

The synthesis and characterization of facial and meridional isomers of *uns-cis*-(ethylenediamine-*N-N'*-di-3-propionato)cobalt(III) complexes with *S*-lysine and *S*-histidine

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In the reaction of sodium *uns-cis*-(ethylenediamine-*N-N'*-di-3-propionato)-(carbonato)cobaltate(III) dihydrate and the corresponding amino acid (*S*-lysine or *S*-histidine) at 70 °C, both the theoretically possible facial and meridional isomers of the *uns-cis*-(ethylenediamine-*N-N'*-di-3-propionato)(aminoacidato)cobalt(III) complexes were prepared. The complexes were isolated chromatographically and characterized by elemental analyses, as well as by electron absorption and infrared spectroscopy.

Keywords: cobalt(III) complexes, ethylenediamine-*N-N'*-di-3-propionato ligand, *S*-lysine, *S*-histidine.

INTRODUCTION

Ethylenediamine-*N-N'*-di-3-propionate (eddp), a linear tetradentate ligand with two nitrogen and two oxygen atoms as donors, can adopt two different configurations in octahedral metal complexes with an additional symmetrical bidentate ligand (*s-cis* and *uns-cis*). Although in most synthetic routes^{1–4} the *uns-cis* geometry of the eddp ligand is favored for eddp-Co(III) complexes, the *s-cis* isomer has also been obtained.⁵ Recently, interest in Co(III) complexes with ligands similar to eddp has increased because of their possible hydrolytic activity on the DNA molecule.^{6,7} For (edda-type)-Co(III) complexes (edda is the ethylenediamine-*N-N'*-diacetate ion) with unsymmetrical bidentate ligands (such as amino acids), three geometric isomers are expected: *s-cis*, *fac-uns-cis* and *mer-uns-cis* (Fig. 1).

Amino acids, as unsymmetrical bidentate ligands, have already been used in the preparation of some edda-Co(III) complexes^{8–10} and eddp-Co(III) complexes.³

In this paper, the synthesis and characterization of both theoretically possible geometrical isomers (facial and meridional) derived from the *uns-cis*-(ethylenedia-

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mine-*N-N'*-di-3-propionato)(carbonato)cobaltate(III) anion by its reaction with aliphatic basic α -amino acids, *S*-lysine and *S*-histidine, are reported. The isolated complexes were characterized by elemental analyses. The geometric configurations of the complexes are proposed on the basis of their electronic absorption and infrared spectra.

EXPERIMENTAL

Materials. Sodium *uns-cis*-(ethylenediamine-*N,N'*-di-3-propionato)(carbonato) cobaltate(III) dihydrate was prepared using a previously described procedure.¹¹ All other reagents were obtained commercially and used without further purification.

1) *Preparation of the facial and meridional isomers of uns-cis-(ethylenediamine-*N,N'*-di-3-propionato)(*S*-lysinato)cobalt(III), [Co(eddp)(*S*-Lys)]*

To a solution of 0.30 g (0.8 mmol) of *uns-cis*-Na[Co(eddp)CO₃] \cdot 2H₂O in 10.0 cm³ of water, 0.146 g (0.8 mmol) of *S*-lysine hydrochloride in 10 cm³ of water, previously neutralized with 0.064 g (1.6 mmol) of NaOH, was added and the pH of the solution adjusted to 8. After heating under stirring for 2 h at 55 °C, the solution was concentrated to 10.0 cm³ and loaded onto a 2.5 \times 32 cm column containing Sephadex G-10. The red-violet eluate was then loaded onto a 2 \times 10 cm column containing Dowex 1-X4 (200-400 mesh) anion-exchange resin in the Cl⁻ form. In both cases, water was used as the eluant.

Two bands appeared on the column: violet (the first) and red (the second). Both eluates were concentrated to a small volume and left in a refrigerator over night. The formed crystals were filtered off, washed with ethanol then ether and air-dried. Yield: 0.17 g (50.07 %) of the violet (meridional) and 0.03 g (8.84 %) of the red (facial) isomer. Anal. Calcd. for *mer-uns-cis*-[Co(eddp)(*S*-lys)] \cdot H₂O = C₁₄H₂₉CoN₄O₇. (FW = 424.34) (%): C, 39.63; H, 6.89; N, 13.20. Found (%): C, 39.38; H, 6.45; N, 13.32. Calcd. for *fac-uns-cis*-[Co(eddp)(*S*-Lys)] \cdot H₂O = C₁₄H₂₉CoN₄O₇. (FW = 424.34) (%): C, 39.63; H, 6.89; N, 13.20. Found (%): C, 39.42; H, 6.91; N, 13.04.

2) *Preparation of the facial and meridional isomers of uns-cis-(ethylenediamine-*N,N'*-di-3-propionato)(*S*-histidinato)cobalt(III), [Co(eddp)(*S*-His)]*

From 0.30 g (0.8 mmol) of *uns-cis*-Na[Co(eddp)CO₃] \cdot 2H₂O and 0.124 g (0.8 mmol) of *S*-histidine, the complexes were obtained by the same procedure as described above. Yield: 0.16 g (51.07 %) of violet (meridional) and 0.025 g (9.01 %) of red (facial) isomer. Anal. Calcd. for *mer-uns-cis*-[Co(eddp)(*S*-His)] \cdot 2H₂O = C₁₄H₂₄CoN₅O₇ (FW = 433.31) (%): C, 38.81; H, 5.58; N, 16.16. Found (%): C, 38.41; H, 5.75; N, 16.23. Calcd. for *fac-uns-cis*-[Co(eddp)(*S*-His)] \cdot 2H₂O = C₁₄H₂₄CoN₅O₇ (FW = 433.31) (%): C, 38.81; H, 5.58; N, 16.16. Found (%): C, 38.62; H, 5.52; N, 15.98.

Characterization

Infrared spectra were recorded on a Perkin-Elmer FTIR 31725-X Spectrophotometer using the KBr pellet technique. Electronic absorption spectra were recorded on a Varian GBC 911A spectrophotometer. Aqueous (1 \times 10⁻³ mol dm⁻³) solutions of the complexes were used for these measurements. Elemental microanalyses for C, H, N were performed by standard methods.

RESULTS AND DISCUSSION

The *uns-cis*-[Co(eddp)CO₃]⁻ complex¹¹ was used as the starting material. Substitution of the CO₃²⁻ ligand by an amino acid should, theoretically, give only two geometric isomers, the *fac-uns-cis* and *mer-uns-cis* isomers of [Co(eddp)(*S*-am)] (Fig. 1). Obviously, both isomers have the same molecular symmetry (C₁) but the symmetry of the ligand field of the facial isomer is higher than that of the corresponding meridional

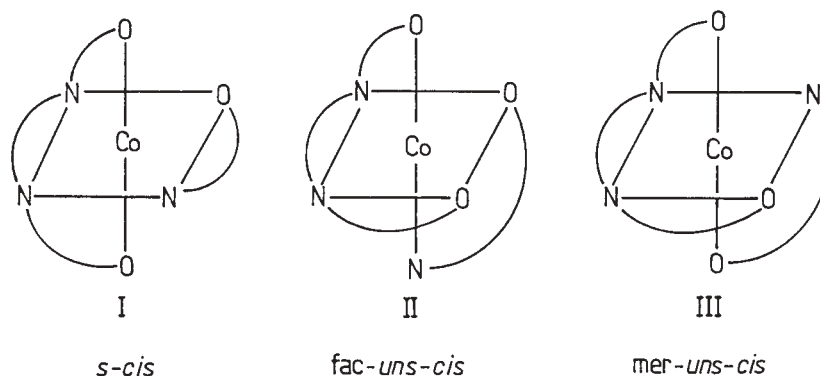


Fig. 1. Possible geometric isomers of $[\text{Co}(\text{eddp})\text{L}]$ complexes: *s-cis*(I), *fac-uns-cis*(II) and *mer-uns-cis*(III), L-unsymmetrical bidentate ligands.

isomer of the same complex. Their molecular symmetries could be compared to the symmetry of the $[\text{Co}(\text{am})_3]$ complex (am = anion of amino-acid), neglecting the backbone diamine ring in the $[\text{Co}(\text{eddp})(\text{am})]$ complexes.

In this work, both the theoretically expected facial (red) and meridional (violet) isomers of *uns-cis*- $[\text{Co}(\text{eddp})(\text{am})]$ (am = anion of *S*-lysine and *S*-histidine) were prepared.

Electronic absorption spectra

The electronic absorption spectra of the isolated *uns-cis*- $[\text{Co}(\text{eddp})(\text{am})]$ complexes are shown in Fig. 2 and their corresponding maxima are summarised in Table I.

The two spin-allowed transitions in the low-spin d^6 system of the Co(III) ion in an octahedral crystal field are ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$, in order of increasing energy. In a tetragonal field, the degeneracies of the excited states are removed, *i.e.*, ${}^1T_{1g} = {}^1A_{2g} + {}^1E_g^a$ and ${}^1T_{2g} = {}^1B_{2g} + {}^1E_g^b$. Additional splitting is expected when the molecular symmetry is further decreased. It has been shown that a small difference between energy states does not cause splitting of the absorption bands when the symmetry is lower than D_{4h} , especially in complexes with edta-type ligands as well as their derivatives.¹² In the *uns-cis-fac* isomer, the holohedrized symmetry of the ligand field is cubic whereas that of the *uns-cis-mer* isomer is rhombic. This loss of symmetry, going from facial to meridional, is expected to cause a splitting, or at least a broadening, of the lowest energy absorption band. This has been observed previously in other CoN_3O_3 systems possessing facial and meridional isomers.³ The electronic absorption spectra of the investigated complexes show big differences in the shape of the band of the lower energy spin-allowed transition (Fig. 2). The violet isomers (I column bands) clearly show band splitting and were assigned meridional geometry; the red isomers (II column bands) exhibit a symmetrical band and were assigned facial geometry.

The maxima of the first absorption band of the *fac* (red) and *mer* (violet) isomers are located at shorter wavelengths than the starting carbonato complex, suggesting that the coordinated amino acids have a stronger ligand field (Table I). Also, the positions of the absorption bands suggest that the eddp tetradentate ligand has the same *uns-cis*-configuration as the starting $[\text{Co}(\text{eddp})\text{CO}_3]^-$ complex.

TABLE I. The absorption band maxima in the visible spectra of some [Co(edda)L] and [Co(eddp)L] complexes*

Complex	I		II		Ref.
	λ_1	ϵ_1	λ_2	ϵ_2	
<i>s-cis</i> -[Co(edda)CO ₃] ⁻	565	114	382	128	16
<i>uns-cis</i> -[Co(edda)CO ₃] ⁻	533	234	390	182	16
<i>uns-cis</i> -[Co(eddp)CO ₃] ⁻	544	232	383	165	11
<i>uns-cis</i> -[Co(eddp)(ox)] ⁻	530	195	384	170	11
<i>fac-uns-cis</i> -[Co(eddp)(Gly)]	529	285	381	126	3a
<i>mer-uns-cis</i> -[Co(eddp)(Gly)]	564	97	381	123	3a
	491	133			
<i>fac-uns-cis</i> -[Co(edda)(Gly)]	520	223	374	–	15
<i>fac-uns-cis</i> -[Co(eddp)(S-Ala)]	528	338	376	170	3b
<i>mer-uns-cis</i> -[Co(eddp)(S-Ala)]	565	117	375	156	3b
	497	166			
<i>fac-uns-cis</i> -[Co(eddp)(S-Val)]	529	185	377	110	3b
<i>mer-uns-cis</i> -[Co(eddp)(S-Val)]	565	117	376	150	3b
	497	157			
<i>fac-uns-cis</i> -[Co(eddp)(S-Leu)]	529	257	377	150	3b
<i>mer-uns-cis</i> -[Co(eddp)(S-Leu)]	566	104	375	150	3b
	498	150			
<i>fac-uns-cis</i> -[Co(eddp)(S-Ile)]	529	308	377	167	3b
<i>mer-uns-cis</i> -[Co(eddp)(S-Ile)]	566	100	376	145	3b
	499	150			
<i>fac-uns-cis</i> -[Co(eddp)(S-Ser)]	527	285	378	138	3c
<i>mer-uns-cis</i> -[Co(eddp)(S-Ser)]	576	108	378	147	3c
	496	153			
<i>fac-uns-cis</i> -[Co(eddp)(S-Cys)]	496	148			3c
<i>mer-uns-cis</i> -[Co(eddp)(S-Cys)]	522	262	370	211	3c
	540	191	378(sh)	260	
<i>fac-uns-cis</i> -[Co(eddp)(S-Lys)]	520	179	375	150	this work
<i>mer-uns-cis</i> -[Co(eddp)(S-Lys)]	570	68	375	97	this work
	495	103			
<i>fac-uns-cis</i> -[Co(eddp)(S-His)]	512	51	365	148	this work
<i>mer-uns-cis</i> -[Co(eddp)(S-His)]	570	53	380	140	this work
	500	119			

* Wavelength (λ) in nm. Extinction coefficient (ϵ) in mol⁻¹ dm³ cm⁻¹ L⁻ represents one bidentate ligand; (sh)=shoulder

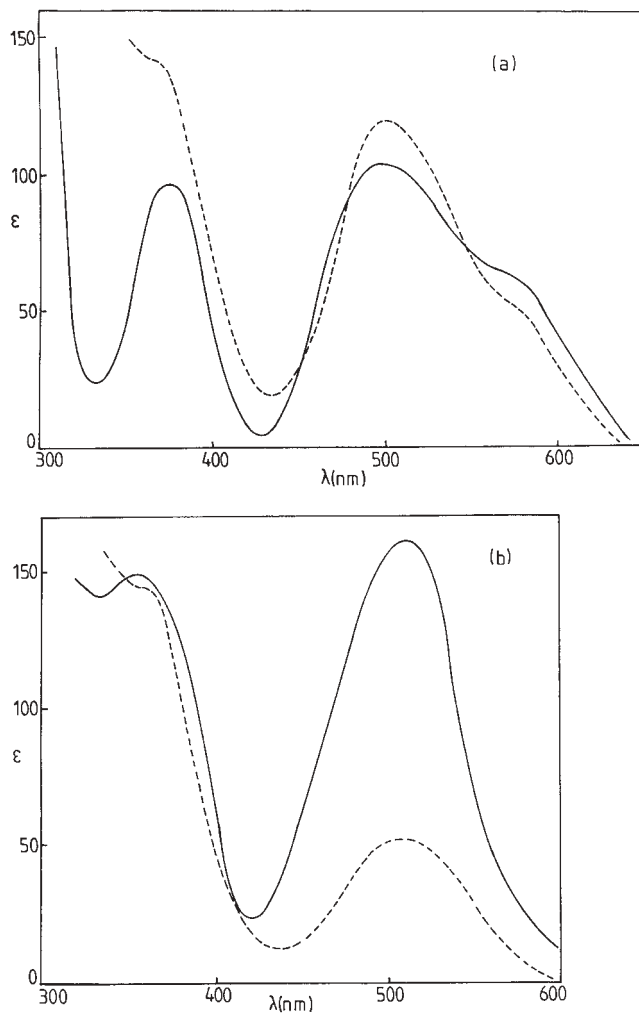


Fig. 2. Electronic absorption spectra of (a) meridional and (b) facial isomers of [Co(eddp)(S-Lys)] (—) and [Co(eddp)(S-His)] (----).

In a previous paper¹ it was reported that complexes with coordinated *s-cis*-*edda*-type tetradentates have the maximum of the first absorption band at a longer wavelength than the corresponding *uns-cis* isomer. Also, it was noted that Co(III) complexes with five-membered carboxylate chelate rings have the first absorption band located at shorter wavelengths than the corresponding complexes with a six-membered chelate ring.^{11,13} Our results confirm these facts (Fig. 2, Table I).

Infrared spectra

The infrared spectra were used to confirm the structure of the isolated complexes. The important IR data for the presently investigated *uns-cis*-[Co(eddp)(S-am)] complexes are given in Table II.

TABLE II. The most important IR bands (cm^{-1}) of the investigated complexes*

Complex	ν_{as} (COO^-)	ν_{s} (COO^-)
<i>fac-uns-cis</i> -[Co(eddp)(<i>S</i> -Lys)]	1597	1395
<i>mer-uns-cis</i> -[Co(eddp)(<i>S</i> -Lys)]	1610(<i>sh</i>) 1595	1393
<i>fac-uns-cis</i> -[Co(eddp)(<i>S</i> -His)]	1641	1397
<i>mer-uns-cis</i> -[Co(eddp)(<i>S</i> -His)]	1636(<i>sh</i>) 1582	1400

*(sh)=shoulder

All of the complexes show a strong, fairly broad absorption around 1650 cm^{-1} , the CO-stretching region. The lack of absorption between $1700\text{--}1750 \text{ cm}^{-1}$ indicates that the carboxyl groups of eddp are coordinated to the central cobalt(III) ion and are not present as free-acid.¹⁴ A distinctive difference between the absorption of facial and meridional isomers is observed in this region; the facial isomer has only one peak whereas the meridional isomer has two split absorption peaks.

Also, it was demonstrated that the asymmetric stretching bands of the carboxylate groups of five-membered chelate rings lie at higher energy than the corresponding bands of six-membered chelate rings.^{1,13} The shapes of the IR spectra of the *fac* and *mer* isomers of the investigated *uns-cis*-[Co(eddp)(*S*-am)] complexes in the carboxylate region are consistent with their assigned geometry. The asymmetric stretching bands of the coordinated carboxylate groups of the meridional (violet) and facial (red) isomers lie in the expected region (*i.e.*, $1700\text{--}1750 \text{ cm}^{-1}$ for free carboxylate groups and $1600\text{--}1650 \text{ cm}^{-1}$ for coordinated carboxylate groups)¹⁴ (Table II). The corresponding symmetrical stretching bands also lie in the expected region (about 1400 cm^{-1}). The stretching bands of the amino groups are also summarized in Table II.

These facts support the conclusion that the investigated red complexes have the facial geometry whereas the violet complexes have meridional geometry.

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ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА ФАЦИЈАЛНИХ И МЕРИДИОНАЛНИХ ИЗОМЕРА
UNS-CIS-(ЕТИЛЕНДИАМИН-*N-N'*-ДИ-3-ПРОПИОНАТО)КОБАЛТ(III) КОМПЛЕКСА СА
S-ЛИЗИНОМ И *S*-ХИСТИДИНОМ

ДАНИЈЕЛА Д. СТАМЕНОВИЋ И СРЕЋКО Р. ТРИФУНОВИЋ

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У реакцији натријум *uns-cis*-(етилендиамин-*N-N'*-ди-3-пропионато)-(карбонато)кобалт(III)-дихидрата и одговарајуће аминокиселине (*S*-лизина и *S*-хистидина) на 70 °C, награвена су оба теоријски очекивана (фацијални и меридионални) изомера *uns-cis*-(етилендиамин-*N-N'*-ди-3-пропионато)(аминоацидато) кобалт(III) комплекса. Комплекси су изоловани хроматографски и карактерисани на бази резултата елементарне микроанализе, као и применом електронске апсорпционе и инфрацрвене спектроскопије.

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