

## Preparation and characterization of facial and meridional isomers of *uns-cis* (ethylenediamine-*N,N'*-di-3-propionato)(*S*-arginine)cobalt(III) chloride dihydrate

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Both theoretically possible geometrical isomers, facial and meridional, of *uns-cis*-(ethylenediamine-*N,N'*-di-3-propionato)(*S*-arginine)cobalt(III) chloride dihydrate were prepared by the reaction of sodium *uns-cis*-(ethylenediamine-*N,N'*-di-3-propionato)(carbonato)cobaltate(III) with *S*-arginine at 75 °C. The complexes were isolated chromatographically and characterized by elemental analysis as well as electron absorption and infrared spectroscopy.

*Keywords:* cobalt(III) complexes, ethylenediamine-*N,N'*-di-3-propionic acid, arginine.

### INTRODUCTION

Eddp is a tetradentate ligand (eddp = ethylenediamine-*N,N'*-di-3-propionate ion) similar to edda ligand (edda = ethylenediamine-*N,N'*-diacetate ion). Metal(III)-complexes with edda-type ligands have been widely investigated.<sup>1–14</sup>

In the case of (edda-type)-M(III)-complexes with symmetrical bidentate ligands (such as oxalate or ethylenediamine), two geometrical isomers *s-cis* and *uns-cis* (Fig. 1a) are to be expected.

However, for (edda-type)-M(III) complexes with unsymmetrical bidentate ligands (such as glycine), three geometrical isomers are theoretically possible, *s-cis*, *fac-uns-cis* and *mer-uns-cis* (Fig. 1b).

Investigations of edda-M(III)-complexes have shown that *s-cis* geometry of edda ligand is favored in most synthetic routes.<sup>1–14</sup> It has been suggested that the observed chelate strain of the carboxylate rings in *uns-cis*-edda complexes may be a contributing factor in determining the configuration of the edda ligand.<sup>13</sup> However, the eddp ligand, having longer carboxylate arms than edda, favored *uns-cis* geometry.<sup>1</sup> Amino acids, as

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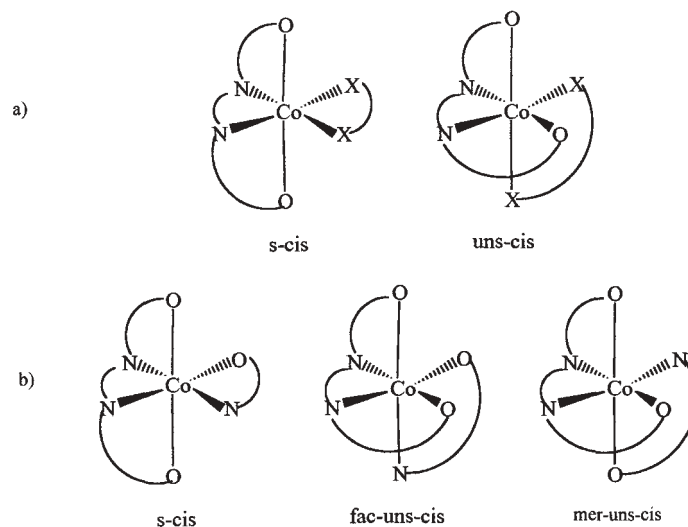


Fig. 1. Possible geometrical isomers of [Co(eddp)L] complexes: (a) *s-cis*(I), *uns-cis*(II), L-symmetrical bidentate ligands; (b) *s-cis*(I), *fac-uns-cis*(II) and *mer-uns-cis*(III), L-unsymmetrical bidentate ligands.

unsymmetrical bidentate ligands, have been used for the preparation of some edda-Co(III)-complexes,<sup>13,15,17</sup> but mixed Co(III) complexes with eddp and *S*-arginine have not been prepared.

In this paper, the facial and meridional isomers of *uns-cis*-(ethylenediamine-*N,N'*-di-3-propionato)(*S*-arginine)cobalt(III) chloride dihydrate are reported. The geometrical configurations of the isolated complexes were determined on the basis of electronic absorption and infrared spectroscopy.

## EXPERIMENTAL

### Materials

Sodium *uns-cis*-(ethylenediamine-*N,N'*-di-3-propionato)(carbonato)cobaltate(III) was prepared using a previously described procedure.<sup>1</sup> Other reagents were obtained commercially and used without further purification.

### Preparation of facial and meridional isomers of *uns-cis*-(ethylenediamine-*N,N'*-di-3-propionato)(*S*-arginine)cobalt(III) chloride dihydrate [Co(eddp)(*S*-argH)Cl·2H<sub>2</sub>O]

To the solution of 1.00 g (2.6 mmol) of *uns-cis*-Na[Co(eddp)CO<sub>3</sub>]·2H<sub>2</sub>O in 20.0 cm<sup>3</sup> water, 0.550 g (2.6 mmol) of *S*-arginine hydrochloride in 10.0 cm<sup>3</sup> water, previously neutralized with 0.146 g (2.6 mmol) KOH, was added and the pH of the solution was adjusted to 8. After heating under stirring for 2 hours at 75 °C, the solution was evaporated to 10.0 cm<sup>3</sup> and introduced onto a 2.5×32 cm column containing Sephadex G-10. The red-violet eluate was then loaded onto a 2×10 cm column containing SP-Sephadex C-25. The column was washed with water to remove the non-adsorbed starting complex and then eluted with 0.2 molar KCl. The adsorbed complex separated into two bands: violet (first) and red (second). The eluates containing the violet and red band were concentrated under reduced pressure. Then methanol was added in order to remove KCl. The chloride salts of the meridional and facial [Co(eddp)(*S*-argH)]<sup>+</sup> complexes were obtained from the desalted violet and red solu-

tions, respectively. Yield: 0.41 g of the violet (meridional) and 0.16 g of red (facial) isomer. Anal. Calcd. for meridional *uns-cis*-[Co(eddp)(*S*-argH)Cl·2H<sub>2</sub>O]: C, 33.18; H, 6.32; N, 16.59. Found: C, 33.03; H, 6.16; N, 17.02. Found for facial: C, 32.89; H, 5.86; N, 16.20.

#### Characterization

Elemental analyses (C, H, N) were performed by standard micromethods at the Department of Instrumental Analysis of the Faculty of Chemistry, Belgrade. 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. For these measurements  $1 \times 10^{-3}$  mol/dm<sup>3</sup> aqueous solutions of the complexes were used. The molar conductivity of an aqueous solutions ( $1 \times 10^{-2}$  mol/dm<sup>3</sup>) was measured at 20 °C with a Jenway-4009 conductivity meter.

### RESULTS AND DISCUSSION

Three geometrical isomers of eddp-Co(III)-complexes, with an ansymmetrical bidentate ligand are theoretically possible, *s-cis*, *fac-uns-cis* and *mer-uns-cis* (Fig. 1b). Since the *uns-cis*-[Co(eddp)CO<sub>3</sub>]- complex<sup>1</sup> was used as the starting material, substitution of the CO<sub>3</sub><sup>2-</sup> ligand with arginine should theoretically give only the *fac-uns-cis* and *mer-uns-cis* geometric isomers of [Co(eddp)(*S*-argH)]<sup>+</sup> (Fig. 1b). Obviously, both isomers have the same molecular symmetry (C<sub>1</sub>) but the facial isomer has the higher symmetry ligand field than the meridional isomer. Their molecular symmetry can be compared with that of the [Co(am)<sub>3</sub>] complex (am = ion of amino-acid) neglecting the backbone diamine ring. In this work, both meridional isomers of the *uns-cis*-[Co(eddp)(*S*-argH)]Cl·2H<sub>2</sub>O complex have been prepared.

The molar conductivity values obtained for a  $1 \times 10^{-2}$  mol/dm<sup>3</sup> solution of the complexes in water [ $\lambda_m(\text{mer}) = 115 \text{ S cm}^2 \text{ mol}^{-1}$ ;  $\lambda_m(\text{fac}) = 99 \text{ S cm}^2 \text{ mol}^{-1}$ ] fall within the range anticipated for a 1:1 electrolyte [ $\lambda_m(\text{NaCl}) = 91 \text{ S cm}^2 \text{ mol}^{-1}$ ].

#### Electronic absorption spectra

The electronic absorption spectra of the *fac* and *mer* isomers of the *uns-cis*-[Co(eddp)(*S*-argH)]<sup>+</sup> complex are shown in Fig. 2 and the absorption data are summarized in Table I.

The two spin-allowed transitions in a low-spin d<sup>6</sup> system in an octahedral crystal field are <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub> and <sup>1</sup>A<sub>1g</sub> → T<sub>2g</sub> in order of increasing energy. In a tetragonal field, the degeneracies of the excited states are removed, *i.e.*, <sup>1</sup>T<sub>1g</sub> = <sup>1</sup>A<sub>2g</sub> + <sup>1</sup>E<sub>g</sub><sup>a</sup> and <sup>1</sup>T<sub>2g</sub> = <sup>1</sup>B<sub>2g</sub> + <sup>1</sup>E<sub>g</sub><sup>b</sup>. On further decreasing the molecular symmetry, further splitting is expected. As has been shown, small differences between states do not cause splitting of the absorption bands, especially of complexes with edta-type ligands and derivatives with symmetry lower than D<sub>4h</sub>.<sup>18</sup> The more symmetrical facial isomer has a subic crystal field while the meridional isomer has a rhombic crystal field. This loss of symmetry in going from facial to meridional is expected to cause a split or at least a broadening of the lowest energy absorption band.<sup>18</sup> This has been observed previously in other CoN<sub>3</sub>O<sub>3</sub> systems possessing facial and meridional isomers.<sup>19</sup> A definite shoulder was found for the low-energy absorption band of meridional *s-cis*-[Co(edda)(*S*-ala)].<sup>4</sup> The electronic absorption spectra of the investigated complexes show large differences in the shape of the lower energy spin-allowed band (Fig. 2). The violet isomer reveals a distinct inflection in the first absorption band, while the red isomer has a symmetrical

first absorption band without splitting. These facts lead to the conclusion that the red isomer has facial geometry while the violet isomer has a lower crystal field symmetry and meridional geometry.

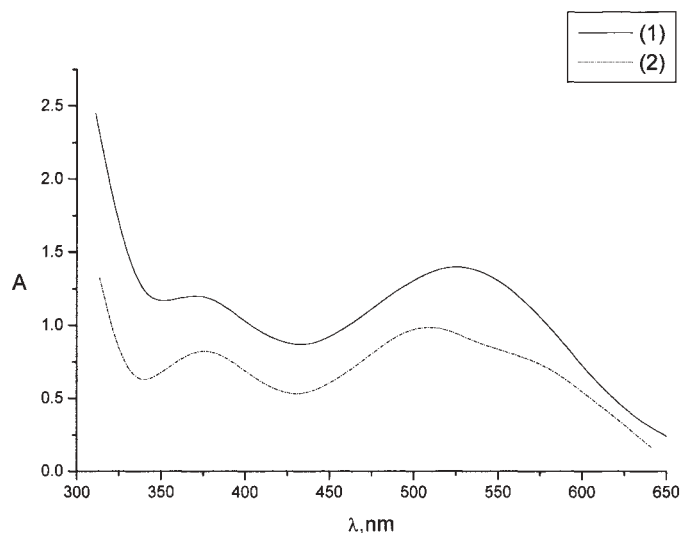


Fig. 2. Electronic absorption spectra of the *uns-cis*-[Co(eddp)(*S*-argH)]Cl complexes: (1) facial, (2) meridional isomers.

TABLE I. Band maxima of the electronic absorption spectra of some (edda-type)-Co(III)-type complexes

Complex	I		II		Ref.
	$\lambda_1$	$\epsilon_1$	$\lambda_2$	$\epsilon_2$	
<i>s-cis</i> -[Co(edda)CO <sub>3</sub> ]-	565	114	382	128	14
<i>uns-cis</i> -[Co(edda)CO <sub>3</sub> ]-	533	234	390	182	14
<i>uns-cis</i> -[Co(eddp)CO <sub>3</sub> ]-	544	232	383	165	1
<i>fac-uns-cis</i> -[Co(eddp)gly]	529	285	381	126	7
<i>mer-uns-cis</i> -[Co(eddp)gly]	564	97	381	123	7
	491	133			
<i>fac-uns-cis</i> -[Co(edda)gly]	520	223	374	—	27
<i>mer-uns-cis</i> -[Co(eddp)( <i>S</i> -argH)]Cl	494	—	375	—	this work
	559	—			
<i>fac-uns-cis</i> -[Co(eddp)( <i>S</i> -argH)]Cl	527	—	376	—	this work

\*Wavelength ( $\lambda$ ) in nm. Extinction coefficient ( $\epsilon$ ) in mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>  
L - one bidentate or two monodentate ligands

In previously reported papers,<sup>1-14</sup> it was shown that complexes with *s-cis* configuration of coordinated edda-type tetradentates have the maxima of the first absorption band located at longer wavelengths than the corresponding *uns-cis* isomers. Also, it was noted that Co(III) complexes with five-membered carboxylate chelate rings have the

first absorption bands located at lower wavelengths than the corresponding complexes with six-membered chelate rings.<sup>1,20</sup>

The maximum of the first absorption band of the *fac* (red) and *mer* (violet) isomers are located at lower wavelengths than the strating carbonato complex, suggesting that the coordinated *S*-arginine has a stronger ligand field (Tabel I). On the other hand, the position of the absorption bands suggests that eddp tetradentate ligand has the same *uns-cis*-configuration as in the starting  $[\text{Co}(\text{eddp})\text{CO}_3]^-$  complex.

### *Infrared spectra*

Asymmetric stretching frequencies of the carboxylate groups are used as a criteria to establish whether carboxylate groups are coordinated ( $1600\text{--}1650\text{ cm}^{-1}$ ).<sup>21</sup> 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.<sup>20,22–26</sup> The asymmetric stretching bands of the coordinated carboxylate groups of the meridional (violet) and facial (red) isomers of the *uns-cis*- $[\text{Co}(\text{eddp})(\text{S-argH})\text{Cl}\cdot 2\text{H}_2\text{O}]$  complex lie in the expected region ( $1642\text{ cm}^{-1}$  and  $1620\text{ cm}^{-1}$ , respectively, Table II). The corresponding symmetrical bands lie at  $1394\text{ cm}^{-1}$  for both the *mer*- and the *fac*-isomer. Also, in the region of the stretching bands of amino groups, the isolated complexes show bands at  $3254$ ,  $3239$  and  $2933\text{ cm}^{-1}$  for the *mer* (violet) isomer, and at  $3250$  and  $2932\text{ cm}^{-1}$  for the *fac* (red) isomer.

These results also suggest that the investigated red complex has a higher ligand field symmetry and facial geometry.

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### ИЗВОД

#### СИНТЕЗА И КАРАКТЕРИЗАЦИЈА ФАЦИЈАЛНОГ И МЕРИДИЈАЛНОГ ИЗОМЕРА *uns-cis*-(ЕТИЛЕНДИАМИН-*N,N'*-ДИ-3-ПРОПИОНАТО)(*S*-АРГИНИН)КОБАЛТ(III)-ХЛОРИДА ДИХИДРАТА

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Оба теоријски могућа геометрјиска изомера, фацијални и меридијални, *uns-cis*-(етилендиамин-*N,N'*-ди-3-пропионато)(*S*-аргинин)-кобалт(III)-хлорида дихидрата су добијена реакцијом натријум-*uns-cis*-(етилендиамин-*N,N'*-ди-3-пропионато)карбонатокобалтата(III) са *S*-аргинином на температури  $75\text{ }^\circ\text{C}$ . Комплекси су изоловани хроматографски и окарактерисани елементарном анализом, електронском апсорпционом и инфрацрвеном спектроскопијом.

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