

NOTE

Synthesis and characterization of *meridional* isomer of *uns-cis*-(ethylenediamine-*N-N'*-di-3-propionato)- (*S*-norleucinato)cobalt(III) semihydrate

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The *meridional* geometrical isomer of *uns-cis*-(ethylenediamine-*N-N'*-di-3-propionato)(*S*-norleucinato)cobalt(III) complex has been prepared by the reaction of sodium *uns-cis*-(ethylenediamine-*N-N'*-di-3-propionato)(carbonato)cobaltate(III) with *S*-norleucine at 75 °C. The complex was isolated chromatographically and characterized by elemental analyses, electron absorption and infrared spectroscopy.

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

Geometrical isomerism in metal complexes of linear flexible tetradentate ligands having the donor atom array ONNO such as edda (ethylenediamine-*N-N'*-diacetate) or eddp (ethylenediamine-*N-N'*-di-3-propionate), is an interesting field that has been studied by a number of workers.¹⁻⁸

For (edda-tupe)-M(III) complexes with unsymmetrical bidentate ligands (as amino acids) three geometric isomers can be expected: *s-cis*, *fac-uns-cis* and *mer-uns-cis* (Fig. 1).

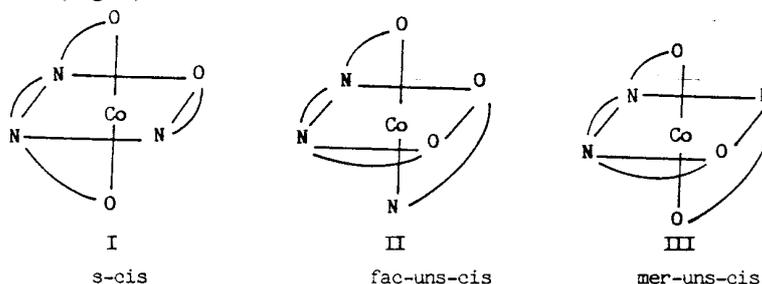


Fig. 1. Possible geometrical isomers of [Co(eddp)L] complexes: *s-cis*(I), *fac-uns-cis*(II) and *mer-uns-cis*(III), L-unsymmetrical bidentate ligands.

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Although for the eddp-Co(III) complexes the *uns-cis* geometry of the eddp ligand is favored in the most synthetic routes,²⁻⁶ the *s-cis* isomer has also been obtained.^{7,8}

Some amino acids, as unsymmetrical bidentate ligands, have already been used for the preparation of some edda-Co(III) complexes^{9,10} and eddp-Co(III) complexes.³⁻⁶

In this paper, the *meridional* isomer of *uns-cis*-(ethylenediamine-*N-N'*-di-3-propionato)cobalt(III) complexes with *S*-norleucine is reported. The geometric configuration of the isolated complex was determined on the basis of electronic absorption and infrared spectroscopy.

EXPERIMENTAL

Sodium *uns-cis*-(ethylenediamine-*N-N'*-di-3-propionato)(carbonato)cobaltate(III) was prepared using a previously described procedure.² Other reagents were obtained commercially and used without further purification.

The infrared spectrum was recorded on a Perkin-Elmer FTIR 31725-X Spectrophotometer using the KBr pellets technique. The electronic absorption spectrum was recorded on a Varian GBC UV/VIS 911A Spectrophotometer, using a 1×10^{-3} mol/dm³ aqueous solution of complex.

Elemental microanalysis for C, H, N was performed by standard micromethods.

*Preparation of the meridional isomer of uns-cis-(ethylenediamine-*N-N'*-di-3-propionato)(*S*-norleucinato)cobalt(III) semihydrate, [Co(eddp)(*S*-nle)]·0.5H₂O*

To a solution of 0.285 g (0.75 mmol) of *uns-cis*-Na[Co(eddp)CO₃]·2H₂O in 10.0 cm³ of water, 0.098 g (0.75 mmol) of *S*-norleucine in 10.0 cm³ of water, previously neutralized by 0.072 g (0.75 mmol) KOH, was added and the pH of the solution was adjusted to 8. After stirring and heating during 2 hours at 75 °C, the solution was evaporated to 5.0 cm³ 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 Dowex 1-X4 (200–400 mesh) anion-exchange resin in the Cl⁻ form. In both cases water was used as the eluent.

Two bands appeared on the column: violet (very intensive) and red (very weak). The eluate containing the violet band was evaporated to a small volume and left in a refrigerator over night.* The crystals were filtered off, washed with ethanol, ether and air-dried. Yield: 0.15 (50.9 %). Anal. Calcd. for *uns-cis*-[Co(eddp)(*S*-nle)]·0.5H₂O = C₁₄H₂₇CoN₃O_{6.5} (*Mr* = 400.36) (%): C, 42.00; H, 6.74; N, 10.49. Found (%): C, 41.77; H, 6.94; N, 10.60.

Infrared data (cm⁻¹): 3240 (*s*), 3133 (*s*), 2957 (*m*), 1602 (*s*), 1397 (*s*) (*s*=strong, *m*=medium).

RESULTS AND DISCUSSION

Three geometric isomers of eddp-Co(III)-complex with unsymmetrical bidentate ligand are theoretically possible: *s-cis*, *fac-uns-cis* and *mer-uns-cis* (Fig. 1). Since the *uns-cis*-[Co(eddp)CO₃]⁻ complex was used, as the starting material, theoretically only two geometrical isomers, the *fac-uns-cis* and *mer-uns-cis* isomers of the [Co(eddp)(*S*-nle)] complex can be expected by substitution CO₃²⁻ ligand with *S*-norleucine.

* The eluate containing red band was evaporated, but the obtained amount of complex could not be quantified

In this work only the *meridional* isomers of *uns-cis*-(ethylenediamine-*N-N'*-di-3-propionato)(*S*-norleucinato)cobalt(III) semihydrate was prepared in preparative yield.

Electronic absorption spectra

The electronic absorption spectrum of the isolated *meridional* isomer of the *uns-cis*-[Co(eddp)(*S*-nle)] complex is shown in Fig. 2. The position of the absorption maxima are tabulated in Table I.

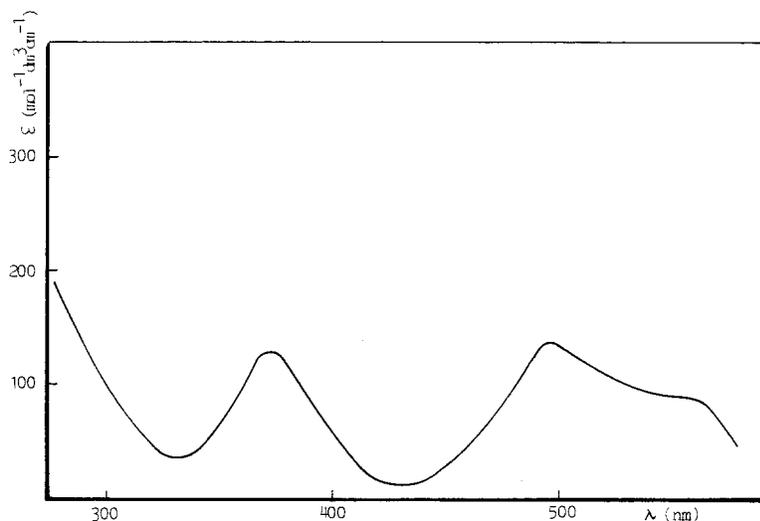


Fig. 2. Electronic absorption spectrum of *meridional* isomer of the *uns-cis*-[Co(eddp)(*S*-nle)] complex.

The characteristic difference between the pairs of *fac-mer* isomers appears in the region of the first absorption band.^{3-6,10} The more symmetrical *facial* isomer has a cubic crystal field while the *meridional* isomer has a rhombic crystal field. This loss of symmetry from *facial* to *meridional* is expected to cause a split or at least a broadening of the lowest energy absorption band. This has been previously observed in other CoN₃O₃ systems possessing *facial* and *meridional* isomers.

The position (Table I) and the shape of the absorption spectrum (Fig. 2) confirm that the configuration of the isolated violet isomer is *meridional* which is consistent with the assignment given by other authors. The inflection in the spectrum of the violet isomer can be attributed to the splitting of the ¹T_{1g} state as result of the rhombic crystal field in the *meridional* isomer. The maximum of the first absorption band of the isolated isomer is located at the lower wavelengths than corresponding starting carbonato-complex suggesting a stronger ligand field of the coordinated *S*-norleucine.

In previous papers, it was reported that complexes with *s-cis* configuration of the coordinated edda-type tetradentates have the maximum of the first absorption

band at a longer wavelength than the corresponding *uns-cis* isomers. The position of this absorption band, also, suggests that the eddp tetradentate ligand has the same *uns-cis*-configuration as in the starting $[\text{Co}(\text{eddp})\text{CO}_3]^-$ complex.

TABLE I. The band maxima of the electronic absorption spectra of some $[\text{Co}(\text{edda})\text{L}]$ and $[\text{Co}(\text{eddp})\text{L}]$ complexes

Complex	I		II		Ref.
	λ_1	ϵ_1	λ_2	ϵ_2	
<i>s-cis</i> - $[\text{Co}(\text{edda})\text{CO}_3]^-$	565	114	382	128	12
<i>uns-cis</i> - $[\text{Co}(\text{edda})\text{CO}_3]^-$	533	234	390	182	12
<i>uns-cis</i> - $[\text{Co}(\text{eddp})\text{CO}_3]^-$	544	232	383	165	2
<i>fac-uns-cis</i> - $[\text{Co}(\text{edda})\text{gly}]$	520	223	374	167	10
<i>mer-uns-cis</i> - $[\text{Co}(\text{edda})\text{gly}]$	525	94	370	128	10
<i>fac-uns-cis</i> - $[\text{Co}(\text{eddp})\text{gly}]$	529	285	381	126	4
<i>mer-uns-cis</i> - $[\text{Co}(\text{eddp})\text{gly}]$	564	97	381	123	4
	491	133			
<i>fac-uns-cis</i> - $[\text{Co}(\text{eddp})\text{S-ala}]$	528	338	376	170	6
<i>mer-uns-cis</i> - $[\text{Co}(\text{eddp})\text{S-ala}]$	565	117	375	156	6
	497	166			
<i>mer-uns-cis</i> - $[\text{Co}(\text{eddp})\text{S-nle}]$	566	112	376	138	this work
	496	143			

Infrared spectra

The asymmetric stretching frequencies of the carboxylate groups were established as criteria for distinguishing between protonated carboxylate groups ($1700\text{--}1750\text{ cm}^{-1}$) and coordinated carboxylate groups ($1600\text{--}1650\text{ cm}^{-1}$).¹¹ The observed frequencies in this region verify that they are all coordinated (1602 cm^{-1}). The complicated shape of IR spectrum in the carboxylate region of the isolated complex is consistent with its molecular symmetry. The symmetric stretching vibration is found at 1397 cm^{-1} .

Also, in the region of the stretching bands of amino groups, the isolated complex shows bands at 3240 , 3143 and 2957 cm^{-1} .

These facts, also, support the conclusion that the investigated violet $[\text{Co}(\text{eddp})(\text{S-nle})]$ complex has *meridional* geometry.

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ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА МЕРИДИЈАЛНОГ ИЗОМЕРА
uns-cis-(ЕТИЛЕНДИАМИН-*N-N'*-ДИ-ПРОПИОНАТО)(*S*-НОРЛЕУЦИНАТО)КОБАЛТ(III)
ХЕМИХИДРАТАТИБОР Ј. САБО¹ и СРЕЂКО Р. ТРИФУНОВИЋ²¹Хемијски факултет, Универзитет у Београду, б. бр. 158, 11001 Београд, и ²Природно-математички факултет, Одсек за хемију, Универзитет у Крагујевцу, б. бр. 60, 34000 Крагујевац

Синтетисан је и окарактерисан *меридијални* изомер *uns-cis*-(етилендиамин-*N-N'*-ди-3-пропионато)(*S*-норлеуцинато)кобалт(III) хемихидрат. Комплекс је добивен реакцијом на тријум-*uns-cis*-(етилендиамин-*N-N'*-ди-3-пропионато)кобалтата(III) дихидрата и *S*-норлеуцина на 75 °С. Комплекс је изолован хроматографски и окарактерисан елементалном анализом, електронско-апсорпционом и инфрацрвеном спектроскопијом.

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