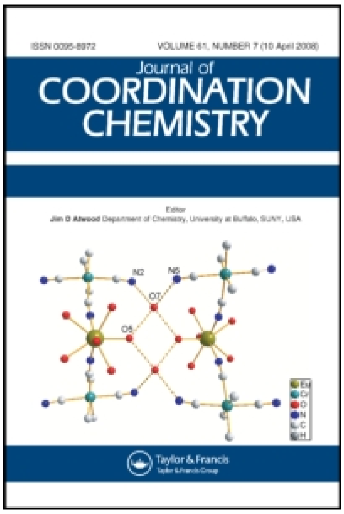

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

PREPARATION AND CHARACTERIZATION OF FACIAL AND MERIDIONAL ISOMERS OF UNS-CIS-(ETHYLENEDIAMINE-*N,N'*-DI-3-PROPIONATO)(GLYCINATO)COBALT(III) SEMIHYDRATE

Tibor J. Sabo[a]; Sanja R. Grgurić[b]; Dragica M. Minić[b]; Srećko R. Trifunović[c]
[a] Faculty of Chemistry, University of Belgrade, Belgrade, Yugoslavia [b] Faculty of Physical Chemistry, University of Belgrade, Belgrade, Yugoslavia [c] Faculty of Sciences, Department of Chemistry, University of Kragujevac, Kragujevac, Yugoslavia

To cite this Article Sabo, Tibor J. , Grgurić, Sanja R. , Minić, Dragica M. and Trifunović, Srećko R.(1998) 'PREPARATION AND CHARACTERIZATION OF FACIAL AND MERIDIONAL ISOMERS OF UNS-CIS-(ETHYLENEDIAMINE-*N,N'*-DI-3-PROPIONATO)(GLYCINATO)COBALT(III) SEMIHYDRATE', Journal of Coordination Chemistry, 44: 1, 47 — 54
To link to this Article: DOI: 10.1080/00958979808022878
URL: http://dx.doi.org/10.1080/00958979808022878

J. Coord. Chem., 1998, Vol. 44, pp. 47–54
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PREPARATION AND CHARACTERIZATION OF FACIAL AND MERIDIONAL ISOMERS OF *UNS-CIS*-(ETHYLENEDIAMINE-*N,N'*-DI-3-PROPIONATO)(GLYCINATO)COBALT(III) SEMIHYDRATE

TIBOR J. SABO[a]* SANJA R. GRGURIĆ DRAGICA M. MINIĆ[c] and
SREĆKO R. TRIFUNOVIĆ[b]

[a]*Faculty of Chemistry, University of Belgrade, P.O. Box 158, 11001 Belgrade, Yugoslavia;* [b]*Faculty of Sciences, Department of Chemistry, University of Kragujevac, P.O. Box 60, 34000 Kragujevac, Yugoslavia;* [c]*Faculty of Physical Chemistry, University of Belgrade, 11001 Belgrade, Yugoslavia*

(Received 7 May 1997)

Both theoretically possible geometrical isomers, *facial* and *meridional*, of *uns-cis*-(ethylenediamine-*N,N'*-di-3-propionato)(glycinato)cobalt(III) semi hydrate have been prepared by reaction of sodium *uns-cis*-(ethylenediamine-*N,N'*-di-3-propionato) (carbonato) cobaltate(III) with glycine at 75°C. The complexes have been isolated chromatographically and characterized by elemental analysis, electron absorption, infrared and nuclear magnetic spectra.

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

INTRODUCTION

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

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

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[*] Author for correspondence.

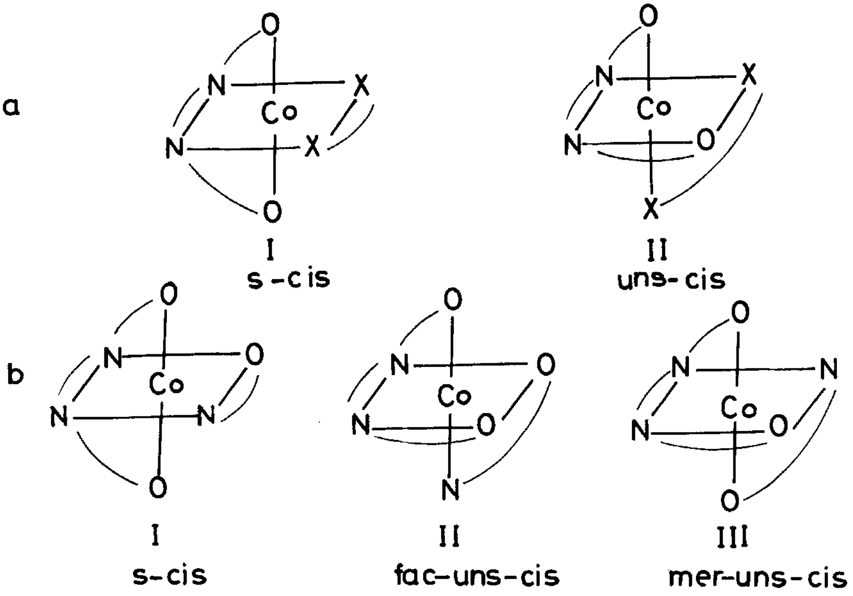

FIGURE 1 Possible geometrical isomers of [Co(eddp)L] complexes: (a) s-*cis* (I), *uns-cis* (II), L is a symmetrical bidentate ligand; (b) s-*cis* (I), *fac-uns-cis* (II) and *mer-uns-cis* (III), L is an unsymmetrical bidentate ligand.

complexes with unsymmetrical bidentate ligands (such as glycine) three geometrical isomers are theoretically possible, *s-cis, fac-uns-cis* and *mer-uns-cis* (Figure 1b). If optical isomers and different modes of coordination of the secondary nitrogen atoms of eddp ligand are also considered, further isomerism can be described[14].

Investigations of the edda-M(III) complexes showed that the *s-cis* geometry of edda ligand is favoured in most synthetic routes[1-14]. It has been suggested that the observed chelate strain of carboxylate rings in *uns-cis*-edda complexes may be a contributing factor in determining the configuration of the edda ligand[13]. However, eddp, with longer carboxylate arms than edda, favoured *uns-cis* geometry[1]. Amino acids, as unsymmetrical bidentate ligands, have been used for the preparation of some edda-Co(III) complexes[13,15,17], but mixed Co(III) complexes with eddp and α-amino acids have not been prepared.

In this paper, the *facial* and *meridional* isomers of *uns-cis*-(ethylenediamine-*N,N'*-di-3-propionato)(glycinato)cobalt(III) are reported. The geometrical configurations of the isolated complexes were determined on the basis of electronic absorption, infrared and ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy.

EXPERIMENTAL

Materials

Sodium *uns-cis*-(ethylenediamine-*N,N'*-di-3-propionato)(carbonato) cobaltate(III) was prepared using a previously described procedure[1]. 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)(glycinato)cobalt(III)semihydrate, $[Co(eddp)(gly)]\cdot 0.5H_2O$

To a solution of 1.00 g (2.6 mmol) of *uns-cis*-$Na[Co(eddp)CO_3]$ dihydrate in 20.0 cm^3 of water, 0.399 g (5.2 mmol) of glycine in 10 cm^3 of water, previously neutralized by 0.291 g (5.2 mmol) of 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 10.0 cm^3 and introduced onto a 2.5 × 32 cm column containing Sephadex G-10. The red-violet eluate was then poured 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 eluant.

Two bands appeared on the column, violet (first) and red (second). Both eluates were evaporated to small volume and left in a refrigerator over night. The resulting crystals were filtered off, washed with ethanol, then ether and air-dried. Yield: 0.62 g of violet (*meridional*) (79.9%) and 0.06 g of red (*facial*) (6.7%) isomer. *Anal.* Calcd. for *mer-uns-cis*-$[Co(eddp)(gly)]\cdot 0.5H_2O$ (%): C, 34.88; H, 5.52; N, 12.20. Found: C, 35.00; H, 5.84; N, 12.14. Calcd for *fac-uns-cis*-$[Co(eddp)(gly)]\cdot 0.5H_2O$: C, 34.88; H, 5.52; N, 12.20. Found: C, 35.13; H, 5.60; N, 12.28.

Spectroscopic Measurements

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 1×10^{-3} mol dm^{-3} aqueous solutions of complexes were used. Proton and ^{13}C NMR spectra were recorded on a Varian Gemini-200 NMR spectrometer using DSS as internal reference in D_2O.

RESULTS AND DISCUSSION

Three geometrical isomers of an eddp-Co(III) complex with an unsymmetrical bidentate ligand are theoretically possible, *s-cis*, *fac-uns-cis* and *mer-uns-cis* (Figure 1b). Since we used as the starting material, *uns-cis*-[Co(eddp)CO_3]$^-$ complex[1], substitution of CO_3^{2-} with glycine should theoretically give only two geometrical isomers, *fac-uns-cis* and *mer-uns-cis* isomers of [Co(eddp)(gly)] (Figure 1b). Obviously, both isomers have the same molecular symmetry (C_1) but the *facial* isomer has the higher symmetry ligand field than the corresponding *meridional* isomer of the same complex. Their molecular symmetry can be compared with that of [Co(am)$_3$] (am = ion of amino-acid) neglecting the backbone diamine ring. In this work we have prepared both *meridional* (violet) isomers of *uns-cis*-[Co(eddp)(gly)].

Electronic Absorption Spectra

Electronic absorption spectra of *fac* and *mer* isomers of *uns-cis*-[Co(eddp)(gly)] complex are shown in Figure 2 and the absorption data are summarized in Table I. The two spin-allowed transitions in a low-spin d^6 system 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 $^1T_{2g} = {}^1B_{2g} + {}^1E_g^b$. With further decreasing 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 lower symmetry than D_{4h}[18]. 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[18]. This has been observed previously in other CoN_3O_3 systems possessing *facial* and *meridional* isomers[19]. A definite shoulder is found for the low-energy absorption band of *meridional* *s-cis*-[Co(edda)(S-ala)][4]. The electronic absorption spectra of the investigated complexes show big differences in the shape of the lower energy spin-allowed region (Figure 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 *meridional* geometry.

The maxima of the first absorption band of the *fac* (red) and *mer* (violet) isomers are located at lower wavelengths than the starting carbonato complex, suggesting the stronger ligand field of coordinated glycine (Table I). On the other hand, the position of the absorption bands suggests that eddp ligand has the same *uns-cis*-configuration as in the starting $[Co(eddp)CO_3]^-$ complex.

In previously papers[1-14] it has been shown that complexes with *s-cis* configuration of coordinated edda-type tetradentates have the maxima of the first absorption bands at longer wavelength than corresponding *uns-cis* isomers. Also, it has been noted that Co(III) complexes with five-membered carboxylate chelate rings have the first absorption bands at lower wavelengths than corresponding complexes with six-membered chelate rings[1,20]. Our results confirm those facts (Figure 2, Table I).

Infrared Spectra

The important IR data for the *fac* and *mer* isomers of *uns-cis*-[Co(eddp)gly] complexes are given in Table II. Asymmetric stretching frequencies of the carboxylate groups were established as criteria for distinguishing between carboxylate groups which are coordinated (1600-1650 cm^{-1})[21]. Also, it was demonstrated that the asymmetric stretching bands of carboxylate groups of five-

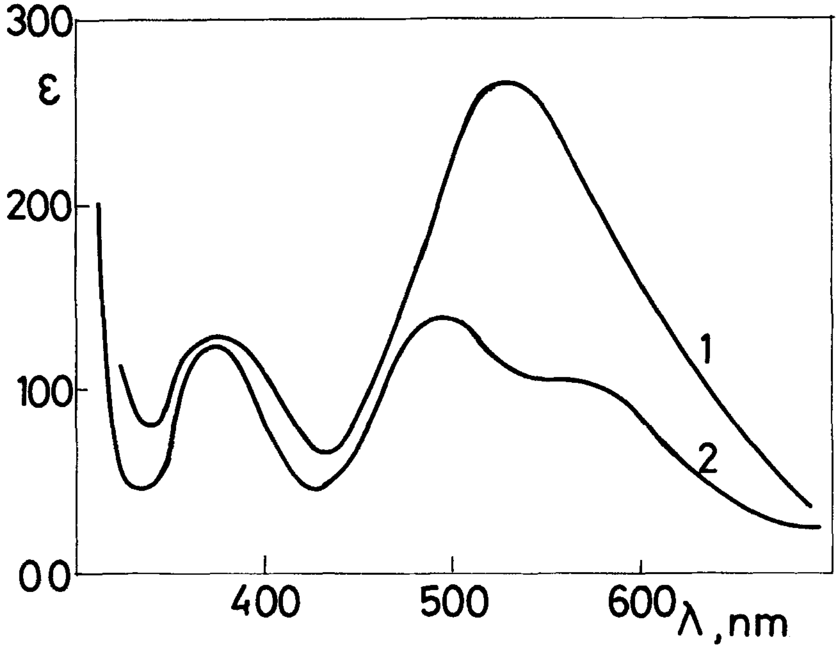

FIGURE 2 Electronic absorption spectra of *uns-cis*-[Co(eddp)gly] complexes: (1) *facial*, (2) *meridional* isomers.

TABLE I Band Maxima in the Visible Spectra of Some [Co(edda)L] and [Co(eddp)L] Complexes*.

Complex	*I*		*II*		*Ref.*
	λ_I	ϵ_I	λ_2	ϵ_2	
s-cis-$[Co(edda)CO_3]^-$	565	114	382	128	14
uns-cis-$[Co(edda)CO_3]^-$	533	234	390	182	14
uns-cis-$[Co(eddp)CO_3]^-$	544	232	383	165	1
uns-cis-$[Co(eddp)ox]^-$	530	195	384	170	1
fac-uns-cis-[Co(eddp)gly]	529	285	381	126	this work
mer-uns-cis-[Co(eddp)gly]	564	97	381	123	this work
	491	133			
fac-uns-cis-[Co(edda)gly]	520	223	374	-	27

Wavelength (λ) in nm, extinction coefficient (ϵ) in M^{-1} cm^{-1} units; L is one bidentate or two monodentate ligands.

membered chelate rings lie at higher energy than corresponding bands of six-membered chelate rings[20,22-26].

The shape of IR spectra in the carboxylate region for *fac* and *mer* isomers of *uns-cis*-[Co(eddp)gly] complex is consistent with their molecular symmetry. The asymmetric stretching bands of coordinated carboxylate groups of *meridional* (violet) and *facial* (red) isomers lie in the expected region (1638, 1600 and 1570 cm^{-1}; and 1617 cm^{-1}, respectively; Table II). Corresponding symmetric bands lie at 1385 cm^{-1} for the *mer* isomer and at 1380 cm^{-1} for the *fac* isomer. These also suggest that the red complex has the higher symmetry of ligand field and *facial* geometry.

Proton and ^{13}C NMR Spectra

The proton NMR spectra of the investigated complexes are shown in Figure 3, but ^1H and ^{13}C NMR does not offer a certain method of distinguishing between isomers. As can be seen, both isomers give a sharp resonance corresponding to glycine methylene protons at 3.32 ppm for *facial* and at 3.55 ppm for *meridional* isomers. Decoupled ^{13}C NMR spectra of both isolated complexes are very simple

TABLE II Characteristic IR Bands (cm^{-1}) for the Complexes.

Complex	$\nu\ (NH_2)$	$\nu_{as}\ (COO^-)$	$\nu_s\ (COO^-)$
mer-uns-cis-[Co(eddp)gly]	3250	1638	
	3156	1600	1385
	2938	1570	
fac-uns-cis-[Co(eddp)gly]	3172	1617	1370
	2938		

(Table III), exhibiting ten signals. This number of signals for carbon atoms indicates retention of *uns-cis* geometry of the eddp ligand in the isolated complexes (as in starting *uns-cis*-[Co(eddp)CO_3]$^-$ complex), but do not establish geometry of the red and violet complexes, separately.

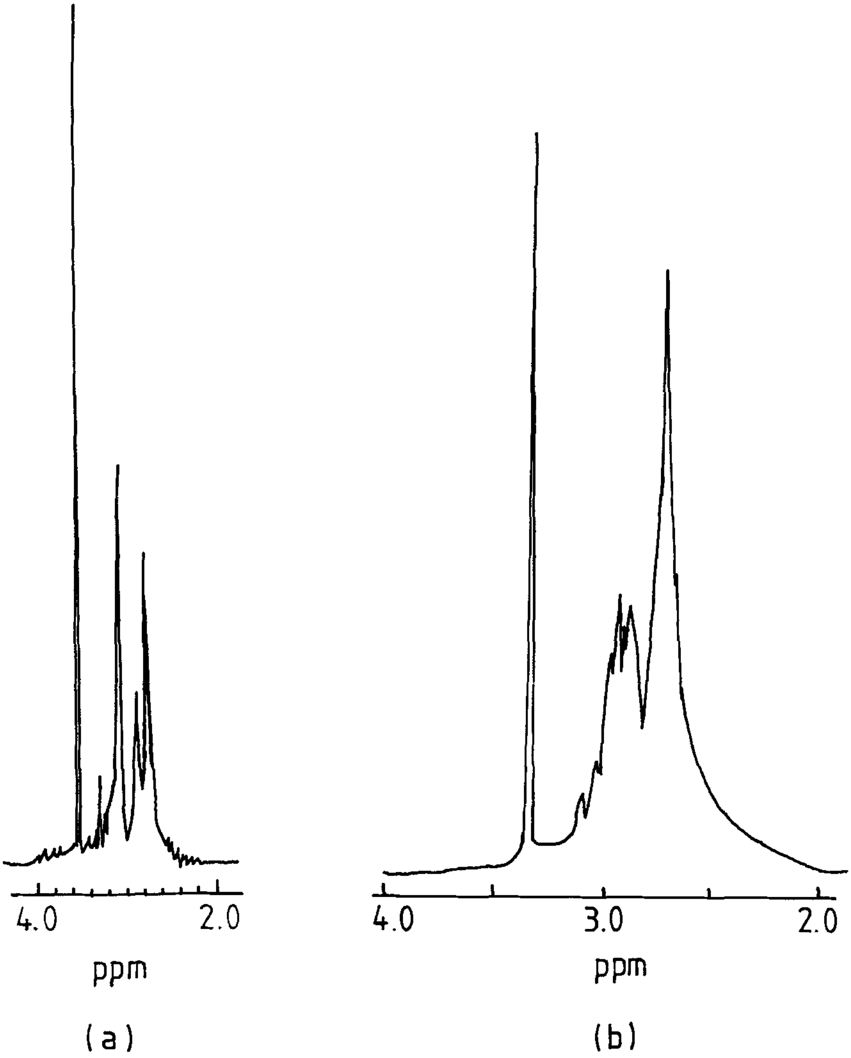

FIGURE 3 PMR spectra of isolated isomers of *uns-cis*-[Co(eddp)gly] complexes: a) *meridional* and b) *facial* isomers.

TABLE III ^{13}C NMR Chemical Shifts of *fac* and *mer* Isomers of *uns-cis*-[Co(eddp)(gly)]^a

	Carbonyl	*Methylene*
mer-uns-cis-[Co(eddp)gly]	177.4 180.6 185.3	28.2 34.2 44.7 45.3 46.5 48.1 50.2
fac-uns-cis-[Co(eddp)gly]	177.9 179.7 184.2	30.1 33.9 43.9 45.9 46.3 50.6 52.2

^{a}Chemical shifts in ppm.

Acknowledgements

The authors are grateful to the Ministry of Science and Technology of the Republic of Serbia for financial support.

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