Inorganica Chimica Acta 399 (2013) 146–153

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Crystal structure, configurational and density functional theory analysis of nickel(II) complexes with pentadentate 1,3-pd3a-type ligands

Svetlana Belošević [a], Marina Ćendić [a], Maja Djukić [a], Miorad Vasojević [a], Auke Meetsma [b], Zoran D. Matović [a,*]

[a] Department of Chemistry, Faculty of Science, University of Kragujevac, Kragujevac SRB-34000, Serbia
[b] Stratingh Institute for Chemistry and Chemical Engineering, University of Groningen, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands

ARTICLE INFO

Article history:
Received 18 October 2012
Received in revised form 4 January 2013
Accepted 20 January 2013
Available online 31 January 2013

Keywords:
Nickel(II) complexes
pd3a-Type ligands
Crystal structure
DFT modeling
NEDA analysis

ABSTRACT

The O–O–N–N–O-type pentadentate ligands $H_3$1,3-pd3a and $H_3$1,3-pd2ap ($H_3$1,3-pd3a stands for 1,3-propanediamine-*N,N,N'*-triacetic acid; $H_3$1,3-pd2ap stands for 1,3-propanediamine-*N,N'*-diacetic-*N*-3-propionic acid) and the corresponding novel octahedral nickel(II) complexes have been prepared and characterized. $H_3$1,3-pd3a and $H_3$1,3-pd2ap ligands coordinate to nickel(II) ion *via* five donor atoms (three deprotonated carboxylate atoms and two amine nitrogens) affording octahedral geometry in case of all investigated Ni(II) complexes. A sixth place within octahedra has been occupied by the molecule of water. A six coordinate, octahedral geometry has been established crystallographically for the K[Ni(1,3-pd3a)(H_2O)]·3H_2O complex. Structural data correlating similar chelate Ni(II) complexes have been used for an extensive strain analysis. This is discussed in relation to information obtained for similar complexes. The infra-red and electronic absorption spectra of the complexes are interpreted and compared with related complexes of known geometries. Density functional theory (DFT) has been used to model the most stable geometry isomer and Natural Energy Decomposition Analysis (NEDA) to reveal the energetic relationship of these compounds. The results from density functional studies have been compared with X-ray data. NEDA has been done for the $[LNi]^-$ and [H_2O] units.

1. Introduction

Nickel and its compounds are released into the atmosphere from natural and anthropogenic sources [1]. Nickel is present in the environment and also it is an important element in modern industry. For many years there has been much more concern about the toxicity of Ni, because Ni is an essential element to plants and many other biota. Human health can be threatened by toxicity of many metals and among other by nickel. Because of the significance of nickel in human health and the environment our research group studied the nature of Ni(II) compounds for many years [2–5]. We also took a survey of polyaminopolycarboxylate which are easily coordinated to ions of metal. A number of edta-type ligands were synthesized in our research group [3,6,7]. Two new edta-type acids, $H_3$1,3-pd3a and $H_3$1,3-pd2ap were prepared and reported here. The 1,3-pd3a-type chelates can surround metal forming 5- and 6-membered rings. Depending on the size of the ring, different isomers can be formed: *cis*-equatorial, *trans*-equatorial and *cis*-polar (Fig. 1.). The previous paper described the $[Cu(pd3a\text{-}type)X]^-$ complex found in *cis*-equatorial configuration which has been crystallographically verified [7]. From a structural point of view, the d-electron configuration and size of the central metal ion are important issues [8–10].

$H_3$1,3-pd3a and $H_3$1,3-pd2ap acids are unsymmetrical ligands of 1,3-pd3a-type which contains one 6-membered 1,3-propanediamine ring, 5-membered acetate rings and one β-propionic ring in case of the $H_3$1,3-pd2ap ligand. Here we reported two new synthesized complexes of Ni(II): K[Ni(1,3-pd3a)(H_2O)]·3H_2O and Ba[Ni(1,3-pd2ap)(H_2O)]$_2$·12H_2O. The IR and electronic spectra are discussed in relation to their geometry.

To confirm the geometry of the isomers we undertook DFT computational experiments [11]. Also, for better understanding of new structures we used DFT (DFT stands for density functional theory) theory in order to determine the actual energetic relationship. Computational calculations are compared with X-ray results in case where they were present. Natural Energetic Decomposition Analysis (NEDA) [12] has been done for the LNi···OH_2 unit.

2. Experimental

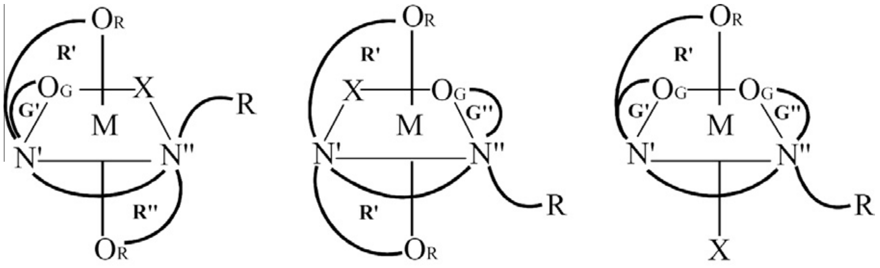
2.1. Materials

Reagent grade, commercially available, chemicals were used without further purification. 1,3-Propanediamine-*N,N'*-diacetic

---

* Corresponding author. Tel.: +381 34336223; fax: +381 34335040.
E-mail address: zmatovic@kg.ac.rs (Z.D. Matović).

0020-1693/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ica.2013.01.014



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

Fig. 1. Geometrical isomerism of six-coordinate [M(pd3a-type)X_n] complexes: $n = 1$.

acid dihydrochloride, $H_2$1,3-pdda·2HCl, was prepared by the method of Igi and Douglas [13]. 3-chloropropionic and chloroacetic acids were purchased from Fluka and used as supplied.

2.2. Physical measurements

Elemental microanalyses for C, H, N were performed at the Microanalytical laboratory, Faculty of Chemistry, University of Belgrade, Serbia. IR spectra in the 400–4000 cm^{-1} region were recorded on a Perkin–Elmer FT-IR spectrophotometer Spectrum One, using the KBr pellets technique. Electronic absorption spectra were recorded on a Perkin–Elmer Lambda 35 spectrophotometer. Melting points were measured by Stuart melting device with accuracy ±1 °C.

2.3. Preparation of compounds

2.3.1. Preparation of condensation mixture containing 1,3-propanediamine-N,N,N′-triacetic acid, $H_3$1,3-pd3a

The 1,3-propanediamine-*N*,*N*,*N*′-triacetic acid, $H_3$1,3-pd3a was prepared by the method described elsewhere [7]. Monochloroacetic acid (11.5 g, 120 mmol) was dissolved in 42 ml of demineralized water and 4.7 g (84 mmol) calcium oxide was added to the solution. The pH rose from 1.0 to 11.2. Subsequently, 3.11 g (42 mmol) of 1,3-propanediamine was added in 10 min. The temperature was kept at about 50 °C without additional heating. After 1 h the temperature was increased to 70 °C and the resulting mixture was left for additional 5.5 h. During the entire reaction, the pH was kept constant at 7.5–8.0 by the addition of calcium oxide. At the end of the reaction, a total of 1.9 g (34 mmol) of calcium oxide was added. The reaction mixture was filtered warm over a glass filter to remove the excess of calcium hydroxide. The reaction mixture (volume 50 ml) contains 1,3-pd3a (50%), 1,3-pdta (18%) i 1,3-pdda (23%) ligands. This was checked by means of chromatography of copper(II) complexes with above mixture.

2.3.2. Preparation of condensation mixture containing 1,3-propanediamine-N,N′-diacetic-N′-3-propionic acid, $H_3$1,3-pd2ap

Solution 1. $H_2$1,3-pdda·2HCl (10.52 g, 40 mmol) was dissolved in 15 ml of water and solution of 6.40 g (160 mmol) NaOH in 16 ml of water was added (pH 5).

Solution 2. 3-Chloropropionic acid (4.34 g, 40 mmol) was dissolved in 8.8 ml of water and solution of 1.6 g (40 mmol) NaOH in 4 ml of water was added (pH 11).

Solutions 1 and 2 were mixed (pH 9–10) and the mixture was stirred and heated at 50 °C for 2 h. After that, the mixture was heated at 70 °C for 32 h. During the entire reaction, the pH was kept constant at 7.0–8.0 by the addition of sodium hydroxide. The reaction mixture was filtered warm over a glass filter to remove the excess of sodium hydroxide and the solution slowly evaporated in the water-bath at 40 °C until it reached small volume (i.e., 20 ml). The reaction mixture (volume 20 ml) was of a light yellow color.

2.3.3. Preparation of the potassium(1,3-propanediamine-N,N,N′-triacetato(aquo)) nickelate(II) trihydrate, K[Ni(1,3-pd3a)(H_2O)]·$3H_2O$ (**1**)

The solution of NaOH (2.52 g, 63 mmol) in 5 ml H_2O was added to the prepared solution containing $H_3$1,3-pd3a (25 ml). That solution was then filtered to remove the excess of calcium hydroxide. The filtrate was then added to the solution of $NiCl_2$·$6H_2O$ (4.99 g, 21 mmol) in 8 ml H_2O. The resulting mixture was stirred at 65 °C for an hour and was then desalted with the gel-filtration technique by a passage through a G-10 Sephadex column, with distilled water as the eluent. The desalted solution was poured into a 5 × 60 cm column containing Dowex 1-X8 (200–400 mesh) anion exchange resin in the Cl^- form. The column was then washed with water (eluting zero charged *cis*-polar-[Ni(1,3pdda)$(H_2O)_2$] complex) and eluted with 0.1 M KCl. Two bands appeared on the column. The obtained eluate of each band was reduced to a small volume and then desalted. The second pale-blue eluate presents K_2[Ni(1,3-pdta)] of known structure. The eluate of the first band (*cis*-polar isomer) was reduced to a volume of 3 ml and stored in a desiccator over ethanol for several days. The blue crystals of *cis*-polar-K[Ni(1,3-pd3a)(H_2O)]·$3H_2O$ were collected, washed with ethanol and then ether, and air-dried (1 g). Melting point: 227 °C. *Anal.* Calc. for $C_9H_{21}KN_2NiO_{10}$; Mw = 415.06: C, 26.04; H, 5.10; N, 6.75. Found: C, 27.00; H, 5.03; N, 6.85%.

2.3.4. Preparation of the barium-bis{(1,3-propanediamine-N,N′-diacetato-N′-propionato)(aquo) nickelate(II)} dodecahydrate, Ba[Ni(1,3-pd2ap)(H_2O)]$_2$·$12H_2O$ (**2**)

The solution of $NiCl_2$·$6H_2O$ (9.50 g, 40 mmol) in 26.66 ml H_2O (pH 2.84) was added to the prepared solution containing $H_3$1,3-pd2ap (40 mmol) acid. The solution was then heated and stirred at 65 °C for an hour with maintained pH at 7.58 (by adding the solution of NaOH). The color of the solution during the reaction and after filtration was blue. The resulting filtrate was then desalted with the gel-filtration technique by passage through a G-10 Sephadex column, with distilled water as the eluent. The desalted solution was poured into a 4 × 40 cm column containing Dowex 1-X8 (200–400 mesh) anion exchange resin in the Cl^- form. The column was then washed with water (eluting again zero charged *cis*-polar-[Ni(1,3pdda)$(H_2O)_2$] complex) and eluted with 0.05 M $BaCl_2$. Two bands appeared on the column. The obtained eluate of each band was reduced to a small volume and then desalted. The second blue eluate presents *trans*(O_5)-Ba[Ni(1,3-pddadp)] isomer of known structure. The eluate of the first band (*cis*-polar Ni-1,3-pda2p isomer) was reduced to a volume of 2 ml and stored in a desiccator over ethanol for a week. The light blue crystals of *cis*-polar-Ba[Ni(1,3-pd2ap)(H_2O)]$_2$·$12H_2O$ were collected, washed with ethanol and then ether, and air-dried

(1.25 g). Melting point: 275 °C. *Anal.* Calc. for $C_{20}H_{58}BaN_4Ni_2O_{26}$; Mw = 1025.39: C, 23.43; H, 5.70; N, 5.46. Found: C, 23.20; H, 5.95; N, 5.16%.

2.4. Crystal structure analysis

Suitable blue-colored, block-shaped crystals were obtained by recrystallisation from a mixture of H_2O and ethanol. A crystal with the dimensions of 0.47 × 0.43 × 0.39 mm was mounted on top of a glass fiber and aligned on a *Bruker* [14] *SMART APEX CCD* diffractometer (Platform with full three-circle goniometer). The crystal was cooled to 100(1) K using the *Bruker KRYOFLEX* low-temperature device. Intensity measurements were performed using graphite monochromated Mo Kα radiation from a sealed ceramic diffraction tube (*SIEMENS*). The final unit cell was obtained from the *xyz* centroids of 5929 reflections after integration. Intensity data were corrected for Lorentz and polarization effects, scale variation, for decay and absorption: a multi-scan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS) [15], and reduced to F_o^2. The program suite SAINTPLUS was used for space group determination (XPREP) [14]. The unit cell [16] was identified as triclinic. Reduced cell calculations did not indicate any higher metric lattice symmetry [17]. Space group, $P\bar{1}$, was determined from considerations of the unit cell parameters, statistical analyses of intensity distributions: the *E*-statistics [18] were indicative of a centrosymmetric space group. Examination of the final atomic coordinates of the structure did not yield extra crystallographic or metric symmetry elements [19,20]. The structure was solved by direct methods using the program SIR2004 [21]. Final refinement on F^2 was carried out by full-matrix least-squares techniques. Crystal data and numerical details on data collection and refinement are given in Table 1. Molecular geometry data are collected in Table 2.

Table 1
Crystal data and details of the structure determination for $K[Ni(pd3a)(H_2O)]\cdot 3H_2O$.

Formula	$K^+\cdot[C_9H_{15}N_2NiO_7]^-\cdot 3(H_2O)$
Formula weight (g mol^{-1})	415.06
Crystal system	triclinic
Space group, No.[22]	$P\bar{1}$, 2
a (Å)	7.2681(5)
b (Å)	7.9578(6)
c (Å)	15.377(1)
α (°)	86.982(1)
β (°)	78.640(1)
γ (°)	63.532(1)
V (Å^3)	779.93(9)
Θ range unit cell: minimum–maximum (°); reflections	2.70–29.70; 5929
Formula Z	2
SpaceGroup Z	2
Z' (=Formula_Z/SpaceGroup_Z)	1
ρ_{calc} (g cm^{-3})	1.767
F(000), electrons	432
μ (Mo K$\bar{\alpha}$) (cm^{-1})	15.64
Color, habit	blue, block
Approx. crystal dimension (mm)	0.47 × 0.43 × 0.39
Radiation type; λ (Å)	Mo K$\bar{\alpha}$, 0.71073
θ range; minimum–maximum (°)	3.12, 28.28
Index ranges	h: −9 → 9; k: −10 → 10; l: −20 → 20
Minimum–maximum absorption transmission factor	0.4894–0.5406
X-ray exposure time (h)	8.0
Total data	7144
Unique data	3710
Data with criterion: ($F_o \geqslant 4.0\sigma(F_o)$)	3596
$R_{int} = \Sigma[\lvert F_o^2 - F_o^2(\text{mean})\rvert]/\Sigma[F_o^2]$	0.0122
$R_{sig} = \Sigma\sigma(F_o^2)/\Sigma[F_o^2]$	0.0195

Table 2
Structural data for $K[Ni(pd3a)(H_2O)]\cdot 3H_2O$ (**1**).

M–L bond lengths (Å)		M–O–C angles (°)	
Ni–O1	2.0235(1)	Ni–O1–C1	114.95(1)
Ni–O3	2.0730(1)	Ni–O3–C7	113.87(9)
Ni–O5	2.0401(1)	Ni–O5–C9	114.97(1)
Ni–O7	2.0899(1)		
Ni–N1	2.0576(1)		
Ni–N2	2.1002(1)		
cis angles (°)			
O1–Ni–O3	99.14(4)	O3–Ni–N2	82.26(5)
O1–Ni–O5	90.91(5)	O5–Ni–N1	91.81(6)
O1–Ni–O7	87.12(5)	O5–Ni–N2	83.78(6)
O1–Ni–N1	82.76(5)	O7–Ni–N1	93.65(6)
O3–Ni–O5	88.52(5)	O7–Ni–N2	98.32(6)
O3–Ni–O7	86.12(5)	N1–Ni–N2	95.89(5)
trans angles (°)			
O1–Ni–N2	174.48(6)	O5–Ni–O7	173.92(5)
O3–Ni–N1	178.07(5)		

2.5. Computational details

After testing various combinations of functional and basis sets, geometries for Ni(II) complexes were optimized using GAUSSIAN 09 A01 program [12]. Starting geometries were taken either from experimental X-ray structures or were pre-optimized using the MM+ implemented in HYPERCHEM 7.01 [23]. For these calculations, we used the unrestricted (triplet) B3LYP hybrid functional and the Ahlrichs TZVP basis set [24]. The Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) with water as a solvent has been employed for all complexes [12]. Subsequent frequency calculations at the same level of theory verified that the optimized structures were true local minima on the potential energy surface i.e. there were no imaginary frequencies. For calculating molecular interactions we used NEDA (NEDA stands for Natural Energy Decomposition Analysis) analyses [12,25].

3. Results and discussion

3.1. Preparation of unsymmetrical diaminotricarboxylate ligands and corresponding Ni(II) complexes and their characterization

This paper deals with the two nickel(II) complexes with pentadentate edta-type ligands containing 5- and/or 6-membered carboxylate arms: 1,3-propanediamine-*N*,*N*,*N′*-triacetate (1,3-pd3a) and 1,3-propanediamine-*N′*-diacetate-*N*-3-propionate (1,3-pd2ap). Chelates of edta-type ligands can be prepared in several ways: with the condensation method starting from neutralized α- or β-monohalogencarboxylic acid and corresponding diamine; by condensation of acrylic acid and diamine (in case you wish to obtain chelates with propionic arms); by condensation of dihalogen derivatives of diamine with diverse amino-acids. In this paper we deal with chelate pentadentate O–O–N–N–O ligands: $H_3$1,3-pd3a and $H_3$1,3-pd2ap. We prepared them using 1,3-propanediamine, neutralized monochloracetic acid or 3-chloropropionic acid (in case of H_3pd2ap). The calcium salt of H_3ed3a acid was successfully isolated with the yield over 80% [7]. On the other hand, in case of $H_3$1,3-pd3a and $H_3$1,3-pd2ap acids we were able to provide only condensation mixtures, and used them for complexation with the Ni(II) ion. Reaction has been done by using the nickel(II) chloride hexahydrate ($NiCl_2\cdot 6H_2O$) salt and neutralized chelate acids as given in the experimental part of work. The chromatography column separation (dowex resin in an anionic Cl^- form) was used. Apart from the isomerism given in Fig. 1., the $H_3$1,3-pd2ap acid upon complexation with the metal ion may actually yield two different *cis*-polar isomers (Fig. 2), that is *cis*-polar(**A**) with a five-membered

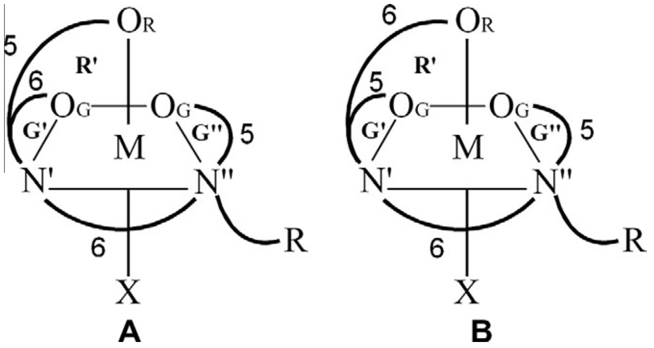


Fig. 2. *cis*-polar isomers of six-coordinate [M(1,3-pd2ap)(H_2O)] complex.

acetate ring in an axial position and *cis*-polar(**B**) with switched acetate and β-propionate rings.

Finally, we isolated: blue crystals of *cis*-polar K[Ni(pd3a)(H_2O)]·3H_2O and a light blue powder of *cis*-polar(**B**)-Ba[Ni(1,3-pd2ap)(H_2O)]$_2$·12H_2O. The complexes were characterized by microanalysis and spectroscopic techniques (IR, UV–Vis). The structural and spectral data of similar complexes are compared and discussed in relation to their geometry. In case of K[Ni(pd3a)(H_2O)]·3H_2O the *cis*-polar geometry was found and confirmed by an X-ray analysis. To explore the geometry of the Ba[Ni(1,3-pd2ap)(H_2O)]$_2$·12H_2O complex we analyzed and compared spectral results (IR and UV–Vis) and computational methods. Results from computational calculations that we used (Gaussian, Firefly and NBO [26]/NEDA) serve for better understanding of energetic and structural properties.

3.2. Description of the crystal structure of K[Ni(1,3-pd3a)(H_2O)]·3H_2O (**1**)

A structural diagram of the *cis*-polar [Ni(1,3-pd3a)(H_2O)]$^-$ anion, with the adopted atom-numbering scheme and the packing of the molecules in the unit cell are shown in Fig. 3. Each asymmetric unit contains one formula unit, consisting of five moieties: a K cation, an anionic Ni-complex and three H_2O molecules. The triclinic unit cell contains ten discrete units: two cations, two anions and six water molecules. A search of the distances yielded intermolecular and intramolecular contacts shorter than the sum of the van der Waals radii [27] for the atoms.

In the crystal structure the Ni(II) ion is coordinated by six donor atoms originating from: three deprotonated oxygen atoms of carboxylate groups, one oxygen atom from water and two nitrogen atoms of diamine. The complex has distorted octahedral geometry. Positions of carboxylate groups define the *cis*-polar geometry of this complex, as one acetate ring occupy nickel in an axial position, while the other two are in the equatorial plane. There are two longer bonds: Ni–O7 (2.0899(15) Å) and Ni–O3 (2.0730(12) Å). The other distances in anionic complex are within the range: from 2.0235(11) Å to 2.0401(14) Å: Ni–N1 2.0576(14) Å; Ni–N2 2.1002(12) Å; Ni–O1 2.0235(11) Å; Ni–O3 2.0730(12) Å; Ni–O5 2.0401(14) Å; Ni–O7 2.0899(15) Å. The *cis* angles are in range from 82.26(5) Å to 99.14(4) Å and *trans* angles in range from 173.92(5) Å to 178.07(5) Å. As can be seen (Fig. 3), the anion unit of [Ni(1,3-pd3a)(H_2O)]$^-$ contains different types of conformation rings. The equatorial 1,3-propanediamine ring is found in a chair conformation. The two five-membered acetate rings in the equatorial plane has a twisted-envelope conformation while the axial acetate ring is planar.

3.3. Structural parameters and strain analysis of nickel(II)-1,3-pd3a-type complexes in relation to their geometry

The strain in complexes of the M(II)edta-type can be considered from [28–30]:

(a) *cis* and *trans* angles located around the central metal ion;
(b) bond angles sum from different rings;
(c) Ni–O–C or Ni–N–C bond angles;
(d) bond angles which coordinated nitrogen build with others.

Structural data related to stereochemistry of Ni(II) complexes are given in Table 3.

The strain analysis has been carried out for *cis*-polar-[Ni(pd3a)(H_2O)]$^-$ for which we obtained crystal structure. Complexes [Ni(pdta)]$^{2-}$ and *cis-eq*-[Ni(ed3a)(H_2O)]$^-$ were taken for the comparison of obtained values (See Table 3). We compared $\Sigma\Delta(O_h)$ (the sum of the absolute values of the deviations from 90° of the L–M–L′ bite angles), $\Delta\Sigma$ (the deviation from the ideal of the corresponding chelate rings' bond angle sum), Δ(M–O–C)

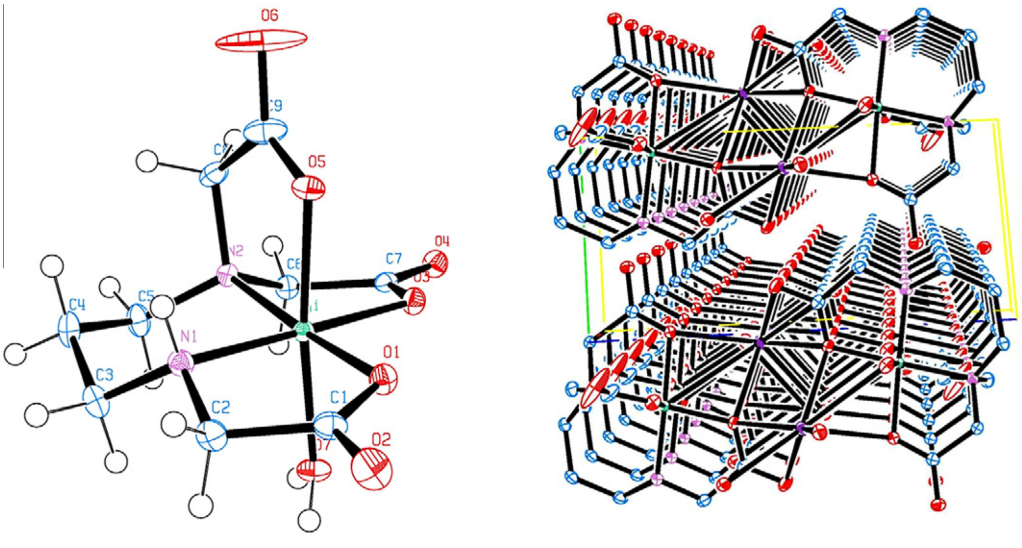


Fig. 3. X-ray crystal structure of the K[Ni(1,3-pd3a)(H_2O)]·3H_2O: Ortep diagram of the [Ni(1,3-pd3a)(H_2O)]$^-$ anion; Crystal packing view along *c* axis.

Table 3
Strain analysis of nickel complexes with pd3a and comparable pdta ligands.

Complex	$\Sigma\Delta(O_h)$[a]	$\Delta\Sigma$(ring)[b]			Δ(M–O–C)[c]		$\Sigma\Delta$(N)[d]	Ref.
		E(*T*)	R	G	R	G		
cis-polar-[Ni(1,3-pd3a)(H_2O)]$^-$	59	+34	+1	−5	+5	+5	+11 +14	This work
cis-eq-[Ni(ed3a)(H_2O)]$^-$	70	−13	−1	−11	+7	+3	16	[31]
[Ni(1,3-pdta)]$^{2-}$	60	+33	+1	−11	+6	+6	11	[32]

[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] $\Delta\Sigma$(ring) is the deviation from the ideal of the corresponding chelate rings' bond angle sum.

[c] Δ(M–O–C) (ring) is the mean value of the deviation of the corresponding rings' M–O–C bond angle from the 109.5°.

[d] $\Sigma\Delta$(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 nitrogens is reported.

(the mean value of the deviation of the corresponding rings' M–O–C bond angle from the 109.5°) and $\Sigma\Delta$(N) (the sum of the absolute values of the deviations from 109.5° of the six bond angles made by nitrogen atoms). The total deviation of octahedral angles ($\Sigma\Delta(O_h)$) depends on the size of the central ion [33] and the complex geometry. Comparing $\Sigma\Delta(O_h)$ values for *cis*-polar [Ni(pd3a)(H_2O)]$^-$, *cis*-equatorial-[Ni(ed3a)(H_2O)]$^-$ and *trans(O$_5$)*-[Ni(pdta)]$^{2-}$, one can see that complexes with the six-membered T backbone ring show lower deviation (59° and 60°) with respect to the E ring of [Ni(ed3a)(H_2O)] (70°). The 1,3-propanediamine (T ring) in *cis*-polar-[Ni(1,3-pd3a)(H_2O)]$^-$ shows a positive value of total deviation by +34° again being quite close to *trans(O$_5$)*-[Ni(pdta)]$^{2-}$ (+33°). According to Table 3 all the examined structural strain parameters, $\Delta\Sigma$(ring), Δ(M–O–C) and $\Sigma\Delta$(N) indicate a slightly lower strain (deviation) of (**1**) than was found for the other two complexes due to a less rigid pentadentate system with the 1,3-propanediamine ring.

3.4. Computational chemistry

Having prepared nickel(II) complexes with pentadentate 1,3-pd3a-type ligands with 5- and 6-membered carboxylate chelates, one can compare their experimental spectroscopic and geometry properties against the results of computational calculations. At the first glance, we optimized the geometries of each of the potential geometric isomers (Figs. 1 and 2.) using DFT method implemented in Gaussian09 [12]. We have modeled all three possible geometrical isomers (*cis*-equatorial, *cis*-polar (**A** and **B** in case of (**2**)) and *trans*-equatorial). The results obtained for (**1**) verified the *cis*-polar isomer as the most energetically stable one: by 4.7 kcal/mol related to the *cis*-equatorial and just 0.1 kcal/mol related to the *trans*-equatorial isomer (Table 4).

As can be seen (see Table 4), observed bond lengths of the experimental structure (**1**) and DFT calculations are in very good agreement. The bond and angle differences were derived as a result of solid state environment influence. In complex (**2**) the calculated *cis*-polar(**B**) isomer (Fig. 4) has been found as the most favorable. Unfortunately, in the last compound, we failed to isolate a crystal suitable for the X-ray to verify the proposed geometry.

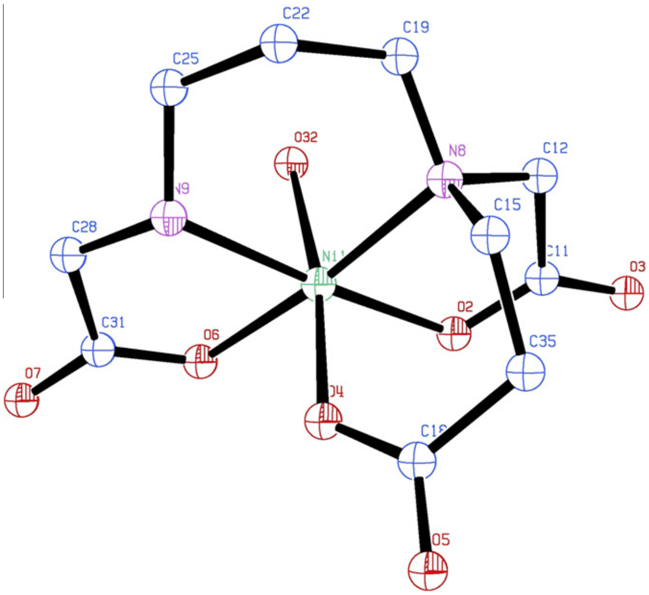


Fig. 4. DFT optimized structure of the *cis*-polar(**B**)-[Ni(1,3-pd2ap)(H_2O)]$^-$ anion.

In addition, we did NEDA calculations [12] using Firefly [25] EES. We were interested to find out the energetics of LNi···OH_2 interaction ([Ni(ed3a)(H_2O)]$^-$ has been taken for comparison) as these usually reflect how easy the pentacoordinated complex turns on the hexacoordinated one. In other words, we were able to see how electron-rich or electron-poor the pentacoordinated complex behave toward the incoming molecule of water (Table 5). Intermolecular forces and energy interactions inside the molecule are the main characteristics of NEDA results.

Table 4
Comparison of experimental (X-ray) and Gaussian (B3LYP/TZVP/PCM) obtained data for [Ni(1,3-pd3a-type)(H_2O)] complex.

Ni–N (Å) in-plane Exp: Gauss	Ni-O (Å) in-plane Exp: Gauss	Ni–O (Å) axial Exp: Gauss	Ni–O–C (°) (av.) Exp: Gauss	*cis*-angles (°) (av.) Exp: Gauss	*trans*-angles (°) (av.) Exp: Gauss
Comparison of experimental (X-ray) and optimized [Ni(1,3-pd3a)(H_2O)]$^-$ structure					
2.058:2.105	2.024:2.066	2.040:2.054	114.6:115.8	90.02:89.98	175.5:177.4
2.100:2.135	2.073:2.061	2.090:2.265[a]			
Geometrical isomer		*cis-polar*-[Ni(1,3-pd3a)(H_2O)]$^-$			*Cis-polar*-[Ni(1,3-pd2ap)(H_2O)]$^-$
Energy differences calculated in kcal/mol[b]					
cis-equatorial		4.7			1.6
cis-polar		0			0
trans-equatorial		0.1			0.16

[a] Water molecule.

[b] The isomer with the lowest energy has been indicated with 0 kcal/mol.

Table 5
Contribution of NEDA (kcal/mol) calculated components.

	CT	ES	POL	XC	DEF(SE) H_2O	DEF(SE) Nipd3a-type	ΔE
$[Ni(ed3a)(H_2O)]^-$	−70.30	−49.10	−43.45	−22.28	115.68	49.40	−20.06
$[Ni(1,3\text{-}pd3a)(H_2O)]^-$	−820.82	−48.95	−39.67	739.82	97.35	55.65	−16.62
$[Ni(1,3\text{-}pd2ap)(H_2O)]^-$	−710.78	−36.90	−42.96	645.70	88.10	41.70	−15.14

In Table 5 the parameters of our interest are listed as follows: CT stands for Charge Transfer; ES stands for Electrostatic component; POL stands for Polarization component; XC stands for Exchange–correlation component; DEF stands for deformation component and ΔE stands for Total energy interaction:

$$\Delta E = \mathrm{CT} + \mathrm{ES} + \mathrm{DEF} + \mathrm{BSSE},$$

where BSSE stands for basis set superposition error [12]. Charge Transfer (CT) and Electrostatic component (ES) terms provide higher contribution to total energy interaction than the other terms. From this point of view [Ni(ed3a)]···water complex is bound by −20.6 kcal/mol, showing the highest ΔE value. The lowest ΔE for (**2**) (−15.14 kcal/mol) makes $[Ni(1,3\text{-}pd2ap)(H_2O)]^-$ the most affordable to release the water molecule in a potential substitution reaction.

3.5. Spectral analysis

3.5.1. IR spectra of Ni(II) complexes with 1,3-pd3a-type ligands

Asymmetric carboxylate stretching frequencies between protonated carboxylate groups (1700–1750 cm^{-1}) and coordinated carboxylate groups (1600–1650 cm^{-1}) [34–36] have long been

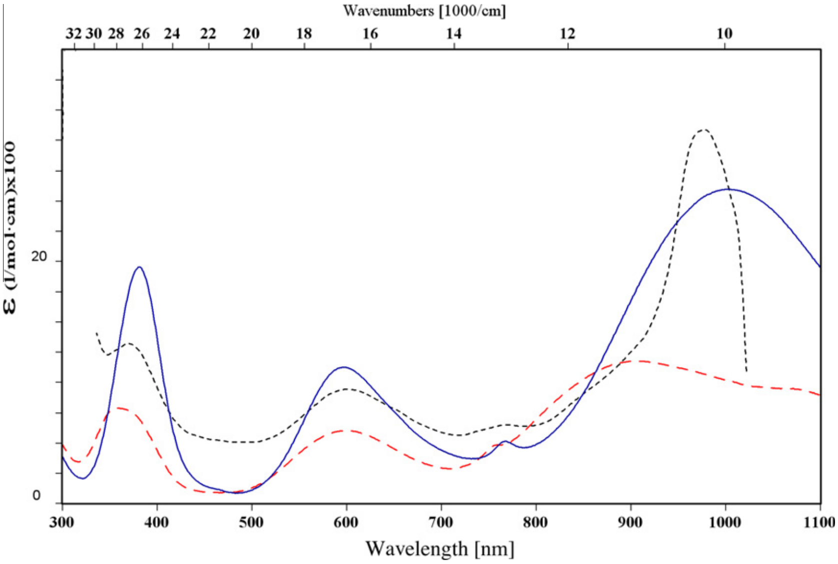


Fig. 5. Electronic absorption spectra of Ni(II) complexes: Nied3a ——; Nipd3a – –; Nipd2ap – –.

Table 6
Electronic absorption data of Ni(II) complexes with pentadentate $H_31,3$-pd3a and $H_31,3$-pd2ap and comparable H_3ed3a ligands.

Complex		Absorption		Assignments (O_h)	Ref.
		λ (cm^{-1})	ε		
cis-equatorial-$[Ni(ed3a)(H_2O)]^-$	I	10.00	26	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	[33]
	II	13.03	5	$\rightarrow {}^1E_g\ (D)$	
	III	16.77	11	$\rightarrow {}^3T_{1g}(F)$	
	IV	26.24	20	$\rightarrow {}^3T_{1g}(P)$	
cis-polar-$[Ni(pd3a)(H_2O)]^-$	I	9.36 (sh)	9.5		This work
	II	11.04	11.8		
	III	13.12	4.8		
	IV	16.67	6		
		27.85	7.9		
	I	9.80 (sh) 10.63	17.9		
cis-polar-[Ni(1,3-pnd3a)]	II	13.14	18.7		[39]
	III	16.84	6.6		
	IV	27.32	11.5		
			16		
cis-polar-$[Ni(1,3\text{-}pd2ap)(H_2O)]^-$	I	10.23	30.9		This work
	II	13.00	6.5		
	III	16.65	9.5		
	IV	27.06	13.2		

established as a criterion for distinguishing them. There is a generally accepted rule that the frequency assigned to five-membered rings [37] lies at a higher energy level than the corresponding frequency of six-membered chelate rings [38]. The IR data reported here for diaminotricarboxylate nickel(II) complexes support the above trend regarding the asymmetric frequencies of carboxylate groups. The frequencies at 1602 cm^{-1} and 1598 cm^{-1} were assigned to the moieties of the five-membered acetato arms of Ni-pd3a and Ni-pd2ap. The shoulder at 1571 cm^{-1} from asymmetric stretching vibrations of the β-propionate six-membered ring proves that we isolated the Ni-pd2ap complex (see Supplementary). The absence of other absorptions at 1700–1750 cm^{-1} show that all carboxylate groups are coordinated.

3.5.2. Electronic absorption spectra of Ni(II) complexes with 1,3-pd3a-type ligands

Electronic absorption spectra were given in Fig. 5. We observed Ni-1,3-pd3a, Ni-1,3-pd2ap and Ni-ed3a or *cis*-polar-[Ni(1,3-pnd3a)]$^{-}$ [39] (1,3-pnd3a stands for 1,3-pentanediamine-*N*,*N*,*N′*-triacetate anion) for the purpose of comparison. In cases of Ni-1,3-pd3a, Ni-1,3-pd2ap and Ni-1,3-pnd3a complexes containing the six-membered 1,3-propanediamine ring, the expansion of the first absorption band on the lower energy side is expected. This occurs as a result of a less pronounced presence of the tetragonal ligand field (D_{4h} model). The best spectral interpretation of Ni(II) complexes can be achieved over (O_h) model: $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (band I), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (band III) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (band IV) (Fig. 5).

Each compound contains shoulder at about 13 000 cm^{-1} (band II) on a higher energy side of the spin-allowed transition (see Table 6). This appearance occurs as a result of spin–orbital coupling.

The bands I, III and IV (usually reflecting an average ligand field strength – LFS) of Ni-1,3-pd3a and Ni-1,3-pd2ap were compared to the Ni-ed3a or Ni-1,3-pnd3a [39] complex. Generally, the bands belonging to complexes with 1,3-propanediamine backbone are moved to higher energy which means that they have a stronger ligand field. Comparing Ni-1,3-pd3a and Ni-ed3a complexes, LFS shift occurs as a consequence of the presence of two carboxylate rings in the equatorial plane that exert greater influence on d-orbital along the *x* and *y* axes. Less molar absorptivity of (**1**) and (**2**) (see Table 6) with regards to the Ni-ed3a complex is a consequence of the presence of a less rigid six-membered 1,3-propanediamine ring.

4. Conclusion

In this paper, we reported the preparation of a new pentadentate H$_3$1,3-pd2ap ligand and two new nickel(II) complexes: potassium-(1,3-propanediamine-*N*,*N*,*N′*-triacetato(aquo))nickelate(II) trihydrate, K[Ni(1,3-pd3a)(H$_2$O)]·3H$_2$O (**1**) and barium-*bis*[(1,3-propanediamine-*N*,*N′*-diacetato-*N*-propionato)(aquo)nickelate(II)]-dodecahydrate, Ba[Ni(1,3-pd2ap)(H$_2$O)]$_2$·12H$_2$O (**2**), containing five- and six-membered rings. Based on experimental data and DFT calculations, we found *cis*-polar geometry as a favored geometry for both complexes. The crystallographically verified isomer for (**1**) also corresponds to the lowest energy structure computed using DFT. The proposed *cis*-polar geometry for (**1**) and (**2**) is consistent with the spectral results. NEDA analysis of [NiL]···[water] adducts has been done. Charge Transfer (CT) and Electrostatic component (ES) terms generaly define the difference between total energy interactions. Therefore, [Ni(ed3a)]···OH$_2$ adduct show the bigest ΔE contribution −20.06 kcal/mol (Table 5). The [Ni(1,3-pd2ap)]···OH$_2$ adduct is bound by 15.14 kcal/mol which makes it the most affordable to release the water molecule in potential substitution reaction. In addition, the presence of the 1,3-propanediamine T ring makes LNi···OH$_2$ energy interaction of nickel(II) complexes lower than complexes imposed by E ring.

Acknowledgments

The authors are grateful to the Serbian Ministry of Science and Education for the financial support (Project No. III41010). We also appreciate Miss Tijana Matović for her help in English.

Appendix A. Supplementary data

CCDC 900434 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article, such as hydrogen-bonding tables, IR spectra can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.01.014.

References

[1] A. Sigel, H. Sigel, R.K.O. Sigel, Metal Ions in Life Sciences, second ed., Nickel and Its Surprising Impact in Nature, John Wiley & Sons Ltd., 2007.
[2] K.K. Das, S.N. Das, S.A. Dhundasi, Indian J. Med. Res. 128 (2008) 412.
[3] V.D. Miletić, A. Meetsma, P.J. van Koningsbruggen, Z.D. Matović, Inorg. Chem. Commun. 12 (2009) 720.
[4] D.J. Radanović, S. Ianelli, G. Pelosi, Z.D. Matović, S. Tasić-Stojanović, B.E. Douglas, Inorg. Chim. Acta 278 (1998) 66.
[5] Z.D. Matović, S. Ianelli, G. Pelosi, S.K. Janićijević, V.M. Ristanović, G. Ponticelli, D.J. Radanović, Polyhedron 21 (2002) 2667.
[6] Z.D. Matović, V.D. Miletić, M.M. Vasojević, M. Cvijović, S. Ćurčić, S.K. Belošević, Monatsh. Chem. 138 (2007) 823.
[7] Z.D. Matović, A. Meetsma, V.D. Miletić, Petra J. van Koningsbruggen, Inorg. Chim. Acta 360 (2007) 2420.
[8] G.H.Y. Lin, J.D. Leggett, R.M. Wing, Acta Crystallogr., Sect. B 29 (1973) 1023.
[9] T. Yamamoto, K. Mikata, K. Miyoshi, H. Yoneda, Inorg. Chim. Acta 150 (1988) 237.
[10] T. Mizuta, T. Yamamoto, N. Shibata, K. Miyoshi, Inorg. Chim. Acta 169 (1990) 257.
[11] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, GAUSSIAN 09, Revision A.1, GAUSSIAN, Inc., Wallingford, 2009.
[12] E.D. Glendening, J. Phys. Chem. A 109 (2005) 11936.
[13] K. Igi, B.E. Douglas, Inorg. Chem. 13 (1974) 425.
[14] Bruker, SMART, SAINTPLUS and XPREP. Area Detector Control and Integration Software. Smart Apex Software Reference Manuals, Bruker Analytical X-ray Instruments. Inc., Madison, Wisconsin, USA, 2000.
[15] G.M. Sheldrick, SADABS. Version 2.03. Multi-Scan Absorption Correction Program, University of Göttingen, Germany, 2001.
[16] A.J.M. Duisenberg, J. Appl. Crystallogr. 25 (1992) 92.
[17] A.L. Spek, J. Appl. Crystallogr. 21 (1988) 578.
[18] M.R. Snow, E.R.T. Tiekink, Acta Crystallogr. 44 (1988) 676.
[19] Y. Le Page, J. Appl. Crystallogr. 20 (1987) 264.
[20] Y. Le Page, J. Appl. Crystallogr. 21 (1988) 983.
[21] M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, J. Appl. Crystallogr. 38 (2005) 381.
[22] T. Hahn, Ed. International Tables for Crystallography, Space-group symmetry, vol. A, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1983.
[23] HyperChem (TM), Hypercube; Inc., 1115 NW 4th Street, Gainesville, Florida 32601, USA.
[24] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 7 (2005) 3297.
[25] A.A. Granovsky, Firefly version 7.1.G, <http://classic.chem.msu.su/gran/firefly/index.html>.
[26] E.D. Glendening, J.K. Badenhoop, A.E. Reed, J.E. Carpenter, J.A. Bohmann, C.M. Morales, F. Weinhold, NBO 5.0, Theoretical Chemistry Institute, University of Wisconsin, Madison, 2001.
[27] A. Bondi, J. Phys. Chem. 68 (1964) 441.
[28] D. Radanović, Coord. Chem. Rev. 54 (1984) 159.
[29] B.E. Douglas, D.J. Radanović, Coord. Chem. Rev. 128 (1993) 139.

[30] B.E. Douglas, D.J. Radanović, Inorg. Chem. 20 (1981) 3208.
[31] S. Belošević, M. Ćendić, A. Meetsma, Z.D. Matović, Polyhedron 20 (2013) 473.
[32] D.J. Radanović, T. Ama, H. Kawaguchi, N.S. Drašković, D.M. Ristanović, S. Janićijević, Bull. Chem. Soc. Jpn. 74 (2001) 701.
[33] R.D. Shaunon, Acta Crystallogr., Sect A 32 (1976) 751.
[34] D.H. Busch, J.C. Bailar Jr., J. Am. Chem. Soc. 75 (1953) 4574;
D.H. Busch, J.C. Bailar Jr., J. Am. Chem. Soc. 78 (1956) 716.
[35] M.L. Morris, D.H. Busch, J. Am. Chem. Soc. 78 (1956) 5178.
[36] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1963.
[37] K. Nakamoto, Y. Morimoto, A.E. Martell, J. Am. Chem. Soc. 83 (1961) 4528.
[38] M.B. Ćelap, S.R. Niketić, T.J. Janjić, V.N. Nikolić, Inorg. Chem. 6 (1967) 2063.
[39] N.S. Drašković, D.D. Radanović, Urszula Rychlewska, B. Warzajtis, I.M. Stanojević, M.I. Đuran, Inorg. Chim. Acta 43 (2012) 185.