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Nickel(II) complexes with *N*-aralkyliminodiacetic acids: Preparation, spectroscopic, structural and thermal characterization



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ABSTRACT

The reactions of *N*-aralkyl derivatives of iminodiacetic acid (H₂Bnida, H₂Peida, H₂Ppida, *o*-H₂Cbida, Bn = benzyl, Pe = 2-phenylethyl, Pp = 3-phenylprop-1-yl, *o*-Cb = *o*-chlorobenzyl) with nickel(II) chloride hexahydrate or nickel(II) acetate tetrahydrate in aqueous solutions were studied. Five new nickel(II) complexes [Ni(Bnida)(H₂O)₃]·H₂O (**1**), [Ni(Peida)(H₂O)₃] (**2**), [Ni(Ppida)(H₂O)₃]·H₂O (**3a**), [Ni(Ppida)(H₂O)₃] (**3b**) and [Ni(*o*-Cbida)(H₂O)₃] (**4**) were prepared and characterized by infrared spectroscopy and thermal analysis (TGA–DTA). The crystal structures of **1** and **3b** were determined by single-crystal X-ray structural analysis. The octahedral coordination environment around the nickel(II) ion in **1** and **3b** consists of an *O*,*N*,*O*'-tridentate *N*-aralkyliminodiacetate ion and three water molecules arranged in a *fac*-position. The molecules in the crystal structures of **1** and **3b** are connected into a complicated hydrogen-bonded 2D network, dominated by the O–H···O hydrogen bonds. These 2D networks are in turn assembled into a 3D architecture only by weak van der Waals interactions.

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1. Introduction

The iminodiacetate ion (ida^{2-}) is a tridentate chelating ligand able to partially satisfy a metal ion coordination, enabling the formation of a large variety of mixed-ligand metal complexes with iminodiacetic acid (H_2 ida) or its derivatives (H_2 Rida; R = alkyl, aryl or an aralkyl group). The available information strongly suggests that the coordination ability of the H₂Rida ligand can be affected by the non-coordinating moiety R [1]. In the octahedral complexes of divalent metals with the metal-to-ligand ratio of 1:1, the tridentate ligands, based on iminodiacetic acid, occupy only three coordination sites of the octahedron. The metal coordination can be completed in different ways, by adding one or more extra ligands or by polymerization [2]. Owing to the various coordination modes of the iminodiacetic acid ligands and the possibility to control dissociation of the carboxylate groups by minor variation in the reaction conditions, the supramolecular structures of the metal complexes can be achieved *via* hydrogen bonds [3].

The hybrid inorganic-organic compounds show considerable promise as a class of porous materials with properties complementary to those seen in aluminosilicates. These materials illustrate the role of higher reaction temperature in reducing the framework water content and the importance of ligand flexibility in

* Corresponding authors. Tel.: +385 1 4606355; fax: +385 1 4606341 (B.-M. Kukovec), tel.: +385 1 4606354; fax: +385 1 4606341 (Z. Popović). determining the metal-oxygen dimensionality in hybrid systems [4]. On the other hand, the study of ternary complexes, involving transition metal ions and nucleobases or their derivatives, is a very important topic because of their presence in the biological systems [5].

Although nickel is an essential element for methanogenic bacteria, its function in human organism is still unknown [6]. However, the metal itself, as well as its alloys and compounds, are considered or known to be human carcinogens [7]. Therefore, removing nickel(II) ions from the environment by complexation should lower the risk from nickel poisoning [6]. Iminodiacetic acid, nitrilotriacetic acid and other similar complexones are very effective for this purpose because of the great stability of their metal complexes over a wide pH range [8].

Phenethylamine behaves as a neuromodulator or neurotransmitter in the mammalian central nervous system. Many substituted aralkylamines are known as stimulants, hallucinogens, psychedelics and antidepressants. Since the aralkyl amines and their derivatives exhibit psychoactive properties [9], the investigation of the *N*-aralkylated iminodiacetic acids and their metal complexes is also of a pharmaceutical interest.

We prepared five new nickel(II) complexes with various N-aralkyliminodiacetic acids: N-benzyliminodiacetic (H₂Bnida), N-(2-phenylethyl)iminodiacetic (H₂Peida), N-(3-phenylprop-1-yl)iminodiacetic (H₂Ppida) and N-(o-chlorobenzyl)iminodiacetic acid (o-H₂Cbida) in order to get more insight into the coordination chemistry of divalent transition metals with iminodiacetic acid derivatives.



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Various cobalt(II), nickel(II) and copper(II) complexes with H₂Bnida and its *para*-substituted derivatives were already described in the literature and most of them contain heterocyclic nitrogen bases (imidazole, pyridine and purine derivatives) or water molecules as additional ligands, including [Ni(Bnida)(H₂O)₃], which is a solvatomorph of our complex [Ni(Bnida)(H₂O)₃]·H₂O (1) [10–15] (*vide infra*). There are also three nickel(II) complexes with H₂Bnida and its *p*-methyl or *p*-methoxy (*p*-X) derivatives, which are salts of the type [Ni(imidazole)₆][Ni(*p*-XBnida)₂] [1] or [Ni(H₂O)₄(imidazole)₂][Ni(Bnida)₂] [2]. As far as we know, no complexes with H₂Ppida were structurally described until now (see Scheme 1).

2. Experimental

2.1. Reagents and physical measurements

All chemicals for the syntheses were purchased from commercial sources (Aldrich, Acros or Merck) and used as received without further purification. The ligands were prepared by a modified method [15]. The CHN analyses were performed on a Perkin-Elmer 2400 Series II CHNS analyzer in the Analytical Services Laboratories of the Ruđer Bošković Institute, Zagreb, Croatia. The FTIR spectra were obtained from KBr pellets in the range 4000–450 cm⁻¹ on a Perkin-Elmer Spectrum RXI FTIR-spectrometer. The TGA-DTA measurements were performed at a heating rate of $10 \,^{\circ}\text{C}\,\text{min}^{-1}$ in the temperature range 25-600 °C, under nitrogen or oxygen flow of 20 mL min⁻¹ on an instrument Mettler-Toledo TGA-SDTA 851^e. Approximately 10 mg of sample were placed in a standard aluminum crucible (40 µL). The DSC measurements were performed at heating rate of 10 °C min⁻¹ in the temperature range 25–500 °C, under nitrogen flow of 180 mL min⁻¹ on an instrument Mettler-Toledo DSC 823^e. Approximately 2–5 mg of sample were placed in the standard aluminum crucible (40 µL). The NMR spectra of the ligands were recorded in the NMR Centre of the Ruđer Bošković Institute, Zagreb, Croatia on a Bruker AV 600 spectrometer, operating at 600 MHz for the ¹H nucleus and at 150 MHz for the ${}^{13}C$ nucleus. The samples were measured in DMSO- d_6 solutions at 298 K, using 5 mm NMR tubes. The chemical shifts in ppm were referenced to TMS. The complexes are paramagnetic and, therefore, not characterized by this method.

2.2. Preparation of the ligands

2.2.1. N-Benzyliminodiacetic acid, H₂Bnida

An aqueous solution of chloroacetic acid (19.0 g; 0.2 mol in 70 mL) was cooled in ice bath to 5 °C and neutralized with an aque-



Scheme 1. Structural formulae of the ligands: *N*-benzyliminodiacetic (H₂Bnida), *N*-(*o*-chlorobenzyl)iminodiacetic (*o*-H₂Cbida), *N*-(2-phenylethyl)iminodiacetic (H₂Peida) and *N*-(3-phenylprop-1-yl)iminodiacetic acid (H₂Ppida).

ous sodium hydroxide solution (8.0 g; 0.2 mol in 40 mL). The alkali was added at such a rate that the temperature of the reaction mixture never reached 20 °C. Then, 11.0 mL (0.1 mol) of the pure (colorless) benzylamine was added [Note 1]. The reaction mixture was refluxed and a solution of 8.0 g NaOH in 40 mL of water was added dropwise into it during one hour period. The clear colorless solution was formed and the refluxing was continued for one additional hour. The reaction mixture was poured into a large beaker, acidified to pH~2 with 34.0 mL [Note 2] of diluted hydrochloric acid (1:1 v/v) (CAUTION – white fumes are evolved!) and cooled to the room temperature. The bottom of the beaker was scratched with a sharp glass rod to induce the precipitation [Note 3] and stirred until the mixture solidified. After standing overnight in a refrigerator, the product was filtered off by suction, washed with 150 mL of ice water and dried by standing in air for a few days. Yield: 18.2 g (82%), m.p. 204.5 °C. White odorless powder, soluble in dimethyl sulfoxide, formic acid, N.N-dimethylformamide and hot water. Very soluble in alkaline aqueous solutions. Anal. Calc. for C₁₁H₁₃NO₄ (223.22): C, 59.18; H, 5.87; N, 6.28. Found: C, 57.86; H, 5.22; N, 6.42%. NMR data: ¹H NMR (600 MHz, DMSO d_6) δ : 3.42 (s, 4H), 3.84 (s, 2H), 7.34 (m, 5H). ¹³C NMR (150 MHz, DMSO-d₆) δ : 53.60 (CH₂), 57.09 (CH₂), 127.08 (CH), 128.18 (CH), 128.66 (CH), 138.57 (C), 172.18 (COOH). The assigned FTIR data (cm^{-1}) : 3025, 2972 (v(CH)); 2700–2300 $(v(NH^{+}))$; ~3450 (m, m)broad), 1729 and 1714, 1248, 703 (ν(OH), ν(C=O), δ(OH) and π (OH) of COOH); 1651 and 1387 (v_{as} and v_s of COO⁻). Other FTIR data (cm⁻¹): 2850(m, br), 1586(m), 1564(m), 1498(m), 1457(m), 1428(s), 1361(s), 1315(m), 1215(s), 1194(s), 1121(m), 1085(m), 1052(m), 1021(m), 956(s), 947(m), 894(m), 878(s), 752(s), 669(w), 624(m), 576(m), 550(w), 529(m), 504(w), 486(w), 472(w), 459(w).

Note 1. When technical (yellow) benzylamine is used in this preparation, a pale pink product is obtained. The color of the product may be removed by adding about 0.5 g of activated carbon to the hot solution before acidification. After 5-10 min of boiling and subsequent filtering, a colorless filtrate is obtained, providing a white product with somewhat lower yield (about 70%).

Note 2. Further acidification must be avoided as it decreases the yield. When 40 mL of hydrochloric acid were added, the yield was only 62%.

Note 3. The product easily forms supersaturated aqueous solutions which may remain for days if not disturbed by scratching. If the sample of this compound is already available, it can be used to initiate the precipitation which then starts more quickly and no scratching is needed.

2.2.2. N-(2-Phenylethyl)iminodiacetic acid, H₂Peida

This ligand was prepared in the same way as reported for H₂Bnida, but using phenethylamine (12.5 mL; 0.1 mol) instead of benzylamine. After the acidification, the product precipitates spontaneously by cooling of the hot solution. Yield: 19.8 g (84%); m.p 181.4 °C. White odorless crystals, soluble in dimethyl sulfoxide, N,N-dimethylformamide and hot water. Very soluble in alkaline aqueous solutions. Anal. Calc. for C₁₂H₁₅NO₄ (237.25): C, 60.75; H, 6.37; N, 5.90. Found: C, 59.86; H, 6.22; N, 6.12%. NMR data: ¹H NMR (600 MHz, DMSO-d₆) δ: 2.73 (t, 2H), 2.89 (t, 2H), 3.49 (s, 4H), 7.21 (m, 5H). ¹³C NMR (150 MHz, DMSO-d₆) δ: 33.65 (CH₂), 54.61 (CH₂), 57.09 (CH₂), 125.86 (CH), 128.20 (CH), 128.56 (CH), 139.84 (C), 172.32 (COOH). The assigned FTIR data (cm⁻¹): 3030, 2991, 2965 and 2840 (v(CH)); 2700-2300 (v(NH⁺)); ~3450 (m, broad), 1709, 1229 and 739 (v(OH), v(C=O), $\delta(OH)$ and $\pi(OH)$ of COOH); 1608 and 1384 (v_{as} and v_s of COO⁻). Other FTIR data (cm^{-1}) : 2840(m), 2648(br,w), 1498(m), 1432(vs), 1347(s), 1325(m), 1292(m), 1196(br, vs), 1083(s), 1032(m), 944(s), 910(m), 895(s), 858(s), 803(w), 782(m), 724(s), 696(s), 600(w), 560(w), 518(w), 478(w).

2.2.3. N-(3-Phenylprop-1-yl)iminodiacetic acid, H₂Ppida

The apparatus for this preparation consists of a hot plate magnetic stirrer and three-necked round bottom flask equipped with a Liebig condenser, dropping funnel and a thermometer reaching below the surface of the reaction mixture. An aqueous solution of chloroacetic acid (9.5 g; 0.1 mol in 50 mL) was cooled in an ice bath to 5 °C and neutralized with an aqueous sodium hydroxide solution (4.0 g; 0.1 mol in 40 mL). The alkali was added at such a rate that the temperature of the reaction mixture never reached 20 °C. Then, 7.2 mL (0.05 mol) of pure (colorless) 3-phenylprop-1-ylamine and 10 mL of ethanol were added [Note 1]. The reaction mixture was stirred and heated in a hot water bath until the temperature of the mixture reached 70 °C and the mixture became yellowish and turbid. Another solution of 4.0 g NaOH (0.1 mol) in 40 mL of water was added dropwise in a 2 h period, maintaining the pH below 11 and the temperature around 75–80 °C. A second portion of ethanol (10 mL) was added after the addition of the first 20 mL of alkali. Finally, the water bath was heated to boiling, the reaction mixture treated with 0.1 g of activated carbon, stirred and heated for 5 additional minutes and filtered. The colorless filtrate was treated with the additional 30 mL of ethanol and acidified with 17.0 mL of diluted hydrochloric acid (1:1 v/v) to pH ≈ 2 . After standing over night, the product crystallized as white needles. The ice-cooled crude product (9.5 g; 76%) [Note 2] was filtered off by suction and washed with 50 mL of water and 100 mL of ethanol. To obtain a pure product, 5.0 g of the substance was dissolved in 150 mL of boiling water and subsequently treated with 300 mL of ethanol. After cooling to the room temperature, the bottom of the flask was scratched with a sharp glass rod and the solution was left to stand in the refrigerator for 2 days. The crystals were filtered off by suction and washed with 50 mL of ice-cold ethanol. The recovery was 4.0 g (80%), making the total yield of the pure product 61%. m.p. 198.0 °C. White odorless needle-like crystals, soluble in dimethyl sulfoxide and boiling water (about 1 g/ 30 mL), almost insoluble in cold water. Soluble in alkaline aqueous solutions. Anal. Calc. for C₁₃H₁₇NO₄ (251.28): C, 62.13; H, 6.82; N, 5.58. Found: C, 61.86; H, 6.99; N, 5.42%. NMR data: ¹H NMR (600 MHz, DMSO-d₆) δ: 1.69 (m, 2H), 2.57 (t, 2H), 2.68 (t, 2H), 3.43 (s, 4H), 7.19 (m, 5H). ¹³C NMR (150 MHz, DMSO-d₆) δ: 29.06 (CH₂), 32.59 (CH₂), 53.58 (CH₂), 54.92 (CH₂), 125.58 (CH), 128.18 (CH), 128.20 (CH), 141.98 (C), 172.27 (COOH). The assigned FTIR data (cm⁻¹): 3017, 2954 and 2867 (v(CH)); 2700–2300 (v(NH⁺)); ~3460 (m, broad), 1738, 1241 and 702 (v(OH), v(C=O), $\delta(OH)$ and $\pi(OH)$ of COOH); 1623 and 1409 (v_{as} and v_s of COO⁻). Other FTIR data (cm⁻¹): 4363(br, w), 1926(br, w), 1497(w), 1328(s), 1264(m), 1190(m), 1077(w), 1024(w), 982(m), 953(m), 916(w), 893(w), 855(w), 759(m), 719(m), 678(w), 613(w), 577(w), 513(w), 491(w).

Note 1. The amine is not very soluble in water and forms white emulsion with aqueous chloroacetate solution. The addition of ethanol increases the solubility of the amine in this medium.

Note 2. The crude product, which was contaminated with the unreacted amine and possessed a strong aromatic odor, was not satisfactory for the preparation of metal complexes.

2.2.4. N-(o-Chlorobenzyl)iminodiacetic acid, o-H₂Cbida

This preparation was performed using the same apparatus as described for H_2 Ppida, but with *o*-chlorobenzylamine (6.0 mL; 0.05 mol) instead of 3-phenylprop-1-ylamine. The reaction mixture was heated to 70 °C and treated dropwise with another equivalent of sodium hydroxide solution during a 2.5 h period, maintaining the pH below 11 and the temperature around 75–80 °C. After the addition of the whole amount of the alkali, the water bath was heated to boiling and the heating continued for one additional hour. To remove the residual yellow oil, the reaction mixture was treated with 0.2 g of activated carbon and filtered

after 10 min of further heating. The almost colorless filtrate was acidified with 17.0 mL of diluted hydrochloric acid (1:1 v/v) to pH \approx 2 and left to cool spontaneously. After the crystallization began, the mixture was left to stand overnight in a refrigerator. The product was filtered off by suction, washed with 100 mL of ice-cold water and 25 mL of ice-cold ethanol. The crude product (9.0 g; 72%), which was contaminated with the unreacted amine, was recrystallized as described for H₂Ppida, with 60% recovery; hence the total yield is 43%. m.p. 197.8 °C. White odorless needles, soluble in dimethyl sulfoxide and boiling water (about 1 g/20 mL), almost insoluble in cold water. Soluble in alkaline aqueous solutions. Anal. Calc. for C₁₁H₁₂NO₄Cl (257.66): C, 51.27; H, 4.69; N, 5.44. Found: C, 50.86; H, 5.12; N, 5.32%. NMR data: ¹H NMR (600 MHz, DMSO-*d*₆) δ: 3.46 (s, 4H), 3.96 (s, 2H), 7.40 (m, 5H). ¹³C NMR (150 MHz, DMSO- d_6) δ : 53.92 (CH₂), 54.32 (CH₂), 127.06 (CH), 128.56 (CH), 129.08 (CH), 130.52 (CH), 132.89 (C), 136.34 (C), 172.25 (COOH). The assigned FTIR data (cm⁻¹): 3078, 3008 and 2966 (v(CH)); 2700–2300 ($v(NH^+)$); ~3430 (m, broad), 1685, 1265, 774 and 672 (v(OH), v(C=O), $\delta(OH)$ and $\pi(OH)$ of COOH); 1597 and 1413 (v_{as} and v_s of COO⁻). Other FTIR data (cm⁻¹): 1519(m), 1479(m), 1367(m), 1265(w), 1212(m), 1051(m), 1017(m), 952(m), 894(w), 857(m), 602(w), 548(w), 520(w), 495(w), 460(w).

2.3. Preparation of the complexes

2.3.1. $[Ni(Bnida)(H_2O)_3] \cdot H_2O(1)$

0.23 g (1.0 mmol) of H₂Bnida was added into a solution of 0.06 g of KOH (1.1 mmol) in 25 mL of water. The mixture was heated until a clear colorless solution was formed and then treated with a solution of 0.12 g (0.5 mmol) NiCl₂·6H₂O in 20 mL of water. The resulting blue-green solution (pH \approx 5) was left to stand overnight. The blue crystals of **1** were filtered off, washed with 5 mL of water and dried in air. Yield: 0.13 g (74%). Soluble in hot pyridine, less soluble in dimethyl sulfoxide or *N*,*N*-dimethylformamide, almost insoluble in water. *Anal.* Calc. for C₁₁H₁₉NO₈Ni (351.96): C, 37.50; H, 5.40; N, 4.00. Found: C, 37.02; H, 5.21; N, 3.91%. The assigned FTIR data (cm⁻¹): ~3450-2900 (s, broad) (ν (OH) of H₂O); 1623 and 1410 (ν_{as} and ν_{s} of COO⁻). Other FTIR data (cm⁻¹): 1580(vs), 1496(m), 1458 (m), 1389(m), 1361(m), 1329(m), 1273(w), 1222(w), 1205(w), 1091(w), 1073(w), 973(w), 944(w), 921(m), 828(w), 765(m), 741 (m), 707(m), 669(w), 632(m), 584(w), 523(m), 496(w), 463(w).

After \approx 4 weeks, blue prismatic crystals of **1** were obtained by the slow evaporation of the filtrate.

2.3.2. [Ni(Peida)(H_2O_3] (2)

An aqueous solution of nickel(II) acetate tetrahydrate (0.25 g; 1.0 mmol in 10 mL) was added to a boiling aqueous solution of H₂Peida (0.24 g; 1.0 mmol in 40 mL). The light green solution (pH \approx 5) became blue-green and light blue needles began to separate after a few minutes. After the reaction mixture was left to stand overnight, the product was filtered off by suction, washed with 15 mL of water and dried in air. Yield: 0.30 g (86%). Soluble in dimethyl sulfoxide and hot pyridine, less soluble in N,N-dimethylformamide, almost insoluble in water. Anal. Calc. for C₁₂H₁₉NO₇Ni (347.97): C, 41.42; H, 5.50; N, 4.03. Found: C, 41.04; H, 5.50; N, 4.12%. The assigned FTIR data (cm⁻¹): 3587 (m), 3180 (s, broad) (v(OH) of H₂O); 1616 and 1411 (v_{as} and v_s of COO⁻). Other FTIR data (cm⁻¹): 2965(m), 1576(s), 1497(m), 1469(m), 1454(m), 1435(m), 1375(m), 1347(m), 1306(w), 1249(w), 1209(w), 1109(m), 1070(w), 1031(w), 1010(w), 979(w), 967(w), 947(w), 913(m), 832(w), 772(m), 748(m), 694(m), 583(w), 535(w), 510(w).

2.3.3. [Ni(Ppida)(H₂O)₃]·H₂O (**3a**) and [Ni(Ppida)(H₂O)₃] (**3b**)

An aqueous solution of nickel(II) acetate tetrahydrate (0.25 g; 1.0 mmol in 10 mL) was added to a boiling aqueous solution of

H₂Ppida (0.25 g; 1.0 mmol in 40 mL). The light green solution (pH \approx 5) became blue-green and pale blue needles began to separate after three days of standing at room temperature. Next day the product was filtered off by suction, washed with 15 mL of water and dried in air to obtain 0.18 g of 3a (Yield: 47%). Soluble in dimethyl pyridine, less sulfoxide and soluble in N,N-dimethylformamide, almost insoluble in water. The sample loses its cocrystallized water after drying in a dessicator over anhydrous CaCl₂. Anal. Calc. for C₁₃H₂₃NO₈Ni (380.01): C, 41.09; H, 6.10; N, 3.69. Found: C, 41.43; H, 6.17; N, 3.85%. The assigned FTIR data (cm⁻¹): 3385 (s, broad) (v(OH) of H₂O); 1611 and 1412 (v_{as} and v_s of COO⁻). Other FTIR data (cm⁻¹): 1589(vs), 1496(w), 1470(w), 1440(w), 1382(m), 1338(w), 1316(w), 1246(w), 1109(w), 1051(w), 987(w), 969(w), 937(w), 904(w), 750(m), 727(w), 697(w), 575(w), 541(w), 490(w).

After one additional day, blue crystals of **3b**, suitable for X-ray structural analysis, were obtained by the slow evaporation of the light blue mother liquor, remained after filtration of 3a. The product was filtered off, washed with 10 mL of water and dried in air. Yield: 0.10 g (28%). Sparingly soluble in dimethyl sulfoxide and pyridine, almost insoluble in *N*,*N*-dimethylformamide and water. Anal. Calc. for C13H21NO7Ni (362.00): C, 43.09; H, 5.80; N, 3.78. Found: C, 43.43; H, 5.94; N, 3.72%. The assigned FTIR data (cm^{-1}) : 3562 (m), 3228 (s, broad) (v(OH) of H₂O); 1613 and 1408 $(v_{as} \text{ and } v_{s} \text{ of COO}^{-})$. Other FTIR data (cm^{-1}) : 2963(m), 1582(vs), 1495(w), 1471(w), 1438(w), 1376(m), 1339(w), 1306(w), 1240(w), 1179(w), 1109(w), 1069(w), 966(w), 943(w), 913(w), 843(w), 749(m), 695(w), 628(w), 586(w), 515(w), 476(w).

2.3.4. Preparation of $[Ni(o-Cbida)(H_2O)_3]$ (4)

An aqueous solution of nickel(II) acetate tetrahydrate (0.25 g; 1.0 mmol in 10 mL) was added to a boiling aqueous solution of o-H₂Cbida (0.26 g; 1.0 mmol in 40 mL). The light green solution (pH 5) became blue-green and light blue needles began to separate after about half an hour. After standing overnight, the product was filtered off by suction, washed with 15 mL of water and dried in air. Yield: 0.31 g (84%). Sparingly soluble in dimethyl sulfoxide and pyridine, almost insoluble in *N*,*N*-dimethylformamide and water. Anal. Calc. for C₁₁H₁₆NO₇ClNi (368.39): C, 35.86; H, 4.38; N, 3.80. Found: C, 35.86; H, 4.15; N, 4.03%. The assigned FTIR data (cm^{-1}) : 3292 (s, broad) (v(OH) of H₂O); 1595 and 1414 (v_{as} and $v_{\rm s}$ of COO⁻). Other FTIR data (cm⁻¹): 2968(m), 1476(m), 1463(m), 1440(m), 1353(w), 1337(m), 1305(w), 1264(m), 1218(w), 1193(w), 1140(w), 1097(w), 1055(w), 1042(m), 974(w), 943(m), 921(m), 818(w), 782(s), 742(m), 725(m), 679(m), 629(w), 590(w), 546(w), 492(w).

2.4. Single crystal X-ray diffraction analysis and structure determination

The suitable single crystals of 1 and 3b were selected and mounted in air onto the thin glass fibers. The data collection for 1 and 3b was carried out by an Oxford Diffraction Xcalibur four-circle kappa geometry diffractometer with Xcalibur Sapphire 3 CCD detector, using a graphite monochromated Mo K α (λ = 0.71073 Å) radiation, and by applying the CrysAlis Software system, Version 1.171.32.29 [16] for 1 and the CrysAlisPro Software system, Version 1.171.33.55 [17] for **3b** at room temperature (296(2) K). The data reduction was done by the same programs [16–17].

The X-ray diffraction data were corrected for Lorentz-polarization factor and scaled for absorption effects by multi-scan. The structure of 1 was solved by direct methods and the structure of 3b by Patterson method, implemented in SHELXS-97 [18]. A refinement procedure by full-matrix least squares methods, based on F^2 values against all reflections, was performed by SHELXL-97 [18], including anisotropic displacement parameters for all non-H atoms.

The position of hydrogen atoms belonging to the carbon atoms was geometrically optimized applying the riding model (0.97 Å, $U_{iso}(H) = 1.2U_{eq}(C)$ for methylen H atoms and 0.93 Å, $U_{iso}(H) =$ $1.2U_{eq}(C)$ for aromatic H atoms). The hydrogen atoms belonging to the water molecules were found in the difference Fourier maps. The distance between the water molecule O atoms and the corresponding hydrogen atoms was restrained to the average value of 0.82 Å using SHELXL-97 DFIX instruction. The isotropic $U_{iso}(H)$ values for these hydrogen atoms were fixed at the same time $(U_{iso}(H) = 1.2U_{eq}(O)).$

The affirmation of chosen space groups and the analysis of the molecular geometry, hydrogen bonds and π - π interactions were performed by PLATON [19]. The molecular graphics were done with ORTEP-3 [20] and MERCURY (Version 3.0) [21].

The crystal parameters, data collection and refinement results for **1** and **3b** are summarized in Table 1.

3. Results and discussion

3.1. Synthesis of the complexes

Complex 1 was prepared from nickel(II) chloride hexahydrate, *N*-benzyliminodiacetic acid and potassium hydroxide in a slightly acidic aqueous solution. Although the ligand-to-metal ratio was 2:1, the nickel(II) ion was found to be coordinated by only one ligand ion. The other possible complexes such as [Ni(HBnida)₂] or $[Ni(HBnida)_2(H_2O)_2]$, which could arise from this combination of reactants, were never isolated. The coordination environment with one fully deprotonated Bnida²⁻ ion and three water molecules

Table 1

Crystal data and details of the structure determination for 1 and 3b.

Compound	1	3b
Formula	C11H19NiNO8	C13H21NiNO7
Mr	351.98	362.02
Color and habit	blue, prism	blue, block
Crystal system	orthorhombic	monoclinic
Space group	Pca2 ₁	$P2_1/c$
Crystal dimensions (mm ³)	$0.49 \times 0.31 \times 0.16$	$0.58 \times 0.53 \times 0.43$
a (Å)	11.3509(2)	18.1964(4)
b (Å)	16.7012(3)	7.7540(2)
c (Å)	7.4757(1)	11.2469(2)
α (°)	90	90
β(°)	90	102.004(2)
γ (°)	90	90
V (Å ³)	1417.20(4)	1552.18(6)
Z	4	4
D_{calc} (g cm ⁻³)	1.650	1.549
$\mu ({\rm mm^{-1}})$	1.408	1.283
F(000)	736	760
θ range (°)	3.79-30.00	4.33-30.00
h,k,l range	–15:15, –23:17,	-25:21, -8:10,
	-10:8	-15:12
Scan type	ω , φ	ω, φ
Number of measured reflections	12162	8455
Number of independent reflections (R_{int})	3802 (0.0201)	4492 (0.0147)
Number of observed reflections $[I \ge 2\sigma(I)]$	2933	3613
Number of refined parameters	214	217
$R^{\rm a}$, w $R^{\rm b}$ $[I \ge 2\sigma(I)]$	0.0275, 0.0585	0.0253, 0.0626
R, wR (all data)	0.0410, 0.0613	0.0347, 0.0644
Goodness of fit (GOF) on F^2 , S^c	0.923	0.975
Maximum, minimum electron density (e Å ⁻³)	0.29, -0.20	0.33, -0.39
Maximum Δ/σ	0.001	0.002

^a $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$.

which was observed in the case of **1** seems to be much more favorable for Ni(II) than the alternative arrangements with two partially deprotonated HBnida⁻ ions. This method of preparation was not satisfactory for the complexes **2-4** because of the low solubility of the higher analogues of H₂Bnida. The second equivalent of the ligand (H₂Peida, H₂Ppida or o-H₂Cbida), which was used to maintain the reaction mixture acidic (to prevent the precipitation of nickel(II)), crystallized out together with its nickel(II) complex, forming the mixtures which could not be easily resolved. That problem was avoided by the use of nickel(II) acetate and only one equivalent of the ligand. This method also gave complex **1** by the reaction of nickel(II) acetate with H₂Bnida. The formation of these complexes was most probably assisted by their low solubility, which allowed these reactions to proceed in a high yield.

3.2. Infrared spectroscopy

The infrared spectra of the ligands indicate that these compounds in the solid state exist in the zwitterionic form with one deprotonated and one protonated carboxylic group [22]. The bands assigned to the antisymmetric stretching (v_{as}) of the carboxylate ion in the spectra of H₂Bnida (1651 cm⁻¹), H₂Peida (1608 cm⁻¹), H₂Ppida (1623 cm⁻¹) and *o*-H₂Cbida (1597 cm⁻¹) are shifted to the lower wavenumbers in the spectra of **1**, **3a**, **3b** and **4**, but to the higher wavenumber in the spectrum of **2**. The bands assigned to the symmetric stretching of the carboxylate ion (v_s), observed at 1387 cm⁻¹ (H₂Bnida), 1384 cm⁻¹ (H₂Peida), 1409 cm⁻¹ (H₂Ppida) and 1413 cm⁻¹ (*o*-H₂Cbida), are shifted to the higher value in the spectra of these complexes. The stretching of the carbonyl group, v(C=0), which appears in the spectra of H₂Bnida (1729 and 1714 cm⁻¹), H₂Peida (1709 cm⁻¹), H₂Ppida (1738 cm⁻¹) and *o*-H₂Cbida (1685 cm⁻¹), is absent in the spectra of the complexes due to deprotonation of the both carboxylic groups [22].

Complexes **1–4** exhibit similar solid-state infrared spectra. The infrared spectrum of **1** shows $v_{as}(COO)$ at 1623 cm⁻¹ and $v_s(COO)$ at 1410 cm⁻¹. Similar peaks of $v_{as}(COO)$ and $v_s(COO)$ are also observed in this region for complexes **2** (1616, 1411 cm⁻¹), **3a** (1611, 1412 cm⁻¹), **3b** (1613, 1408 cm⁻¹) and **4** (1595, 1414 cm⁻¹). The difference between $v_{as}(COO)$ and $v_s(COO)$, Δ value, is greater than 200 cm⁻¹ for complexes **1**, **2** and **3b** and is negligibly smaller than 200 cm⁻¹ for complex **3a** (199 cm⁻¹),







Fig. 2. The packing diagram of $[Ni(Bnida)(H_2O)_3]$ -H₂O (1) (a view in the (100) plane). In this projection, the 2D network (described in Crystal structures section) is represented as an endless double chain, extending in the [001] direction. The $[Ni(Bnida)(H_2O)_3]$ and co-crystallized water molecules are connected into the chain by intermolecular O-H···O hydrogen bonds (shown by the dotted lines).



Fig. 3. The packing diagram of $[Ni(Ppida)(H_2O)_3]$ (**3b**) (a view in the (010) plane). In this projection, the 2D network (described in Crystal structures section) is represented as an endless double chain, extending in the [001] direction. The molecules are connected into the chain by intermolecular O-H···O hydrogen bonds (shown by the dotted lines).

indicating the monodentate coordination of the carboxylate group [23,24]. Complex **4** is an exception with Δ = 181 cm⁻¹, probably because of the steric or electronic influence of the chlorine atom attached to the aromatic ring in the *ortho* position. The broad bands observed in the range of 2300–3500 cm⁻¹ indicate numerous hydrogen bonds of the O-H···O type.

3.3. Thermal analysis (TGA-DTA, DSC)

The free ligands, when heated in the nitrogen atmosphere, melt with decomposition. The melting points, obtained from DSC curves, are 204.5, 181.4, 198.0 and 197.8 °C for H₂Bnida, H₂Peida, H₂Ppida and o-H₂Cbida. The decomposition of H₂Bnida starts at 201.1 °C, yielding a black residue (15.1% of its initial mass). The decomposition of H₂Peida and H₂Ppida starts at 182.3 and 198.6 °C, and no residue is obtained. o-H₂Cbida decomposes above 197.9 °C, yielding a black residue (2.2%).

Complex **1**, when heated in nitrogen, loses its water molecules in two partially overlapped consecutive steps: 13.7% at 149.2 °C and 6.7% at 196.0 °C, the sum of which corresponds to the calculated value of 20.5% for the total loss of four water molecules. Further heating leads to the complete degradation of the sample. The mass loss of 61.2% between 200 and 600 °C corresponds to the calculated value for the Bnida^{2–} ion (62.8%). The residue at 600 °C amounts to 18.4%. The same experiment, when performed in the oxygen atmosphere, also shows two partially overlapped steps: 13.2% at 153.2 °C and 7.1% at 206.7 °C for the total loss of four water molecules. Further heating leads to a very exothermic decomposition of the sample. The mass loss at 404.9 °C equals 63.1%, leaving a black residue (16.7%) at 600 °C.

Complex **2** decomposes in three steps. The sample loses its water molecules in two overlapped consecutive steps: 6.7% at 138.9 °C and 8.3% at 180.6 °C, the sum of which corresponds to the calculated value of 15.5% for the total loss of three water molecules. Further heating leads to the complete degradation of the sample. The mass loss of 70.2% between 200 and 600 °C corresponds to the calculated value for the Peida^{2–} ion (67.6%). The residue at 600 °C amounts to 14.8%. The sample of **2** decomposes also in three steps in the oxygen atmosphere: 5.6% at 140.2 °C and 9.2% at 186.7 °C for all three water molecules and a very exothermic decomposition between 300 and 400 °C (67.0%; two peaks found at 363.8 and 385.2 °C). The residue at 600 °C amounts to 18.1%.

Complex **3a** loses its water molecules in three overlapped steps: 6.8% at 100.6 °C, 6.9% at 119.6 °C and 6.6% at 167.5 °C, the sum of which corresponds to the calculated value of 18.9% for the total loss of four water molecules. The mass loss of 64.7% at 380.4 °C

T - 1	1.1		2
13	n	ρ	
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Selected bond distances (Å) and angles (°) for **1** and **3b**.

	1	3b
Bond distances		
Ni1-01	2.067(2)	2.0415(9)
Ni1-02	2.038(2)	2.0578(9)
Ni1-03	2.067(2)	2.079(1)
Ni1-04	2.041(2)	2.0448(9)
Ni1-05	2.017(1)	2.0297(9)
Ni1-N1	2.130(2)	2.122(1)
Bond angles		
05-Ni1-02	176.49(8)	175.59(4)
05-Ni1-O4	90.70(8)	87.48(4)
02-Ni1-04	92.72(8)	88.18(4)
05-Ni1-01	90.42(7)	91.85(4)
02-Ni1-01	86.16(8)	92.43(4)
04-Ni1-01	178.87(9)	176.43(4)
05-Ni1-O3	89.10(6)	89.25(4)
02-Ni1-03	91.80(7)	91.75(4)
04-Ni1-03	88.85(8)	92.53(4)
01-Ni1-03	91.35(8)	90.97(4)
05-Ni1-N1	82.95(6)	83.53(4)
02-Ni1-N1	96.65(6)	95.10(4)
04-Ni1-N1	82.65(6)	82.42(4)
01-Ni1-N1	97.31(6)	94.02(4)
03-Ni1-N1	168.27(8)	171.34(4)

corresponds to the calculated value for the Ppida^{2–} ion (65.6%). The residue at 600 °C amounts to 14.4%. The sample of **3a** also decomposes in four steps in the oxygen atmosphere: mass losses of 6.5% at 101.1 °C, 7.2% at 121.7 °C and 7.0% at 169.2 °C correspond to the release of all four water molecules and are followed by a very exothermic decomposition between 250 and 350 °C (62.2%; two peaks found at 328.5 °C and 367.7 °C). The residue at 600 °C amounts to 17.5%.

Complex **3b** loses its water molecules in two steps: 4.9% at 120.2 °C and 8.9% at 140.0 °C, which is in agreement with the calculated value of 4.9% per one water molecule. Further heating (two peaks observed at 252.6 °C and 381.3 °C) leads to the loss of the ligand (70.2% observed, 68.9% calculated for the Ppida^{2–} ion). The residue at 600 °C amounts to 16.0%. The decomposition of **3b** in oxygen starts with the loss of one water molecule at 119.8 °C (4.8% observed). The other two water molecules (10.4% observed) are lost between 120 and 250 °C (one weak endothermic peak at 252.5 °C observed). A further heating leads to a very exothermic decomposition, in the range 250–400 °C (67.4%; two peaks found at 337.0 and 395.1 °C). The residue at 600 °C amounts to 17.5%.

Complex **4** decomposes in only two steps in the nitrogen atmosphere. After the loss of all three water molecules at 155.7 $^\circ$ C

Table 3						
Hydrogen	bond	geometry	for	1	and	3b.

(14.7% calculated; 14.3% observed), the sample loses 62.3% of its initial mass (69.4% calculated for the *o*-Cbida^{2–} ion) between 200 and 600 °C (an endothermic peak at 397.2 °C observed), leaving a black residue (23.3%). The decomposition of **4** in oxygen starts with the loss of three water molecules at 149.5 °C (14.6% observed). After further heating a very exothermic decomposition occurs. The loss of 67.1% at 411.1 °C corresponds to 70.0%, calculated for the molecule of *o*-H₂Cbida. The residue at 600 °C amounts to 18.7%.

3.4. Crystal structures

ORTEP-3 drawings of the molecular structures of **1** and **3b** are depicted in Fig. 1. The crystal structures of **1** and **3b** are shown in Figs. 2 and 3, respectively. The selected molecular geometry parameters are listed in Table 2, and the hydrogen bond geometry in Table 3.

Nickel(II) ion is octahedrally coordinated by three water molecules (O1, O2 and O3 atoms) and by *O*,*N*,*O'*-tridentate Bnida^{2–} (in **1**) or Ppida^{2–} ligand (in **3b**), resulting with the formation of *fac* isomer in both cases. Bnida^{2–} and Ppida^{2–} are coordinated to nickel(II) ion via imino N1 and carboxylate O4 and O5 atoms, forming two five-membered chelate rings (defined by Ni1/O4/C1/C2/N1 and Ni1/O5/C3/C4/N1 atoms) (Fig. 1). The dihedral angle between these rings amounts to 82.7(1)° in **1** and to 87.88(5)° in **3b**. The distortion of the octahedron is indicated by the bond angles around the nickel(II) ion in **1** and **3b**, involving *cis* and *trans* pairs of donor atoms (Table 2). The distortion is also observed in the bite angles $\angle O4-Ni1-N1$ (82.65(6)° for **1** and 82.42(4)° for **3b**) and $\angle O5-Ni1-$ N1 (82.95(6)° for **1** and 83.53(4)° for **3b**) (Table 2). There is a cocrystallized water molecule (O8 atom) in the structure of **1**.

The analogous bond distances and angles in **1** and **3b** are comparable to each other (Table 2). The Ni–N and Ni–O bond distances (N and O atoms from Bnida^{2–} and Ppida^{2–}) in **1** and **3b** are in accordance with the corresponding ones, reported in the literature for nickel(II) complexes with *N*-aralkyl derivatives of iminodiacetic acid [1–2,14]. Complexes **1** and **3b** are closely related to the published [Ni(*p*-XBnida)(H₂O)₃] (*p*-X = *p*-methyl or *p*-methoxy). All of these complexes have analogous molecular structures, but some of them contain different number of cocrystallized water molecules [1,14].

There are numerous intermolecular $O-H\cdots O$ hydrogen bonds in the crystal structures of both **1** and **3b**, formed between water molecule O atoms as proton donors and carboxylate O atoms as proton acceptors (Table 3). Some water molecule O atoms also act as proton acceptors in the structure of **1**. The molecules of [Ni(Bnida)(H₂O)₃] and cocrystallized water molecules in the crystal structure of **1**

$D{-}H{\cdot}{\cdot}{\cdot}A$	d(D-H) (Å)	$d(H \cdot \cdot \cdot A)(Å)$	$d(\mathbf{D}\cdot\cdot\cdot\mathbf{A})$ (Å)	\angle (D–H···A) (°)	Symmetry code on A
1					
01-H1106	0.78(2)	2.01(3)	2.760(2)	161(3)	x, y, -1 + z
01-H12···07	0.82(2)	1.93(2)	2.748(2)	178(2)	-1/2 - x, y, $-1/2 + z$
02-H2106	0.83(2)	2.02(2)	2.810(2)	161(2)	1/2 - x, y, $-1/2 + z$
02-H22···08	0.83(2)	1.79(2)	2.610(3)	171(3)	-
03-H31···01	0.74(2)	2.36(3)	2.973(2)	142(3)	-x, $1 - y$, $1/2 + z$
03-H32···04	0.79(2)	2.08(2)	2.858(2)	169(2)	-x, $1 - y$, $-1/2 + z$
08-H8105	0.80(3)	2.07(3)	2.845(3)	163(4)	-x, $1 - y$, $-1/2 + z$
08-H82···05	0.78(4)	2.05(3)	2.808(3)	165(3)	1/2 + x, $1 - y$, z
3b					
01-H1104	0.81(1)	1.93(1)	2.738(1)	175(2)	x, $5/2 - y$, $-1/2 + z$
01-H12···05	0.81(2)	1.93(2)	2.738(1)	178(2)	1 - x, 2 - y, 1 - z
02-H21···07	0.76(2)	2.04(2)	2.787(1)	170(2)	x, 1 + y, z
02-H22···06	0.82(2)	1.87(2)	2.676(2)	173(2)	x, $5/2 - y$, $-1/2 + z$
03-H31···07	0.83(2)	2.09(2)	2.909(2)	168(2)	1 - x, $1/2 + y$, $3/2 - z$
03-H32···07	0.87(1)	2.27(2)	3.075(2)	155(2)	x, 1 + y, z

are connected into a complicated hydrogen-bonded 2D network which is parallel to the (010) plane. These 2D networks are in turn assembled only by weak van der Waals interactions in the [010] direction (Fig. 2). The molecules in the crystal structure of **3b** are also connected into the hydrogen-bonded 2D network, parallel to the (100) plane. The 2D networks are in turn assembled by weak van der Waals interactions in the [100] direction (Fig. 3).

There are π - π interactions between the phenyl rings defined by atoms C8/C9/C10/C11/C12/C13 and C8ⁱ/C9ⁱ/C10ⁱ/C11ⁱ/C12ⁱ/C13ⁱ [symmetry code (i): -x, 2 - y, -z; centroid-centroid distance 3.614(1) Å, the angle between the planes 0°; the perpendicular distance between the planes 3.333(1) Å; the slippage 1.396 Å] in the structure of **3b**.

4. Conclusions

Several nickel(II) complexes were prepared by the reactions of nickel(II) salts with various *N*-aralkyliminodiacetic acids in aqueous solutions. Their molecular structures were determined by X-ray diffractometry. All these complexes are monomer (not polymeric) compounds and have analogous molecular structures with *fac*-conformation of the chelators. Some of them contain cocrystallized water molecules.

Due to their insolubility in the aqueous medium, the formation of these complexes could find its application in the removal of nickel(II) ions from water contaminated with the soluble nickel(II) salts.

Metal complexes with N-(2-phenylethyl)iminodiacetic acid (H₂-Peida), are scarce in the literature, as only three metal complexes of this ligand are known [15,25]. Complex **3b** is the first prepared and structurally characterized metal complex with N-(3-phenylprop-1yl)iminodiacetic acid (H₂Ppida), a new ligand for the complexation of metal ions.

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Appendix A. Supplementary material

CCDC 907170 and 907171 contain 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 can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.02.017.

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