ (478.34) calculated: 44.53% C, 8.32% H, 8.65% N; found: 45.00% C, 8.48% H, 8.69% N.

Results and Discussion

Tris(*s*-aminoacidato)cobalt(III) complexes form two geometrical isomers, which are enantiomorphous at the cobalt atom, giving rise to the absolute configuration *Λ* and *Δ*, corresponding to the left-handed and right-handed helicity about a three-fold axis of rotation. The presence of optically active amino acid causes that isomers, which are diastereoisomers differ in their thermodynamic stabilities due to the non-bonding interactions.

The direct oxidation of CoSO₄ in the presence of *s*-leucine yields 3.9 g of *Λ,Λ-trans* and 0.18 g of *Λ-cis* isomers. On the other hand, when activated charcoal was added, the following quantities were obtained: 4.3 g of *Λ,Λ-trans*, 0.20 g of *Λ-cis* and 0.16 g of *Δ-cis*. The reaction yield depends somewhat on the reaction time. The amount of *cis* isomers obtained by increasing of the prolonged reaction time, whilst the amount of *trans* isomers decreased. Co²⁺ ions could be parallelly detected. The low yield of *cis* isomers might be result of *trans-Δ* → *trans-Λ* inversion, which is accompanied by the bond rupture or by the dissociation mechanism [6]. Absence of *Δ-cis* (without catalysis) is not surprising because of the axial character of leucine alkyl groups. Catalysis with activated charcoal generally enhances reaction yields together with the formation of the *Δ-cis* isomer. Both these effects are in agreement with the mechanism of charcoal catalysis [7].

Predominance of *trans* over *cis* isomers may be discussed in terms of higher stability of the former, where nonbonding interactions are smaller than in *cis* complexes [6]. Equilibration of *Δ-trans*-tris(*s*-leucinato)cobalt(III) in 1-butanol gives a mixture of both *Λ* and *Δ* isomers and only a small amount of *cis* one [6], suggesting higher thermodynamic stability of *trans* isomers in the comparison with *cis*. However, it must be taken into account that synthetic reactions in dependence on the reaction conditions may reflect both kinetic and thermodynamic control of the reaction.

The isolated geometrical isomers were identified by using electronic absorption spectra (region of *d-d* transitions), which corresponded to the proper symmetries. Absorption spectra show two expected absorption peaks: *Λ,Λ-trans*: λ_{max} = 375 and 535 nm (ε = 184 and 108); *Λ-cis*: λ_{max} = 370 and 520 nm (ε = 210 and 205); *Δ-cis*: λ_{max} = 370 and 520 nm (ε = 180 and 210). In the case of *trans* isomers the absorption peak (band I) is somewhat splitted (Fig. 1).

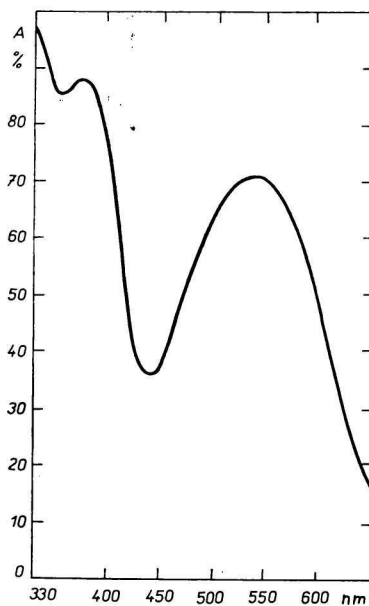


Fig. 1. Absorption spectrum of *trans-Λ,Δ*-Co(*s*-leucinate)₃ · 3H₂O.

Configuration of isomers was established comparing of the optical rotatory dispersion curves with those prepared according to *Denning* and *Piper* [6]. These results show that *trans-Λ* and Δ forms were synthesized in the roughly equal amounts. We were not successful in the total resolution of the mixture of *trans-Λ* and Δ isomers even when we used different solvent systems with alumina as sorbent. This is probably on account of the small differences between equatorial and axial *sec*.butyl groups in Δ or Λ isomers, respectively. Questions concerning separability of diastereoisomers of the Co^{III}(aminoacidate)₃ type will be described elsewhere.

The isolated compounds were further characterized by infrared spectra, which are closely similar to those of the other Co(aminoacidate)₃ complexes [3].

The elemental analysis showed that isomers were obtained as hydrated compounds. Thermal gravimetric analysis indicated that the dehydration of *trans* isomers occurred at the temperature intervals of 40–160°C. Further increasing of the temperature resulted in a total decomposition.

Thanks are due both to Dr. F. Kůtek for the gravimetric thermal analysis and Mr. J. Marc for the measurement of optical rotatory dispersion spectra.

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Translated by F. Jursik