Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polyhedron 22 (2003) 3265–3276
POLYHEDRON
www.elsevier.com/locate/poly

Crystal structure of *cis*-polar,*trans*(Cl,O_5)-$Na_2[Rh(1,3\text{-pddadp})Cl] \cdot 7H_2O$ and structural correlations between octahedral pentadentate metal(III) complexes with diaminopolycarboxylato-type ligands

Urszula Rychlewska [a,*], Miloš I. Djuran [b,*], Beata Warżajtis [a], Dušanka D. Radanović [c], Miorad M. Vasojević [b], Dušan J. Radanović [b]

[a] *Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, Poznan 60-780, Poland*
[b] *Department of Chemistry, Faculty of Science, University of Kragujevac, R. Domanovića 12, P.O. Box 60, Kragujevac YU-34000, Yugoslavia*
[c] *Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, P.O. Box 815, Belgrade YU-11001, Yugoslavia*

Received 22 April 2003; accepted 21 July 2003

Abstract

The pentadentate complex *cis*-polar,*trans*(Cl,O_5)-$Na_2[Rh(1,3\text{-pddadp})Cl] \cdot 7H_2O$ (where 1,3-pddadp is the 1,3-propanediamine-*N*,*N′*-diacetate-*N*,*N′*-di-3-propionate ion) was prepared and characterized. The structure of the complex was determined by X-ray analysis. The rhodium(III) ion is surrounded octahedrally by the two N and three O atoms of the 1,3-pddadp ligand and one chloride anion. The chloride anion occupies the *trans* position with respect to the oxygen atom of the axial glycinate ring and the *cis*-polar orientation with respect to the tertiary nitrogen atom bonded to the uncoordinated 3-propionate group. The investigated pentadentate complex derives directly from the *trans*(O_5O_6) isomer of the corresponding hexadentate $[Rh(1,3\text{-pddadp})]^-$ complex. The conformations of the chelate rings were found to be *envelope* and *flat* for in-plane (G″) and axial (R′) glycinate rings, and *sofa* and *chair* for in-plane β-alaninate (G′) and 1,3-propanediamine (T) rings, respectively. The electronic absorption spectrum of *cis*-polar,*trans*(Cl,O_5)-$[Rh(1,3\text{-pddadp})Cl]^{2-}$ is also given and compared with those of hexadentate *trans*(O_5O_6)-$[Rh(1,3\text{-pddadp})]^-$ and *trans*(O_5)-$[Rh(1,3\text{-pddadp})]^-$ complexes.

Keywords: Pentadentate Rh(III) complex; Crystal structure; Ring conformations

1. Introduction

The analysis of structural data of hexadentate $[M(edta)]^{n-}$ (edta is the ethylenediaminetetraacetate ion) complexes shows that the system is strained [1]. The ethylenediamine ring (E ring) and two glycinate rings (G rings) in-plane are considerably more strained than the out-of-plane glycinate rings (R rings) [1,2]. Also, it is well known that hexadentate edta complexes are susceptible to substitution reactions in which certain monodentate ligands can displace the in-plane (G) glycinate ring [3]. In general, for pentadentate octahedral complexes with edta- or ed3a-type (ed3a is the ethylenediamine-*N*,*N*,*N′*-triacetate ion) ligands containing carboxylate arms of the same length three geometrical isomers are possible [*cis*-equatorial (*cis*-eq), *trans*-equatorial (*trans*-eq) and *cis*-polar, Fig. 1 [1]]. Although the majority of six-coordinate pentadentate complexes with ed3a or *N*-substituted ed3a ligands adopt *cis*-eq geometry [1] the other two geometrical isomers (*trans*-eq and

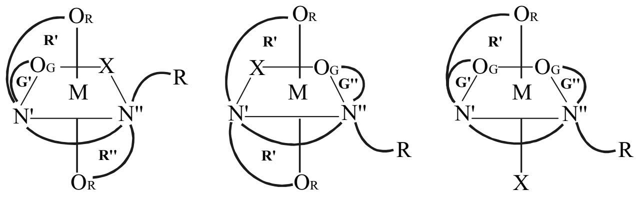
---

* Corresponding authors. Tel.: +48-61-865-8008 (U. Rychlewska); Tel.: +381-34-335-039; fax: +381-34-335-040 (M.I. Djuran).

E-mail addresses: urszular@amu.edu.pl (U. Rychlewska), djuran@knez.uis.kg.ac.yu (M.I. Djuran).

[1] Fig. 1 illustrates the three isomers derived for the Δ configurational isomer. The N′ label is assigned to the three-ring nitrogen and N″ to the two-ring nitrogen. The chelate rings are assigned depending on the nitrogen atoms (N′ or N″) from which they stem from.

0277-5387/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2003.07.012



cis-Equatorial *trans*-Equatorial *cis*-Polar

Fig. 1. Possible geometrical isomers of octahedral pentadentate complexes with edta- or ed3a-type ligands (edta is ethylenediaminetetraacetate and ed3a is ethylenediamine-N,N,N'-triacetate; R is CH_2COOH, $–CH_2COO^-$, –H or any other alkyl substituent and X is a monodentate ligand).

cis-polar) also have been established in some cobalt(III) complexes [4–6]. In the case of $[Co(ed3a)(NO_2)]^-$ [4,5] (where R is H and X is NO_2^-) two geometrical isomers (*cis*-eq and *trans*-eq) have been isolated and spectroscopically assigned, whereas the *cis*-polar isomer was described for the $[Co(Hedta)(Br)]^-$ [6] complex (where R is $-CH_2COOH$ and X is Br^-) (Fig. 1). In addition, it has been found that the variation of N-substituents in Co(III)-ed3a-type complexes has an important influence on the chiral properties of these systems [4,5,7–9].

X-ray data concerning *trans*-eq configuration have been reported by Sakagami and Kaizaki [10] for ed3p-type (ed3p is the ethylenediamine-N,N,N'-tri-3-propionate ion) complexes of chromium(III): *trans*-eq-$[Cr\{(S)\text{-}1,2\text{-pd3p}\}(H_2O)]\cdot 4H_2O$ [10] and *trans*-eq-$[Cr\{(SS)\text{-cyd3p}\}(H_2O)]\cdot 4.5H_2O$ [10] [(*S*)-1,2-pd3p = (*S*)-1, 2-propanediamine-N,N,N'-tri-3-propionate and (*SS*)-cyd3p = (1*S*, 2*S*)-*trans*-1,2-cyclohexanediamine-N,N,N'-tri-3-propionate]. The same authors have also prepared and characterized two geometrical isomers (*cis*-eq and *trans*-eq) of the “acidic” complex $[Cr(Hedtp)(H_2O)]$ [11] (Hedtp is the ethylenediamine-N,N,N'-tri-3-propionate-N'-3-propionic acid) of which the *cis*-eq isomer was established by X-ray analysis. Recently, the conformational analysis of chromium(III) complexes with the ed3p ligand revealed the *trans*-eq isomer to be the most stable one for the $[Cr(ed3p)(H_2O)]$ species [12]. These results are in agreement with X-ray experimental data [13,14].

With respect to edta, the symmetrical hexadentate edta-type ligands such as ethylenediamine-N,N'-diacetate-N,N'-di-3-propionate and 1,3-propanediamine-N,N'-diacetate-N,N'-di-3-propionate ions (eddadp and 1,3-pddadp, respectively), differing only in the length of the diamine chain, are able to form less strained octahedral systems with metal ions of different size [1]. These ligands can form a maximum of three geometrical isomers on hexadentate coordination: *trans*-(O_5) (**I**), *trans*-(O_5O_6) (**II**) and *trans*-(O_6) (**III**) (Fig. 2) (O_5 and O_6 refer to the five- and six-membered N–O rings, respectively). It is commonly accepted that the six-membered β-alaninate rings serve better for the formation of less-strained G rings thus favoring the *trans*-(O_5) isomers of $[M(eddadp)]^{n-}$ complexes [15–21]. Contrary to this, all possible isomers of the $[M(1,3\text{-pddadp})]^{n-}$ complex have been reported for Cr(III) [22], but only two isomers (*trans*-(O_5O_6) and *trans*-(O_6)) for Co(III) [23,24] and (*trans*-(O_5) and *trans*-(O_5O_6)) for Rh(III) [25,26] and Ni(II) [27] have been isolated and characterized.

Recently, we have reported the structural studies on hexadentate *trans*(O_5)-$[Rh(1,3\text{-pddadp})]^-$ and *trans* (O_5O_6)-$[Rh(1,3\text{-pddadp})]^-$ complexes [26]. This paper is a continuation of our previous work on Rh(III)-edta-type complexes. Here, we report the synthesis and X-ray analysis of the pentadentate *cis*-polar,*trans*(Cl,O_5)-$Na_2[Rh(1,3\text{-pddadp})Cl]\cdot 7H_2O$ complex, and present the structural characteristics of octahedral pentadentate M(III) complexes with diaminopolycarboxylato ligands. The electronic absorption spectrum of the reported pentadentate complex is displayed and correlated with the electronic absorption spectra of the hexadentate *trans*(O_5) and *trans*(O_5O_6) geometrical isomers of $[Rh(1,3\text{-pddadp})]^-$ for which the crystal structures are known.

2. Experimental

The 1,3-propanediamine-N,N'-diacetic-N,N'-di-3-propionic acid ($H_4$1,3-pddadp) was prepared using a previously described procedure [23]. $RhCl_3\cdot 3H_2O$ (purchased from Fluka) and all other commercially obtained chemicals were used as supplied.

2.1. Preparation of *cis*-polar,*trans*(Cl,O_5)-$Na_2[Rh(1,3\text{-pddadp})Cl]\cdot 7H_2O$

This complex was prepared by the procedure used to make Rh(III) complexes with hexadentate edta-type ligands [25,26,28,29]. Solid $RhCl_3\cdot 3H_2O$ (1.32 g, 5 mmol) and 15 ml of Na_4-1,3-pddadp solution, which was obtained by neutralization of the corresponding acid (1.72 g, 5 mmol) with four equivalents of NaOH, were mixed in a Pyrex tube. The tube was sealed and then heated at 145 °C on an oil-bath for 7 h. After cooling to room temperature the yellow solution was filtered off and the filtrate containing different 1,3-pddadp-Rh(III) complexes was passed through a column supplied with the QAE A-25 Sephadex in the Cl^- form. After elution with 0.1 M NaCl, five yellow bands were detectable on the column after two days. The first two bands were separated and by UV–Vis spectroscopy it was found that they represent previously characterized *trans*(O_5) (eluate I) and *trans*(O_5O_6) (eluate II) geometrical isomers of $[Rh(1,3\text{-pddadp})]^-$ [26]. The elution with 0.1 M NaCl was continued and next two bands were separated. The last band, remaining on the top of the column after elution with 0.1 M NaCl, was eluted with concentrated NaCl. We believe that this elute is a mixture of different

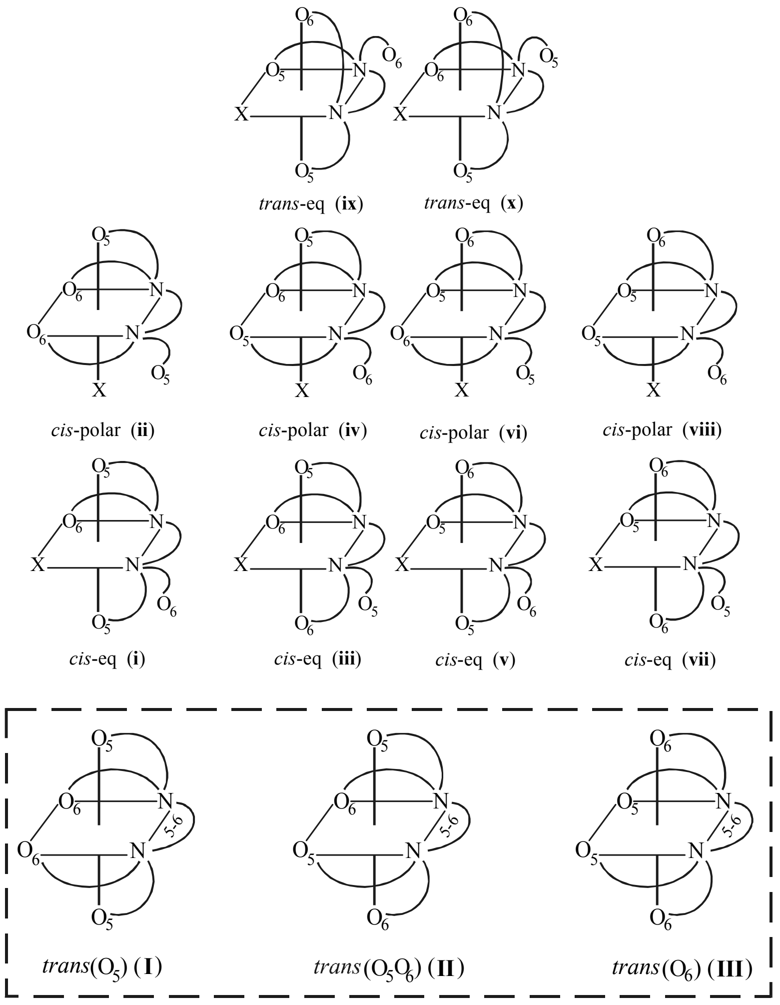


Fig. 2. Possible geometrical isomers of $[M(eddadp)]^{n-}$ (eddadp is the ethylenediamine-*N*,*N*′-diacetato-*N*,*N*′-di-3-propionato ion) or $[M(1,3\text{-}pddadp)]^{n-}$ (1,3-propanediamine-*N*,*N*′-diacetato-*N*,*N*′-di-3-propionato ion) complexes with these ligands acting as hexadentate and $[M(eddadp)X]^{n-}$or $[M(1,3\text{-}pddadp)X]^{n-}$ type complexes derived from the corresponding *trans*(O_5), *trans*(O_5O_6) and *trans*(O_6) isomers (X is a monodentate ligand; eddadp and 1,3-pddadp are pentadentate ligands).

hydroxo species with higher than −2 charge. Since some thermal decomposition of the ligand is expected [10,30,31], the formation of these complexes involves decarboxylation of 1,3-pddadp. The elute III was obtained in a very small yield and after additional chromatography we found that it contains at least two complexes which have not been identified yet. The elute IV was evaporated to 10 ml and desalted by passage through a G-10 Sephadex column with distilled water as eluent. The elute was evaporated to ca. 3 ml and *cis*-polar,*trans*(Cl,O_5)-$Na_2[Rh(1,3\text{-}pddadp)Cl] \cdot 7H_2O$ was crystallized after adding ethanol and cooling the solution in a refrigerator. The crystals were collected, washed with ethanol, and air-dried. Yield 0.25 g. *Anal.* Calc. for *cis*-polar,*trans*(Cl,O_5)-$Na_2[Rh(1,3\text{-}pddadp)Cl]$ $\cdot 7H_2O{=}Na_2RhC_{13}H_{32}N_2O_{15}Cl$ (FW = 640.70): C, 24,37; H, 5.03; N, 4.37. Found: C, 25.07; H, 5.22; N, 4.84%.

2.2. Physical measurements

The electronic absorption spectra were recorded on a Perkin–Elmer spectrophotometer and for these measurements about 10^{-3} M aqua solutions were used. Elemental microanalyses for carbon, hydrogen, and nitrogen were done by the Faculty of Chemistry, University of Belgrade.

2.3. Crystallographic data collection and refinement of the structure

A yellow prismatic crystal having approximate dimensions of $0.5 \times 0.3 \times 0.2$ mm was used for data collection at 295 K. Worth to mention is the observed decrease of the diffracting power of the crystal during the process of lowering the temperature for data collection. Therefore, the reported results correspond to the room temperature structure.

Crystal data: $C_{13}H_{32}ClN_2Na_2O_{15}Rh$ (FW = 640.75), triclinic, space group $P\bar{1}$, $a = 9.536(2)$, $b = 9.761(2)$, $c = 13.153(3)$ Å, $\alpha = 103.40(3)°$, $\beta = 94.64(3)°$, $\gamma = 90.19(3)°$, $V = 1186.8(4)$ Å^3, $Z = 2$, $D_c = 1.793$ g cm^{-3}, λ (Mo Kα) = 0.71073 Å, $T = 295(2)$ K, $\mu = 0.943$ mm^{-1}, $F(000) = 656$.

Intensity measurements were made on a KM4CCD κ-geometry diffractometer [32]. The structure was solved by direct methods using SHELXS-97 [33] and refined by least-squares techniques with SHELXL-97 [34], to $R = 0.0634$ and $R_w = 0.1065$ for 3651 reflections ($I > 2\sigma(I)$) of 4778 reflections collected in the range $3.13° < \theta < 26.37°$ using the ω scan method (index ranges: $h = -11 \rightarrow 8$, $k = -12 \rightarrow 12$, $l = -16 \rightarrow 16$). The intensity data were corrected for Lp effects as well as for absorption ($T_{\min} = 0.907$, $T_{\max} = 0.988$). Anisotropic thermal parameters were employed for the non-hydrogen atoms. The positions of the hydrogen atoms attached to the C-atoms were calculated at standardized distances of 0.96 Å. Water hydrogen atoms were located from difference Fourier maps and their bond distances have been standardized to a value of 0.85 Å. All hydrogen atoms were refined using a riding model with isotropic temperature factors 30% higher than the isotropic equivalent for the atom to which the H-atom was bonded. A Siemens Stereochemical Workstation was used to prepare drawings [35].

3. Results and discussion

In the reaction between $RhCl_3 \cdot 3H_2O$ and the hexadentate 1,3-pddadp ligand (1,3-pddadp is the 1,3-propanediamine-*N,N'*-diacetato-*N,N'*-di-3-propionato ion) 10 geometrical isomers of octahedral pentadentate [Rh(1,3-pddadp)X]$^{n-}$ (X is a monodentate ligand) are theoretically possible. Schematic presentation of these geometrical isomers is given in Fig. 2. Eight geometrical isomers of the 10 presented in this figure (*cis*-eq and *cis*-polar) can directly be derived from the corresponding *trans*(O_5) (**I**), *trans*(O_5O_6) (**II**) and *trans*(O_6) (**III**) isomers of the [Rh(1,3-pddadp)]$^-$ complex with 1,3-pddadp coordinated as a hexadentate ligand. Among the Rh(III) complexes with diaminopolycarboxylato-type ligands, the only octahedral pentadentate complex for which the crystal structure has been reported so far is *cis*-eq-[Rh(Hedta)(H_2O)] [36]; see Fig. 1. This paper presents the structural characteristics of a new pentadentate rhodium(III) complex, the *cis*-polar,*trans*(Cl,O_5)-isomer of Na_2[Rh(1,3-pddadp)Cl] · $7H_2O$, obtained in the reaction with 1,3-pddadp ligands having mixed five and six carboxylate arms.

3.1. Description of the crystal structure of *cis*-polar,*trans*(Cl,O_5)-Na_2[Rh(1,3-pddadp)Cl] · $7H_2O$

The Ortep drawing of *cis*-polar,*trans*(Cl,O_5)-Na_2[Rh(1,3-pddadp)Cl] · $7H_2O$ is depicted in Fig. 3, where the labelling schemes adopted for the respective atoms and rings are also given. Selected bond distances and valence angles are listed in Table 1. The rhodium(III) ion is surrounded octahedrally by two N and three O atoms of the 1,3-propanediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate ion (1,3-pddadp) and a chloride anion. The chloride anion occupies the *trans* position with respect to the oxygen atom of the axial glycinate ring and the *cis*-polar orientation with respect to the tertiary nitrogen atom bonded to the uncoordinated 3-propionate group. The 1,3-pddadp ligand forms an in-plane six-membered diamine (T) ring, five-membered glycinate (G″) and six-membered β-alaninate (G′) rings. The other glycinate ring (R′) is coordinated in the axial position. The uncoordinated 3-propionate group, attached to N(2) nitrogen, adopts an axial orientation with respect to the N–Rh–N plane and is situated on the same side of the complex as the R′ ring, as indicated by the value of the torsion angle C(11)–N(2)–Rh(1)–O(5) equal to −1.6(1)°. The *cis*-polar,*trans*(Cl,O_5)-[Rh(1,3-pddadp)Cl]$^{2-}$ ion (isomer **iv**, Fig. 2) derives directly from the *trans* (O_5O_6) isomer (**II**) of the corresponding hexadentate

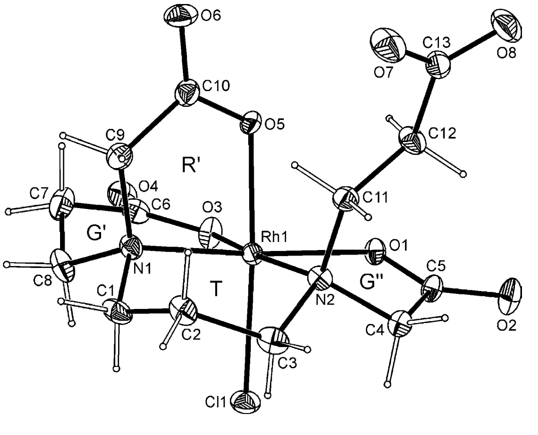


Fig. 3. A view of the *cis*-polar,*trans*(Cl,O_5)-[Rh(1,3-pddadp)Cl]$^{2-}$ ion as the sodium heptahydrate salt, showing the labelling scheme of atoms and rings. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are represented as spheres of arbitrary radius.

Table 1
Bond distances (Å) and valence angles (°) with e.s.d. around Rh(III)

Bond distances			
Rh1–O3	2.030(4)	Rh1–N1	2.065(6)
Rh1–O5	2.035(5)	Rh1–N2	2.092(5)
Rh1–O1	2.046(4)	Rh1–Cl1	2.338(2)
Valence angles			
O3–Rh1–O5	86.6(2)	O3–Rh1–Cl1	86.8(2)
O3–Rh1–O1	86.4(2)	O1–Rh1–Cl1	88.8(1)
O5–Rh1–O1	92.2(2)	N1–Rh1–Cl1	95.5(2)
O3–Rh1–N1	95.4(2)	N2–Rh1–Cl1	91.6(2)
O5–Rh1–N1	83.7(2)	O5–Rh1–Cl1	173.2(2)
O5–Rh1–N2	95.2(2)	O1–Rh1–N1	175.4(2)
O1–Rh1–N2	82.4(2)	O3–Rh1–N2	168.6(2)
N1–Rh1–N2	95.9(2)		

complex in which the chloro ligand displaced the six-membered β-alaninate R-ring. The X-ray data for the hexadentate Λ-*trans*(O_5O_6)-[Rh(1,3-pddadp)]$^-$ complex has already been reported [26]. The difference in conformation between the two complex anions can be readily seen from Table 2 which presents the endocyclic torsion angles and a set of Cremer and Pople parameters [37] for the two structures, and from Fig. 4 which is an orthogonal fit of the two molecules. To allow a direct comparison of the two structures, an inversion of configuration of the *trans*(O_5O_6) isomer from Λ to Δ was necessary, as the reported co-ordinates for the *cis*-polar structure refer to the Δ isomer. The most dramatic changes in conformation take place in the two rings to which the nitrogen carrying the uncoordinated propionate arm belongs, i.e., T and G″. The two diamine T rings differ in both the mode and degree of ring puckering. The flexible twist boat conformation with the average torsion angle magnitude of 42.5°, observed in the *trans*(O_5O_6)-[Rh(1,3-pddadp)]$^-$ complex [26], is contrasted with the rigid chair form in the pentadentate complex, in which the average torsion angle magnitude is 55.2°. An increase of the T-ring puckering is accompanied by a decrease of the diamine bite angle from 97.0(1)° to 95.9(2)°. The flexible twist boat conformation of the T ring has also been observed in other hexadentate Rh(III) complexes, *trans*(O_5)-[Rh(1,3-pddadp)]$^-$ [26] and [Rh (1,3-pdta)]$^-$ [38] (1,3-pdta is the 1,3-propanedia- minetetraacetate ion). This seems to indicate that the rigid and highly puckered conformation of the T ring is one of the characteristic features of the *cis*-polar pentadentate complex. As far as the G″ ring is

Table 2
Endocyclic torsion angles (°) in the pentadentate *cis*-polar,*trans*(Cl,O_5)-[Rh(1,3-pddadp)Cl]$^{2-}$ complex and its congener the hexadentate *trans* (O_5O_6)-[Rh(1,3- pddadp)]$^-$ isomer[a] and Cremer and Pople puckering parameters [37]

Ring (size) torsion angle	*cis*-polar,*trans*(Cl,O_5)-[Rh(1,3-pddadp)Cl]$^{2-}$ Δ, N′(R), N″(R) this work	*trans*(O_5O_6)-[Rh(1,3-pddadp)]$^-$ Δ, N′(R), N″(S) Ref. [26]
T (6)	$QT = 0.590$, $\varphi_2 = -152.3°$, $\theta_2 = 6.8°$, $q_2 = 0.070$, $q_3 = 0.586$	$QT = 0.746$, $\varphi_2 = 94.1°$, $\theta_2 = 90.6°$, $q_2 = 0.746$, $q_3 = -0.008$
Rh–N′–C_α–C_β	54.7	63.3
N′–C_α–C_β–C_γ	−68.0	−39.5
C_α–C_β–C_γ–N″	70.0	−31.4
C_β–C_γ–N″–Rh	−58.7	63.2
C_γ–N″–Rh–N′	40.8	−32.0
N″–Rh–N′–C_α	−38.7	−25.4
G′ (6)	$QT = 0.533$, $\varphi_2 = -54.7°$, $\theta_2 = 121.2°$, $q_2 = 0.456$, $q_3 = -0.276$	$QT = 0.554$, $\varphi_2 = -102.9°$, $\theta_2 = 127.5°$, $q_2 = 0.440$, $q_3 = -0.337$
Rh–N′–C_α–C_β	−59.8	−67.6
N′–C_α–C_β–C_γ	71.2	50.6
C_α–C_β–C_γ–O	−33.1	−8.5
C_β–C_γ–O–Rh	−4.6	−5.9
C_γ–O–Rh–N′	8.6	−10.9
O–Rh–N′–C_α	22.3	42.8
G″ (5)	$\varphi_2 = 30.2°$, $q_2 = 0.402$	$\varphi_2 = -149.3°$, $q_2 = 0.382$
Rh–O–C_β–C_α	1.4	1.1
O–C_β–C_α–N″	−25.4	24.1
C_β–C_α–N″–Rh	36.4	−34.9
C–N″–Rh–O	−29.0	27.9
N″–Rh–O–C_β	18.3	−17.6
R′ (5)	$\varphi_2 = 22.4°$, $q_2 = 0.159$	$\varphi_2 = -160.3°$, $q_2 = 0.105$
Rh–N′–C_α–C_β	13.3	−8.4
N′–C_α–C_β-O	−7.1	4.0
C_α–C_β–O–Rh	3.4	2.9
C_β–O–Rh–N′	9.0	−6.4
O–Rh–N′–C_α	−11.8	7.9
R″ (6)		$QT = 0.661$, $\varphi_2 = 136.5°$, $\theta_2 = 82.8°$, $q_2 = 0.655$, $q_3 = -0.083$
Rh–O–C_γ–C_β		32.4
O–C_γ–C_β–C_α		22.6
C_γ–C_β–C_α-N″		−69.1
C_β–C_α–N″–Rh		50.4
C_α–N″–Rh–O		−3.9
N″–Rh–O–C_γ		−38.9

[a] The published coordinates for the *trans*-(O_5O_6) isomer [26], correspond to Λ configuration at the metal center. For the purpose of comparison, torsion angle values given in the table correspond to Δ configuration.

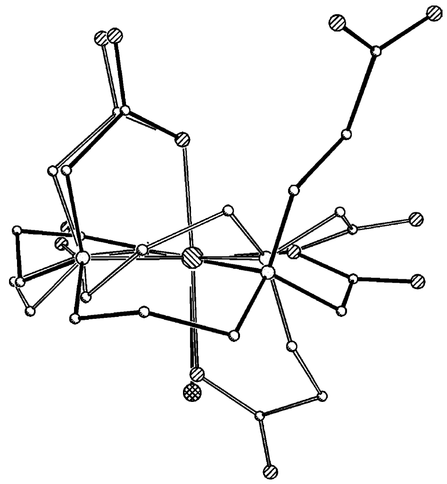


Fig. 4. The result of a least-squares fit to the N1, O1 and O3 donor atoms of the *trans*(O_5O_6)-[Rh(1,3-pddadp)]$^-$ and *cis*-polar,*trans*(Cl,O_5)-[Rh(1,3-pddadp)Cl]$^{2-}$ isomers. The isomers are distinguished by open and full lines, respectively.

concerned, the degree of its puckering is nearly the same in the *cis*-polar,*trans*(Cl,O_5)-[Rh(1,3-pddadp)Cl]$^{2-}$ pentadentate complex and its hexadentate analog [26] (the average of the endocyclic torsion angle magnitudes is 22.1° and 21.1°, respectively) but the signs of the endocyclic torsion angles are interchanged, indicating the inverted conformations (λ and δ, respectively, Table 2, Fig. 4). Judging from the average deviations from octahedral angles (average (ΔO_h) parameter), the investigated *cis*-polar,*trans*(Cl,O_5)-[Rh(1,3-pddadp)Cl]$^{2-}$ pentadentate complex shows a higher degree of the octahedral distortion than its hexadentate analogue (4.9° versus 3.9°, respectively).

In Rh(III)-edta-type complexes [26], there is a tendency for axial bonds to be significantly shorter than equatorial ones, and the average values are in the range 2.003–2.020 versus 2.038–2.045 Å. Contrary to this, in the *cis*-polar isomer the axial Rh–O(R) bond length (2.035(5) Å) is the same as the average equatorial Rh–O(G) bond length (2.038 Å). In addition, in the investigated *cis*-polar isomer the in-plane average Rh–N bond length is somewhat larger than those found in hexadentate *trans*(O_5)-[Rh(1,3-pddadp)]$^-$ [26] and *trans*(O_5O_6)-[Rh(1,3-pddadp)]$^-$ [26] complexes (2.079 versus 2.058 and 2.045 Å). Besides that, the axial bond formed between Rh(III) and the monodentate chloro ligand in *cis*-polar,*trans*(Cl,O_5)-[Rh(1,3-pddadp)Cl]$^{2-}$ is significantly longer than all other metal–ligand bonds found in Rh(III)-edta-type complexes, and sums 2.338(2) Å. Thus, the ligand field strength along the *z*-axis of the complex should be significantly lower in the investigated complex *cis*-polar,*trans*(Cl,O_5)-[Rh(1,3-pddadp)Cl]$^{2-}$ than in both hexadentate Rh(III) complexes with the same 1,3-pddadp ligand. In addition, *trans* influence and chelate constraint effects should also be considered in explanation of the differences in Rh–O distances between the investigated Rh(III) complexes.

Each sodium ion is coordinated by six oxygen atoms which are situated at the corners of a distorted octahedron. The Na–O distances vary from 2.386(3) to 2.481(3) Å. The Na1 cation is surrounded by five water molecules and one carbonyl oxygen atom O4 from an equatorial β-alaninate G′ ring. The Na2 cation is surrounded by three water molecules and three carbonyl oxygen atoms: two from the equatorial β-alaninate G′ ring (O4 and its symmetrical equivalent at $2-x$, $1-y$, $2-z$) and O6 at x, $y-1$, z from the axial glycinate R′ ring. By sharing three of its vertices, the Na1 octahedron is joined to the neighboring Na1 octahedron and to two neighboring Na2 octahedra. On the other hand, each Na2 octahedron, in addition to sharing one of its edges with the nearest Na1 octahedron, shares an edge with the neighboring Na2 octahedron. To a cluster consisting of two Na2 and one Na1 octahedra four Rh complex anions are connected by fragments of 1,3-pddadp. In this way the chains of edge sharing sodium octahedra that are formed along the *x*-axis carry on both sides as well as on the top and the bottom the rhodium(III) complex anions. Of the two bridging carboxylate oxygens (O4 and O6) which belong to G′ and R′ rings, respectively, the O4 oxygen is surrounded by three different Na cations which, together with the C6 carbon atom to which the O4 is bonded, form a nearly tetrahedral environment around this oxygen atom.

3.2. Structural correlations between octahedral pentadentate metal(III) complexes with diaminopolycarboxylato-type ligands

Examination of crystal structures is a good starting point to gain more insight into the configurational and conformational preferences of pentadentate complexes as compared with their hexadentate analogs and to study the mechanism of the M–O bond rupture. The conformations of chelate rings and ring strains, expressed by the average value of the torsion angle moduli ($|\omega|$), the sum of the chelate ring bond angles [2] and the mean deviation from octahedral angles (average (ΔO_h)) in *cis*-polar,*trans*-(Cl,O_5)-[Rh(1,3-pddadp)Cl]$^{2-}$ and selected other M(III) pentadentate complexes with diaminopolycarboxylato ligands are given in Table 3 (values calculated from the coordinates deposited at the Cambridge Crystallographic Data Base [1] and from [13,14]).

In a group of octahedral edta and ed3a complexes, with the ligand acting as pentadentate, there is no real exception from the *cis*-equatorial configuration. The conformational characteristics of octahedral pentadentate Rh(III) [36], Ru(III) [39,40], Cr(III) [13] and Co(III) [9,41] complexes with ed3a or *N*-substituted ed3a ligands seems to be quite uniform (Table 3). Of the three types of rings (R, G and E), the two R rings are the least puckered but differ between each other in the degree of puckering. Ring R′ is usually flat, with the average torsion angle magnitude not exceeding 9° while R″ is more puckered with the average torsion angle magnitude in the range 14.4°–17.4°. The [Rh(Hedta)(H_2O)] [36] complex (Table 3), having the R″ ring flat and R′ puckered, constitutes an exception in this respect. G′ rings are more puckered than R rings (the average torsion angle magnitude in the range 21.0°–26.4°) and seem to prefer an envelope conformation when connected to bigger size ions, and a twist form when connected to smaller size ions. Still more puckered are the E rings having the average torsion angle moduli in the range 31.4°–33.6°. The degree of puckering of the corresponding rings is strikingly similar in all analyzed *cis*-equatorial M(III) edta and ed3a octahedral pentadentate complexes, independent whether they carry an uncoordinated carboxylate arm or not, whether this carboxylate group is protonated and whether the sixth position is occupied by a water or chloride ligand. However the mode of puckering varies. The distortions from octahedral geometry, measured as the mean deviation from octahedral angles (average (ΔO_h), Table 3) are significant for Rh(III), Ru(III) and Cr(III) ions (the (ΔO_h) values vary from 4.7° to 5.4°) and smaller for Co(III) ions ((ΔO_h) values 3.1° and 3.4°). For detailed elucidation of pentadentate complexes that display octahedral geometry it might be desirable to compare their geometry with the geometry of their hexadentate analogs. However, such comparison is possible only for edta-type complexes with ions of smaller size such as Co(III), because metals with ionic radii higher than the reported critical value of 0.79 [18] form solely pentadentate complexes with solvent occupying the sixth position. Comparison of Co(III) ed3a complexes with their hexadentate analogs [2,42–44] reveals very close structural similarity except, perhaps, that in hexadentate complexes the two R-rings display more uniform ring puckering and the total distortion from octahedral geometry is slightly higher ((ΔO_h) values are in the range 4.0°–4.6°) [2,42–44]. An analogous comparison of the *cis*-equatorial isomer of [Cr(Hedtp)(H_2O)] [11] with its hexadentate congener, the $[Cr(edtp)]^-$ complex [21] (edtp is the ethylenediamine-*N*,*N*,*N*′,*N*′-tetra-3-propionate ion) also indicates the lack of conformational changes upon dissociation of one of the carboxylate arms. Table 4 illustrates close configurational and conformational similarity of the *cis*-equatorial isomer derived from the Δ $[Cr(edtp)]^-$ isomer. It might be of interest to note that despite an increase of pucker of all the carboxylate rings due to an increase of the ring size from 5 to 6, the degree of the E-ring puckering in the *cis*-equatorial isomer [11] is the same as in the ed3a (or edta) complexes (Table 3). We may thus conclude that on the pathway from hexadentate octahedral complexes with edta and edtp ligands to *cis*-equatorial pentadentate isomers, no significant change of complex geometry occurs. It should be mentioned, however, that as a result of bond cleavage, a new chiral center is created at N″ which for the Δ isomer has the (R) configuration.

As mentioned above, the investigated *cis*-polar isomer can formally be derived from the (*trans*(O_5O_6)-$[Rh(1,3\text{-pddadp})]^-$) isomer in which the M–O bond cleavage occurs in the β-alaninate R-ring. There are two independent sources of chirality in the two compounds. One is the configuration at the metal center (Δ, Λ), the other is the configuration at the nitrogen atoms (R, S). The *cis*-polar,*trans*(Cl,O_5)-$[Rh(1,3\text{-pddadp})Cl]^{2-}$ pentadentate complex having Δ configuration can be considered as being derived from its hexadentate analog of the same Δ configuration. However, while in the parent compound the Δ configuration is accompanied by the R, S configuration at N1 and N2, respectively, in its pentadentate analog it is accompanied by the same (R, R) configuration at the two nitrogen atoms. Hence, the investigated *cis*-polar isomer cannot be directly derived from *trans*(O_5O_6)-$[Rh(1,3\text{-pddadp})]^-$ by simple bond rupture in the β-alaninato R-ring and subsequent replacement of the chelate by the chloride ligand, but requires an inversion of configuration at the N(2) nitrogen atom. Besides the fact that the hypothetical M–O bond cleavage that would lead to the *cis*-polar isomer imposes a change of configuration at the nitrogen atom carrying the uncoordinated propionate arm, it also affects the conformation of the two rings to which this nitrogen atom belongs. This can be readily seen from Table 2 by comparing the values of the endocyclic torsion angles and Cremer and Pople puckering parameters [37] for the T and G″ rings, and is also clearly demonstrated in Fig. 2. We may thus conclude that, contrary to the situation observed for *cis*-equatorial isomers, the hypothetical M–O bond rupture leading to the formation of the *cis*-polar isomer from its hexadentate congener, would have to be accompanied by significant structural changes within the complex anion.

Crystal structures of chromium(III) complexes with ed3p [14] and 1,2-pd3p ligands [10] provide information about the structure of the *trans*-equatorial isomers. It has been suggested [10] that these isomers result from the C–N bond cleavage in the β-alaninate R-ring, which leads to the *cis*-polar isomer, and subsequent interchange of the coordination site between the propionate arm of the G-ring on the three-ring amine and the solvent ligand. Compared with its hexadentate congener (Table 4), the *trans*-equatorial isomer lacks chirality at the metal center but gains chirality at the two-ring nitrogen (N″). For the isomer with (R) configuration at N″, the conformation of the E-ring is δ and the ethylenic gauche conformation of the propionato G″ ring is λ. This is contrasted with the *cis*-equatorial isomer [11] in which the (R) configuration at N″ corresponds to λ

Table 3
Average values of torsion angles and sums of the chelate ring bond angles (°) in pentadentate complexes of Rh(III), Ru(III), Cr(III) and Co(III) with diaminopolycarboxylato ligands

Complex	Ring (size)	Conformation	$\lvert\omega\rvert$[a]	Bond-angles sum[b]	Av. ΔO_h	Reference
cis-polar,*trans*(Cl,O$_5$)-[Rh(1,3-pddadp)(Cl)]$^{2-}$	R′ (5)	*flat*	8.9	538.2	4.9	This work
	T (6)	*chair*	55.2	666.8		
	G′ (6)	*sofa*	33.3	686.0		
	G″ (5)	*envelope*	22.1	527.5		
cis-eq-[Rh(Hedta)(H$_2$O)]	R′ (5)	*envelope*	11.1	537.2	4.7	[36]
	R″ (5)	*flat*	6.5	539.0		
	E (5)	*twist*	33.6	514.7		
	G′ (5)	*envelope*	26.4	522.5		
cis-eq-K[Ru(Hedta)(Cl)] · 2H$_2$O	R′ (5)	*flat*	8.1	538.6	5.3	[39]
	R″ (5)	*envelope*	16.7	533.2		
	E (5)	*envelope*	31.6	516.8		
	G′ (5)	*envelope*	23.5	525.8		
cis-eq-NH$_4$[Ru(Hedta)Cl] · 2H$_2$O	R′ (5)	*flat*	8.7	525.4	5.4	[40]
	R″ (5)	*envelope*	16.5	533.3		
	E (5)	*envelope*	31.6	517.2		
	G′ (5)	*envelope*	24.0	525.4		
cis-eq-K[Ru(1,2-Hpdta)Cl] · 0.5H$_2$O[c]	R′ (5)	*flat*	5.7	539.3	5.1	[39]
	R″ (5)	*envelope*	14.4	535.2		
	E (5)	*twist*	32.8	515.2		
	G′ (5)	*envelope*	21.0	529.5		
cis-eq-[Cr(ed3a)(H$_2$O)]	R′ (5)	*flat*	7.1	538.9	5.1	[13]
	R″ (5)	*envelope*	15.7	534.5		
	E (5)	*twist*	31.8	517.4		
	G′ (5)	*envelope*	23.6	526.7		
NH$_4$*cis*-eq-[Co(ed3a)(CN)] · H$_2$O · 0.5CH$_3$OH	R′ (5)	*flat*	6.4	539.1	3.1	[41]
	R″ (5)	*envelope*	16.5	533.2		
	E (5)	*twist*	31.4	517.7		
	G′ (5)	*twist*	24.8	525.6		
K(-)-*cis*-eq-[Co(hed3a)(CN)] · 1.5H$_2$O[d]	R′ (5)	*flat*	5.1	539.4	3.4	[9]
	R″ (5)	*intermediate*	17.4	532.7		
	E (5)	*twist*	32.2	516.3		
	G′ (5)	*twist*	23.7	527.1		
cis-eq-[Cr(Hedtp)(H$_2$O)] · 5H$_2$O	R′ (6)	*twist-boat*	33.5	687.9	2.6	[11]
	R″ (6)	*twist-boat*	36.2	676.7		
	E (5)	*twist*	32.5	511.9		
	G′ (6)	*chair*	38.6	686.0		

trans-eq-[Cr(ed3p)(H_2O)]	R′ (6)	*sofa*	29.9	691.1	2.4	[13,14]
	R′ (6)	*chair*	39.5	686.7		
	E (5)	*envelope*	28.4	520.8		
	G″ (6)	*half-chair*	36.9	687.4		
trans-eq-[Cr{(S)-1,2-pd3p}(H_2O)]	R′ (6)	*sofa*	30.2	691.1	2.2	[10]
	R′ (6)	*1,3-diplanar*	31.8	687.3		
	E (5)	*envelope*	27.2	522.5		
	G″ (6)	*sofa*	34.9	687.2		
trans-eq-[Cr{(S)-1,2-pd3p}(H_2O)]	R′ (6)	*sofa*	30.3	690.7	3.0	[10]
	R′ (6)	*1,3-diplanar*	33.0	691.9		
	E (5)	*envelope*	28.3	520.9		
	G″ (6)	*sofa*	34.6	684.5		

[a] $|\omega|$ = Average torsion angle magnitude.

[b] Ideal values: 528.0° and 637.5° for the five- and six-membered diamine ring, respectively, and 538.5° and 648.0° for the five- and six-membered carboxylate ring, respectively.

[c] 1,2-Hpdta = 1,2-propanediamine-*N*,*N*,*N*′-triacetate-*N*′–acetic acid.

[d] hed3a = *N*-(Hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetate.

conformation of the E-ring and δ conformation of the ethylenic C–C bonds in the G′ ring (Table 4). The R rings in the *trans*-equatorial isomer are both attached to the same three-ring nitrogen (N′) and have nearly enantiomeric conformations (δ, λ), as evident by comparing the torsion angle signs listed in Table 4. The geminal R rings belong to the rigid chair family of conformers (flattened around the carboxylate), while the R rings in the parent hexadenate [Cr(edtp)]$^-$ complex (connected to different nitrogens) display flexible *twist-boat* conformations. The diamine chelates in *trans*-equatorial isomers are significantly less puckered than those in the *cis*-equatorial isomers (Tables 3 and 4), independent of whether the latter ones are derived from edta or edtp type of ligands. Moreover, the degree of puckering of both R rings and G rings in pentadentate edtp isomers is comparable while in the *cis*-equatorial edta isomers the R-rings are always significantly flatter.

3.3. Electronic absorption spectra

The electronic absorption spectrum of the *cis*-polar,*trans*(Cl,O_5)-Na_2[Rh(1,3-pddadp)Cl] with pentadentate coordination of the 1,3-pddadp ligand is given in Fig. 5. This spectrum has been compared with the corresponding spectra for *trans*(O_5) and *trans*(O_5O_6) geometrical isomers of [Rh(1,3-pddadp)]$^-$ in which 1,3-pddadp acts as a hexadentate ligand. In our previous work, the electronic absorption spectra of the latter two complexes have been discussed in detail [26] and here they have only been repeated for the sake of comparison with the spectrum of the corresponding pentadentate complex. The shape of the electronic spectrum of *cis*-polar,*trans*(Cl,O_5)-[Rh(1,3-pddadp)Cl]$^{2-}$ is different from those for *trans*(O_5) and *trans*(O_5O_6) geometrical isomers of [Rh(1,3-pddadp)]$^-$; see Fig. 5. Both absorption maxima of the pentadentate rhodium(III) complex are significantly shifted to lower energy. It can also be seen that the electronic absorption spectrum of the examined Rh(III) complex shows a lower intensity of the first, as well as a slight splitting in the region of the second absorption maximum. These differences can be attributed to the fact that the *cis*-polar,*trans*(Cl,O_5)-[Rh(1,3-pddadp)Cl]$^{2-}$ isomer with a five-coordinated 1,3-pddadp ligand and a ring-opened 3-propionate arm in the axial position constitutes a less strained system than the other two geometrical isomers of the hexadentate [Rh(1,3-pddadp)]$^-$ complex. The presence of such strain in hexadentate complexes manifests itself in shortening of the Rh–N bonds to values comparable with, or smaller than, the equatorial Rh–O bonds. This contraction of the Rh–N bond lengths has not been observed in the *cis*-polar complex and, consequently, the average value of the Rh–N bond distances (2.079 Å) in this complex is by 0.04 Å greater than the average value of the equatorial Rh–O bond lengths (2.038 Å). The absence of the Rh–N

Table 4
Endocyclic torsion angles (°) in Cr(III) complexes with edtp and ed3p type ligands[a]

Ring (size) Torsion angle	Hexadentate	Pentadentate						
		cis-equatorial	*trans*-equatorial					
	Δ [Cr(edtp)]⁻ [21]	Δ, N″(R)[b] $[Cr(Hedtp)(H_2O)]$ [11]	N″(R)[b] $[Cr(ed3p)(H_2O)]$ [13,14]		N″(R) $[Cr\{(S)\text{-}1,2\text{-}pd3p\}(H_2O)]$[c] [10]			
R′ (6)								
	λ	*λ*	*λ*	*δ*	*λ*	*δ*	*λ*	*δ*
Cr–N′–C_α–C_β	28.4	30.4	63.8	−60.6	62.8	−66.9	64.7	−57.6
N′–C_α–C_β–C_γ	−65.0	−62.5	−63.0	61.5	−58.4	53.5	−54.4	63.2
C_α–C_β–C_γ–O	45.6	37.0	35.0	−25.3	18.4	−4.7	10.2	−33.6
C_β–C_γ–O–Cr	9.2	19.1	−20.0	−3.0	8.6	−23.6	15.5	9.2
C_γ–O–Cr–N′	−35.1	−39.9	19.4	0.6	−1.7	7.5	−3.5	−6.9
O–Cr–N′–C_α	12.7	12.0	−35.8	28.8	−31.2	34.7	−33.3	27.6
R″ (6)								
	λ	*λ*						
Cr–N″–C_α–C_β	32.9	38.1						
N″–C_α–C_β–C_γ	−65.5	−75.7						
C_α–C_β–C_γ–O	43.0	51.4						
C_β–C_γ–O–Cr	11.6	8.6						
C_γ–O–Cr–N′	−34.2	−34.9						
O–Cr–N′–C_α	8.7	8.2						
E (5)								
	λ	*λ*	*δ*		*δ*		*δ*	
Cr–N′–C_α–C_β	43.3	42.2	−21.7		−25.1		−22.7	
N′–Cα–C_β–N″	−60.5	−61.6	45.1		45.0		45.1	
C_α–C_β–N″–Cr	42.5	43.8	−45.6		−41.9		−44.6	
C_β–N″–Cr–N′	−14.6	−16.2	26.9		22.9		26.8	
N″–Cr–N′–C_α	−15.8	−13.6	−2.6		1.0		−2.2	
G′ (6)								
	δ	*δ*						
Cr–N′–C_α–C_β	−69.8	−66.6						
N′–C_α–C_β–C_γ	46.9	52.2						
C_α–C_β–C_γ–O	−2.0	−22.0						
C_β–C_γ–O–Cr	−10.4	16.5						
C_γ–O–Cr–N′	−11.4	−27.1						
O–Cr–N′–C_α	47.3	47.1						
G″ (6)								
	δ		*λ*		*λ*		*λ*	
Cr–N″–C_α–C_β	−65.6		57.1		60.7		62.6	
N″–C_α–C_β–C_γ	44.1		−67.2		−65.6		−67.7	
C_α–C_β–C_γ–O	−7.8		44.3		37.9		26.2	
C_β–C_γ–O–Cr	2.9		−17.2		−9.9		13.4	
C_γ–O–Cr–N″	−21.5		8.6		5.5		−12.3	
O–Cr–N″–C_α	48.9		−27.1		−29.9		−25.5	

[a] Symbols Δ, (R) and (S) describe chirality of the presented enantiomorph, and *λ* and *δ* the ethylenic gauche conformation of the chelate rings.

[b] Original coordinates correspond to enantiomeric structures.

[c] Two independent molecules.

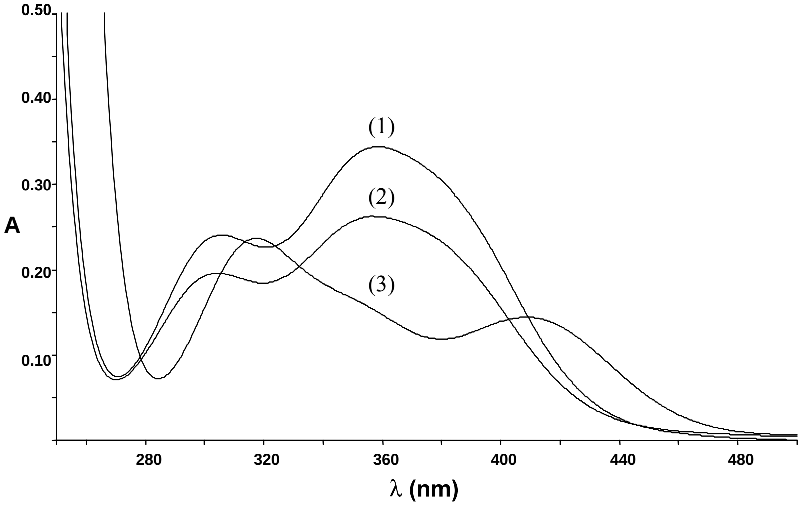


Fig. 5. Electronic absorption spectra of Rh(III) complexes: (1) *trans*(O_5O_6)-Na[Rh(1,3- pddadp)] · 3H_2O, (2) *trans*(O_5)-Na[Rh(1,3-pddadp)] · H_2O, (3) *cis*-polar,*trans*(Cl,O_5)-Na_2[Rh(1,3-pddadp)Cl] · 7H_2O.

bonds contraction combined with the fact that the axial Rh–Cl bond (2.338(2) Å) in the *cis*-polar complex is significantly longer than all other metal–ligand bonds found in [Rh(edta-type)]$^-$ complexes may indicate the lower ligand field strength in the *cis*-polar complex as compared with the other two hexadentate [Rh(1,3-pddadp)]$^-$ complexes. Recently, the electronic absorption spectra of hexadentate cobalt(III) complexes with edta and edta-related ligands, ed3ap, eddadp, eda3p and edtp, have been investigated [45]. These spectra showed significant shifting of the first absorption maxima to the lower energy field upon introduction of a less-strained six-membered chelate ring into the octahedral cobalt(III) system. By analogy, the observed shift of both absorption maxima of the *cis*-polar,*trans*(Cl,O_5)-[Rh(1,3-pddadp)Cl]$^{2-}$ complex to the lower energy field (in relation to those for the corresponding hexadentate [Rh(1,3-pddadp)]$^-$ complexes) may be interpreted as resulting from the release of its ring strain. Additionally, the mixed N_2O_3Cl ligand field arrangement around the Rh(III) center in [Rh(1,3-pddadp)Cl]$^{2-}$ and the lower symmetry of this complex should also be considered in explanation of the differences in shape of the above-mentioned electronic spectra.

4. General conclusions

This study contributes to a better understanding of very complicated coordination chemistry of metal ions with hexadentate aminopolicarboxylate edta-type ligands having mixed acetate and 3-propionate carboxylate arms. The coordination chemistry of these ligands is particularly very complicated if their pentadentate coordination mode is present in octahedral geometry. In this study, the *cis*-polar,*trans*(Cl,O_5)-[Rh(1,3-pddadp)Cl]$^{2-}$ isomer has been characterized. This isomer is one of the 10 theoretically possible geometrical isomers of the octahedral pentadentate [Rh(1,3-pddadp)Cl]$^{2-}$ complex that can be derived directly from the *trans*(O_5O_6) isomer of the corresponding hexadentate [Rh(1,3-pddadp)]$^-$ complex. To the best of our knowledge, among the metal complexes with edta-type ligands having mixed five and six-membered carboxylate chelate rings, this isomer is the first octahedral pentadentate complex for which the crystal structure has been reported and it is the only *cis*-polar isomer among the edta-type complexes ever deposited in the CSD [1]. Weaker metal–ligand interactions in the investigated isomer as compared with those in the hexadentate *trans*(O_5)-[Rh(1,3-pddadp)]$^-$ and *trans*(O_5O_6)-[Rh(1,3-pddadp)]$^-$ complexes are reflected in their electronic absorption spectra.

5. Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk), quoting the deposition number CCDC 155912.

Acknowledgements

The authors M.I.D., D.D.R. and M.M.V. are grateful to the Ministry of Science, Technologies and

Development of the Republic of Serbia for the financial support (Projects No. 1254 and No. 1569).

References

[1] F.H. Allen, O. Kennard, Chem. Des. Autom. News 8 (1993) 1, 31.
[2] H.A. Weakliem, J.L. Hoard, J. Am. Chem. Soc. 81 (1959) 549.
[3] H. Ogino, M. Shimura, Adv. Inorg. Bioinorg. Mech. 4 (1986) 107.
[4] C.W. Maricondi, C. Maricondi, Inorg. Chem. 13 (1974) 1110.
[5] D.E. Bause, C.A. Chang, B.E. Douglas, J. Coord. Chem. 6 (1979) 211.
[6] O.W. Howarth, P. Moore, N. Winterton, Inorg. Nucl. Chem. Lett. 10 (1974) 553.
[7] C.W. Van Saun, B.E. Douglas, Inorg. Chem. 7 (1968) 1393.
[8] C.W. Maricondi, C. Maricondi, Inorg. Chem. 12 (1973) 1524.
[9] D.J. Radanović, S.R. Trifunović, D.E. Bause, C. Maricondi, J.E. Abola, B.E. Douglas, Inorg. Chem. 26 (1987) 3994.
[10] N. Sakagami, S. Kaizaki, J. Chem. Soc., Dalton Trans. (1992) 291.
[11] N. Sakagami, S. Kaizaki, Inorg. Chim. Acta 195 (1992) 187.
[12] S. Grubišić, M. Gruden, S.R. Niketić, N. Sakagami-Yoshida, S. Kaizaki, J. Mol. Struct. 609 (2002) 1.
[13] N. Sakagami, Ph. D. Thesis, Osaka University, 1993.
[14] S. Grubišić, M. Gruden, S.R. Niketić, N. Sakagami-Yoshida, S. Kaizaki, Transition Met. Chem. 28 (2003) 37.
[15] T. Mizuta, T. Yamamoto, N. Shibata, K. Miyoshi, Inorg. Chim. Acta 169 (1990) 257.
[16] R. Herak, L.J. Manojlović-Muir, M.I. Djuran, D.J. Radanović, J. Chem. Soc., Dalton Trans. (1985) 861.
[17] F.T. Helm, W.H. Watson, D.J. Radanović, B.E. Douglas, Inorg. Chem. 16 (1977) 2351.
[18] T. Yamamoto, K. Mikata, K. Miyoshi, H. Yoneda, Inorg. Chim. Acta 150 (1988) 237.
[19] K. Kanamori, J. Kumada, M. Yamamoto, T. Okayasu, K. Okamoto, Bull. Chem. Soc. Jpn. 68 (1995) 3445.
[20] D.J. Radanović, S. Ianelli, G. Pelosi, Z.D. Matović, S. Tasić-Stojanović, B.E. Douglas, Inorg. Chim. Acta 278 (1998) 66.
[21] M. Parvez, C. Maricondi, D.J. Radanović, M.I. Djuran, B.E. Douglas, Inorg. Chim. Acta 182 (1991) 177.
[22] S. Kaizaki, M. Byakuno, M. Hayashi, J.I. Legg, K. Umakoshi, S. Ooi, Inorg. Chem. 26 (1987) 2395.
[23] D.J. Radanović, S.R. Trifunović, M.S. Cvijović, C. Maricondi, B.E. Douglas, Inorg. Chim. Acta 196 (1992) 161.
[24] M. Parvez, C. Maricondi, D.J. Radanović, S.R. Trifunović, V.D. Miletić, B.E. Douglas, Inorg. Chim. Acta 248 (1996) 89.
[25] D.J. Radanović, M.I. Djuran, T.S. Kostić, B.E. Douglas, Inorg. Chim. Acta 211 (1993) 149.
[26] U. Rychlewska, M.I. Djuran, M.M. Vasojević, D.D. Radanović, V.M. Ristanović, D.J. Radanović, Inorg. Chim. Acta 328 (2002) 218.
[27] Z.D. Matović, S. Ianelli, G. Pelosi, S.K. Janiæijević, V.M. Ristanović, G. Ponticelli, D.J. Radanović, Polyhedron 21 (2002) 2667.
[28] D.J. Radanović, K.D. Gailey, M.I. Djuran, B.E. Douglas, J. Coord. Chem. 10 (1980) 115.
[29] D.J. Radanoviæ, M.I. Djuran, K.D. Gailey, B.E. Douglas, J. Coord. Chem. 11 (1982) 247.
[30] S. Kaizaki, M. Hayashi, J. Chem. Soc., Chem. Commun. (1988) 613.
[31] N. Sakagami, M. Hayashi, S. Kaizaki, J. Chem. Soc., Dalton Trans. (1992) 285.
[32] KM4CCD Software. Version 1.163 KUMA Diffraction, Wroclaw, Poland, 1999.
[33] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.
[34] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
[35] Stereochemical Workstation Operation Manual, Release 3.4. Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1989.
[36] G.H.Y. Lin, J.D. Leggett, R.M. Wing, Acta Crystallogr., Sect. B 29 (1973) 1023.
[37] D. Cremer, J.A. Pople, J. Am. Chem. Soc. 97 (1975) 1354.
[38] R. Herak, G. Srdanov, M.I. Djuran, D.J. Radanović, M. Bruvo, Inorg. Chim. Acta 83 (1984) 55.
[39] M.M.T. Khan, D. Chatterjee, R.R. Merchant, P. Paul, S.H.R. Abdi, D. Srinivas, M.R.H. Siddiqui, M.A. Moiz, M.M. Bhadbhade, K. Venkatasubramanian, Inorg. Chem. 31 (1992) 2711.
[40] J. Jolley, C.J. Campbell, A. Castineiras, A.I. Yanovsky, K.B. Nolan, Polyhedron 18 (1999) 49.
[41] C. Maricondi, S. Utsuno, D.J. Radanović, S.R. Trifunović, J.E. Abola, B.E. Douglas, Inorg. Chim. Acta 142 (1988) 135.
[42] K.I. Okamoto, T. Tsukihara, J. Hidaka, Y. Shimura, Bull. Chem. Soc. Jpn. 51 (1978) 3534.
[43] R.M.L. Warren, K.J. Haller, A. Tatehata, A.G. Lappin, Inorg. Chem. 33 (1994) 227.
[44] L.A. Zasurskaya, A.L. Pozdnyak, T.N. Polynova, V.B. Rybakov, M.A. Porai-Koshits, Zh. Neorg. Khim. 41 (1996) 1647.
[45] D.J. Radanović, M.I. Djuran, T.S. Kostić, C. Maricondi, B.E. Douglas, Inorg. Chim. Acta 207 (1993) 111.