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New polynuclear compounds based on *N*-benzyliminodipropionic acid: solution studies, synthesis, and X-ray crystal structures

Emiliano Braña^a, Delfina Quiñone^a, Sebastián Martínez^a, Joaquín Grassi^b, Ignacio Carrera^b, Julia Torres^a, Javier González-Platas^c, Gustavo Seoane^b, Carlos Kremer^a and Carolina Mendoza^a

^aCátedra de Química Inorgánica, Departamento Estrella Campos, Facultad de Química, Universidad de la República, Montevideo, Uruguay; ^bLaboratorio de Síntesis Orgánica, Departamento de Química Orgánica, Facultad de Química, Universidad de la República, Montevideo, Uruguay; ^cDepartamento de Física, Servicio de Difracción de Rayos X, Universidad de La Laguna, Tenerife, Spain

ABSTRACT

Three new polynuclear compounds based on a dicarboxylic acid ligand are reported. In particular, two Cu(II) coordination compounds, $[Cu_2(H_2O)_{\epsilon}(Hbzlidp)_2](CF_2SO_2)_2 \cdot 2H_2O$ (1) and $[Cu(NO_2)(Hbzlidp)]_{\epsilon}$ (2) $(bzlidp^{2-} = N-benzyliminodipropionate anion)$, and a Ni(II) dinuclear compound, $[Ni_2(H_2O)_4(bzlidp)_2]$ (3), were synthesized and characterized by IR spectroscopy, elemental analysis and single crystal X-ray diffraction. Different structures were obtained depending on the reaction conditions. The structural analyses reveal that **1** was formed by dinuclear $[Cu_{2}(H_{2}O)_{c}(Hbzlidp)_{2}]^{2+}$ units built by two copper(II) ions joined through two Hbzlidp ligands, while 2 was formed by pairs of Cu(II) centers bridged by four syn, syn carboxylate groups to generate "paddle wheel" units. The dinuclear copper units are arranged in a rhombus type grid, in a 2-D layer structure. In both cases, the N was protonated and not coordinated to the metal center. Compound 3 was formed by [Ni₂(H₂O)₄(bzlidp)₂] neutral dinuclear units, with octahedral Ni(II) centers. Solution studies of the ligand-M(II) systems (M(II) = Mn, Co, Ni, Cu, Zn, Cd, and Pb) were also carried out.

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1. Introduction

Coordination polymers are infinite crystalline lattices composed of inorganic nodes (metal ions or clusters) connected by organic polytopic ligands that act as linkers [1]. Solid-state materials with different architectures, linear, bi- or tri-dimensional arrays, are formed by a self-assembly process [2]. The design and preparation of coordination polymers is of current interest due to their promising applications in gas storage, catalysis, drug delivery, magnetochemistry, or supramolecular chemistry [1, 3–8]. Initially, rigid, highly directional ligands were used to connect the metal ions, an approach of choice if specific crystal motifs are desired [9]. Recently, the use of flexible ligands in the synthesis of coordination polymers has caught the attention of several groups [10–18]. Examples of flexible ligands employed in the preparation of coordination polymers are dicarboxylic acid compounds such as 1,4-cyclohexanedicarboxylic acid (H₂chdc) [19] or 1,4-phenylenediacetic acid (H₂pda) [20], dipyridine derivatives such as 1,2-bis(4-pyridyl) ethane (bpe) [21] or tricarboxylic acids such as nitrilotriacetic acid (H₃nta) [22] and nitrilotripropionic acid (H₃ntp) [23]. In these ligands, the flexibility is due to the rotation of the single bonded carbon chains [22]. The existence of different conformations may lead to different final structures [12]. The use of flexible ligands is of interest because flexibility is essential in the design of molecular devices whose functionality is based on conformational changes. The breathing ability of certain solid-state polymers or the possibility of adaptive recognition of guests are good examples [4, 24, 25].

In comparison to rigid connectors, the use of flexible ligands to build coordination polymers is more difficult [12]. The reasons for this include: (a) the ligand can adopt different conformations which are difficult to control, making the design of polymers complicated; (b) the self-assembly process is sensitive to many factors related to the reaction conditions, in particular the metal ion, the reactant concentration, and the solution pH; and finally, (c) flexible ligands can also act as polydentate ligands forming mononuclear entities, a competitive process that should be avoided.

Polycarboxylate ligands are frequently selected as flexible organic linkers in the construction of metal clusters, because they show different coordination modes, resulting from completely or partially deprotonated sites, allowing for various structural topologies [26]. They can act as terminal unidentate, chelating, bridging bidentate, or bridging tridentate ligands [27]. They also present the ability to act as hydrogen bond acceptors to assemble supramolecular structures [28].

We are interested in the design of coordination polymers using flexible polytopic ligands. In previous work, we reported the preparation of polymers $[Ln(Hida)_3] \cdot xH_2O$ (Ln = lanthanide ion; H_2 ida = iminodiacetic acid) [29]. Although this is a typical tridentate ligand, if the synthesis is performed under acidic conditions, nitrogen protonation occurs, and Hida⁻ becomes a ditopic flexible ligand. It is able to build polymeric complexes, which exhibit, in the solid state, large hexagonal channels with more than 11 Å diameters. We also reported the preparation and X-ray crystal structure of trinuclear copper(II) complexes with nitrilotripropionate (ntp³⁻), working at acidic pH values. The structure of the polynuclear complexes shows the presence of well-defined capsules formed by three Cu(II) cations and two protonated Hntp²⁻ ligands in a tritopic arrangement. The counter ion of the copper salt used in the preparation influences the final structure by changing the connection between the capsules [30].

With these examples in mind, we started study of iminodipropionic acid derivatives, in particular *N*-benzyliminodipropionic acid (H₂bzlidp, figure 1) as flexible ligand to connect metal ions. H₂bzlidp is a dicarboxylic acid that has been scarcely studied as a ligand in coordination chemistry. To our knowledge, the three compounds reported here are the first examples of polynuclear complexes containing this



Figure 1. Structure of *N*-benzyliminodipropionic acid (H₂bzlidp).

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ligand. H₂bzlidp was prepared based on a slight modification of a previously reported protocol for the synthesis of the *N*-methyliminodipropionic acid (H₂midp) [31]. The authors reported the preparation of a Cu(II) compound ([Cu(H₂O)midp]·H₂O) where the coordination geometry of each Cu ion can be described as a slightly distorted square pyramid and the midp²⁻ is a tetradentate bridging ligand resulting in infinite chains, which extend along [010]. Other related iminodipropionic ligands have been employed in the preparation of Cu(II) mononuclear coordination compounds. For instance, with the *o*-anisidine-*N*,*N*-di-3-propionate anion (*o*-Andp²⁻) a mononuclear compound, [Cu(*o*-Andp)(H₂O)₂]·2H₂O, was obtained where the Cu coordination polyhedron is a distorted tetragonal bipyramid (4 + 2) and the ligand is a tetradentate chelator, forming three chelate rings [32]. With *p*-toluidine-*N*,*N*-di-3-propionate (P-Tdp²⁻) amononuclear complexes [CuL(H₂O)₂] (L = *p*-Tdp²⁻ or Adp²⁻) were prepared and show a square pyramid Cu coordination polyhedron with the ligand as tridentate chelator. However, no polynuclear species were reported with these ligands [33, 34].

2. Experimental

2.1. General information

All common laboratory chemicals were reagent grade, purchased from commercial sources and used without purification. Infrared spectra, as KBr pellets, were obtained from a FTIR Shimadzu IR-Prestige-21 spectrophotometer from 4000 to 400 cm⁻¹. Elemental analyses (C, H, N, and S) were performed on a Flash 2000 instrument. NMR spectra were obtained on a Bruker Avance DPX-400 instrument. Proton chemical shifts (δ) are reported in ppm downfield from TMS as an internal reference. Thermogravimetric analyses (TGA) were performed in a Shimadzu TGA-50 instrument with a TA 50 I interface using platinum cells. TGA results were recorded under a nitrogen stream (50 mL min⁻¹) and with a heating rate of 1.0 °C min⁻¹ from 18 to 300 °C and 30 °C min⁻¹ from 300 to 700 °C.

For solution studies, $MnCl_2 \cdot 4H_2O$ (98%, Merck), $CoCl_2 \cdot 6H_2O$ (98%, Carlo Erba), $NiCl_2 \cdot 6H_2O$ (98%, Merck), $CuCl_2 \cdot 2H_2O$ (99.2%, Baker), $ZnCl_2$ (98%, Sigma Aldrich), $CdCl_2$ (99%, Fluka), and $Pb(NO_3)_2$ (99%, Sigma Aldrich) were used as metal cation sources. The standard HCl and NaOH solutions were prepared by diluting Merck standard ampoules. Me_4NCl solutions were prepared from Me_4NCl (98% from Fluka). Acid and base stock solutions were standardized against sodium borate and potassium hydrogen phthalate, respectively. All solutions were prepared with analytical grade water (18 μ S cm⁻¹) and were freed of carbon dioxide by bubbling with argon.

2.2. Equilibrium studies

The protonation constants of bzlidp^{2–} were determined through four potentiometric titrations (*ca.* 100–150 experimental points each) in the concentration range 1–4 mmol L⁻¹. Then, the behavior of the ligand in the presence of metal cations M(II) (M = Mn, Co, Ni, Cu, Zn, Cd, and Pb) was analyzed through at least six potentiometric titrations (*ca.* 100–150 experimental points each) for each system, at metal cation concentrations ranging from 1 to 3 mmol L⁻¹, and ligand to metal cation total molar ratios varying from 5:1 to 1:2. The pH interval from 2 to the pH where solid formation was evidenced was covered (pH value for the solid formation was always higher than six). In those cases, the formation of solid M(II) hydroxide was consistent with previous reports on metal hydroxide solubilities [35]. The formation constants of soluble hydroxo species of M(II) were also determined analogously under the same experimental conditions. Four titrations of M(II) solutions (*ca.* 80 experimental points each) were carried out in the concentration interval 1–3 mmol L⁻¹. The obtained values for these hydrolysis constants were taken into account in the Hyperquad input for the subsequent formation constants calculation.

In each potentiometric experiment, the solutions were poured into a 50 mL titration cell. After thermal equilibrium was reached, hydrogen ion concentrations were determined by successive readings, each performed after a small incremental addition of standard 0.1 mol L⁻¹ NaOH solution. The titrant addition and e.m.f. measurements were carried out using an automatic titrator, Mettler–Toledo

DL50-Graphix. The ionic strength was kept almost constant throughout the titrations by using solutions containing 0.50 mol L⁻¹ Me₄NCl and relatively low initial concentrations of metal ions and bzlidp (the sum of these reactants initial concentrations did not contribute more than 2% to the total ionic strength). Pre-saturated argon (free of CO₂) was bubbled through the solutions during titrations to eliminate the effect of atmospheric carbon dioxide, and the temperature was kept at 20.0 (±0.1) °C. Equilibrium attainment after each titrant addition was verified by controlling the deviation of successive e.m.f. readings. Independent stock solutions were used in some titrations to check reproducibility. The cell electrode potential *E*° and the acidic junction potential were determined according to reported procedure [36] from independent titrations of the strong acid with the titrant solution. In this way, the pH scale was the free hydrogen concentration scale. The calibration in the alkaline range was checked by recalculating *K*_w values for each system. The obtained values (average $\log_{10} K_w = -13.90$) were always checked to assure they were in line with previously reported data under similar experimental conditions [35].

Data were analyzed using the HYPERQUAD program [37], and species distribution diagrams were produced using the HySS program [38]. The fit of the values predicted by the model to the experimental data was estimated on the basis of the σ parameter, corresponding to the scaled sum of squared differences between predicted and experimental values. Many other possible stoichiometries were tried for each system, and final models were selected on the basis of the σ parameter, the model confidence level estimator, Chi squared, and the internal consistency of data reflected in standard deviations of the formation constants [37].

2.3. Synthesis of N-benzyliminodipropionic acid (H,bzlidp)

N-benzyliminodipropionic acid (H₂bzlidp) was prepared based on a slight modification of a previously reported protocol [31]. Acrylic acid (31.7 g, 0.44 mol) was added to 20 mL of an 8 mol L⁻¹ solution of benzylamine in dry ethanol (17.1 g, 0.16 mol). The mixture was heated overnight at boiling. The product precipitated as a white solid which was filtered and washed with cold ethanol (32.97 g, 0.13 mol, 82%. yield). ¹H NMR (400 Hz, DMSO-d₆, δ , ppm): 7.36–7.31 (m, 5H), 3.62 (s, 2H) 2.71 (t, *J* = 2.7 Hz, 4H), 2.41 (t, *J* = 2.4 Hz, 4H); ¹³C NMR (100 Hz) 174.0, 139.4, 129.1, 129.1, 128.6, 128.6, 127.4, 57.5, 48.9, 32.1. Selected IR data (v_{max} /cm⁻¹): 3017, 3003, 2765, 1701, 1396, 1223, 1095; Anal. Calcd for C₁₃H₁₇NO₄ (%): C, 62.14; H, 6.82; N, 5.57. Found: C, 61.60; H, 7.13; N, 5.88.

2.4 Synthesis of the complexes

2.4.1. Synthesis of bis-(μ -hydrogen-N-benzyliminodipropionato-κO, κO)bis[triaquacopper(II)] ditrifluoromethanesulfonate dihydrate [Cu₂(H₂O)₆(Hbzlidp)₂](CF₃SO₃)₂·2H₂O (1)

H₂bzlidp (0.626 g, 1.17 mmol) and copper trifluoromethanesulfonate (0.307 g, 0.85 mmol) were dissolved in 10 mL of distilled water by addition of 1 M NaOH solution to pH 3. The blue solution was filtered and the solvent was slowly evaporated at room temperature. After a few days, blue crystals appeared and were separated by filtration, washed with water and allowed to dry in the open air. In this manner, 0.243 g of blue crystals were obtained. Yield 53% (based on copper trifluoromethanesulfonate). Anal. Calcd for C₁₄H₂₄CuNO₁₁F₃S (%): C, 31.43; H, 4.52; N, 2.62; S, 5.99. Found: C, 31.65; H, 4.54; N, 1.84; S, 6.65. Selected IR data (v_{max} /cm⁻¹): 3470, 3385, 3129, 1597, 1447, 1421, 1375, 1330, 1261, 1180, 1031, 745, 638. TGA (18–700 °C, N₂) % weight loss: 10.9 (left limit 18 °C–right limit 100 °C), 32.6 (left limit 100 °C–right limit 285 °C), 28.5 (left limit 285 °C–right limit 700 °C).

2.4.2. Synthesis of catena-poly[nitratocopper(II)-μ-(hydrogen-N-benzyliminodipropionato-(κO, (κO')] [Cu(NO₃)(Hbzlidp)]_∞(2)

 H_2 bzlidp (0.626 g, 1.17 mmol) and copper nitrate trihydrate (0.411 g, 1.7 mmol) were dissolved in 10 mL distilled water by addition of 5 M NaOH solution to pH 3.0. The solvent was slowly evaporated at room temperature. After a few days, a green-blue solid appeared that was separated by filtration, washed with a few drops of water and allowed to dry in the open air (0.288 g). Yield 65% (based on H_2 bzlidp).

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Table 1. Crystallographic data for 1–3.

	1	2	3
Empirical formula	C14H34CuNO11E3S	C ₁₃ H ₁₆ CuN ₂ O ₇	C ₁₃ H ₁₀ NNiO ₆
Formula weight	534.94	375.82	344.00
Т(К)	200(1)	293(2)	150(1)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P 2,/n	P 2,/c
a (Å)	7.3233(3)	9.2620(2)	12.0502(5)
b (Å)	9.8634(4)	11.2106(3)	6.8629(3)
c (Å)	15.2034(7)	14.5082(3)	17.7884(7)
α (°)	89.815 (4)	90	90
β (°)	86.776(4)	90.298(2)	93.019(4)
γ (°)	88.033(4)	90	90
V (Å ³)	1095.80(8)	1506.40(6)	1469.04(11)
Z	2	4	4
D_{Calcd} (g cm ⁻³)	1.621	1.657	1.555
μ (Cu Ka) (mm ⁻¹)	3.053	2.423	2.161
F (0 0 0)	550	772	720
Crystal dimensions (mm)	$0.286 \times 0.191 \times 0.147$	$0.090 \times 0.062 \times 0.053$	$0.176 \times 0.120 \times 0.0940$
2θ range for data collection (°)	8.97-134.16	9.972-134.12	7.346-134.146
Limiting indices	$-8 \le h \le 8$	<i>−</i> 11 ≤ <i>h</i> ≤ 11	$-12 \le h \le 14$
	−11 ≤ <i>k</i> ≤ 9	−13 ≤ <i>k</i> ≤ 13	$-5 \le k \le 8$
	−13 ≤ <i>l</i> ≤ 18	−17 ≤ <i>l</i> ≤ 15	−21 ≤ / ≤ 16
Reflections (collected/unique, (Rint))	7192/3902/0.0205	6220/2685/0.0183	5071/2613/0.0204
Data/restraints/parameters	3902/0/297	2685/0/212	2613/0/206
$R_1^{a}, WR_2 [F^2 > 2\sigma(F^2)]^{b}$	0.0355/0.0915	0.0282/0.0736	0.0289/0.0816
Goodness-of-fit on F ²	1.04	1.06	1.03
Largest diff. peak and hole (e Å ⁻³)	0.51/-0.45	0.41/-0.26	0.38/-0.38
CCDC	1454769	1454770	1454771

 ${}^{a}R_{1} = \Sigma ||F_{0}| - |F_{c}||/\Sigma |F_{c}| \cdot {}^{b}wR_{2} = (\Sigma [w(F_{0}^{2} - F_{c}^{2})^{2}]/\Sigma [w(F_{0}^{2})^{2})^{1/2}.$

Green-blue crystals adequate for X-ray analysis were obtained from a water solution of the product by slow diffusion of acetonitrile. Anal. Calcd for $C_{13}H_{16}CuN_2O_7$ (%): C, 41.55; H, 4.29; N, 7.45. Found: C, 41.52; H, 4.70; N, 7.28. Selected IR data (v_{max}/cm^{-1}): 3073, 3009, 2961, 2895, 1636, 1416, 1373, 1360, 1321, 1227, 1047, 702. TGA (18–700 °C, 1.0 °C min⁻¹, N₂) % weight loss: 59.5 (left limit 100 °C–right limit 280 °C), 8.39 (left limit 280 °C–right limit 520 °C).

2.4.3. Synthesis of bis(μ -benzyliminodipropionato)tetraaquadinickel(II) [Ni₂(H₂O)₄(bzlidp)₂] (3) H₂bzlidp (0.125 g, 0.5 mmol) and nickel acetate tetrahydrate (0.125 g, 0.5 mmol) were dissolved in 10 mL distilled water at 80 °C. The pH was set to 4.2 by addition of 1 M NaOH solution. A 5 mL portion of this pale green solution was allowed to crystallize by slow diffusion of acetone vapors. After five days, pale green crystals were obtained from the acetone diffusion (12.3 mg). Yield 14%. Anal. Calcd for C₁₃H₁₉NNiO₆ (%): C, 45.39; H, 5.57; N, 4.07. Found: C, 45.09; H, 5.79; N, 3.95. Selected IR data (v_{max} / cm⁻¹): 3264, 3030, 2965, 2880, 1578, 1416, 1383, 1114, 894.

2.5. X-ray crystallography

The X-ray diffraction data for all compounds were collected with an Agilent SuperNOVA diffractometer with microfocus X-ray using Cu K α radiation ($\lambda = 1.54184$ Å). CrysAlisPro [39] software was used to collect, index, scale, and apply analytical absorption correction based on the faces of the crystal. The structure was solved by a dual-space algorithm using the SHELXT program [40]. Fourier recycling and least-squares refinement were used for the model completion with SHELXL-2014 [41–43]. All non-hydrogen atoms have been refined anisotropically and all hydrogens have been placed in geometrically suitable positions and refined as riding with isotropic thermal parameters related to the equivalent isotropic thermal parameter of the parent. Hydrogens were geometrically positioned with C–H = 0.93 Å and Uiso(H) = 1.2 Ueq(C), except for hydrogens on N in **1** and **2** that were determined by Fourier differences

and refined freely. Also hydrogens from water molecules of **3** and one water molecule of compound **1** could be localized in this form and refined.

Crystal data, collection procedures, and refinement results are summarized in table 1.

3. Results and discussion

3.1. Solution studies

Values for the protonation equilibrium constants of bzlidp²⁻ were required to study the metal complexation reactions. The obtained results at 20.0 °C in 0.50 mol L⁻¹ Me₄NCl are: log $K_1^{H} = 8.856(3)$; log $\beta_2^{H} = 12.789(5)$; log $\beta_3^{H} = 15.624(7)$; $\sigma = 0.2$. The titration curves of H₂bzlidp with base have three equivalent points, the third one corresponding to the presence of the N-connecting atom. No previous reports are available for comparison [35]. The first protonation constant shows lower basic character than that reported for iminodipropionato ligand, due to the presence of the benzyl substituent on nitrogen, an electron-withdrawing group [44]. *N*-benzyliminodiacetate also shows the same behavior. In fact, its first protonation constant has a very similar value to that of bzlidp: log $K_1^{H} = 8.87$ at 25 °C and 0.1 M ionic strength [35]. Also in line with previous reports, the protonation constants of the propionic carboxylate groups in bzlidp are higher than those of the iminodiacetato ligand or *N*-benzyliminodiacetate, the amino group is expected to be predominantly protonated in aqueous solution below pH 8.8.

The following step was the study of the M(II)–bzlidp interaction. The divalent cations used for this study were Mn, Co, Ni, Cu, Zn, Cd, and Pb, and the results are shown in table 2. Stability of complexes containing 3d metal ions follows the Irving-Williams trend. The species detected were in all cases [ML] and [M(HL)]⁺ (L = bzlidp^{2–}). Complex species [ML] (Co, Ni, Cu) had been reported for various dipropionic acid ligands [31, 44, 46]. In this work, we have additionally detected the protonated species, with a stability constant value that is fairly independent of the identity of the metal ion.

Figure 2 shows the speciation diagrams for the copper and nickel containing systems. It is important to note that protonated species are not predominant, but they are formed for pH values around 4. The speciation diagrams for the rest of the metal ions that were analyzed can be found in the Supporting Information, figures S1–S5.

3.2. Synthesis of the complexes

The copper complexes were prepared by direct reaction of copper salts with H₂bzlidp in aqueous solution at pH 3.0–4.0 and in different ligand to metal molar ratios. According to the solution studies, this pH, where the predominant form of the ligand is HL⁻, should be adequate to favor formation of complexes bearing the monoprotonated form of the ligand. [Cu(Hbzlidp)]⁺ was detected in this pH interval. The nickel complex was prepared by reaction of nickel acetate with H₂bzlidp in a 1:1 metal to ligand molar ratio, in aqueous solution at pH 4.2, followed by diffusion of acetone. Even though at this acidic pH the species [Ni(HL)]⁺ is expected to be present, **3** was the only product obtained by this synthetic procedure.

	log K ₁	$\log \beta_{111}$	σ
Mn	2.42(2)	10.26(4)	0.3
Со	2.28(5)	10.33(3)	0.2
Ni	2.76(2)	10.43(2)	0.2
Cu	6.49(1)	10.74(4)	0.4
Zn		10.61(1)	0.1
Cd		10.15(3)	0.2
Pb		10.86(1)	0.2

Table 2. Overall formation constants for M(II)-bzlidp complexes determined at 20.0 °C in 0.50 mol L⁻¹ Me₄NCI.



Figure 2. Species distribution diagram of the M(II)–bzlidp system in 0.50 mol L⁻¹ Me₄NCl at 20.0 °C (total [M²⁺] = 5 mmol L⁻¹ and total [bzlidp] = 5 mmol L⁻¹). The fully deprotonated ligand is represented as L²⁻. (a) M = Cu; (b) M = Ni.

The crystalline solids were characterized by elemental analysis and infrared (IR) spectroscopy. IR spectra of **1** and **3** show broad bands at 2800–3600 cm⁻¹, which suggests the presence of water in the structures. This signal is absent in **2**. The three complexes exhibit bands at 2800–2970 cm⁻¹ that correspond to the v_{C-H} vibrations of the $-CH_2$ - groups in the carbon chains on bzlidp ligands. The absence of the characteristic absorption of v_{as} (COOH) near 1700 cm⁻¹ indicates that carboxylate groups of the ligand are not fully protonated in the complexes. The v_{as} (COO⁻) vibrations occurred at *ca*. 1600 cm⁻¹, while those of v_s (COO⁻) appeared at *ca*. 1420 cm⁻¹. The large difference in the v_{as} - v_s values (around 180 cm⁻¹) excludes the presence of chelating bidentate coordination modes of the ligand [47]. The bands at 1261, 1031, and 638 cm⁻¹ account for the presence of the CF₃SO₃⁻ in **1** [48]. The coordinated NO₃⁻ in **2** has bands at 1416 and 1321 cm⁻¹ which correspond to the asymmetric and symmetric stretching vibrations in a monodentate coordination mode [49]. The TGA curves for **1** and **2** show a decomposition process that begins about 200 °C. For **1**, a dehydration process (with a weight loss of 10.9%) is shown below 100 °C.

3.3. Crystal structures

It was possible to obtain single crystals for **1** by slow evaporation of the solvent at room temperature, while crystals of **2** and **3** were obtained by slow diffusion of acetonitrile or acetone, respectively.

Compound 1		Compound 2		Compound 3	
Distances					
Cu1-01	1.9743(15)	Cu101	1.9588(15)	Ni1-01	2.0527(11)
Cu1-03#1	1.9928(14)	Cu1-02#2	1.9630(15)	Ni1-03	2.0003(12)
Cu1–O1W	1.9321(15)	Cu1–O3 ^{#3}	1.9616(13)	Ni1–O1W	2.0837(12)
Cu1–O2W	2.2572(19)	Cu1–05	2.1429(16)	Ni1–O2W	2.0600(12)
Cu1–O3W	1.9172(19)	Cu104#4	1.9765(13)	Ni1-01#5	2.1336(11)
		O5–N2	1.239(2)	Ni1–N1	2.1003(13)
Angles					
03 ^{#1} Cu1O2W	94.80(7)	01–Cu1–O5	93.97(9)	01 W-Ni1-02 W	90.50(5)
01–Cu1–O3 ^{#1}	170.45(7)	02 ^{#2} -Cu1-05	99.03(9)	01W-Ni1-01	84.05(5)
01–Cu1–O2W	94.29(7)	02 ^{#2} -Cu1-01	166.90(7)	O1W-Ni1-N1	97.88(5)
01W-Cu1-03#1	86.81(6)	02 ^{#2} -Cu1-04 ^{#4}	87.98(7)	01W-Ni1-01#5	84.54(5)
01W–Cu1–O1	90.14(7)	02 ^{#2} -Cu1-03 ^{#3}	89.65(7)	03-Ni1-01	89.54(5)
01W-Cu1-02W	91.79(8)	03 ^{#3} -Cu1-05	104.15(6)	03-Ni1-02W	94.32(5)
O3W-Cu1-O3 ^{#1}	93.28(7)	03 ^{#3} -Cu1-01	88.73(7)	03-Ni1-N1	92.23(5)
03W–Cu1–01	88.67(7)	03 ^{#3} -Cu1-04 ^{#4}	166.82(6)	03-Ni1-01W	168.40(5)
03W–Cu1–O2W	96.04(10)	04 ^{#4} Cu105	89.03(6)	03-Ni1-01 ^{#5}	84.88(5)
03W–Cu1–01W	173.13(10)	04 ^{#4} Cu101	90.65(7)	01-Ni1-02W	169.87(5)
				01-Ni1-N1	94.43(5)
				01-Ni1-01 ^{#5}	80.57(5)
				O2W-Ni1-N1	94.77(5)
				02W-Ni1-01#5	90.44(5)
				N1-Ni1-01#5	174.22(5)

Table 3. Selected	bond distances	(Å) and	angles (°) for	1-3.ª

^aSymmetry codes for #1 = 1 - x, -y, 1 - z; #2 = -x, 1 - y, 1 - z; #3 = 1/2 - x, -1/2 + y, 3/2 - z; #4 = -1/2 + x, 3/2 - y, -1/2 + z; #5 = 2 - x, 1 - y, 1 - z.



Figure 3. Molecular structure of 1, showing $[Cu_2(H_2O)_6(Hbzlidp)_2]^{2+}$, with labeling. Thermal ellipsoids are shown at 50% probability. Hydrogens are omitted for clarity. Color code: copper, orange; oxygen, red; nitrogen, blue; carbon, gray; sulfur, yellow; fluorine, green.

Table 4. Selected bond lengths (Å) and angles (°) of hydrogen b	oonds in 1	1 .ª
• • • • •		

D–H···A	D–H (Å)	H…A (Å)	D…A (Å)	D−H…A (°)
N1H1…O2	0.86(3)	2.24(2)	2.831(2	126(2)
N1H1…O3	0.86(3)	2.28(3)	2.887(2)	128(2)
O2WH2WA····O6 ⁱ	0.78(3)	2.16(3)	2.940(3)	171(3)
O2WH2WB···O5 ⁱⁱ	0.80(4)	2.04(4)	2.826(3)	169(4)

^aSymmetry codes: i = 2 - x, 1 - y, 1 - z; ii = 1 - x, 1 - y, 1 - z.

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Figure 4. Inter- and intramolecular hydrogen bonds in 1. Color code: copper, orange; oxygen, red; nitrogen, blue; carbon, gray; hydrogen, white.



Figure 5. Coordination environment of Cu(II) in 2, with labeling. Thermal ellipsoids are shown at 50% probability. Color code: copper, orange; oxygen, red; nitrogen, blue; carbon, gray. Hydrogens are omitted for clarity.

3.3.1. Crystal structure of $[Cu_2(H_2O)_6(Hbzlidp)_2](CF_3SO_3)_2 \cdot 2H_2O(1)$

Selected bond lengths and angles for **1** are presented in table 3. The structure is formed by a dinuclear $[Cu_2(H_2O)_6(Hbzlidp)_2]^{2+}$ unit, two trifluoromethanesulfonate anions, and two crystallization water molecules. The $[Cu_2(H_2O)_6(Hbzlidp)_2]^{2+}$ units are built by two copper(II) ions joined through two Hbzlidp⁻ ligands as shown in figure 3. The ligand is protonated at N, with a N1–H1 distance of 0.85(3) Å, avoiding the direct union to the copper ions. Hence, this potentially tridentate ligand is ditopic, through two oxygens of different carboxylate groups. Each Cu(II) is square pyramidal ($\tau = 0.08$) [50], being the donor atoms two oxygen from independent Hbzlidp⁻ ligands (Cu1–O1 1.9743(15) Å and Cu1–O3 1.9928(14) Å), and three other oxygens from coordinated water. Of these water molecules, two are in the equatorial plane,



Figure 6. Cu(II) dinuclear units bridged by carboxylates in 2, showing the "paddle wheel" conformation. Hydrogens are omitted for clarity. Color code: copper, orange; oxygen, red; nitrogen, blue; carbon, gray.



Figure 7. The 2-D array of Cu(II) dinuclear units in 2. The benzyl groups and the hydrogens are omitted for clarity. Color code: copper, orange; oxygen, red; nitrogen, blue; carbon, gray.

at an average Cu–O distance of 1.9247(19) Å. The third water occupies the apical position of the square pyramid (Cu1–O2W distance 2.2572(19) Å). In the dimer, the Cu–Cu average distance is 4.8551(5) Å. Intramolecular H-bonds are present (table 4) between the protonated N and the O of the carboxylate groups and also between the equatorial water molecules and the carboxylates (figure 4). The packing of **1** is supported by a hydrogen bond network involving water molecules, trifluoromethanesulfonates, and carboxylate groups (table S1, Supplementary Material).



Figure 8. Molecular structure of 3, with labeling. Thermal ellipsoids are shown at 50% probability. Hydrogens are omitted for clarity. Color code: nickel, green; oxygen, red; nitrogen, blue; carbon, gray.



Figure 9. Unit cell of the structure of 3. Hydrogens are not shown for clarity. Color code: nickel, green; oxygen, red; nitrogen, blue; carbon, gray.

3.3.2. Crystal structure of [Cu(NO₃)(Hbzlidp)]₍₂₎

Selected bond lengths and angles for **2** are presented in table 3. Cu(II) centers are connected by Hbzlidp⁻ in the structure. Each Cu(II) is five coordinate with a slightly distorted square pyramidal geometry ($\tau = 0.05$) [50], the donors are four oxygens of four different Hbzlidp⁻ anions (average Cu–O distance 1.9650(15) Å) and O of a nitrate in the apical position of the square pyramid (figure 5) with a Cu–O5 distance of 2.1429(16) Å. Again, the organic ligand is protonated at N (the N1–H1 distance is 0.92(2) Å), avoiding direct union to copper ions and acting as bridging ligand. The ligand connects four different Cu(II) ions through oxygens of two carboxylate groups, resulting in pairs of Cu(II) centers bridged by four *syn,syn* carboxylate groups to generate dinuclear "paddle wheel" units (figure 6) [51–54]. The



Figure 10. Molecular structure of 3 showing the intramolecular hydrogen bond between carboxylate O and water molecules. Color code: nickel, green; oxygen, red; nitrogen, blue; carbon, gray; hydrogen, white.

Cu–Cu distance in the dimer is 2.6776(5) Å. The dinuclear copper units are arranged in a rhombus type grid (figure 7) in a 2-D layer structure. Intramolecular and intermolecular hydrogen bonds are present in the structure and relevant distances and angles are included in table S2 (Supplementary Material).

3.3.3. Crystal structure of $[Ni_2(H_2O)_4(bzlidp)_2]$ (3)

Selected bond lengths and angles for **3** are presented in table 3. The structure is formed by $[Ni_2(H_2O)_4(bzlidp)_2]$ neutral dinuclear units, built by two nickel ions joined through two bzlidp²⁻ ligands as shown in figure 8. The bzlidp²⁻ are tridentate ligands, coordinating through two oxygens of the carboxylate groups, one of which is bridging and coordinated to the other Ni(II) of the molecule. Each Ni(II) is octahedral, and the coordination sphere is completed by nitrogen of bzlidp²⁻ and two water molecules (average Ni–OW distance 2.0719(12) Å) in a *cis* position. The intramolecular Ni–Ni average distance is 3.1938(5) Å. The unit cell of **3** is shown in figure 9. The units present intramolecular hydrogen bonds, between the free carboxylate oxygen O2 of one half of the molecule, and one of the water molecules in the other half, and between carboxylic O3 and the O1W of a coordinated water (figure 10 and table S3, Supplementary Material).

4. Conclusion

The dicarboxylic acid compound $H_2bzlidp$ showed interesting versatility as a ligand. It can assemble metal ions into polynuclear systems with different patterns of connection. In this way, it was possible to synthesize and determine the structure of three different polynuclear complexes, in which the ligand was a bridge, although with different coordination modes. Control of the coordination abilities of *bzlidp* was achieved by appropriate selection of the reaction conditions. In particular, acidic pH values led this tridentate ligand to be ditopic due to the N protonation, and a dinuclear, cyclic structure was obtained. When an excess of copper was employed, a more extended system was obtained, with each carboxylate group connecting two copper centers. Finally, in the case of nickel, which favors octahedral geometries, a dinuclear, more compact structure was formed, with the deprotonated N also coordinated to the metal center.

Supplementary material

CCDC 1454769–1454771 contains the supplementary crystallographic data for 1–3. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Disclosure statement

No potential conflict of interest was reported by the authors.

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