

which should be cited to refer to this work.

Structural analysis of conformational flexibility in (aqua) (propanediamine-*N,N'*-diacetato-*N*-propionato)chromium(III) dihydrate. Crystal structure of *cis*-polar, *trans*(H₂O,O⁵)-[Cr(1,3-pddap)(H₂O)] · 2H₂O

SONJA GRUBIŠIĆ*†, MAJA GRUDEN-PAVLOVIĆ‡, SVETOZAR R. NIKETIĆ‡§||, NARUMI SAKAGAMI-YOSHIDA¶ and SUMIO KAIZAKI¶

†Center for Chemistry, Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, PO Box 815, 11001 Belgrade, Serbia & Montenegro

‡Faculty of Science, Department of Chemistry, University of Belgrade, Studentski Trg 16, PO Box 158, 11001 Belgrade, Serbia & Montenegro

§Department of Chemistry, University of Fribourg-Pèrolles, CH-1700 Fribourg, Switzerland

¶Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

The quinquedentate complex *trans*(H₂O,O⁵)-[Cr(1,3-pddap)(H₂O)] · 2H₂O (where 1,3-pddap is the 1,3-propanediamine-*N,N'*-diacetate-*N*-3-propionate ion) was prepared and its structure established by X-ray diffraction method. It crystallizes in the orthorhombic space group *Pna*2₁, *a* = 17.290(2), *b* = 10.821(2), *c* = 7.872(1) Å, *Z* = 4. The metal atom is surrounded octahedrally with two nitrogen and three oxygen donors of (1,3-pddap)³⁻, forming two six-membered and two five-membered metal chelate rings, and with one water molecule occupying the *trans* position with respect to the oxygen of the axial glycinate ring. Conformational analysis of the five geometrical isomers of [Cr(1,3-pddap)(H₂O)], performed with the Consistent Force Field (CFF) program and recently developed edta force field, revealed that the global minimum is indeed the *trans*(H₂O,O⁵) isomer with the geometry in a very good agreement with the crystallographic structure. General patterns for the conformational preferences of edta-type complexes of trivalent first-row transition metals are exposed and discussed.

1. Introduction

From a stereochemical point of view, edta-type complex provide a wide range of structures suitable for studying isomerism and chelate ring conformations. Series of compound with various denticities, chelate ring sizes, and the branching patterns of edta-type ligands are synthetically readily accessible. But in spite of their

*Corresponding author. Email: grubisic@chem.bg.ac.yu

||Permanent address: University of Belgrade.

rich stereochemistry conformational studies on edta-type complexes they are surprisingly rare (cf [1–4], and to some extent [5]).

For a reliable conformational analysis on the structures of (poly)amino-(poly)carboxylate complexes and for the elucidation of factors which determine the preferred conformation mode and the geometry in such systems there is a need for a specific force field. In our recent studies, focused at a development of a consistent force field for edta-type complexes, we investigated the conformations of Cr(III), Co(III) and Rh(III) complexes containing 5-membered as well as mixed 5- and 6-membered metal chelate rings of edta-type ligands. The following systems were treated: [Cr(ed3p)(H₂O)] [6], [Cr(ed3a)(H₂O)] [7], [Co(1,3-pddadp)][−] [8], [Rh(1,3-pddadp)][−] and [Rh(1,3-pddadp)Cl]^{2−} [9]. Each study contributed at refining a common force field in a consistent way, and at the same time aided in building up a general pattern of conformational preferences for edta-type complexes. In this work we complete the series with the conformational analysis of [Cr(1,3-pddap)(H₂O)] isomers, and the X-ray structure of the *cis*-polar, *trans*(H₂O,O⁵)-[Cr(1,3-pddap)(H₂O)] · 2H₂O species, which was found to correspond to the global minimum of [Cr(1,3-pddap)(H₂O)].

2. Stereochemistry

In general, quinquedentate octahedral complexes with ed3a or ed3p ligands containing carboxylate arms of the same length, can exist in three theoretically possible geometries: *cis*-equatorial, *trans*-equatorial and *cis*-polar. Earlier it was found that the *cis*-equatorial isomer is the most stable one for the [Cr(ed3a)(H₂O)] complex, whereas *trans*-equatorial is more favored for the [Cr(ed3p)(H₂O)], and these results are in agreement with the reported X-ray structures [6, 7, 10].

For the ed3a-type complexes containing ligands with mixed carboxylate arms (acetate and propionate), geometrical isomerism is more elaborate with respect to the complexes with ed3a and ed3p ligands in the sense that *cis*-polar and *cis*-equatorial isomers dualize into *trans*(H₂O,O⁵) + *trans*(H₂O,O⁶), and *trans*(O⁵,O⁵) + *trans*(O⁵,O⁶), respectively. For that reason we chose to abandon the common “trivial” labels (*cis*-polar, *cis*-equatorial and *trans*-equatorial), widely used hitherto [6–11], rather than no attempt to extend them, and to revert to the standard stereochemical designators and superscripted numerals on oxygen symbols to indicate the corresponding chelate ring size. Occasionally, in this text we will use both labeling schemes in order to provide continuity with previous papers.

3. Experimental

3.1. Preparation of the complex

The [Cr(1,3-pddap)(H₂O)] complex, used subsequently in structure determination, was obtained from the reaction solution of sexidentate [Cr(1,3-pddadp)][−] complex

(where 1,3-pddadp is the 1,3-propanediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate ion) [12]. After pouring the reaction solution onto a column of QAE A-25 Sephadex in the Cl^- form, the non-charged complex $[\text{Cr}(1,3\text{-pddap})(\text{H}_2\text{O})]$ was eluted with distilled water. The complex was recrystallized, as a dihydrate, by adding acetone to the aqueous solution. Anal. Calc. for $[\text{Cr}(1,3\text{-pddap})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$, $\text{C}_{10}\text{H}_{21}\text{N}_2\text{O}_9\text{Cr}$ (FW = 365.28): C, 32.88; H, 6.79; N, 7.67%. Found: C, 32.94; H, 5.92; N, 7.54%.

3.2. Structure determination

A single crystal suitable for X-ray measurements, with approximate dimensions of $0.1 \times 0.1 \times 0.4 \text{ mm}^3$, was loaded into a glass capillary. Measurements were made on a Rigaku AFC5R diffractometer using graphite monochromated Mo- $\text{K}\alpha$ radiation. The calculations were performed using TEXSAN crystallographic software package of Molecular Structure Corporation [13] on a VAX computer.

The data were collected at $296 \pm 1 \text{ K}$ using the ω - 2θ scan technique. Three representative reflection were monitored every 100 scans and their intensities showed no decay. The intensity data were corrected for Lp effects as well as for absorption.

The structure was solved by direct methods. The positional and thermal parameters were refined by the block-diagonal least-squares refinement. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found in the difference Fourier map, and refined isotropically.

Crystallographic data are listed in table 1. The fractional atomic coordinates and equivalent isotropic thermal parameters, anisotropic thermal parameters for non-hydrogen atoms and selected torsional angles are summarized in tables S1–S3 (of the Supplementary material). Molecular diagrams were produced with *Ortep-3* (V1.08) for Windows XP [14]. CCDC reference number is 608189.

Table 1. Crystal data summary for *cis*-polar, *trans*($\text{H}_2\text{O}, \text{O}^5$)- $[\text{Cr}(1,3\text{-pddap})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (**I**).

Chemical formula	$\text{C}_{10}\text{H}_{17}\text{O}_7\text{N}_2\text{Cr} \cdot 2\text{H}_2\text{O}$
Formula weight	365.28
Space group	<i>Pna</i> 2 ₁
Crystal system	Orthorhombic
<i>a</i> (Å)	17.290(2)
<i>b</i> (Å)	10.821(2)
<i>c</i> (Å)	7.872(1)
$\alpha = \beta = \gamma$ (°)	90.0
<i>V</i> (Å ³)	1472.9
<i>Z</i>	4
<i>D</i> _{Calcd} (g cm ⁻³)	1.647
Crystal size (mm ³)	0.1 × 0.1 × 0.4
μ (Mo-K α) (cm ⁻¹)	8.03
<i>hkl</i> range	$0 \leq h \leq 24, 0 \leq k \leq 15, -10 \leq l \leq 0$
No. of total reflections	2485
No. of unique reflections	1108
$R = \Sigma[F_o - F_c]/ F_o $	0.042
$R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2}$	0.040

3.3. Molecular mechanics calculations

Conformational analysis of five geometrical isomers of (aqua)(1,3-propanediamine-*N,N'*-diacetato-*N*-propionato)chromium(III) has been performed with the Consistent Force Field (CFF) programme [15]. The edta force field (FF) was developed to include parameters describing force constants and equilibrium values for bonds, angles, torsions, as well as parameters describing van der Waals and electrostatic interactions for all atoms. The force field development and its application is described previously [6, 16]. The most recent refinement of the parameters is documented in [7] and in this work.

The principal revisions were in the M–O–C' angle bending parameters ($k_{\theta}(\text{M–O–C}') = 180.01 \text{ kcal mol}^{-1} \text{ rad}^2$ and $\theta_0(\text{M–O–C}') = 2.184 \text{ rad}$), and in the bond stretching parameter for the M–O bond ($r_0(\text{M–O}) = 1.96 \text{ \AA}$). The former parameters were modified due to the fact that in five- and six-membered carboxylate chelate rings the M–O–C' angles are different, which necessitated a decrease in k_{θ} parameter in order to maintain the force field transferability. The correction of the M–O equilibrium bond length improved the fit to experimental geometries in the present as well as in all the previous studies by this FF.

All the stable conformers were found by energy minimization of the complete sets of theoretically possible initial structures having all the permissible conformations of diamine and carboxylato metal chelate rings. By this strategy [6] we believe that we have achieved a comprehensive and reliable spanning of the conformational space for all five geometrical isomers of [Cr(1,3-pddap)(H₂O)]. The procedure used for the generation of initial coordinates was the same as the one described in detail in our previous paper [6].

Geometry optimizations were carried out using the combination of steepest-descent, Davidson–Fletcher–Powell and Newton–Raphson minimization methods [6–10, 15]. The former two algorithms were generally used in initial exploratory searches allowing, if necessary, for repeated alternations between them. To approach true minima Newton–Raphson iterations were always employed. Geometry optimizations were carried down to the energy rms gradient of $<10^{-6} \text{ kJ mol}^{-1} \text{ \AA}$. Ortep-3 (V1.08) for Windows XP [14] was used to depict energy-minimized structures.

4. Results and discussion

4.1. Description of the molecular structure of [Cr(1,3-pddap)(H₂O)] · 2H₂O and structural correlation between octahedral quinquedentate metal(III) complexes with ed3a-type ligands

The dihydrate of [Cr(1,3-pddap)(H₂O)] crystallizes as red stick-like crystals in the *Pna*2₁ space group. Its molecular structure corresponds to the *cis*-polar, *trans*(H₂O,O⁵) isomer.

The Ortep drawing of *trans*(H₂O,O⁵)-[Cr(1,3-pddap)(H₂O)] · 2H₂O is depicted in figure 1, where the labeling scheme adopted for the respective atoms and rings is also shown. Selected bond distances and angles are listed in table 2. The chromium(III) ion is surrounded octahedrally by two N and three O atoms of 1,3-propanediamine-*N,N'*-diacetate-*N*-3-propionate ion and one water molecule. Coordinated water occupies the *trans* position with respect to the oxygen atom of the axial glycinato ring stemming from the tertiary nitrogen of the propanediamine ring (and the *cis*-polar orientation

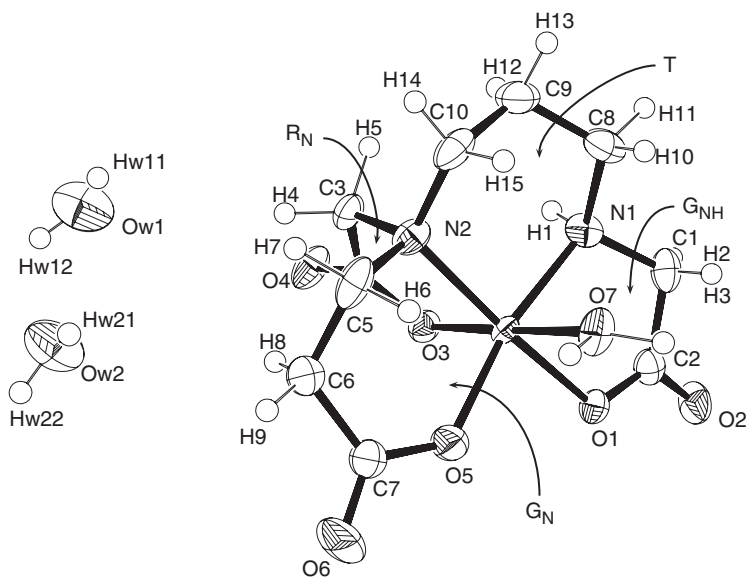


Figure 1. ORTEP representation of the molecular structure of *cis*-polar, *trans*(H₂O,O⁵) (I) [Cr(1,3-pddap)(H₂O)], as determined by X-ray crystallography, with the atom and ring labeling scheme adopted.

with respect to the secondary nitrogen atom). The 1,3-pddap ligand forms an in-plane six-membered diamine (T) ring, five-membered glycinato (G_{NH}) and six-membered β -alaninato (G_N) rings.¹ The other glycinato ring (R_N) is coordinated in the axial position. The R,G labels for describing various metal chelate rings formed in edta-type structures is credited to Weakliem and Hoard [17]. The conformations of the chelate rings are found to be *half-chair* and *envelope* for the in-plane (G) and axial (R) glycinato rings, respectively, and 1,3-*dipplanar* and *chair* for the inplane β -alaninato (G_N) and 1,3-propanediamine (T) rings, respectively. The investigated *trans*(H₂O,O⁵)-[Cr(1,3-pddap)(H₂O)] (isomer I) theoretically derives from the *trans*(O⁵,O⁶) isomer of corresponding sexidentate [Cr(1,3-pddap)]⁻ complex having Δ absolute configuration. In recently investigated *cis*-polar, *trans*(Cl,O⁵) isomer of Na₂[Rh(1,3-pddap)Cl] · 7H₂O [18], which is similar in structure to the *trans*(H₂O,O⁵)-[Cr(1,3-pddap)(H₂O)] · 2H₂O (*cis*-plar), the same R,R configuration at nitrogen atoms was observed with respect to the sexidentate *trans*(O⁵,O⁶)-[Rh(1,3-pddap)]⁻ isomer [19] from which it derives. However, in *trans*(H₂O,O⁵)-[Cr(1,3-pddap)(H₂O)] · 2H₂O the S,R absolute configuration at N1 and N2, respectively, was found. This comparison of the configurations at N atoms applied to the Δ absolute configuration of complexes.

4.2. Strain analysis

In crystallographic studies on edta-type complexes it is customary to report sums of deviations of the bond angles on selected atoms from their ideal values, or the

¹ Additional designators for the G and R rings, used in this article, are explained in the footnote to table 3.

Table 2. Selected bond distances (Å) and angles (°) for *cis*-polar, *trans*(H₂O,O⁵)-[Cr(1,3-pddap)(H₂O)]·2H₂O (I).

Cr(1)–O(1)	1.966(5)	O(1)–Cr(1)–O(7)	92.4(2)
Cr(1)–O(3)	1.919(5)	O(1)–Cr(1)–N(1)	80.9(2)
Cr(1)–O(5)	1.936(5)	O(1)–Cr(1)–N(2)	170.3(2)
Cr(1)–O(7)	2.021(5)	O(3)–Cr(1)–O(5)	92.5(3)
Cr(1)–N(1)	2.061(6)	O(3)–Cr(1)–O(7)	178.4(2)
Cr(1)–N(2)	2.069(6)	O(3)–Cr(1)–N(1)	93.0(3)
O(1)–C(2)	1.270(9)	O(3)–Cr(1)–N(2)	83.0(2)
O(2)–C(2)	1.23(1)	O(5)–Cr(1)–O(7)	87.7(3)
O(3)–C(4)	1.277(9)	O(5)–Cr(1)–N(1)	168.8(3)
O(4)–C(4)	1.24(1)	O(5)–Cr(1)–N(2)	96.6(2)
O(5)–C(7)	1.286(9)	O(7)–Cr(1)–N(1)	87.1(3)
O(6)–C(7)	1.22(1)	O(7)–Cr(1)–N(2)	95.4(2)
N(1)–C(1)	1.47(1)	N(1)–Cr(1)–N(2)	93.7(2)
N(1)–C(8)	1.50(1)	Cr(1)–O(1)–C(2)	119.3(5)
N(2)–C(3)	1.50(1)	Cr(1)–O(3)–C(4)	119.5(5)
N(2)–C(5)	1.49(1)	Cr(1)–O(5)–C(7)	131.1(6)
N(2)–C(10)	1.48(1)	Cr(1)–N(1)–C(1)	109.1(5)
C(1)–C(2)	1.53(1)	Cr(1)–N(1)–C(8)	117.3(4)
C(3)–C(4)	1.50(1)	Cr(1)–N(2)–C(3)	107.7(4)
C(5)–C(6)	1.52(1)	Cr(1)–N(2)–C(5)	109.4(5)
C(6)–C(7)	1.48(1)	Cr(1)–N(2)–C(10)	114.6(5)
C(8)–C(9)	1.50(1)	C(1)–N(1)–C(8)	111.0(6)
C(9)–C(10)	1.53(1)	C(3)–N(2)–C(5)	109.4(6)
O(1)–Cr(1)–O(3)	89.2(2)	C(3)–N(2)–C(10)	109.9(6)
O(1)–Cr(1)–O(5)	89.5(2)	C(5)–N(2)–C(10)	105.7(6)

deviations from ideal bond angle sums for chelate rings, in the form of the so-called *strain analysis*. However, detailed partition of strain among all internal coordinates available in molecular mechanics results eliminates the need for such kind of strain analysis, which is mentioned here solely for the sake of comparison with other similar hitherto published results.

Strain analysis of Cr(III) complexes with quinquedentate ed3a-type ligands (table 3) for *trans*(H₂O,O⁵)-[Cr(1,3-pddap)(H₂O)] (*cis*-polar), *cis*-equatorial [Cr(ed3a)(H₂O)], and *trans*-equatorial [Cr(ed3p)(H₂O)] shows that the degree of octahedral distortion ($\Sigma\Delta O_h$) is smaller when the number of glycinato rings present in the Cr(III) ed3a-type complexes decreases. The ethylenediamine ring (E ring) in *cis*-equatorial isomer of [Cr(ed3a)(H₂O)] shows a greater negative total deviation in comparison with the *trans*-equatorial isomer of [Cr(ed3p)(H₂O)] (−11 vs. −7°), indicating that the strain of E ring is greater for the system containing five-membered rings only. In *trans*(H₂O,O⁵)-[Cr(1,3-pddap)(H₂O)] the deviation of six-membered diamine ring is positive and sums to +32°. Six-membered β -alaninato rings coordinated in the equatorial plane in *trans*(H₂O,O⁵)-[Cr(1,3-pddap)(H₂O)] and *trans*-equatorial [Cr(ed3p)(H₂O)] complexes, as well as the one geminal R_N ring in the latter structure have the same deviation (+39°) from the ideal chelate ring bond angles sum. The deviation from ideal chelate ring bond angles sum of the other R_N geminal ring in *trans*-equatorial isomer of [Cr(ed3p)(H₂O)] is slightly greater and amounts to +43°.

Thus it appears that axial or equatorial orientation of β -alaninato ring has no significant influence on the strain of these systems. However, the equatorially coordinated five-membered glycinato rings are more strained than those

Table 3. Strain analysis of [Cr(ligand)(H₂O)] complexes with quinquedentate ed3a-type ligands.

Ligand isomer	$\Sigma\Delta^a(O_h)$	<i>E</i> or <i>T</i>	R_N^d	$\Sigma\Delta^b R_{NH}^c$	G_N^f	G_{NH}^g	$\Sigma\Delta^c N$	$\Sigma\Delta^c N_H$	Ref.
1,3-pddap <i>trans</i> (H ₂ O, O ⁵)	46	+32	0		+39	-5	11	20	This work
ed3a <i>cis</i> -eq	53	-11	0	-4	-12		17	37	[7]
ed3p <i>trans</i> -eq	24	-7	+43			+39	10	16	[10]
			+39						

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

^b $\Delta\Sigma(\text{ring})$ is the deviation from the ideal of the corresponding chelate rings' bond angle sum. Ideal values: 528 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 $\Sigma\Delta(N)$ is the sum of the absolute values of the deviations from 109.5° of the six bond angles on the nitrogen atoms.

^d R_N = carboxylate rings coordinated axially (*relaxed*) that contain tertiary nitrogen atom.

^e R_{NH} = carboxylate rings coordinated axially (*relaxed*) that contain secondary nitrogen atom.

^f G_N = carboxylate rings coordinated equatorially (*girdle*) that contain tertiary nitrogen atom.

^g G_{NH} = carboxylate rings coordinated equatorially (*girdle*) that contain secondary nitrogen atom.

coordinated axially; cf complexes *trans*(H₂O, O⁵)-[Cr(1,3-pddap)(H₂O)] (*cis*-polar) and *cis*-equatorial [Cr(ed3a)(H₂O)]. In all the observed complexes the strain formed around secondary chelating nitrogen atoms is greater than that found for tertiary nitrogen atoms.

4.3. Hydrogen bonding in the crystal structure of *trans*(H₂O, O⁵)-[Cr(1,3-pddap)(H₂O)] · 2H₂O

In the crystal structure of *trans*(H₂O, O⁵)-[Cr(1,3-pddap)(H₂O)] · 2H₂O (*cis*-polar) there is an intricate three-dimensional pattern of hydrogen bonds. The most prominent strand of this web consists of short hydrogen bonds (1.83 Å) between carbonyl oxygens of five-membered R_N rings, O(4), and hydrogens from coordinated H₂O ligands, H(71), of adjacent [Cr(1,3-pddap)(H₂O)] species. These hydrogen bonds produce parallel threads of complex species, hereafter called *principal strands*, two of which are depicted with continuous thick gray lines (extending semi-vertically) in figure 2. Another set of hydrogen bonds (1.96 Å) are formed between carbonyl oxygens of five-membered G_{NH} rings, O(2), and imino hydrogens, H(1). They connect complex species from two adjacent *principal strands* in a zigzag manner (since each of the G_{NH} rings is engaged in two such H-bonds), and are depicted with dashed thick gray lines in figure 2. Both lattice water molecules are also engaged in hydrogen bonding. One of them forms a very short H-bond (1.76 Å) to the hydrogen, H(2), of coordinated water, which is not involved in the *principal strand*. Finally, the other lattice water molecule bridges two complex species via H-bonds involving carbonyl oxygens, O(6), from the six-membered G_N ring (1.99 Å) as well as carbonyl oxygens, O(2), from five-membered G_{NH} rings (2.02 Å). Carbonyl oxygen O(2) is thus engaged in two types of H-bonds: one with imino hydrogen, H(1), and the other with one of lattice water molecules. The latter strands are approximately transverse with respect to the *principle strands*. However, unlike the 1.96 Å-threads, they join the other pairs of complex species, which, for example, lie above or below the plane containing the principal strands (*viz.*, the plane of figure 2) and, therefore, complete the specific three-dimensional web of

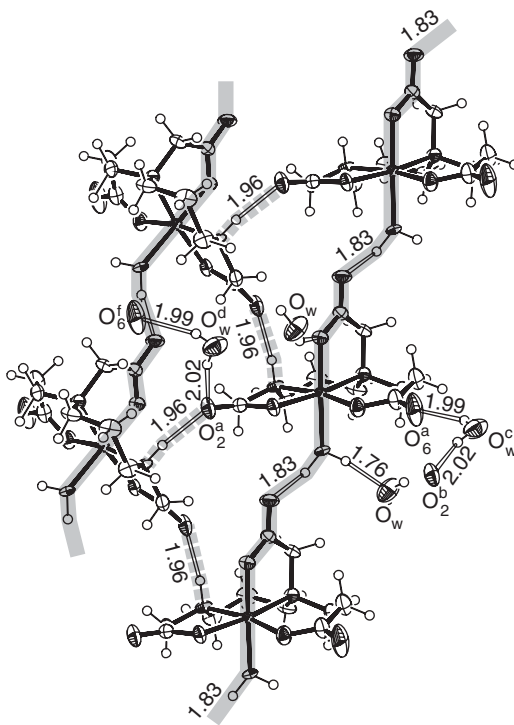


Figure 2. The network of hydrogen bonds in the crystal structure of *cis*-polar, *trans*(H₂O, O⁵) (I) [Cr(1,3-pddap)(H₂O)].

hydrogen bonds in the crystal structure of *trans*(H₂O, O⁵)-[Cr(1,3-pddap)(H₂O)] · 2H₂O (*cis*-polar).

4.4. Molecular mechanics results

Energy minimization/geometry optimization procedure resulted in several stable conformation for each geometrical isomer *trans*(H₂O, O⁵), *trans*(H₂O, O⁶), *trans*(H₂O, N_H), *trans*(O⁵, O⁶), and *trans*(O⁵, O⁵) of [Cr(1,3-pddap)(H₂O)] (table 4). The present calculations show that the most stable one of the *trans*(H₂O, O⁵) isomers, having 5-6-6 combination of the ring sizes in the G plane, represents the global minimum for the [Cr(1,3-pddap)(H₂O)] species. The lowest energy conformer corresponds to the configuration that has been found in the X-ray structure of [Cr(1,3-pddap)(H₂O)] · 2H₂O.

The energies (relative and absolute), structural parameters for the most stable energy-minimized structures, as well as comparison with the X-ray structure, are also presented in tables 4 and 5, respectively. Ortep illustrations for each of the resulting structures are shown in figure 3.

Endocyclic torsional angles for the energy-minimized structures and for the X-ray structure are shown in table 6. The total energy of minimized structures for five geometrical isomers of [Cr(1,3-pddap)(H₂O)] increases in the order: E_{total}

Table 4. Relative energies (ΔE) and energy contributions (in kcal mol⁻¹) of the MM optimized structures of [Cr(1,3-pddap)(H₂O)] isomers.^a

Isomer	ΔE	E_{total}	E_{bond}	E_{angle}	E_{torsion}	E_{vdw}	E_{c}
I	0.0	19.17	4.16	18.06	0.74	13.75	-17.54
II	1.6	20.77	4.32	15.99	3.31	14.32	-17.17
III	5.1	24.24	4.39	19.64	3.78	13.70	-17.27
IV	6.2	25.39	5.32	20.78	2.28	16.11	-19.10
V	7.2	26.34	5.13	19.67	3.18	15.91	-17.55

^aRoman numerals indicate the order of stability; isomer labels are as follows: **I**=*trans*(H₂O,O⁵); **II**=*trans*(H₂O,O⁶); **III**=*trans*(O⁵,O⁶); **IV**=*trans*(H₂O,N_H); **V**=*trans*(O⁵,O⁵) (see also figure 3).

(*trans*(H₂O,O⁵)) < E_{total} (*trans*(H₂O,O⁶)) < E_{total} (*trans*(O⁵,O⁶)) < E_{total} (*trans*(H₂O,N_H)) < E_{total} (*trans*(O⁵,O⁵)) (table 4).

4.5. Ring puckering analysis

The conformations of six-membered propanediamine and β -alaninato rings are conveniently described with Cremer–Pople puckering parameters, θ and ϕ [20]. A pair of ring-puckering parameters defines a unique point on the surface of the Cremer–Pople sphere. An azimuthal equidistant projection of the first octant of such a sphere showing the ring-puckering parameters for all six-membered rings in [Cr(1,3-pddap)(H₂O)] conformers investigated in this work is presented in figure 4.

As can be seen from the graph, the six membered propanediamine ring in the minimized structures of the *trans*(H₂O,O⁵), *trans*(H₂O,O⁶), and *trans*(H₂O,N_H) isomers of the [Cr(1,3-pddap)(H₂O)] species is *chair*, and in minimized structures of the *trans*(O⁵,O⁶) and *trans*(O⁵,O⁵) isomers is either *twist-boat* or *boat*. This seems to indicate that the rigid and highly puckered conformation of the T ring is favored for the *cis*-polar and *trans*-equatorial isomers, whereas the flexible *twist boat* (or *boat*) conformations are more favored for *cis*-equatorial isomers of the quinquedentate complex. The conformations of six-membered β -alaninato rings of the R type are irregular *boats* or *twist-boats*, and for the G type are best described as *1,3-diplanar* and *twist-boat* forms. However, the demarcation is not clear-cut due to the general tendency of all β -alaninato rings to flatten at the carboxylate part.

It is interesting to note that the axial five-membered glycinato rings are flattened in almost all of the minimized structures, but when a five-membered glycinato ring is positioned in the equatorial plane an *envelope* conformation is favoured (table 6). This is in agreement with the fact that the steric crowding in the equatorial plane is reduced when five-membered glycinato rings are highly puckered.

5. General conclusion

This work aims at rationalizing the complex coordination stereochemistry of metal ions with (poly)amino(poly)carboxylate edta-type ligands having mixed acetato (glycinato)

Table 5. Selected average values of bond lengths (Å) and angles (°) in MM optimized structures of [Cr(1,3-pddap)(H₂O)] isomers.^a X-ray data are given in bold, and the corresponding MM calculated values are given in slanted type.

Isomer	M–N	M–O	C ^α –O	C ^α –C ^β	C ^α –C	C ^α –C ^β	C ^α –C	N–C ^α	N–C ^β	N–C
X-ray										
I	2.065	1.960	1.277	1.500	1.516	1.520	1.484	1.484	1.492	1.490
<i>II</i>	<i>2.085</i>	<i>1.954</i>	<i>1.275</i>	<i>1.518</i>	<i>1.540</i>	<i>1.540</i>	<i>1.497</i>	<i>1.489</i>	<i>1.489</i>	<i>1.488</i>
III	2.073	1.928	1.277	1.524	1.548	1.544	1.496	1.494	1.494	1.490
<i>IV</i>	<i>2.077</i>	<i>1.926</i>	<i>1.277</i>	<i>1.525</i>	<i>1.544</i>	<i>1.544</i>	<i>1.499</i>	<i>1.497</i>	<i>1.497</i>	<i>1.484</i>
V	2.087	1.916	1.277	1.530	1.532	1.563	1.498	1.498	1.499	1.485
<i>V</i>	<i>2.082</i>	<i>1.919</i>	<i>1.277</i>	<i>1.527</i>	<i>1.548</i>	<i>1.546</i>	<i>1.501</i>	<i>1.501</i>	<i>1.505</i>	<i>1.483</i>
Isomer	NMO	MOC'	OC' ^α	C' ^α C' ^β	C ^α NM	C ^α C ^β N	C ^β NM	NCC	NMN	MNC
X-ray										
I	86.8	123.2	116.5	116.6	108.4	115.4	109.4	113.8	93.7	115.9
<i>II</i>	<i>87.4</i>	<i>122.4</i>	<i>119.1</i>	<i>111.8</i>	<i>107.4</i>	<i>115.7</i>	<i>110.6</i>	<i>115.8</i>	<i>96.2</i>	<i>112.0</i>
III	87.0	120.1	118.7	111.3	106.6	116.7	110.9	115.7	99.2	111.3
<i>IV</i>	<i>87.0</i>	<i>119.9</i>	<i>118.8</i>	<i>111.6</i>	<i>105.9</i>	<i>117.3</i>	<i>112.6</i>	<i>117.0</i>	<i>96.8</i>	<i>111.1</i>
V	87.4	119.6	119.1	119.2	106.0	117.0	110.7	113.6	97.6	113.4
<i>V</i>	<i>86.9</i>	<i>118.9</i>	<i>118.4</i>	<i>109.9</i>	<i>106.6</i>	<i>118.6</i>	<i>111.0</i>	<i>117.0</i>	<i>96.4</i>	<i>111.3</i>

^aRoman numerals indicate the order of stability; for isomer labels see footnote to table 4 or figure 3.

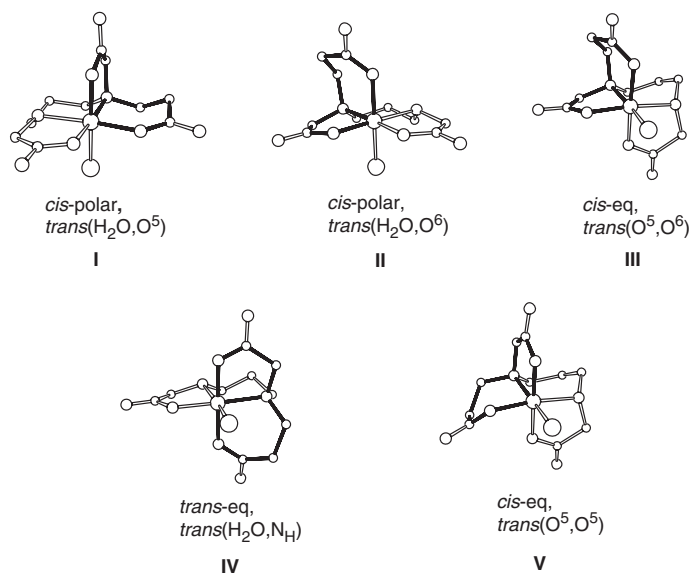
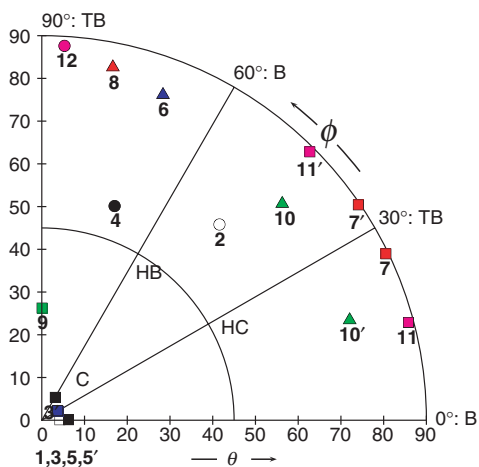


Figure 3. ORTEP illustrations of the energy-minimized structures of *trans*(H₂O,O⁵) (I), *trans*(H₂O,O⁶) (II), *trans*(H₂O,N_H) (IV), *trans*(O⁵,O⁶) (III), and *trans*(O⁵,O⁵) (V) isomers of [Cr(1,3-pddap)(H₂O)] complex. Roman numerals indicate the order of stability. The global minimum is labeled in bold. Hydrogens are omitted for clarity.



Legend: Squares: six-membered diamine rings, T; circles: in-plane (*girdle*) β -alaninato rings, G_N; triangles: out-of-plane (*relaxed*) β -alaninato rings, R_N; empty squares and circles: X-ray structure of [Cr(1,3-pddap)(H₂O)]·2H₂O.

1 T	X-ray <i>trans</i> (H ₂ O,O ⁵)	7 T	<i>trans</i> (O ⁵ ,O ⁶)
2 G _N	X-ray <i>trans</i> (H ₂ O,O ⁵)	8 R _N	<i>trans</i> (O ⁵ ,O ⁶)
3 T	<i>trans</i> (H ₂ O,O ⁵)	9 T	<i>trans</i> (H ₂ O,N _H)
4 G _N	<i>trans</i> (H ₂ O,O ⁵)	10 R _N	<i>trans</i> (H ₂ O,N _H)
5 T	<i>trans</i> (H ₂ O,O ⁶)	11 T	<i>trans</i> (O ⁵ ,O ⁵)
6 R _N	<i>trans</i> (H ₂ O,O ⁶)	12 G _N	<i>trans</i> (O ⁵ ,O ⁵)

Figure 4. Azimuthal equidistant projection of the first octant of the sphere of puckering parameters θ and Φ showing the normalized distribution of values for the six-membered β -alaninato and propanediamine rings in [Cr(1,3-pddap)(H₂O)] species.

Table 6. Endocyclic torsional angles (°) in MM optimized structures of [Cr(1,3-pddap)(H₂O)] isomers.^a

Ring size torsional angle	X-ray	I	II	III	IV	V
6-membered tn						
M–N–C–C	55.8	54.0	–53.6	–62.8	44.7	–60.9
N–C–C–C	–67.0	–66.5	66.6	32.2	–72.2	21.8
C–C–C–N _H	65.1	68.8	–67.2	39.7	81.5	48.9
C–C–N _H –M	–56.2	–62.5	57.1	–63.6	–65.2	–62.9
C–N _H –M–N	41.4	45.5	–42.3	26.1	36.5	19.2
N _H –M–N–C	–40.1	–39.2	39.6	30.9	–24.7	36.9
6-membered						
	G _N	G _N	R _N	R _N	R _N	G _N
M–O–C'–C	–5.1	6.0	–40.9	–37.4	31.7	–37.8
O–C'–C–C	–35.3	–39.5	–14.3	–20.2	–46.7	–29.1
C'–C–C–N	71.3	72.1	68.0	67.3	–0.4	69.6
C–C–N–M	–55.2	–60.8	–57.6	–49.6	47.8	–35.6
C–N–M–O	17.2	22.9	8.8	1.3	–51.0	–16.8
N–M–O–C'	12.6	2.5	41.0	44.2	13.4	58.3
5-membered						
	R _N	R _N	G _N	G _N	R _N	R _N
M–O–C'–C	–0.3	7.3	4.2	0.4	–5.4	–5.2
O–C'–C–N	–8.6	–13.8	–20.8	–21.1	11.5	12.9
C'–C–N–M	12.2	12.5	24.6	27.9	–10.7	–12.8
C–N–M–O	–9.9	–7.7	–19.1	–23.3	6.9	8.8
N–M–O–C'	6.2	0.5	9.0	13.7	–1.2	–2.3
5-membered						
	G _{NH}	G _{NH}	G _{NH}	R _{NH}	G _{NH}	R _{NH}
M–O–C'–C	5.9	8.7	–7.5	–0.3	7.3	4.8
O–C'–C–N	–22.1	–19.5	16.8	–8.3	–23.8	–15.9
C'–C–N–M	26.3	19.5	–16.6	11.7	26.4	17.6
C–N–M–O	–19.2	–13.1	11.1	–9.9	–19.5	–13.0
N–M–O–C'	7.7	2.9	–2.4	6.0	7.4	5.0

^aRoman numerals indicate the order of stability; for isomer labels see footnote to table 4 or figure 3.

and 3-propionato (β -alaninato) carboxylate arms. With optimized MM force field, used before in the study of the analogous ed3p and ed3a structures containing carboxylate arms of the sample length [6, 7], we succeeded here at correctly reproducing the conformations and explaining the calculated stabilities of the [Cr(1,3-pddap)(H₂O)] species with mixed-length carboxylate arms. Excellent agreement between available X-ray data and our MM results on six different families of edta-type structures with Cr(III), Co(III) and Rh(III), studied so far [6–9], validates the consistency of the present edta force field.

These investigations include the two hexidentate [M(1,3-pddap)] (M = Co(III) and Rh(III)) complexes [8, 9], where it was found that the lowest energy conformer corresponds to the *trans*(O⁵,O⁶) configuration, with an inversion of the stability order among the other two isomers (*trans*(O⁵) and *trans*(O⁶)) for Rh(III) and Co(III) complexes. For ten geometrical isomers of the quinquedentate [Rh(1,3-pddap)Cl]²⁻ complex [9] we showed that the lowest energy conformer corresponds to the *cis*-polar, *trans*(Cl,O⁵) configuration. A similar result was obtained in the investigation of Cr(III) complex with the quinquedentate 1,3-pddap ligand (lacking one 3-propionate arm in comparison to the 1,3-pddap), where the calculated energies showed that the *trans*(H₂O,O⁵) isomer is the most stable. The computational and experimental results are in agreement since the structures corresponding to the lowest energy conformers with the 5-6-6 combination of the chelate rings in the G-plane are the only ones obtained and characterized by X-ray analysis.

Furthermore, our recent MM results for chromium(III) complexes with ed3p [6] and ed3a [7] ligands clearly demonstrate that in ed3a-type structures fused five-membered rings preferentially adopt facial configuration with the 5-5 combination of the ring members in the G-plane (*cis*-equatorial), whereas in the ed3p-type structures six-membered rings preferentially adopt meridional configuration (*trans*-equatorial). This is corroborated by X-ray results on a number of similar structures [18]. The present results for [Cr(1,3-pddap)(H₂O)] show that fused five- and six-membered chelate rings (glycinato in R position and β -alaninato in G position) prefer that facial configuration, which parallels the stereochemical behavior calculated for the above-mentioned [Rh(1,3-pddadp)Cl]²⁻ species [9]. Work in progress from this laboratory on similar aminocarboxylato complexes of lower denticities [21] support the generality of this pattern.

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