

The preparation and characterization of *uns-cis*-(ethylenediamine-*N,N'*-di-3-propionato)(*N*-alkylethylenediamines)cobalt(III) complexes

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(Received 15 March, revised 29 October 1999)

Three octahedral cobalt(III) complexes of the general formula *uns-cis*-[Co(eddp)(*R-en*)]Cl·2H₂O, where eddp = the tetradentate ONNO-type ligand ethylenediamine-*N,N'*-di-3-propionate and *R-en* = a bidentate NN-type ligand, either *N*-methyl, *N*-ethyl or *N*-isopropylethylenediamine. The complexes were prepared by the reaction of sodium *uns-cis*-(ethylenediamine-*N,N'*-di-3-propionato)(carbonato)cobaltate(III)dihydrate with the corresponding diamine. They were isolated chromatographically and characterized by elemental analysis, infrared and electronic absorption spectroscopy.

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

INTRODUCTION

Cobalt(III) complexes with the ethylenediamine-*N,N'*-di-3-propionate ion (eddp) have been investigated in the past few years.¹⁻⁶ The ethylenediamine-*N,N'*-di-3-propionate ion is an ONNO type ligand and is similar to the ethylenediamine-*N,N'*-diacetate ion (edda), except that the former has a longer carboxylate moiety. Such ligands can occupy four of the octahedral sites around a Co(III) ion and the other two sites may be occupied by other ligands, whereby two geometrical isomers are possible as shown in Fig. 1.

The eddp complexes were obtained only with *uns-cis* geometry, except the ethylenediamine complex^{5,6}, while the edda complexes have been isolated with both geometries, *s-cis* and *uns-cis*.⁷ It was noted that the complexes containing eddp, which forms a six-membered amino-carboxylato backbone, prefer the *uns-cis* configuration suggesting that the size of the chelate ring has a profound effect on the distribution of the geometrical isomers.¹

As part of our continuing study of cobalt(III) complexes containing edda-type ligands²⁻⁴ the synthesis of *uns-cis* isomers of (ethylenediamine-*N,N'*-di-3-propionato)cobalt(III) complexes with some diamines, *N*-methylethylenediamine(meen), *N*-ethylethylenediamine(eten) and *N*-isopropylethylenediamine(*i*-pren) is reported here. The

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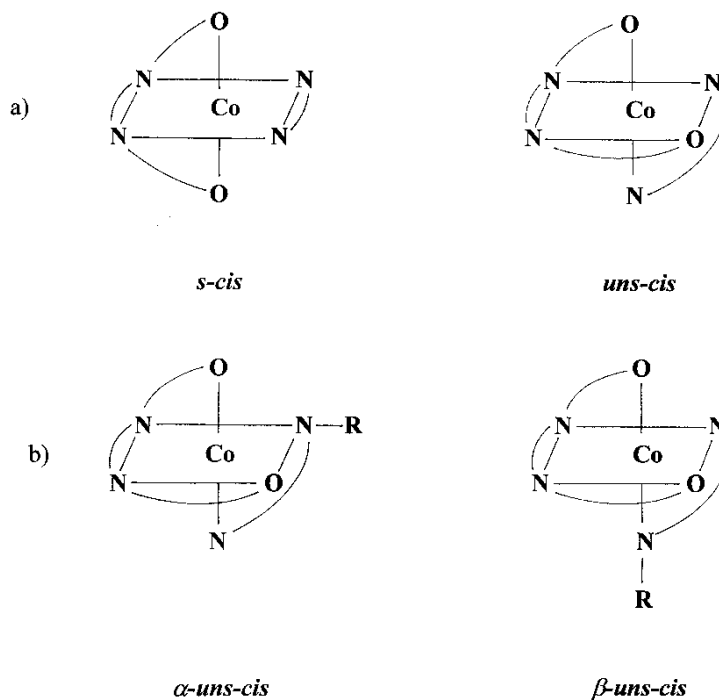


Fig. 1. Possible geometrical isomers of the $[\text{Co}(\text{eddp})(R\text{-en})]^+$ complexes.

geometric configuration of the isolated complexes was determined 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 procedure¹. Other reagents were obtained commercially and used without further purification.

*Preparation of uns-cis (ethylenediamine-*N,N'*-di-3-propionato) (N-methylethylenediamine)cobalt(III)chloridedihydrate, $[\text{Co}(\text{eddp}) (\text{meen})]\text{Cl}\cdot 2\text{H}_2\text{O}$*

To a solution of 0.38 (1 mmol) of *uns-cis*- $\text{Na}[\text{Co}(\text{eddp})\text{CO}_3]\cdot 2\text{H}_2\text{O}$ in 10.0 cm³ of water, 1.20 cm³ (1.5 mmol) of a 10% aqueous solution of *N*-methylethylenediamine was added, and the pH of the resulting solution adjusted to 9 with 0.2 mol dm⁻³ HCl. After heating under stirring for 2 h at 55 °C, the solution was concentrated to 5.0 cm³ and charged onto a 2.5 × 30 cm column containing Sephadex G-10. The red-violet eluate was then charged onto a 2.5 × 3.2 cm column containing SP-Sephadex C-25. The column was washed with water to remove non-adsorbed starting complex and then eluted with 0.2 mol dm⁻³ KCl. The eluate of the red-purple band was concentrated under reduced pressure. Then methanol was added in order to eliminate KCl. The *uns-cis*- $[\text{Co}(\text{eddp})(\text{meen})]\text{Cl}$ complex was obtained from the desalted solution.

Yield: 0.14 g (34.4%) *Anal.* Calcd. for $\text{C}_{11}\text{H}_{28}\text{ClCoN}_4\text{O}_6$ ($M_r=406.84$): C, 32.47; H, 6.95; N, 13.80%. Found: C, 32.58; H, 7.06; N, 13.72%.

Preparation of uns-cis-(ethylenediamine-N,N'-di-3-propionato)(N-ethylethylenediamine)cobalt(III)-chloridedihydrate, [Co(eddp) (eten)] Cl·2H₂O

From a solution containing 0.38 g (0.1 mmol) of *uns-cis*-Na[Co(eddp)CO₃] \cdot 2H₂O in 10 cm³ of water and 1.40 cm³ (1.5 mmol) of a 10% aqueous solution of *N*-ethylethylenediamine, the corresponding complex was obtained in the same manner as described above. Yield: 0.16 g (38.0%) *Anal.* Calcd. for C₁₂H₃₀ClCoN₄O₆ (M_r=420.84): C, 34.24; H, 7.20; N, 13.32%. Found: C, 34.26; H, 7.29; N, 13.23%.

Preparation of uns-cis-(ethylenediamine-N,N'-di-3-propionato)(N-isopropylethylenediamine)cobalt(III)-chloridedihydrate, [Co(eddp) (i-pren)] Cl·2H₂O

From a solution containing 0.38 g (0.1 mmol) of *uns-cis*-Na[Co(eddp)CO₃] \cdot 2H₂O in 10 cm³ of water and 1.70 cm³ (1.5 mmol) of 10% aqueous solution of *N*-isopropylethylenediamine, the corresponding complex was obtained by the same procedure as described above. Yield: 0.13 g (29.9%) *Anal.* Calcd. for C₁₃H₃₂ClCoN₄O₆ (M_r=434.87): C, 35.90; H, 7.43; N, 12.88%. Found: C, 35.40; H, 7.27; N, 13.28%.

Analytical methods

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 \cdot 10⁻³ mol dm⁻³ solutions of the complexes were used for these measurements. Elemental microanalysis for C, H, N were performed by standard methods.

RESULTS AND DISCUSSION

Two geometrical isomers of a Co(eddp)-complex are theoretically possible, *s-cis* and *uns-cis* (Fig. 1a), when the bidentate ligand has the same two donor atoms. If substituents on the N-atoms are also considered, further isomerism can be described, a and b (Fig. 1b). Since we used as the starting material the *uns-cis*-Na[Co(eddp)CO₃] complex, only the *uns-cis* isomer was expected on substituting the CO₃²⁻ ligand with a diamine, assuming that *s-cis*–*uns-cis* isomerization does not occur.

Electronic absorption spectra

The maxima in the electronic absorption spectra of the isolated [Co(eddp)*R*en]⁺ complexes are listed in Table I. The *uns-cis* isomers are readily distinguished from the *s-cis* isomers on the basis of their electronic absorption spectra. It is well known, both experimentally and theoretically, that *trans*(O)-[Co(N₄O₂)] type complexes exhibit large splittings of the first absorption band, while for *cis*(O)-[Co(N₄O₂)] type complexes this band is nearly symmetrical because of the smaller splitting⁸.

The first absorption bands for the complexes shown are nearly symmetrical. If only coordinated atoms are considered, these complexes have holohedrized tetragonal symmetry. Under tetragonal (*D*_{4h}) symmetry, the T_{1g} (*O_h*) level is split into A₂ and E levels. In the present complexes (Fig. 1) there is a stronger ligand along the unique axis (N-N) than in the plane perpendicular to it. Therefore it is predicted that the A₂(*D*_{4h}) level lies lower in energy than the E(*D*_{4h}) level, contrary to the situation in complexes of *s-cis* geometry where the weaker field is along the unique (O-O) axis.^{9,11} In the literature,⁷ it has been reported that the maximum of

the first absorption band of complexes with coordinated *s-cis* edda-type tetradentates appears at a longer wavelength than the corresponding *uns-cis* isomer. The position and the shape of this band of the prepared complexes strongly suggests that the eddp tetradentate ligand has the same *uns-cis* configuration as in the starting Na[Co(eddp)CO₃] complex (Table I).

TABLE I. Band maxima in the visible spectra of some (Co(edda)L)⁺ complexes*

Complex	λ_1	ϵ_1	λ_2	ϵ_2	λ_3	ϵ_3	Ref.
<i>s-cis</i> -[Co(edda)en] ⁺	528	87.3	449	sh	364	113	9
<i>uns-cis</i> -[Co(edda)en] ⁺	493	170			359	169	10
<i>s-cis</i> -[Co(eddp)en] ⁺	542	93	455	33	362	81	5
<i>uns-cis</i> -[Co(eddp)en] ⁺	508	218			367	120	5
<i>uns-cis</i> -[Co(eddp)meen] ⁺	513	165			365	115	this work
<i>uns-cis</i> -[Co(eddp)eten] ⁺	517	175			369	130	this work
<i>uns-cis</i> -[Co(eddp) <i>i</i> -pren] ⁺	519	180			373	140	this work

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

Table I also shows that the first absorption band is progressively shifted to lower energy as the hydrogen of the nitrogens on the ethylenediamine are substituted by methyl (meen), ethyl (eten) and isopropyl (*i*-pren). This shift is probably due to the lengthening of the metal-ligand bonds to accommodate the *N*-substituted alkyl groups.

Infrared spectra

All the complexes showed a strong or very strong absorption around 1600 cm⁻¹, the COO-asymmetric stretching region. The lack of absorption between 1700–1750 cm⁻¹ indicates that the carboxyl groups of eddp are certainly coordinated to the central cobalt (III) ion¹². The presence of only one band in this region is not consistent with the lower molecular symmetry of the prepared *uns-cis* complexes. However, these bands show evidence of broadening and splitting. These results lead to the conclusion that the isolated complexes have lower molecular symmetry and *uns-cis* geometry. The strong symmetric stretching bands of the coordinated carboxylate groups (1397 cm⁻¹) lie in the expected region (about 1400 cm⁻¹).

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

ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА *UNS-CIS*-(ЕТИЛЕНДИАМИН-*N,N'*-ДИ-3-ПРОПИОНАТО) (*N*-АЛКИЛЕТИЛЕНДИАМИН) КОБАЛТ(III) КОМПЛЕКСА

ТИБОР Ј. САБО И САЊА Р. ГРГУРИЋ

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У овом раду су синтетисана и окарактерисана три октаедарска кобалт(III) комплекса опште формуле *uns-cis*-[Co(eddp) (*R-en*)]Cl·2H₂O, где је eddp тетрадентатни ONNO-тип лиганда етилендиамин-*N,N'*-ди-3-пропионат, а *R-en* бидентатни *NN* лиганд, *N*-метил, *N*-етил или *N*-изопропилетилендидамин. Комплекси су синтетисани полазећи од *uns-cis*-натријум(етилендиамин-*N,N'*-ди-3-пропионато)(карбонато)кобалтат(III)-дихидрата и одговарајућих диамина, изоловани хроматографски и окарактерисани елементалном анализом, инфрацрвеном и електронско-апсорпционом спектроскопијом.

(Примљено 15. марта, ревидирано 10. октобра 1999)

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