

# Structural and theoretical investigations of the Rh(III) and Co(III) complexes containing symmetrical edta-type ligands with mixed carboxylate and diamine rings: Quantum-mechanical/NBO insight into stability of geometrical isomers

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## ABSTRACT

The *trans*(O<sub>5</sub>O<sub>6</sub>) isomer of the Na[Rh(eddadp)]·4H<sub>2</sub>O and the K[Co(eddadp)]·3H<sub>2</sub>O (eddadp = ethylenediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate) were synthesized and Na[Rh(eddadp)]·4H<sub>2</sub>O structure was confirmed by X-ray diffraction analysis. The percentage of particular isomers found in reaction equilibrium mixtures of [M(eddadp)]<sup>−</sup> complex has been reported. Single crystal X-ray diffraction of the complex revealed an octahedral geometry of the Rh(III) centre. Improved structural distortion analysis of M(III) (M = Rh, Co) complexes with symmetric edta-type of ligands containing mixed carboxylate and diamine rings was made. Structural distortion analysis has determined high values of total deviation of the octahedral angles ( $\Delta(O_h)$ ) for both existing *trans*(O<sub>5</sub>) (34°) and *trans*(O<sub>5</sub>O<sub>6</sub>) (41°) isomers of [Rh(eddadp)]<sup>−</sup> complex, while in the case of a similar Co(III) complex, relatively low value (31°) for *trans*(O<sub>5</sub>) has been established. Extensive QM/NBO calculations were made for both systems [M(eddadp)]<sup>−</sup> and [M(1,3-pddadp)]<sup>−</sup> using different DFT methods (B3LYP/SDD, M06/SDD, MP2/SDD). By correlating the structural parameters obtained from X-ray and DFT optimized 3D structures, the B3LYP/SDD method was used as the method of choice. Based on the correlation between the energies of the optimized systems and the strain parameters, the existence of the *trans*(O<sub>6</sub>) isomer of the [Rh(1,3-pddadp)]<sup>−</sup> complex was predicted. NRT (Natural Resonance Theory) analysis gave the best resonances for each isomer. Here the stability of particular isomer has been described in terms of 3-CHB bonds involving metal ions and Second Order Perturbation Theory analysis using Donor/Acceptor energies. Further, to explain the bonding nature of M-edta-type complexes the Natural Coulomb Electrostatics (NCE) analysis has been done as well. The pairwise steric exchange interaction  $E_{ij}^{P_{\text{max}}}$  results obtained for the best-ranked resonances of different isomers are in excellent agreement with favored isomers reported so far. For the energy limit of the possibility of forming geometric isomers, a value of about 6 kcal mol<sup>−1</sup> is proposed.

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## 1. Introduction

The cobalt(III) and rhodium(III) and their coordination chemistry have been extensively investigated for many decades. Special attention is devoted to its complexes with edta-type ligands (edta = ethylenediamine-*N,N,N',N'*-tetraacetate) which are largely studied [1–11]. Polyaminopolycarboxylate chelate ligands have a wide application in coordination chemistry. Metal complexes with

these ligands are used in environmental field [12–14], laboratory settings [15,16], industrial processes [17–19], biological systems [20–23], in medicine [24–31]. Of all known chelators, edta is the most commonly used [32–38]. Edta and similar ligands are used to remove heavy metals from the soil and water [39,40], as well as from the human body [41], as antioxidants for food preservation [42]. [M(edta-type)] complexes usually exist as biological redox reagents and there is a series of such complexes (M = Al, Sc, V-Co) [43].

In the case of edta-type ligands with variations in the length of the carboxylate chains, the eddadp (ethylenediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate) is one of the most distinguished [2,6].

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When the eddadh is found in a coordinated form attached to the central metal ion, it consists of 5 chelate rings: three five-membered (one ethylenediamine and two acetates) and two six-membered propionate rings. Depending on which type of ring is located in-plane (G) and out-plane (R), three geometric isomers are possible:  $trans(O_5)$ ,  $trans(O_5O_6)$  and  $trans(O_6)$ , where  $O_5$  and  $O_6$  relate to the five-membered and six-membered ring. (Fig. 1). The literature data show that the  $trans(O_5)$  isomer of eddadh is the most stable and favored in relation to the remaining two [2c,44–48]. Also,  $trans(O_5O_6)$  isomer for Rh(III) [2a] and Co(III) [6b] were obtained, but their X-ray structures were not confirmed until now, while the  $trans(O_6)$  isomer is obtained only in the case of heptacoordinated Ti(III) [49]. This outcome can be explained by the high strain in the equatorial plane at the  $trans(O_6)$  isomer because the in-plane 5-5-5 arrangement of the rings makes the acetate rings more strained than the propionic ones. The six-membered propionate rings serve better for the formation of the less-strained G rings favoring the  $trans(O_5)$  isomers of  $[M(\text{eddadh})]^-$  complexes, with 6-5-6 in-plane arrangement of rings.

Contrary to this, when it comes to the 1,3-pddadh (1,3-propanediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate ion) ligand, the dominant isomer was found to be  $trans(O_6)$  for Cr(III) [50], Co(III) [9a] and Cu(II) [51], while  $trans(O_5O_6)$  is isolated and X-ray confirmed in case of Rh(III) [5b] and Co(III) [9b]. Surprisingly, the less expected  $trans(O_5)$  isomer was isolated and its 3D structure confirmed for Rh(III) [5b] and Ni(II) [52]. The explanation for such a behavior is based on the size of a central metal ion that grows in the following order: Co(III) < Fe(III) < Cr(III) < Rh(III) < Ni(II) < Cu(II). The formation of  $trans(O_5)$  isomer is accompanied by the presence of the various strain in the G plane as well.

In addition, DFT (Density Functional Theory) methods have been used for the purpose of energetic and structural comparison and analysis [1b]. Unfortunately, most of the data obtained in this way were just tabulated usually without any practical purpose. We tried to compare energies and plot them against common structural features responsible for the complex stability and consequently for their possible co-existence in solution. That means we tried to select the best DFT method among several the most used and correlate such isomer energies with strain parameters in order to predict existence and possibility of isolation or exclude any chance for isomer to be formed in the usual way of preparation.

From the above, we may see that in the case of the complex  $[M(\text{eddadh})]^-$  the  $trans(O_5O_6)$  isomer has been prepared but never isolated in the crystal form suitable for X-ray analysis. Accordingly, there is no data on the 3D structure of such complexes with any metal. Therefore, the aim of this paper is to prepare and try to isolate the crystals of the mentioned isomer in the case of Co(III) and Rh(III) in order to evaluate its structural parameters. This means

that we might be able more reliable to discuss the structure and energetic dependence. This paper deals with structural parameters and strain analysis data of this and similar complexes of known structures that are discussed in relation to the structure of the ligand, geometry of complexes, octahedral distortion and their mutual energetic dependence (DFT-NBO). What was not our goal in this paper is to monitor the distribution of geometric isomers depending on the reaction conditions. We have tried to produce a thermodynamic equilibrium of final isomer mixtures (for both reactions involving both metallic ions with the  $H_4\text{eddadh}$  ligand). In addition, X-ray diffraction analysis performed on  $trans(O_5O_6)$ - $[Rh(\text{eddadh})]^-$  ion served for a better structural description of analogous of this kind of complexes.

## 2. Experimental section

### 2.1. Chemicals and physical measurements

All chemicals were purchased from Sigma-Aldrich and were used without any further purification.  $H_4\text{eddadh}$  was prepared using a previously described procedure [6a]. Elemental (C, H, N) analysis of the sample was carried out in the Center for Instrumental Analysis, Faculty of Chemistry, Belgrade. IR spectra (in KBr pellets) were recorded on a Perkin Elmer FT-IR spectrophotometer SpectrumOne. Electronic absorption spectra were obtained using a double beam UV-Vis spectrophotometer model Cary 300 (Agilent Technologies, Santa Clara, USA) with 1.0 cm quartz cells. NMR spectra were performed at 25 °C in  $D_2O$  with TSP as the internal standard using a Varian Gemini 200 MHz NMR spectrometer ( $^1H$  at 200 and  $^{13}C$  at 50 MHz).

### 2.2. Syntheses

#### 2.2.1. Synthesis of the $trans(O_5O_6)$ - $Na[Rh(\text{eddadh})]\cdot 4H_2O$ (1)

The complex was prepared by the previously reported procedure [2b].  $RhCl_3\cdot 3H_2O$  (1.32 g, 5 mmol) was dissolved in 1 mL of water in a Pyrex tube. To this mixture, a solution obtained by dissolving 1.6 g (5 mmol)  $H_4\text{eddadh}$  in 5 mL 4 M of NaOH (20 mmol) was added, the tube sealed and the mixture heated at 145 °C on an oil-bath for 7 h. After cooling to room temperature, the tube was chilled in ice and opened carefully. The yellow solution (pH = 4) was filtered off and a little rhodium metal removed. The exact portion of filtrate was then introduced into a column containing Sephadex QAE A-25 anion exchange resin in the  $Cl^-$  form. After the column was washed with  $H_2O$ , 0.1 M NaCl solution was used for elution (ca. 0.5 mL  $min^{-1}$ ).

After elution with 0.1 M NaCl, two yellow bands were detected on the chromatographic column. Both bands were evaporated, desalted using Sephadex G-10 resin and evaporated again to ca.

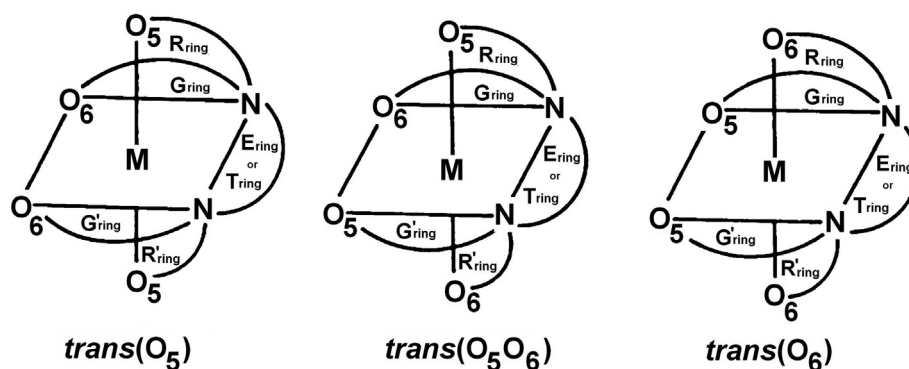


Fig. 1. Geometrical isomerism of six-coordinate  $[M(\text{eddadh})]^-$  and  $[M(1,3\text{-pddadh})]^-$  complexes.

3 mL. After addition of 2–3 mL of ethanol, the solutions were left in a refrigerator for two days. The first band represents the *trans*(O<sub>5</sub>)-[Rh(eddadp)]<sup>-</sup> which is earlier synthesized with confirmed X-ray structure [2c]. The yellow crystals of the second band were collected, washed with ethanol and air-dried. The last band, remaining on the top of the column was eluted with concentrated NaCl. This band is a mixture of different hydroxo species with charge higher than -2 [1].

Yield: 0.4 g (11.68%). Melting point: >305 °C (from ethanol). Anal. Calc. for C<sub>12</sub>H<sub>24</sub>N<sub>2</sub>O<sub>12</sub>RhNa (514.23 g mol<sup>-1</sup>): C, 28.03; H, 4.70; N, 5.45. Found: C, 28.30; H, 4.55; N, 5.60%. IR (KBr, ν<sub>max</sub> cm<sup>-1</sup>): 1573, 1625, 1641<sub>(sh)</sub>, 1667 ν(COO<sup>-</sup>). UV-Vis (H<sub>2</sub>O, c = 10<sup>-3</sup> M): λ<sub>max</sub> (ε) = 298<sub>(sh)</sub> (291 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>), 344 nm (519 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) and 380<sub>(sh)</sub> nm (319 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>). <sup>1</sup>H NMR δ (200 MHz, D<sub>2</sub>O, TSP): 3.92 (AB pattern, R ring), 3.92 (AB pattern, G ring); <sup>13</sup>C NMR δ (50 MHz, D<sub>2</sub>O, TSP): 186.64, 185.96, 183.45, 180.90 (C=O), 67.88, 66.20, 64.02, 62.83, 59.55, 58.79, 36.07 (CH<sub>2</sub>).

### 2.2.2. Synthesis of the *trans*(O<sub>5</sub>O<sub>6</sub>)-K[Co(eddadp)]·3H<sub>2</sub>O (2)

This complex was prepared by the previously reported procedure [6b].

H<sub>4</sub>eddadp, 4.8 g (15 mmol), was dissolved at 55° in 300 mL of water. To this solution, freshly prepared Na<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>], 6.06 g (15 mmol), in 10 mL of water was then added, and heating and stirring at the same temperature were continued for 3 h. After that, the temperature was increased to 85° for 5 h more. The resulting blue-violet solution (ca. 100 mL) was then introduced into a column containing Dowex 1-X8 (200–400 mesh) anion-exchange resin in the NO<sub>3</sub><sup>-</sup> form. The column was then washed with H<sub>2</sub>O and eluted with 0.1 M KNO<sub>3</sub> solution (ca. 0.5 mL min<sup>-1</sup>). Two similarly coloured bands, the first of which was blue-violet and the second violet, were obtained (ca. 4:1), in addition to a third, brown-violet, band which was more strongly bound to the column. The brown-violet band was eluted with 0.2 M KNO<sub>3</sub>. The first eluate (blue violet) was evaporated under vacuum at 50 °C to 30 mL and then cooled in a refrigerator for 2 h. The deposited KNO<sub>3</sub> was removed by filtration. To the filtrate was added 30 mL of ethanol, precipitating the complex. The complex was filtered off, washed with ethanol and then acetone, and air-dried; yield 3.0 g. This complex was recrystallized from a 1:1 water-ethanol mixture and identified by means of its electronic absorption spectrum as the earlier characterized *trans*(O<sub>5</sub>) geometrical isomer of K[Co(eddadp)]. The second eluate (violet) was evaporated under vacuum at 30° to a volume of 15 mL and then cooled. KNO<sub>3</sub> was removed and 20 mL of ethanol was added to the filtrate. A precipitate formed which was filtered off, and the solution was cooled again for 3 h. After removing some solid KNO<sub>3</sub>, 15 mL more of ethanol was added to the filtrate and the solution was left in the refrigerator to stand for 6 h to crystallize the second geometrical isomer of K[Co(eddadp)]. This complex was filtered, washed with acetone, and air-dried; yield 0.6 g. The isomer was recrystallized from water/ethanol mixture and identified by means of its electronic absorption spectrum as the earlier characterized *trans*(O<sub>5</sub>O<sub>6</sub>) geometrical isomer of K[Co(EDDDA)].

Unfortunately, after a number of attempts where we've changed a counter ion (Ba<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Li<sup>+</sup>, Na<sup>+</sup>) during column elution and crystallization solvent (methanol, ethanol, acetone-water, DMSO, etc.) we were unable to prepare a crystal of *trans*(O<sub>5</sub>O<sub>6</sub>) isomer suitable for X-ray analysis.

### 2.3. X-ray crystallographic analysis

Details of crystal data, data collection, and refinement for *trans*(O<sub>5</sub>O<sub>6</sub>)-Na[Rh(eddadp)]·4H<sub>2</sub>O are given in Table 1. Intensity data were collected using Mo Kα radiation (λ = 0.71073 Å) on a Bruker-Nonius KappaCCD diffractometer (graphite monochromator).

**Table 1**  
Selected crystallographic data for *trans*(O<sub>5</sub>O<sub>6</sub>)-Na[Rh(eddadp)]·4H<sub>2</sub>O.

<i>Crystal data</i>	
Empirical formula	C <sub>12</sub> H <sub>24</sub> N <sub>2</sub> O <sub>12</sub> RhNa
Formula weight	514.23
Radiation	Mo Kα (λ = 0.71073 Å)
Crystal system, space group	Triclinic, P $\bar{1}$
a, b, c (Å)	6.3075(3), 8.7637(8), 16.2724(12)
α, β, γ (°)	89.236(8), 89.299(6), 84.116(7)
V (Å <sup>3</sup> )	894.6(2)
Z	2
F(000)	524
D <sub>calc</sub> (Mg m <sup>-3</sup> )	1.909
Cell parameters from 102 reflections	
θ (°)	6.0–20.0
μ (mm <sup>-1</sup> )	1.05
T (K)	200
Crystal shape, color, size (mm)	Needle, yellow, 0.23 × 0.06 × 0.04
<i>Data collection</i>	
T <sub>min</sub> , T <sub>max</sub>	0.901, 0.959
No. of measured, independent and observed [I > 2σ(I)] reflections	23968, 4446, 4028
R <sub>int</sub>	0.029
θ values (°)	θ <sub>max</sub> = 28.3, θ <sub>min</sub> = 3.4
Index ranges	h = -8 → 8, k = -11 → 11, l = -21 → 21
<i>Refinement</i>	
Refinement method on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
R[F <sup>2</sup> > 2σ(F <sup>2</sup> ), wR(F <sup>2</sup> ), S	0.018, 0.042, 1.05
No. of reflections	4446
No. of parameters/restraints	325/8
Hydrogen site location	Difference Fourier map; Only H-atom coordinates refined
Weighting scheme	w = 1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> ) + (0.018P) <sup>2</sup> + 0.4755P], where P = (F <sub>o</sub> <sup>2</sup> + 2F <sub>c</sub> <sup>2</sup> )/3
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.43, -0.51

Data were corrected for Lorentz and polarization effects, semiempirical absorption corrections were performed on the basis of multiple scans using SADABS V2.06 [53]. The structure was solved by direct methods (SHELXTL NT 6.12) [54] and refined by full-matrix least-squares procedures on F<sup>2</sup> using SHELXL2016/6 [55]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were derived from a difference Fourier map and their positional parameters were refined. The isotropic displacement parameters of all H atoms were tied to those of their corresponding carrier atoms by a factor of 1.2 or 1.5. Fixed distance restraints were applied to the O–H bonds of the water molecules that coordinate to the Na<sup>+</sup> cation. Olex2 was used to prepare material for publication [56].

### 2.4. Isomer proportions in aqueous solution

The following procedure is in according to the earlier reported paper by Keene and Searle [57]. The filtrate from each preparation was diluted so that the concentration of the -1 anions was less than 0.1 M, and aliquots were applied to two columns (20 × 1 cm) of Sephadex QAE A-25 in the Cl<sup>-</sup> form (in case of Rh) or Dowex 1-X8 (200–400 mesh) in the NO<sub>3</sub><sup>-</sup> form (in case of Co). The absorbed complexes on each column were eluted with 0.1 M NaCl (in case of Rh) and 0.1 M KNO<sub>3</sub> (in case of Co) to separate the isomers *trans*(O<sub>5</sub>) (eluted first) and *trans*(O<sub>5</sub>O<sub>6</sub>) (eluted second). The separated bands were collected and subsequently made up to standard volumes (50 or 100 mL) in volumetric flasks. The solu-

tions were estimated by spectrophotometry in 1 cm quartz cells. The absorbances of the eluted isomer bands from each chromatographic separation were measured at the first and second band maximum for Rh (ca. 296 and 344 nm) and both bands maximum for Co (ca. 539 and 389 nm) on a double beam UV–Vis spectrophotometer model Cary 300 against water reference. The isomer percentage values given in Table 2 are the means from the duplicate separations for each run.

### 2.5. Computational details

Gaussian 09 D.01 program has been used for this part of the study [58]. Starting geometries were taken either from experimental X-ray structures or were modeled (Hyperchem MM+ [59], and the best hit from conformational search taken in order to pre-optimize them using the molecular mechanics and semi-empirical methods (MOPAC PM6 [60]). Obtained geometries were fully optimized using different QM methods: Møller–Plesset second-order perturbation theory (MP2) [61], M06 hybrid meta-exchange–correlation functional [62], as well as the standard Becke three-parameter exchange functional in conjunction with the Lee–Yang–Parr correlation hybrid functional (B3LYP) [63]. In all cases, the SDD basis set was used [64]. The systems were treated within the restricted formalism. All the calculations were performed with H<sub>2</sub>O as a solvent using the Polarizable Continuum Model (PCM) as implemented in Gaussian 09. Geometry optimizations were conducted without symmetry constraints. The minimum energy is achieved in all cases which were confirmed by the frequency calculations for each optimized structure. BSSE were not calculated as energy (E-E<sub>zero-point</sub>) values have been used just for comparison purpose between structurally same compounds. For further calculation of intra-molecular orbital interactions, we used NBO7.0 code [65].

## 3. Results and discussion

### 3.1. Synthesis of complexes and spectral analysis

The hexadentate H<sub>4</sub>eddp ligand was used for the synthesis of the *trans*(O<sub>5</sub>O<sub>6</sub>) complexes of Rh(III) and Co(III). The reactions of the equimolar amounts of RhCl<sub>3</sub>·3H<sub>2</sub>O and Na<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>] with H<sub>4</sub>eddp in the water at 145 °C and 85 °C, respectively, were carried out and column chromatography was used to separate isomers from the resulting mixture as described earlier [2,6b]. As expected, two bands in each case were obtained. The first band represents *trans*(O<sub>5</sub>) geometrical isomer of [M(eddp)]<sup>−</sup> complex, while the second band represents *trans*(O<sub>5</sub>O<sub>6</sub>) one.

Generally, preparation of trivalent transition metal (Cr(III), Co(III), Rh(III)) complexes with edta-type chelates starts from pure acid or a mixture of different acids. Further, reactants may involve metal salts (CrCl<sub>3</sub>, RhCl<sub>3</sub>, Co(CH<sub>3</sub>COO)<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub>) or

hydroxide (Co(OH)<sub>3</sub>, Rh(OH)<sub>3</sub>) or complex species [Co(NO<sub>2</sub>)<sub>6</sub>]<sup>3−</sup>. The distribution of geometric isomers depends both on the electronic configuration of the metal ion and on the configuration of edta-type ligands. The geometry of the complex and its structural parameters and octahedral distortion are usually mutually dependent. Certainly, a chemist may change the usual reaction conditions to contribute to the different distribution of isomers [57]. In addition, we used the procedure of Keen&Searle [57] to establish the thermodynamic equilibrium of reaction mixtures and therefore to determine the percentage contribution of each isomer (see Experimental). The UV–Vis spectrum of the thermodynamic mixtures and their double chromatogram picture are given in Fig. 2. Finally, the percentages of obtained isomers from the reaction mixture, in the case of studied complexes, is given in Table 2. These numbers from equilibrium determination follow in good order the quantities reported here and elsewhere (molar ratio). The absence of *trans*(O<sub>6</sub>) isomer in case of eddp and relative abundance of all 1,3-pdddp isomers (depending on the metal) are noticeable.

If the *trans*(O<sub>5</sub>) isomer is stabilized by the less equatorial strain with smaller Co(III) cation (Co(III) < Fe(III) < Cr(III) < Rh(III) < Ni(II) < Cu(II)), to an extent designated  $\Delta G_{trans(O_5)}^0$ , then it is clear that *trans*(O<sub>5</sub>O<sub>6</sub>) isomers is additionally stabilized with larger Rh(III) cation and higher reaction temperature (145 °C in case of Rh(III)) as their proportion increase relative to the *trans*(O<sub>5</sub>) form (see Table 2). This additional stabilization of the *trans*(O<sub>5</sub>O<sub>6</sub>) isomers can be evaluated from the isomer distributions:  $\Delta G_{Rh\_mix}^0 - \Delta G_{Co\_mix}^0 = -RT\ln(60/40) - RT\ln(79/21) = -1 \text{ kcal mol}^{-1}$ .

In the case of rhodium(III), the yellow crystals of *trans*(O<sub>5</sub>O<sub>6</sub>)-Na [Rh(eddp)]·4H<sub>2</sub>O were collected. Gailey et al. characterized the powder form of this complex in terms of <sup>1</sup>H, <sup>13</sup>C NMR and IR spectra [2a], as well as by UV–Vis and CD spectra [2b]. Despite that, in Experimental part, we gave the data sets of the IR, UV–Vis and NMR spectra that slightly differ from previously published. We believe this is because they relate to the crystalline and powder form that most probably include impurities. The IR spectrum shows three clearly defined bands at 1573, 1625 and 1667 cm<sup>−1</sup>, as well as one shoulder at 1641 cm<sup>−1</sup> (Fig. S1, Supplementary material), which confirms the *trans*(O<sub>5</sub>O<sub>6</sub>) geometry. The lack of other bands in the range 1700–1750 cm<sup>−1</sup> indicates that all the carboxylate groups are coordinated. The UV–Vis spectrum of *trans*(O<sub>5</sub>O<sub>6</sub>)-Na[Rh(eddp)]·4H<sub>2</sub>O is presented in Fig. S2 (Supplementary material). In addition, the shapes of *trans*(O<sub>5</sub>)-[Rh(eddp)]<sup>−</sup> [2b] and *trans*(O<sub>5</sub>O<sub>6</sub>)-[Rh(1,3-pdddp)]<sup>−</sup> [5b] are also presented for comparison purpose. The molar absorptivity, ε, are less (291, 519, 319) than previously reported (380, 565, 390) for *trans*(O<sub>5</sub>O<sub>6</sub>) complex in the form of powder [2b]. The NMR spectra obtained in D<sub>2</sub>O solution gave evidence of the structure of *trans*(O<sub>5</sub>O<sub>6</sub>)-Na[Rh(eddp)]·4H<sub>2</sub>O complex (Figs. S3 and S4, Supplementary material) and they are in accordance with published data [1,2,5]. There is nothing unusual which could be

**Table 2**  
Isomer ratio for [M(edta-type)]<sup>−</sup> complexes.

Ligand	eddp						Ref.	1,3-pdddp						
	<i>trans</i> (O <sub>5</sub> )		<i>trans</i> (O <sub>5</sub> O <sub>6</sub> )		<i>trans</i> (O <sub>6</sub> )			<i>trans</i> (O <sub>5</sub> )		<i>trans</i> (O <sub>5</sub> O <sub>6</sub> )		<i>trans</i> (O <sub>6</sub> )		Ref.
	mol <sup>a</sup>	% <sup>b</sup>	mol	%	mol	%		mol	% <sup>c</sup>	mol	%	mol	%	
Rh(III)	1.5		1		–		[2b]	1	40	1.5	60	–	0	[5b]
	2	60	1	40	–	0		This work						
Co(III)	6		1		–		[6b]	–	0	1	29	2.5	71	[9]
	5	79	1	21	–	0		This work						

<sup>a</sup> Molar ratio of precipitated isomers.

<sup>b</sup> Equilibrium geometric isomer percentages in preparations of [M(eddp)]<sup>−</sup> complexes at 85 °C (M = Co) and 145 °C (M = Rh).

<sup>c</sup> Geometric isomer percentages in preparations of [M(1,3-pdddp)]<sup>−</sup> complexes calculated from published data.

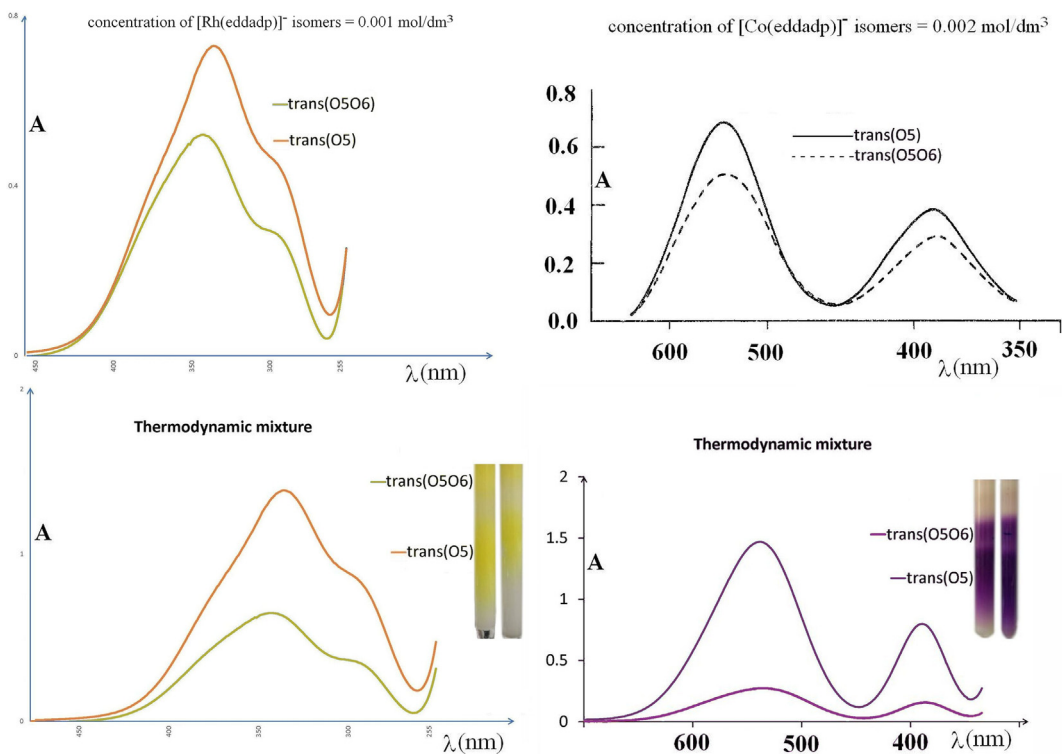


Fig. 2. UV-Vis spectra and double chromatograms of the thermodynamic mixture of  $[M(eddap)]^-$  isomers.

pointed out with spectral data (UV-Vis, NMR, IR) already reported for  $trans(O_5O_6)-K[Co(eddap)] \cdot 3H_2O$  compared to those already published by Radanović and Douglas for this complex [6b].

### 3.2. Description of the crystal structure of $trans(O_5O_6)-Na[Rh(eddap)] \cdot 4H_2O$

The molecular structure of  $trans(O_5O_6)-[Rh(eddap)]^-$  along with the packing in the crystals is illustrated in Fig. 3, while selected bond distances and angles are listed in Table 3.

The asymmetric unit contains one formula unit, comprising of three moieties: the negatively charged rhodium complex  $[Rh$

$(eddap)]^-$ , a  $Na^+$  ion coordinated to three water molecules, and one additional water molecule of crystallization. Therefore, the triclinic unit cell contains 6 units: two cations, two anions, and two water molecules. The two cationic species ( $Na^+$ ) are partially (triply) hydrated. The  $trans(O_5O_6)$  geometry of  $[Rh(eddap)]^-$  entity contains Rh(III) center in a well approximated octahedral geometry. The rhodium(III) ion coordinates six donor atoms from the ligand: four deprotonated carboxylic oxygens and two amine nitrogen atoms.

The equatorial positions of the octahedron are occupied by two deprotonated carboxylic oxygens (Rh–O3 2.053(1) Å, Rh–O7 2.053(2) Å) and the two nitrogen atoms of the ligand (Rh–N1 2.015(2) Å,

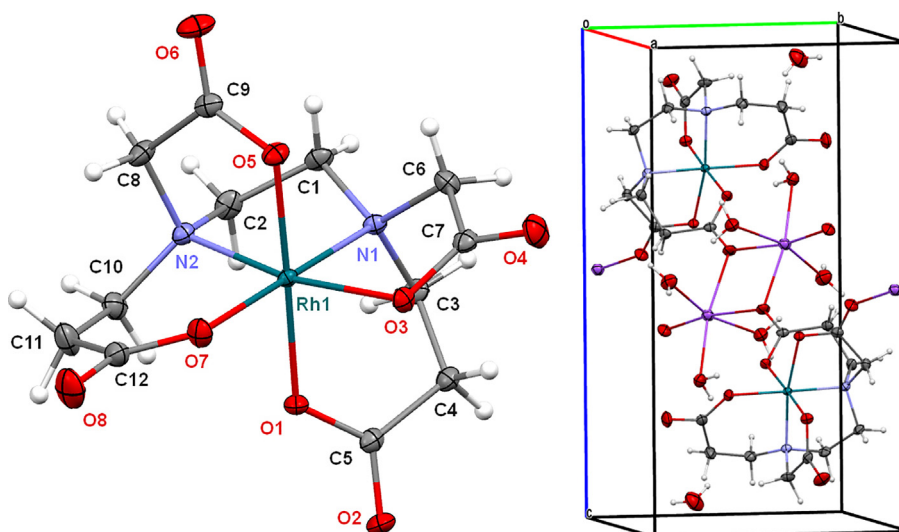


Fig. 3. Ortep diagram of the  $trans(O_5O_6)-[Rh(eddap)]^-$  complex anion and crystal packing view along  $a$  axis (50% probability ellipsoids).

**Table 3**  
Selected bond distances and angles for *trans*-(O<sub>5</sub>O<sub>6</sub>)-Na[Rh(eddap)]·4H<sub>2</sub>O.

M–L bond lengths (Å)		Valence angles (°)			
Rh(1)–O(1)	2.032(2)	O(1)–Rh(1)–O(3)	90.43(4)	N(1)–Rh(1)–O(5)	88.64(5)
Rh(1)–O(3)	2.053(1)	O(1)–Rh(1)–O(7)	86.48(4)	N(1)–Rh(1)–N(2)	89.16(5)
Rh(1)–O(5)	2.017(2)	O(5)–Rh(1)–O(3)	89.55(4)	N(2)–Rh(1)–O(1)	97.08(5)
Rh(1)–O(7)	2.053(2)	O(5)–Rh(1)–O(7)	91.27(4)	N(2)–Rh(1)–O(7)	91.89(5)
Rh(1)–N(1)	2.015(2)	O(5)–Rh(1)–N(2)	83.25(5)	N(2)–Rh(1)–O(3)	169.30(5)
Rh(1)–N(2)	2.026(2)	O(7)–Rh(1)–O(3)	96.19(4)	O(5)–Rh(1)–O(1)	177.73(4)
		N(1)–Rh(1)–O(1)	93.61(5)	N(1)–Rh(1)–O(7)	178.93(5)
		N(1)–Rh(1)–O(3)	82.74(5)		

Rh–N2 2.026(2) Å). The axial positions are occupied by two more oxygen donor atoms of the third and fourth carboxyl (Rh–O5 2.017(2) Å, Rh–O1 2.032(2) Å). The second oxygen atom of the propionic axial carboxylic group interacts with the sodium ion (O2–Na1 2.374(2) Å). The Rh–L bond distances and angles (Table 3) are comparable with the corresponding ones of analogous complexes [1–5]. The *cis* angles are in the range of 82.74(5)° to 97.08(5)° and the *trans* angles vary between 169.30(5)° and 178.93(5)°.

The ethylenediamine E ring is in a twisted conformation. The puckering parameters, which relate to deviations of the ring atoms from the mean plane, are  $q_2 = 0.461(2)$  Å and  $\varphi_2 = 264.9(1)^\circ$ . The ideal values for a twisted conformation are  $q_2 > 0$  Å,  $\varphi_2 = 90^\circ$  [66]. The two five-membered acetate rings adopted a twisted conformation. Their puckering parameters are  $q_2 = 0.242(1)$  Å,  $\varphi_2 = 129.3(3)^\circ$  (RhO5C9C8N2) and  $q_2 = 0.453(1)$  Å,  $\varphi_2 = 159.3(2)^\circ$  (RhO3C7C6N1). The equatorial six-membered propionate ring is in a twist-boat conformation (RhO7C12C11C10N2) with puckering parameters:  $q_2 = 0.419(2)$  Å,  $q_3 = -0.356(1)$  Å,  $\varphi_2 = 213.9(1)^\circ$ ,  $\theta = 130.4(2)^\circ$ . Also, the axial ring is in a twist-boat conformation (RhO1C5C4C3N2) and its puckering parameters are:  $q_2 = 0.679(1)$  Å,  $q_3 = 0.067(1)$  Å,  $\varphi_2 = 213.9(1)^\circ$ ,  $\theta = 84.4(1)^\circ$ .

Two centrosymmetric sodium ions are linked *via* O2 bridging carboxylate oxygen atoms of two neighboring complex units (that are also related by a crystallographic inversion centre). Together with an O4 carboxylate atom and three water molecules an approximated octahedral coordination geometry (Figs. 3 and S5, Supplementary material) around sodium is realized. Two water molecules occupy the axial positions, while one water molecule and three carboxylic oxygens are located on the equatorial plane.

### 3.3. Structural distortion analysis of [M(edta-type)]<sup>−</sup> complexes in relation to their geometry

Structural distortion analysis of [M(edta-type)]<sup>−</sup> complexes (M = Rh, Co) has been performed and discussed in detail. The structural data related to the stereochemistry of Rh(III) and Co(III) complexes are given in Table 4.

Grubišić et al. described the structural and molecular mechanics study of edta-type complexes of some divalent and trivalent metal ions [67]. However, the research has been structurally limited on 1,3-propanediamine backbone of edta-type ligands and use of molecular mechanics as a unique theoretical approach [67]. The Rh(III) and Co(III) ions adopted octahedral geometry with different degrees of distortion within the complexes depending on the arrangement of the carboxylate ring in the equatorial plane. As expected, the total deviation of the octahedral angles is greater for an Rh(III) complexes than for a group of related Co(III) complexes (Table 4). Complex 1 shows a moderate distortion that is in accordance with its *trans*-(O<sub>5</sub>O<sub>6</sub>) geometry and the rings position at the equatorial plane (5–5–6), while similar Co(III) complex (2) with same ring arrangement show less distortion (31°), which can be attributed to the size of the central metal ion (Co(III) < Rh(III)). Previously synthesized complexes 3 and 5 show less distortion than 1 (34° and 31°) because of the more favorable layout of the rings in the plane (6–5–6) [2c,46a]. Considering only ethylenediamine complexes, we may see that 4 and 6 show the greatest deviation from the octahedron because the arrangement of the rings in the plane is very unfavorable (5–5–5). These two complexes were not isolated. The 1,3-propanediamine complexes

**Table 4**  
Structural distortion analysis of [M(edta-type)]<sup>−</sup> complexes with five and/or six-membered carboxylate rings.

Complex	$\Sigma\Delta(O_h)^a$	$\Delta\Sigma(\text{ring})^b$			$\Delta(M-O-C)^c$		$\Delta(M-O-C=O)^d$		$\Sigma\Delta(N)^e$	Ref.
		E or T	R	G	R	G	R	G		
<i>trans</i> -(O <sub>5</sub> )-[Rh(eddap)] <sup>−</sup> (3)	34	−12	−1	+41	+5	+18	5	14	12	[2c]
<i>trans</i> -(O <sub>5</sub> O <sub>6</sub> )-[Rh(eddap)] <sup>−</sup> (1) <sup>f</sup>	41	−13	−4(+32)	−14(+43)	+6(+14)	+1(+17)	7(23)	11(1)	19	This work
<i>trans</i> -(O <sub>6</sub> )-[Rh(eddap)] <sup>−</sup> (4) <sup>g</sup>	66	−10	+39	−19	+20	+1	14	13	30	This work
<i>trans</i> -(O <sub>5</sub> )-[Co(eddap)] <sup>−</sup> (5)	31	−11	−1	+38	+6	+18	10	26	13	[46a]
<i>trans</i> -(O <sub>5</sub> O <sub>6</sub> )-[Co(eddap)] <sup>−</sup> (2) <sup>f,g</sup>	31	−10	−5(+33)	−12(+33)	+7(+17)	+4(+18)	6(26)	11(22)	12	This work
<i>trans</i> -(O <sub>6</sub> )-[Co(eddap)] <sup>−</sup> (6) <sup>g</sup>	45	−15	+31	−17	+18	+2	29	14	33	This work
<i>trans</i> -(O <sub>5</sub> )-[Rh(1,3-pddadp)] <sup>−</sup> (7)	55	+37	−6	+27	+5	+14	4	15	17	[5b]
<i>trans</i> -(O <sub>5</sub> O <sub>6</sub> )-[Rh(1,3-pddadp)] <sup>−</sup> (8) <sup>f</sup>	42	+33	+1(+32)	−10(+41)	+5(+14)	+4(+21)	1(30)	3(7)	13	[5b]
<i>trans</i> -(O <sub>6</sub> )-[Rh(1,3-pddadp)] <sup>−</sup> (9) <sup>g</sup>	53	+35	+40	−15	+20	+4	12	9	16	This work
<i>trans</i> -(O <sub>5</sub> )-[Co(1,3-pddadp)] <sup>−</sup> (10) <sup>g</sup>	42	+39	−6	+27	+7	+17	5	17	18	This work
<i>trans</i> -(O <sub>5</sub> O <sub>6</sub> )-[Co(1,3-pddadp)] <sup>−</sup> (11) <sup>f</sup>	36	+34	0(+36)	−9(+44)	+6(+19)	+5(+24)	2(16)	4(5)	16	[9b]
<i>trans</i> -(O <sub>6</sub> )-[Co(1,3-pddadp)] <sup>−</sup> (12)	38	+28	+33	−11	+17	+4	26	10	16	[9a]

<sup>a</sup>  $\Sigma\Delta(O_h)$  is the sum of the absolute values of the deviations from 90° of the twelve L–M–L' angles. All values rounded off to the nearest degree.

<sup>b</sup>  $\Delta\Sigma(\text{ring})$  is the deviation from the ideal of the corresponding chelate rings' bond angle sum. Ideal values: 528° for the five-membered ethylenediamine (E) ring, 637.5° for the six-membered 1,3-propanediamine (T) ring, 538.5° and 648° for the five- and six-membered carboxylate (R in axial position and G in-plane) ring, respectively.

<sup>c</sup>  $\Delta(M-O-C)$  (ring) is the mean value of the deviation of the corresponding rings' M–O–C bond angle from the 109.5°.

<sup>d</sup> (M–O–C=O) is the mean value of the absolute values of deviations from 180° of the corresponding M–O–C=O bond angle.

<sup>e</sup>  $\Sigma\Delta(N)$  is the sum of the absolute values of the deviations from 109.5° of the six bond angles made by nitrogen atoms. A mean value for the two nitrogen atoms is reported.

<sup>f</sup> Values in parentheses are given for the 3-propionate rings.

<sup>g</sup> DFT calc. structure (B3LYP/SDD).

(7–12) show an expected distortion (36–55°). If we compare the same isomers, differing only in the size of the diamine ring, ((3 vs. 7); (1 vs. 8); (5 vs. 10); (2 vs. 11); (6 vs. 12)), can be seen that greater octahedral distortion was found for 1,3-propanediamine complexes. Besides, the value of the equatorial *cis* angle O–M–O decreases with the increasing number of six-membered rings in the equatorial plane (108.2° for 4 (5-5-5), 97.9° for 9 (5-6-5), 96.2° for 1 (6-5-5), 87.5° for 3 (6-5-6), 87.5° for 8 (5-6-6), 83.4° for 7 (6-6-6)). The angle influence is the same in the case of Co (III) complexes: 99.7° for 6 (5-5-5), 92.9° for 2 (6-5-5), 92.0° for 12 (5-6-5), 85.3° for 11 (5-6-6), 84.0° for 5 (6-5-5), 84.0° for 10 (6-6-6). The ethylenediamine (E) rings in the 1–6 show a negative value of total deviation, contrary to complexes 7–12 containing T ring (1,3-propanediamine) which are more relaxed. The five-membered G (in-plane) rings, as supposed, are less than the ideal sum (538.5°), i.e. they are more strained, while six-membered G rings have a positive deviation. The rings in the axial position (R rings) are less strained comparing to G rings due to the presence of a smaller number of rings in the environment (Table 4). All complexes show the positive deviation of the Rh–O–C(R, G) bond angles. Complexes 4 and 6 show the greatest deviation of the tetrahedral angles around the nitrogen (30° and 33°). It is to be noted that we observed significant torsional deviation of M–O–C=O angle (Table 4) that belongs to the 3-propionate ring. These torsions vary from 1° to 22° for G rings and 16° to 30° for the R rings. Therefore, it can be concluded that DFT modeled complexes 4 and 6 are the most unstable of all the presented compounds with the unfavorable layout of the rings in the plane (5-5-5).

### 3.4. Computational chemistry

#### 3.4.1. DFT

In order to interpret the stability of different geometric isomers of the [M(edta-type)]<sup>−</sup> complexes, calculations of their energy by different DFT theoretical models (B3LYP/SDD, M06/SDD, MP2/SDD) have been performed. The starting geometries were taken from the X-ray structures or the conformational analyses were made for different isomers whose structures were not determined by X-ray (Table 5). In order to use the most valuable DFT method, we've made a comparison of the total deviation of the octahedral angles calculated from the X-ray and DFT optimized structures (Fig. 4). At first glance, the B3LYP/SDD method gave the closest view (position and numerical values) to the strain parameters of X-ray structures. Accordingly, in further structural evaluation, we'll use the results obtained by this method.

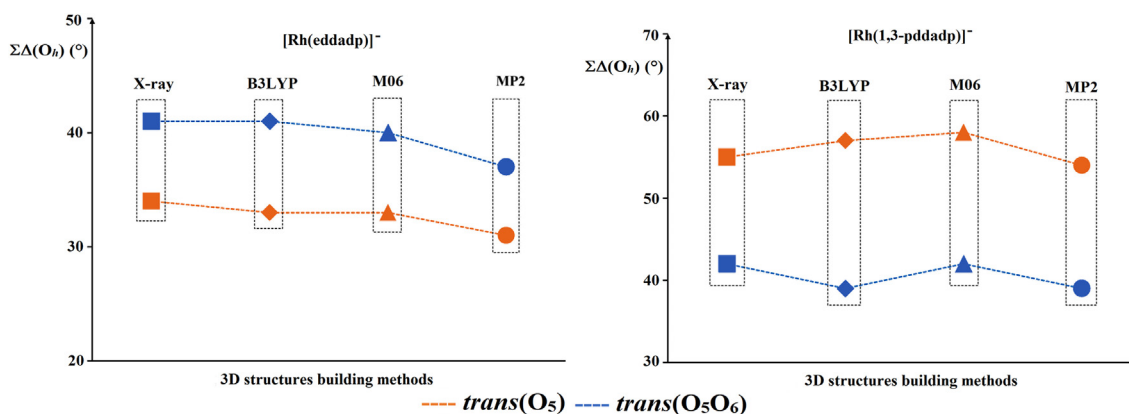
By insight in Table 5, we have primarily established the energy dependence on the structure of the geometric isomer. The obtained results show that the *trans*(O<sub>5</sub>) isomer of [M(eddadp)]<sup>−</sup> complex is the most stable regardless of which model of calculation was used: *trans*(O<sub>5</sub>) < *trans*(O<sub>5</sub>O<sub>6</sub>) < *trans*(O<sub>6</sub>). The small difference between first two isomers of [M(eddadp)]<sup>−</sup> complex (Table 5) indicates the simultaneous existence of both *trans*(O<sub>5</sub>) and *trans*(O<sub>5</sub>O<sub>6</sub>) isomers in the reaction mixture. Also, the same calculations were performed for structurally similar [M(1,3-pddadp)]<sup>−</sup> complex, where the situation is a little different. In case of rhodium calculation, models showed the same results: the most stable isomer is *trans*(O<sub>5</sub>O<sub>6</sub>) (X-ray confirmed here) with the small difference with respect to *trans*(O<sub>6</sub>) (never isolated). Quite unusually we found that

**Table 5**  
Relative energies (kcal mol<sup>−1</sup>) for [M(edta-type)]<sup>−</sup> complexes.<sup>a,b</sup>

Ligand	eddadp			1,3-pddadp		
	<i>trans</i> (O <sub>5</sub> )	<i>trans</i> (O <sub>5</sub> O <sub>6</sub> )	<i>trans</i> (O <sub>6</sub> )	<i>trans</i> (O <sub>5</sub> )	<i>trans</i> (O <sub>5</sub> O <sub>6</sub> )	<i>trans</i> (O <sub>6</sub> )
<i>Rhodium(III)</i>						
B3LYP	0	2.28	10.44	5.75	0	2.14
M06	0	1.07	8.66	5.94	0	1.46
MP2	0	0.05	7.45	4.74	0	0.70
<i>Cobalt(III)</i>						
B3LYP	0	1.12	7.56	7.94	2.81	0
M06	0	0.45	6.54	10.44	3.67	0
MP2	0	0.25	5.77	12.59	6.17	0

<sup>a</sup> The isomer with the lowest energy minimum has been indicated with 0 kcal mol<sup>−1</sup>.

<sup>b</sup> SDD basis set was used for all cases.



**Fig. 4.** Comparison of  $\Sigma\Delta(O_h)$  values depending on 3D structure building methods.

*trans*(O<sub>5</sub>) isomer (isolated and X-ray resolved, [5b]) adopt energetically the most unfavorable position: *trans*(O<sub>5</sub>O<sub>6</sub>) < *trans*(O<sub>6</sub>) < *trans*(O<sub>5</sub>). When the results of cobalt are considered, a more logical order is obtained: *trans*(O<sub>6</sub>) < *trans*(O<sub>5</sub>O<sub>6</sub>) < *trans*(O<sub>5</sub>). This means that both isomers *trans*(O<sub>6</sub>) and *trans*(O<sub>5</sub>O<sub>6</sub>) were isolated and structurally resolved [9]. The most energetically unfavorable isomer is found to be *trans*(O<sub>5</sub>) differing for roughly 8 kcal mol<sup>-1</sup> from the most stable one.

As seen, energetic analysis (Table 5) gave the expected results that agree with the stability of these complexes interpreted from the aspect of strain analysis (Table 4). All DFT calculation models are in agreement with each other and give the same order of stability to the isomers, i.e. for [M(eddadp)]<sup>-</sup> complexes, and for [M(1,3-pddadp)]<sup>-</sup> complexes. In this paper, we tried to enter deeper into the energy dependence of geometrical isomers and the usual strain parameters.

The basic correlation diagram between isomer energies and values of strain parameters (the total deviation of the octahedral angles, ΣΔ(O<sub>h</sub>), the mean value of the deviation of the corresponding rings' M–O–C bond angle, Δ(M–O–C) and the sum of the absolute values of the deviations of the six bond angles made by nitrogen atoms, ΣΔ(N)) is given in Fig. 5. These comparisons have been done for both [M(eddadp)]<sup>-</sup> and [M(1,3-pddadp)]<sup>-</sup> systems.

Carefully examining the components of the diagram, we can conclude that there is no apparent dependence of the M–O–C angles on the energies of the isomers. Rather, these isomers vary in the range of several degrees regardless of the energy value (Fig. 5 right end of the diagram). Similar behavior also shows energetic dependence on ΣΔ(N) deviations, except [M(eddadp)]<sup>-</sup> complexes. In this case, the deviation of *trans*(O<sub>6</sub>) isomers correlates with the rise in energy and reaches values of 10–20°. In our opinion, the determining strain parameter is the octahedral deviation ΣΔ(O<sub>h</sub>) which, according to the diagram (left side), indicates a good correlation with the energy values. This is more pronounced in case of [M(eddadp)]<sup>-</sup> and vary for [M(1,3-pddadp)]<sup>-</sup> complexes. The [M(eddadp)]<sup>-</sup> complexes show the increasing linear dependence of the ΣΔ(O<sub>h</sub>) values on the energy of the system. In the case of [M(1,3-pddadp)]<sup>-</sup> complexes we were not able to determine the

full correlation of the ΣΔ(O<sub>h</sub>) with energy values. For [Rh(1,3-pddadp)]<sup>-</sup> complexes the ΣΔ(O<sub>h</sub>) values are almost in correlation with corresponding energies but this is not true when [Co(1,3-pddadp)]<sup>-</sup> chelates are in question.

When considering the [M(eddadp)]<sup>-</sup> system, the values of the three parameters: energetics, ΣΔ(O<sub>h</sub>) and ΣΔ(N) values (see Table 5), unambiguously indicate the inability for *trans*(O<sub>6</sub>)-[M(eddadp)]<sup>-</sup> complexes to be formed. In addition, low energy profile in case of *trans*(O<sub>6</sub>)-[Rh(1,3-pddadp)]<sup>-</sup> complex (E = 2.14 kcal mol<sup>-1</sup>) allow and high energy of *trans*(O<sub>5</sub>)-[Co(1,3-pddadp)]<sup>-</sup> (E = 7.94 kcal mol<sup>-1</sup>) exclude possibility for these complexes to be formed under common reaction conditions. Perhaps the greatest surprise is the absence of *trans*(O<sub>6</sub>) isomer of [Rh(1,3-pddadp)]<sup>-</sup> complex in experimental conditions (column chromatography). There is a possibility that *trans*(O<sub>6</sub>) isomer might be found in the fourth band (splitting further into two bands) as reported by Radanović et al. [5b].

In an attempt to define the boundary energy beyond which it is impossible to expect the formation of a geometric isomers by careful analysis of the diagram (Fig. 5), we have come to the conclusion that this could be energy with a value of roughly 6 kcal mol<sup>-1</sup> for the both [Rh(eddadp)]<sup>-</sup> and the [Rh(1,3-pddadp)]<sup>-</sup> systems.

#### 3.4.2. NBO

In order to further reinforce all the above written, we have performed NBO orbital analysis. Generally, all the isomers represent strongly delocalized structures. NBO search for the best Lewis structure, calculated from .47 files, gave just one resonance's complex form. However, to be able to discuss energetic details (orbital and donor/acceptor energies) of these strongly delocalized structures the Natural Resonance Theory (NRT) analysis had to be done. Therefore, using \$NRT keyword we were able to calculate a set of different resonance structures (for each CHOOSE structure proposed by NBO search) and left the NBO program to analyze the resonance structures ranking by their weight (Figs. S6–S17, Supplementary material). 3D structures of the best-ranked resonances for each isomer are depicted in Fig. 6.

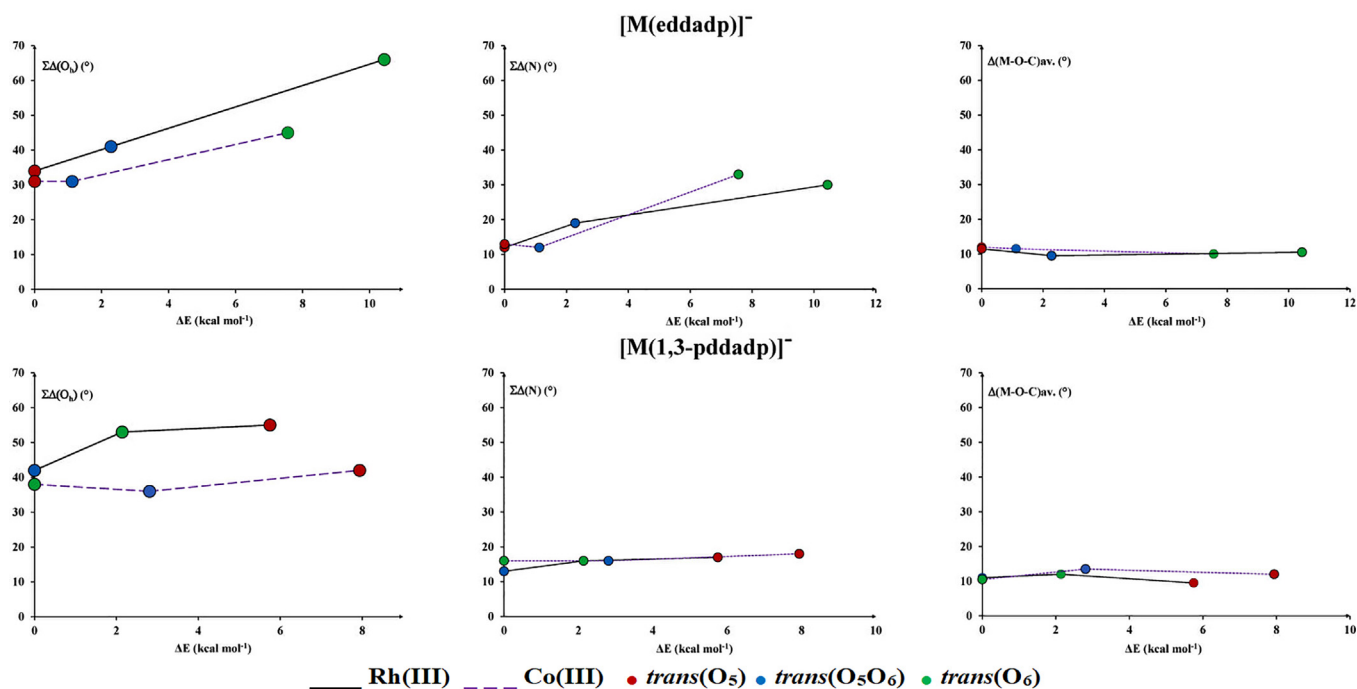
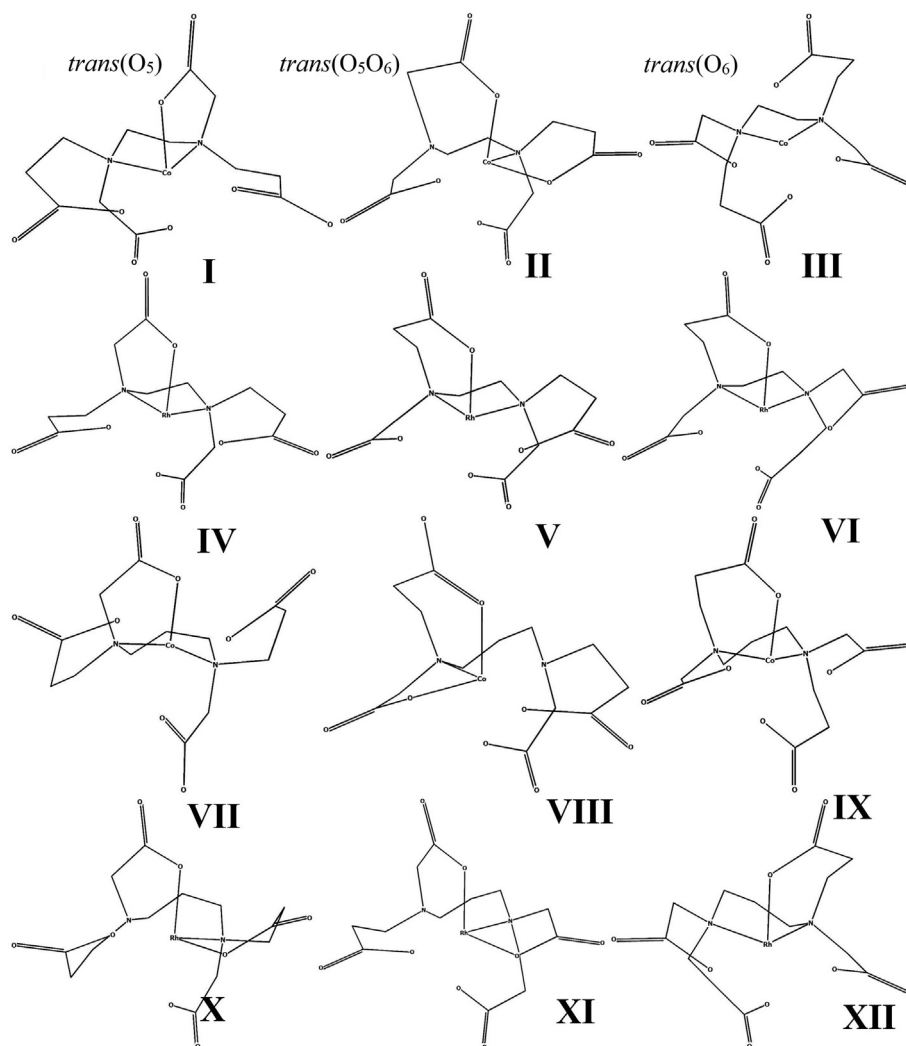


Fig. 5. Correlation diagram between DFT energies (B3LYP/SDD) of geometrical isomers and their basic structural strain-parameters.





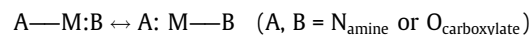
**Fig. 6.** The best-ranked resonances as a result of NRT analysis on different isomers: I–VI [M(eddadp)]<sup>−</sup>; VII–XII [M(1,3-pddadp)]<sup>−</sup> complex anions, (M = Co(III), Rh(III)).

All these resonances (Fig. 6) have an almost unique feature that is both metals are tri-coordinated except Co(III) in *trans*(O<sub>6</sub>)-[Co(eddadp)]<sup>−</sup> complex ion (III) which adopt di-coordination in an octahedral surrounding. For the former group, tri-coordination is provided by N2O or NO2 chromophore and for the latter, two diamine nitrogen atoms coordinate cobalt(III) ion.

Generally, natural bond order for complexes (NRT analysis) containing cobalt(III) ion roughly ranges from 2.5 to 3. For example, the complex *trans*(O<sub>6</sub>)-[Co(1,3-pddadp)]<sup>−</sup> shows that Co–N bond is made up of 27% of the covalent and 73% of the ionic character while the Co–O bond involve about 20% of the covalent and 80% of the ionic character. On the other hand rhodium(III) ion's natural bond order is approximately 3.1 and for the corresponding compound *trans*(O<sub>6</sub>)-[Rh(1,3-pddadp)]<sup>−</sup> shows that Rh–O and Rh–N bonds have 10% higher covalent character. Therefore, covalency is more pronounced in the complexes of rhodium(III) than in the case of cobalt(III) complexes.

All the isomers give roughly 98.1% of Lewis (L) occupancies and 1.7% of valence non-Lewis (NL) orbitals. The rest of ~0.2% occupancies belong to Rydberg and Core orbitals. There are three M–N or M–O bonds (M = Co(III) or Rh(III)) which are described with three L bonding (BD) orbitals followed by three high-energy valence NL antibonding (BD\*) orbitals. Further, NBO search found two, three or four 3-center 4-electrons A:–M:–B (A, B = N<sub>amine</sub> or O<sub>carboxylate</sub>)

hyperbonds ( $\omega$  bonds) along with O–C:–O carboxylate triads. These 3-center metal bonds, constituting of A(N<sub>amine</sub> or O<sub>carboxylate</sub>), M and B(N<sub>amine</sub> or O<sub>carboxylate</sub>) atoms, with strongly interacting valence hybrids  $h_A$ ,  $h_M$ ,  $h_B$ , are described as a strong resonance hybrid of the two localized L structure representations:



These triad resonances account on interactions between LP  $n_{B(A)}$  and BD  $\sigma_{MA(B)}$  orbitals.

Each A:–M:–B triad corresponds to strong  $n_B \rightarrow \sigma_{MA}^*$  delocalization in the A–M :B Lewis structure, or equivalently, strong  $n_A \rightarrow \sigma_{MB}^*$  delocalization in the alternative A: M–B Lewis structure, leading to nearly equivalent NRT weightings of these structures ( $w_{A-M :B} \approx w_{A: M-B}$ ) [68]. The BD\* (valence shell NL orbitals) typically play the primary role in departures (delocalization) from the idealized Lewis structure. The second-order perturbative estimates, donor(D)-acceptor(A) (bond-antibond) theory analysis of Fock matrix, interactions in the NBO basis. This is carried out by examining all possible interactions between “filled” (donor, L) NBOs and “unfilled” (acceptor, NL) NBOs, and estimating their energetic importance by 2nd-order perturbation theory. We already mentioned above that molecular stabilization comes from delocalization caused by  $n_A \rightarrow \sigma_{MB}^*$  or  $n_B \rightarrow \sigma_{MA}^*$  charge transfer.

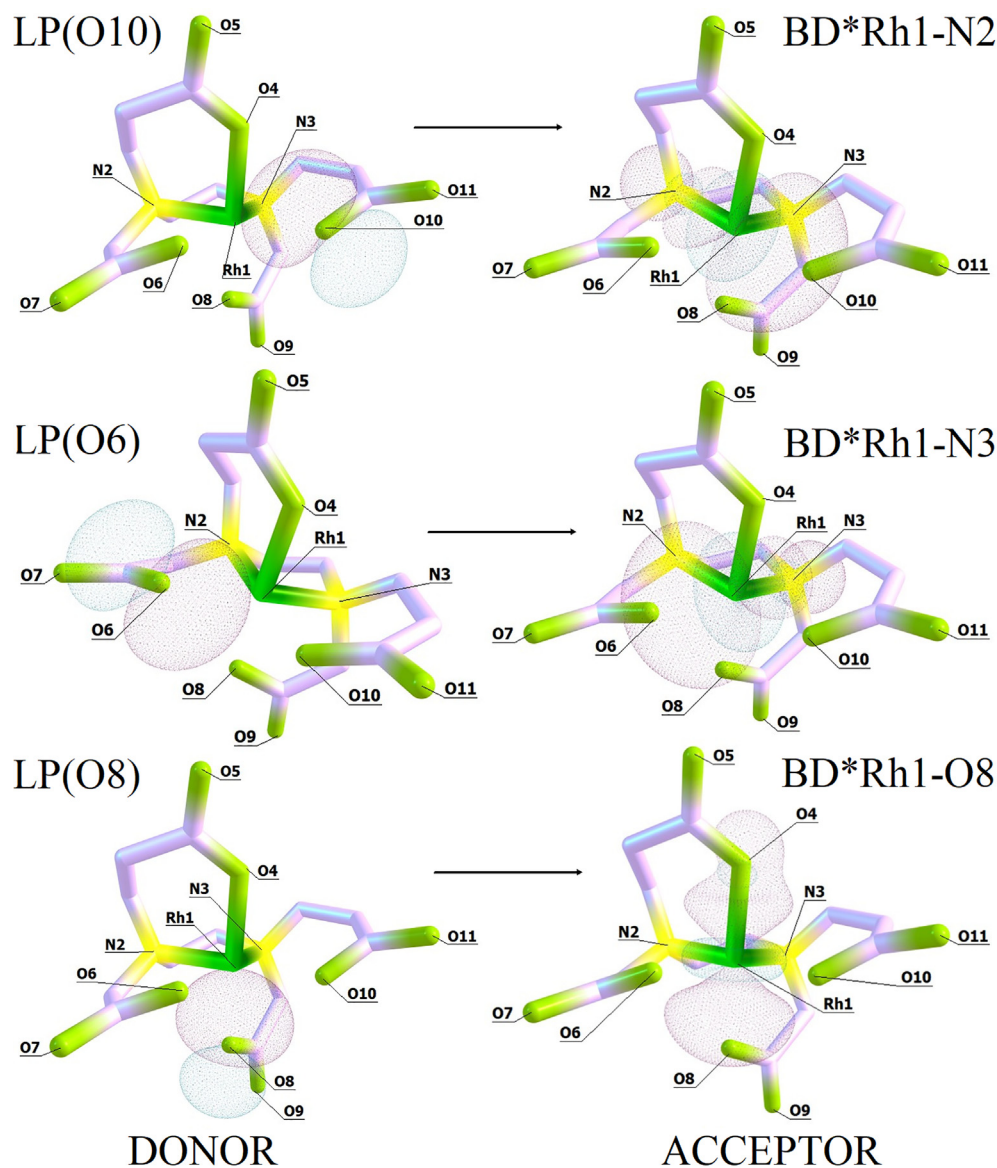


Fig. 7. PNBO Donor/Acceptor orbitals referred to as resonance hybrid stabilization of  $trans(O_5O_6)-[Rh(1,3-pddadp)]^-$  complex anion.

NBO really found three (or two in case of Co(III)-eddadp, see Fig. 6, III) high-energy valence NL  $BD^*$  orbitals, containing metal, for each isomer structure. In the case of  $trans(O_5O_6)-[Rh(eddadp)]^-$  isomer, these valence NL  $BD^*$  orbitals are: 93. (0.33044)  $BD^*Rh1-N2$ , 94. (0.32594)  $BD^*Rh1-N3$  and 95. (0.35539)  $BD^*Rh1-O4$  (Fig. 7 – Acceptor). One may see (numbers in parentheses) significantly large NL occupation (roughly 0.33 electrons) for each antibonding orbital. Each of these orbitals expect a donation of electron density from, symmetry-related, Lewis non-bonding lone pairs (LP),  $sp^n$  orbitals. These LP orbitals are depicted in Fig. 7. (Donor):  $sp^{5.71}$  (O6),  $sp^{3.40}$  (O8) and  $sp^{7.01}$  (O10). Therefore, according to D/A mechanism we are estimating three electron density transfers (Fig. 7):

1. LP (O10)  $\rightarrow$   $BD^*(Rh1)^{sd2.13} - (N2)^{sp5.06}$  equatorial donation
2. LP (O6)  $\rightarrow$   $BD^*(Rh1)^{sd2} - (N3)^{sp5.05}$  equatorial donation
3. LP (O8)  $\rightarrow$   $BD^*(Rh1)^{sd1.73} - (O4)^{sp8.65}$  axial donation

Thus, making a comparison between energies that come from electron density transfers of different isomers the next order has been established:

$$trans(O_5):trans(O_5O_6):trans(O_6) = 379.11:362.40:355.09 \text{ kcal mol}^{-1}$$

Such an energy relationship tells us that the stabilization of the hybrid structure is the greatest in the case of the  $trans(O_5)$  isomer and amounts  $\sim 12 \text{ kcal mol}^{-1}$ . This could be a rational explanation of why the  $trans(O_5)$  and  $trans(O_5O_6)$  isomers are found in reaction mixture what's in a full agreement with the established order of their electronic energies (Table 5). Similarly, rhodium(III)-eddadp donor–acceptor energies follow the order of QM electronic states. The D/A energies of Rh(III) isomers in case of 1,3-pddadp ligand also suggest the existence of  $trans(O_6)$  geometry (see above). Only discrepancy may be seen for  $[Co(1,3-pddadp)]^-$  isomers (Table 6). Namely, both symmetrical isomers  $trans(O_5)$  and  $trans(O_6)$  are of more intense donor–acceptor interactions than  $trans(O_5O_6)$  isomer.

Since we established a bit higher ion's bonding character within  $[Co(1,3-pddadp)]^-$  unit a natural Coulombic energy analysis has been done for all the isomers investigated (Table 6). One may see that there is no substantial shift in total natural Coulomb electrostatics potential energy ( $NCE_{total}$ ) for all complexes except  $[Co(1,3-pddadp)]^-$  isomers (Table 6). Here, the total NCE potential energy shifts in the next order:

**Table 6**NBO Donor/Acceptor energies<sup>a</sup> of 3-CHB bonds, pairwise steric exchange interactions  $E_{ij}^{pw}$  and Natural Coulomb Electrostatics (NCE) Analysis of  $[M(\text{edta-type})]^-$  complexes.

Acceptor	Donor					
	edddap			1,3-pdddap		
	<i>trans</i> (O <sub>5</sub> )	<i>trans</i> (O <sub>5</sub> O <sub>6</sub> )	<i>trans</i> (O <sub>6</sub> )	<i>trans</i> (O <sub>5</sub> )	<i>trans</i> (O <sub>5</sub> O <sub>6</sub> )	<i>trans</i> (O <sub>6</sub> )
Rh(III)	379.11	362.40	355.09	335.19	346.77	358.30
Co(III)	341.29	327.03	277.50	365.99	328.36	382.70
Rh(III) <sub><math>E_{ij}^{pw}</math></sub>	1026.48	1057.80	1072.23	1151.44	1096.85	1103.96
Co(III) <sub><math>E_{ij}^{pw}</math></sub>	1079.54	1149.04	1177.37	1171.51	1144.48	1151.16
NCE Potential energy <sup>b</sup>	[Rh(edddap)] <sup>-</sup>			[Rh(1,3-pdddap)] <sup>-</sup>		
	<i>trans</i> (O <sub>5</sub> )	<i>trans</i> (O <sub>5</sub> O <sub>6</sub> )	<i>trans</i> (O <sub>6</sub> )	<i>trans</i> (O <sub>5</sub> )	<i>trans</i> (O <sub>5</sub> O <sub>6</sub> )	<i>trans</i> (O <sub>6</sub> )
Lewis	-4.87451	-4.91143	-4.88222	-5.03605	-5.05614	-5.00669
Non-Lewis	2.18730	2.22420	2.18872	2.28615	2.29314	2.24761
total	-2.68721	-2.68723	-2.69351	-2.74990	-2.76300	-2.75908
	[Co(edddap)] <sup>-</sup>			[Co(1,3-pdddap)] <sup>-</sup>		
	<i>trans</i> (O <sub>5</sub> )	<i>trans</i> (O <sub>5</sub> O <sub>6</sub> )	<i>trans</i> (O <sub>6</sub> )	<i>trans</i> (O <sub>5</sub> )	<i>trans</i> (O <sub>5</sub> O <sub>6</sub> )	<i>trans</i> (O <sub>6</sub> )
Lewis	-5.61248	-5.32442	-5.52337	-5.61861	-5.63819	-5.37922
Non-Lewis	2.70975	2.41792	2.62078	2.65556	2.65979	2.38507
total	-2.90273	-2.90650	-2.90258	-2.96305	-2.97840	-2.99415

<sup>a</sup> kcal mol<sup>-1</sup>.<sup>b</sup> a.u.
$$\text{trans}(O_6):\text{trans}(O_5O_6):\text{trans}(O_5)$$

$$= -2.99415 < -2.97840 < -2.96305 \text{ a.u.}$$

This means that ionic bonding character within  $[\text{Co}(1,3\text{-pdddap})]^-$  predominates over covalent ones (or semi-covalent-like coordination bonds are supposed to be). This is in accordance with the isomers favored, so far, in the reaction between  $\text{Co}^{3+}$  and  $1,3\text{-pdddap}^{4-}$  under common reaction conditions.

Natural steric analysis expresses steric exchange repulsion as the energy difference due to orbital orthogonalization. Replacement of NBOs by NLMOs (natural localized molecular orbitals) significantly improve the description of steric effects in strongly delocalized species (such as transition metal complexes). The natural steric analysis also approximates the important pairwise steric exchange interaction  $E_{ij}^{pw}$  between two semi-localized NLMOs  $I$  and  $J$  [68]. These interactions (Table 6) summarize a pairwise-additive estimate (based on partial orthogonality involving only two pairs simultaneously)  $E_{ij}^{pw}$  within different geometrical isomers of  $[\text{M}(\text{edddap})]^-$  and  $[\text{M}(1,3\text{-pdddap})]^-$  complex ions. This parameter is less accurate, but more closely related to the concept of steric “contact” between individual electron pairs. The  $E_{ij}^{pw}$  results obtained for the best-ranked resonances of different isomers are in excellent agreement with favoured geometries reported by different authors so far. This means that in the case of  $[\text{M}(\text{edddap})]^-$  anion the *trans*(O<sub>5</sub>) and *trans*(O<sub>5</sub>O<sub>6</sub>) isomers are under lower steric exchange repulsion than *trans*(O<sub>6</sub>) isomer. In order to be more specific in clarifying this phenomenon, the main difference in steric interactions within *trans*(O<sub>5</sub>) and *trans*(O<sub>6</sub>) isomers lies in the repulsions of the NLMO orbitals which include oxygen atoms coordinated in the equatorial plane. The sum of  $E_{ij}^{pw}$  energies involving equatorial oxygens follows the next order: *trans*(O<sub>5</sub>):*trans*(O<sub>6</sub>) = 117.38:186.14 kcal/mol.

When  $[\text{M}(1,3\text{-pdddap})]^-$  ion is in question again the low steric exchange interactions for “disjoint” pairs of NLMOs (i.e. sharing no common atom) of *trans*(O<sub>6</sub>) and *trans*(O<sub>5</sub>O<sub>6</sub>) isomer indicates higher stability and relative ease of their preparation.

#### 4. Conclusions

In summary, the percentage of particular isomers found in reaction equilibrium mixtures of  $[\text{M}(\text{edddap})]^-$  complex has been reported. The molecular structure of *trans*(O<sub>5</sub>O<sub>6</sub>)-Na[Rh(edddap)]·4H<sub>2</sub>O was confirmed by X-ray analysis. This complex adopts an

octahedral geometry where the arrangement of five-membered and six-membered rings is such as to make the *trans*(O<sub>5</sub>O<sub>6</sub>) isomer. We investigated the stability of different geometric isomers of  $[\text{M}(\text{edta-type})]^-$  complexes using different DFT theoretical models (B3LYP/SDD, M06/SDD, MP2/SDD) as well. All DFT calculation models are in agreement with each other and giving the same order of stability to the isomers, i.e. for  $[\text{M}(\text{edddap})]^-$  and for  $[\text{M}(1,3\text{-pdddap})]^-$  complexes (M = Co(III), Rh(III)). Small energy difference between first two geometries of  $[\text{M}(\text{edddap})]^-$  complex indicates the simultaneous existence of both *trans*(O<sub>5</sub>) and *trans*(O<sub>5</sub>O<sub>6</sub>) isomers in the reaction mixture, which is confirmed in case of Rh(III). When we talk about  $[\text{M}(1,3\text{-pdddap})]^-$  complexes, the most energetically unfavorable isomer is found to be *trans*(O<sub>5</sub>). This is strange for Rh(III) complex because this isomer was X-ray confirmed, contrary to *trans*(O<sub>6</sub>) isomer which is never isolated, but adopt energy that is quite close to *trans*(O<sub>5</sub>O<sub>6</sub>) which was found to be in the most favorable position. In case of Co(III), more logical order was obtained: *trans*(O<sub>6</sub>) < *trans*(O<sub>5</sub>O<sub>6</sub>) < *trans*(O<sub>5</sub>), where *trans*(O<sub>5</sub>) (never isolated) isomer energetically differ for roughly 8 kcal mol<sup>-1</sup> from the most stable one.

The boundary energy beyond which it is impossible to expect the formation of geometric isomers, we proposed, that this could be energy with a value of roughly 6 kcal mol<sup>-1</sup> for the both  $[\text{Rh}(\text{edddap})]^-$  and the  $[\text{Rh}(1,3\text{-pdddap})]^-$  systems. On the basis of energetic and structural evaluation, we are convinced in the possibility of formation of *trans*(O<sub>6</sub>)-[Rh(1,3-pdddap)]<sup>-</sup> complex. We propose that attention should be paid to careful examination of chromatographic bands [5b] allowing the *trans*(O<sub>6</sub>) isomer to be isolated. NBO analysis suggests a strongly delocalized structure for all the complexes under investigation. Second order perturbation analysis estimated donor-acceptor energies that agree very well with QM electronic energies. The only departure has been recorded in the case of  $[\text{Co}(1,3\text{-pdddap})]^-$  isomers. This exception is explained by the total natural Coulomb electrostatics potential energy (NCE<sub>total</sub>) that favor the formation of *trans*(O<sub>5</sub>) and *trans*(O<sub>5</sub>O<sub>6</sub>) isomers. The  $E_{ij}^{pw}$  results obtained for the best-ranked resonances of different isomers are in excellent agreement with favoured isomers reported so far.

#### Declaration of Competing Interest

The authors declare that no conflicts of interests.

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## Appendix A. Supplementary data

CCDC 1876886 contains the supplementary crystallographic data for the compound (1). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2019.04.053>.

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