

ISOMERS OF BIS((S)-LYSINATO-O,N,N)COBALT(III) CATION: PREPARATION AND PROPERTIES

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In the complex cation of the compound $[\text{Co}((S)\text{-Lys})_2]\text{NO}_3$ (*S*)-lysine is coordinated as a tridentate ligand, giving rise to $\Lambda\Delta\Delta\Delta$ -*cis,cis,trans* and *cis,trans,cis* isomers. Yields of both isomers are higher in dimethyl sulfoxide than in water. Their structure was derived from ^1H NMR, CD and electronic absorption spectra.

(*S*)-Diaminocarboxylic acids represent tridentate ligands whose coordination in octahedral complexes can lead to three geometric isomers with different size of the chelate rings. The hitherto published studies of cobalt(III) complexes with (*S*)-2,3-diaminopropionic acid^{1,2} (2,3-Dap), (*S*)-2,4-diaminobutyric acid³ (2,4-Dab) and (*S*)-ornithine⁴ (Orn) proved the existence of isomers with chelate rings ($\text{O}-\text{N}_\alpha$, $\text{N}_\alpha-\text{N}_\omega$) of the size 5-5, 5-6 and 5-7, respectively. In order to extend this homologous series we describe here the preparation and properties of the complex with (*S*)-lysine, containing chelate rings of the size 5-8.

EXPERIMENTAL

Chemicals and Instruments

(*S*)-Lysine ($[\alpha]_D +25.9^\circ$) was a Calbiochem (USA) product; $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ was prepared according to the literature⁵. Electronic absorption spectra were taken on Specord UV-VIS and VSU 2 spectrophotometers (both Carl Zeiss, G.D.R.). ^1H NMR spectra were measured on a Varian XL-100 instrument, using sodium 2,2-dimethylsilapentane-5-sulfonate as a standard. CD spectra were taken on a CARY 61 instrument, calibrated with (+)-10-camphorsulfonic acid.

Preparation of $[\text{Co}((S)\text{-Lys})_2]\text{NO}_3$

a) *In water*: A solution of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (2.67 g; 0.01 mol) and (*S*)-lysine (2.29 g; 0.02 mol) in water (500 ml) was treated with charcoal (0.7 g) and the mixture was worked up according to the literature⁴. The reaction mixture was applied on a column of Dowex 50WX8 (NH_4^+ cycle; 100-200 mesh, 750 mm length, 25 mm diameter). Elution with a solution of NH_4NO_3 (0.75 mol \cdot dm^{-3}) afforded fractions I and II. Material which was slowly eluted only with eluant of con-

centration higher than 1.0 mol dm^{-3} was not studied further. The eluates *I* and *II* were evaporated *in vacuo*, the residues were extracted with methanol and freed of NH_4NO_3 by chromatography on Sephadex G 10 column.

b) *In dimethyl sulfoxide*: The compound $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ was converted into $[\text{Co}(\text{NH}_3)_6](\text{ClO}_4)_3$. A solution of $[\text{Co}(\text{NH}_3)_6](\text{ClO}_4)_3$ (3.14 g; 0.007 mol) and (*S*)-lysine (2.0 g; 0.014 mol) in dimethyl sulfoxide (500 ml) was treated with charcoal and worked up as described under a). For $[\text{Co}(\text{C}_6\text{H}_{13}\text{N}_2\text{O}_2)_2]\text{NO}_3 \cdot \text{H}_2\text{O} \cdot 2 \text{NH}_4\text{NO}_3$ (595.3) (*I*) calculated: 24.18% C, 6.04% H, 21.17% N; found: 24.00% C, 6.20% H, 21.66% N. For $[\text{Co}(\text{C}_6\text{H}_{13}\text{N}_2\text{O}_2)_2]\text{NO}_3 \cdot 2 \text{H}_2\text{O} \cdot 0.5 \text{NH}_4\text{NO}_3$ (487.3) (*II*) calculated: 29.55% C, 6.56% H, 17.24% N; found: 29.57% C, 6.55% H, 17.51% N.

RESULTS AND DISCUSSION

Coordination of (*S*)-lysine as a tridentate ligand with a cobalt(III) ion gives rise to the complex $[\text{Co}((\text{S})\text{-Lys})_2]^+$ which, in principle, can exist in three geometrical isomers. These are described on the basis of mutual relations of the oxygen, α -nitrogen and ω -nitrogen donor atoms (Fig. 1).

The complex $[\text{Co}((\text{S})\text{-Lys})_2](\text{NO}_3)$ was prepared in the presence of charcoal. Chromatographic separation of the reaction mixture on a cation-exchange resin afforded two fractions, identified as *cis,trans,cis* and *cis,cis,trans* isomers. Predominant part of the material remained adsorbed on the top of the column and was not eluted even with solutions of concentrations higher than 1.0 mol dm^{-3} . In the case

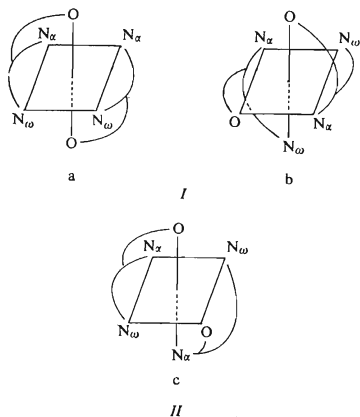


FIG. 1
Geometric isomers of $[\text{Co}((\text{S})\text{-Lys})_2]^+$. a *trans(O)cis(N_α)cis(N_ω)*, b *cis(O)trans(N_α)-cis(N_ω)* (*I*), c *cis(O)cis(N_α)trans(N_ω)* (*II*)

of lysine the amount of these complexes with charge probably higher than +1 (polymeric products) is greater than in the preparation of $[\text{Co}((S)\text{-Orn})_2]\text{NO}_3$. The lysine complex was prepared in water or in dimethyl sulfoxide. In both solvents under charcoal catalysis only two isomers were formed reflecting their higher thermodynamic stability. The total yield was higher in dimethyl sulfoxide, the polymers being still the main product. This observation is in accord with results obtained by Ogino and Fujita⁶ who found that the yield of monomeric cobalt(III) complexes of α,ω -diaminoalkanes sharply dropped, if the ligand coordination led to an eight-membered chelate ring. Also here the use of a non-aqueous medium increased the monomer yield.

On the basis of electronic absorption spectra, similar to those of isomers of the same donor type¹⁻⁴ CoN_4O_2 , we can exclude the *trans*(O)-isomer (no splitting of the absorption band in the region of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transitions) and ascribe the spectral data to the *cis*(O) isomers. A distinction between the *cis*(O) isomers from these spectra was not possible (Fig. 2). Thus obtained isomers were assigned the *cis,trans,cis* and *cis,cis,trans* configuration on the basis of their ${}^1\text{H}$ NMR spectra. The measurements were performed in ${}^2\text{H}_2\text{O}$, *i.e.* under conditions of a rapid exchange of N—H protons with the solvent. In the spectra of both isomers we can distinguish three regions. The lowest-field multiplets correspond to the proton at the α -carbon atom (~ 3.5 ppm), the 3 ppm region contains signals due to protons

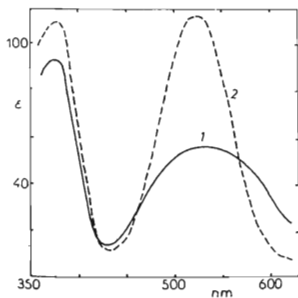


FIG. 2

Electronic absorption spectra of the isomers of $[\text{Co}((S)\text{-Lys})_2]\text{NO}_3$. 1 *cis,trans,cis* (I), 2 *cis,cis,trans* (II)

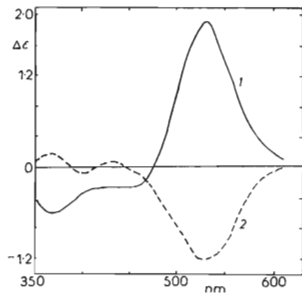


FIG. 3

CD Spectra of the isomers of $[\text{Co}((S)\text{-Lys})_2]\text{NO}_3$. 1 *cis,trans,cis* (I) 2 *cis,cis,trans* (II)

on terminal carbon atoms of the ligand, the remaining proton signals being located more upfield. This is in accord with the integrated intensities of the signals. Analogously to cobalt(III) complexes with (S)-2,3-Dap, (S)-2,4-Dab and (S)-Orn¹⁻⁴, the spectra of the isomers differ in the C_α proton signal chemical shifts. For the *cis,trans,cis*-isomer I this signal is located more downfield (3.75 ppm) than for the *cis,cis,trans*-isomer II (3.42 ppm). This difference is obviously due to different interligand interactions in the single geometric arrangements (different shielding constants). Absolute configuration was assigned to the geometric isomers using the ring-pairing method⁷. It follows from application of this method that the CD contribution of the *cis,trans,cis* isomer is caused only by the vicinal effect due to the presence of the (S)-ligand and the absolute configuration of the *cis, cis, trans* isomer is $\Lambda\Delta\Delta\Delta$. The isomers were distinguished also by their CD spectra (Fig. 3). As mentioned above, the absolute configuration of the *cis, cis,trans*-isomer is $\Lambda\Delta\Delta\Delta$ (as determined by ring-pairing method⁷). This corresponds to the CD curve found for the isomer which was eluted as the second. The CD spectrum of the remaining isomer displays a curve, corresponding to those¹⁻⁴ of *cis,trans,cis*-isomers of the complexes $[\text{Co}((\text{S})\text{-}2,3\text{-Dap})_2]^+$, $[\text{Co}((\text{S})\text{-}2,4\text{-Dab})_2]^+$ and $[\text{Co}((\text{S})\text{-Orn})_2]^+$ which have a positive maximum in the longer-wavelength region.

Comparison of the whole series of trivalent cobalt complexes with α,ω -diaminocarboxylic acids shows that the geometric isomers are eluted from a cation exchange resin column in the same order, *i.e.* *trans,cis,cis* (not available in case of $[\text{Co}((\text{S})\text{-Lys})_2]^+$), *cis,trans,cis* and *cis,cis,trans*. The yield ratio is 1 : 1 : 1 for $[\text{Co}((\text{S})\text{-}2,4\text{-Dab})_2]^+$ (ref.³) and 1 : 10 : 2 for $[\text{Co}((\text{S})\text{-Orn})_2]^+$ (ref.⁸); no data were published for $[\text{Co}((\text{S})\text{-}2,3\text{-Dap})_2]^+$. No *trans,cis,cis*-isomer of $[\text{Co}((\text{S})\text{-Lys})_2]^+$ was observed and the remaining isomers were formed in a 1 : 1 ratio in a 10x lower yield than in the case of $[\text{Co}((\text{S})\text{-Orn})_2]^+$.

The CD curves of the geometric isomers of the compared complexes are analogous but their intensities do not show any simple dependence on the size of the chelate rings. This dependence, described by Legg and Neal⁹ for five- and six-membered chelate rings in $[\text{Co}(\text{Ida})_2]^-$, $[\text{Co}(\text{Ida})(\text{Asp})]^-$ and $[\text{Co}(\text{Asp})_2]^-$ (where Ida designates iminodiacetic acid) holds for bis(α,ω -diaminocarboxylato)cobalt(III) complexes only in the case of $[\text{Co}((\text{S})\text{-Orn})_2]^+$. The deviations, observed for $[\text{Co}((\text{S})\text{-Lys})_2]^+$ can be ascribed to contribution of the eight-membered chelate ring which is conformationally more complex than five to seven-membered rings, or to a possible gradual change in the vicinal effect¹⁰.

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