Polyhedron 29 (2010) 683-690

Contents lists available at ScienceDirect

### Polyhedron

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

# Nickel(II) derivatives of N-benzyliminodiacetate(2–) ligands, with and without imidazole: Synthesis, crystal structure and properties

D.K. Patel<sup>a</sup>, D. Choquesillo-Lazarte<sup>b</sup>, J.M. González-Pérez<sup>a</sup>, A. Domínguez-Martín<sup>a</sup>, A. Matilla-Hernandez<sup>a</sup>, A. Castiñeiras<sup>c</sup>, J. Niclós-Gutiérrez<sup>a,\*</sup>

<sup>a</sup> Department of Inorganic Chemistry, Faculty of Pharmacy, University of Granada, E-18071 Granada, Spain

<sup>b</sup> Laboratorio de Estudios Cristalográficos, IACT-CSIC, P.T. Ciencias de la Salud, Granada, Spain

<sup>c</sup> Department of Inorganic Chemistry, Faculty of Pharmacy, University of Santiago de Compostela, E-15782 Santiago de Compostela, Spain

#### ARTICLE INFO

Article history: Received 20 June 2009 Accepted 30 September 2009 Available online 30 October 2009

Keywords: Nickel(II) complexes Iminodiacetate Imidazole Crystal structure

#### 1. Introduction

The iminodiacetate(2–) ion (IDA) is a tridentate chelating ligand, able to partially satisfy a metal ion's coordination. That enables the formation of a large variety of mixed-ligand metal complexes with IDA and/or IDA-like derivatives, and aqua or other ligands. Structural studies of these complexes, based on crystallographic data, have proved interesting changes of the IDA moiety's conformation that can be rationalized according to the metal ion's coordination requirements and the metal binding possibilities of other ligands involved in the coordination polyhedron.

Our group has been contributing in this field for two decades, working on metal-iminodiacetates, mainly with first row transition metal ions. Most metal-IDA-like derivatives are obtained from aqueous solutions. Thus, in the absence of other ligands other than from water, complexes of the general formula  $[M(IDA-like)(-H_2O)_x] \cdot nH_2O$  are formed. This kind of compounds will hereafter be referred to as a binary compound, assuming that the  $xH_2O$  ligands are metal linkers to satisfy the coordinating requirements of the metal ion M. A general strategy to obtain ternary compounds is to react the binary compound (in solution) with other ligands (L), frequently so-called secondary or auxiliary ligands. Statistical results show that the formation of a ternary complex, for example [MAB], is favored against a salt such as [MA\_2][MB\_2].

Currently, we are interested in the study of nickel(II)-iminodiacetates because of two main reasons, firstly due to the limited struc-

Corresponding author.
 E-mail address: jniclos@ugr.es (J. Niclós-Gutiérrez).

#### ABSTRACT

In an attempt to prepare binary and ternary compounds, we have obtained two molecular complexes  $[Ni(MEBIDA \text{ or } MOBIDA)(H_2O)_3] \cdot nH_2O$  (n = 0 or 1) and two iso-type salts  $[Ni(Him)_6][Ni(MEBIDA \text{ or } MOB-IDA)_2] \cdot 4H_2O$  [MEBIDA = N-(p-methylbenzyl)iminodiacetate(2–) and MOBIDA = N-(p-methylbenzyl)-iminodiacetate(2–) ligands, Him = imidazole]. Our results are discussed with regard to related copper(II) and nickel(II) compounds. The reasons for which these chelating ligands produce nickel(II) salts instead of ternary compounds remain unclear since other iminodiacetate-like ligands give true ternary Ni(II) compounds with imidazole and other N-heterocyclic ligands.

© 2009 Elsevier Ltd. All rights reserved.

tural information available [1-16] and secondly because Ni(II) allows ternary compounds to be obtained as well as salts with similar composition, in addition to related binary compounds or closely similar polymeric compounds. The available information strongly suggest that the non-coordinating moiety of the N-R-IDA ligand (R = H, alkyl, benzyl or phenyl) can influence the system towards a true mixed-ligand complex or to the corresponding salt. Under the same conditions, the behavior of these systems noticeably differs from that observed for the copper(II) analogues, for which salt formation has not been observed [17-32]. In particular, it is known that N-methyliminodiacetate (MIDA) and N-benzyliminodiacetate (NBzIDA) ligands yield salts with Ni(II) and imidazole (Him), but not the corresponding ternary complexes [4]. In this context, the aim of the present work is to contribute to this field by means of the study of binary and ternary systems having Ni(II), an IDA-like para-substituted ligand (see MEBIDA and MOBIDA in the Scheme 1) and Him. The need to carry out crystallographic studies is founded in: (1) to distinguish whether the obtained crystals are salts or ternary compounds; (2) to appreciate if the iminodiacetate moiety experiences conformational changes between the binary compound and the IDA derivative also containing imidazole.

#### 2. Experimental

#### 2.1. Materials

The chelating ligands were synthesized in the acid form  $(H_2MEBIDA \text{ or } H_2MOBIDA)$  as reported for N-benzyliminodiacetic acid  $(H_2NBzIDA)$  [26], but using 4-methylbenzylamine or





<sup>0277-5387/\$ -</sup> see front matter  $\odot$  2009 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2009.09.034



4-methoxybenzylamine instead of benzylamine. These latter amines and imidazole were purchased from Aldrich, whereas nickel(II) basic carbonate [NiCO<sub>3</sub>·2Ni(OH)<sub>2</sub>·4H<sub>2</sub>O] was purchased from Merck. Related salts are also available from Aldrich, such as 2Ni-CO<sub>3</sub>·3Ni(OH)<sub>2</sub>·4H<sub>2</sub>O, or from various suppliers as NiCO<sub>3</sub>·2Ni(OH)<sub>2</sub>· xH<sub>2</sub>O. In order to accurately determine the amount of this Ni(II) source required for each synthesis, elemental and thermo-gravimetric analysis of this reagent was encouraged. These reagents were used as received.

#### 2.2. Synthesis of the nickel(II) derivatives

#### 2.2.1. Molecular nickel(II)-chelates

In a Kitasato flask, 237 mg of H<sub>2</sub>MEBIDA or 253 mg of H<sub>2</sub>MOB-IDA (1 mmol) was added to a slurry of Ni(II) basic carbonate (124 mg, 0.33 mmol) in 120 mL of distilled water. The reacting mixture was heated (70 °C) and stirred well under reduced pressure (20 min) to remove CO<sub>2</sub> (by-product) for ca. 2 h until a clear solution seemed to be obtained. To remove a small amount of unreacted metal basic carbonate, the solution was filtered without vacuum through a sintered disk filter funnel (Ø 10–16 µm) onto a crystallization device. Evaporation of the solvent was controlled by covering the device with a plastic film. After a few days, well shaped light bluish crystals appeared. Some of these were used for single-crystal X-ray diffraction purposes. Additional samples were collected, washed with cool water and air dried for analytical studies. Typical yields are ca. 50-60%. Anal. Calc. for [Ni(MEB-IDA)(H<sub>2</sub>O)<sub>3</sub>] (C<sub>12</sub>H<sub>19</sub>NNiO<sub>7</sub>, hereafter **1**): C, 41.42; H, 5.50; N, 4.03. Found: C, 41.07; H, 5.70; N, 4.14%. Anal. Calc. for [Ni(MOB-IDA)(H<sub>2</sub>O)<sub>3</sub>]·H<sub>2</sub>O (C<sub>12</sub>H<sub>21</sub>NNiO<sub>9</sub>, hereafter **2**): C, 37.73; H, 5.54; N, 3.67. Found: C, 37.87; H, 5.64; N, 3.60%.

#### 2.2.2. Novel salts with the $[Ni(Him)_6]^{2+}$ ion

In a series of attempts to obtain ternary complexes of the formula  $[Ni(IDA-like)(Him)_3] \cdot nH_2O$ , we proceeded as follows: to a slurry of Ni(II) basic carbonate (124 mg, 0.33 mmol) in 120 mL of distilled water in a Kitasato flask, 237 mg of H<sub>2</sub>MEBIDA or 253 mg of H<sub>2</sub>MOBIDA (1 mmol) was added. The reacting mixture was heated (70 °C) and stirred well under reduced pressure (20 min) to remove CO<sub>2</sub> (by-product) over ca. 2 h until a clear solution was obtained, then Him (204 mg, 3 mmol) was added to each binary complex solution. After a few minutes, the intensity of the blue color of the solutions increased. These solutions were filtered without vacuum on the appropriate crystallization device and left to evaporate at room temperature, controlling the process with the aid of a plastic film. In these cases, no unreacted residue of nickel(II) basic carbonate was observed on the disk filter funnels. After 3 weeks, well shaped crystals were formed, many of them suitable for X-ray crystallographic purposes. Additional samples were also collected to give a yield of ca. 70%. Anal. Calc. for [Ni(Him)<sub>6</sub>]-[Ni(MEBIDA)<sub>2</sub>]·4H<sub>2</sub>O (C<sub>42</sub>H<sub>58</sub>N<sub>14</sub>Ni<sub>2</sub>O<sub>12</sub>, hereafter **3**): C, 47.22; H, 5.47; N, 18.35. Found: C, 46.99; H, 5.48; N, 18.27%. Anal. Calc. for

[Ni(Him)<sub>6</sub>][Ni(MOBIDA)<sub>2</sub>]·4H<sub>2</sub>O (C<sub>42</sub>H<sub>58</sub>N<sub>14</sub>Ni<sub>2</sub>O<sub>14</sub>, hereafter **4**): C, 45.84; H, 5.32; N, 17.82. Found: C, 45.63; H, 5.17; N, 17.71%.

#### 2.3. Physical measurements

Analytical data were obtained in a Fisons–Carlo Erba EA 1108 elemental micro-analyzer. TG analysis (pyrolysis) of the studied compounds (295–800 °C) were carried out in CO<sub>2</sub>-free dry-air flow (100 mL/min) by a Shimadzu Thermobalance TGA-DTG-50H instrument, meanwhile a series of FT-IR spectra (20–22 per sample) were recorded in order to identify the evolved gases, using a coupled FT-IR Nicolet Magma 550 spectrometer. Infrared spectra (KBr pellets, 4000–400 cm<sup>-1</sup>) were recorded on a Jasco FT-IR 410 spectrometer. Electronic (diffuse reflectance) spectra were obtained in a Varian Cary-5E spectrophotometer.

#### 2.4. X-ray data collection and structure refinement

Suitable crystals were mounted on glass fibers and these samples were used for data collection. Data were collected with Bruker X8 Kappa APEXII (1, 100 K), Bruker SMART CCD 1000 (2, 100 K) or Bruker X8 Proteum (3 and 4, 293 K) diffractometers. The data were processed with sAINT (2) [33] or APEX2 (1, 3 and 4) [34] and corrected for absorption using sadabs [35]. The structures were solved by direct methods [36], which revealed the position of all the nonhydrogen atoms. These atoms were refined on  $F^2$  by a full-matrix least-squares procedure using anisotropic displacement parameters [37]. All hydrogen atoms were located in difference Fourier maps and included as fixed contributions riding on their attached atoms with isotropic thermal displacement parameters 1.2 times those of the respective atoms. Geometric calculations were carried out with PLATON [38] and drawings were produced with PLATON [38] and MERCURY [39]. A summary of crystal data is reported in Table 1. Selected coordination bonds and angles are listed in Table 2.

#### 3. Results and discussion

#### 3.1. Structure and properties of binary compounds 1 and 2

As a part of the present study, we have made an effort to obtain the structures of appropriate binary compounds of Ni(II) and MEB-IDA (Fig. 1, left) or MOBIDA (Fig. 2, left), compounds **1** and **2**, respectively. These compounds do not have the same type of formula but consist of [Ni(MEBIDA or MOBIDA)(H<sub>2</sub>O)<sub>3</sub>] molecules, without (**1**) or with (**2**) non-coordinated water molecules. In these complex molecules, the Ni(II) atom exhibits the expected octahedral coordination and the IDA-like ligand only plays a tridentate chelating role, adopting a *fac*-NO<sub>2</sub> conformation. All Ni–O coordination bond length are in the range 2.00–2.07 Å, whereas the Ni– N(MEBIDA or MOBIDA) bond distance is near 2.14 Å. It is interesting to note that the lowest value of the *trans*-angle is the N(MEB-IDA or MOBIDA)–Ni–O(aqua) one (~170°), whereas the trans O– Ni–O(aqua) angle values are 175–177°.

The large difference between compounds **1** and **2** refers to crystal packing forces. There are no  $\pi$ , $\pi$ -stacking interactions between the aromatic rings of neighboring MEBIDA or MOBIDA ligands in these compounds. In the crystal of **1**, all O–H(aqua) bonds are involved in (aqua)O–H···O(carboxylate) interactions between four different neighboring molecules, forming 2D frameworks parallel to the *ab* plane, where the MEBIDA hydrophobic arms fall towards the external faces (Fig. 1, right). These layers are connected by hydrophobic contacts along the *c*-axis of the crystal. Again in the crystal of **2**, (aqua or water)O–H···O(aqua, water or carboxylate) interactions build 2D frameworks parallel to the *ab* plane, with the MOBIDA non-coordinating arms oriented towards the external

Table 1
Crystal and structure refinement data

Compound	1	2	3	4
Empirical formula	C12H19NNiO7	C <sub>12</sub> H <sub>21</sub> NNiO <sub>9</sub>	C42H58N14Ni2O12	C42H58N14Ni2O14
Formula weight	347.99	382.01	1068.40	1100.44
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	P21	P21	ΡĪ	ΡĪ
Unit cell dimensions				
a (Å)	7.1474(16)	7.5845(4)	8.9079(18)	9.0570(4)
b (Å)	7.4206(16)	6.9195(3)	11.051(2)	11.0641(5)
<i>c</i> (Å)	14.346(3)	15.3709(6)	12.953(3)	12.8792(5)
α (°)	90	90	87.781(7)	88.1960(10)
β (°)	94.011(4)	101.903(2)	74.283(7)	74.4480(10)
γ (°)	90	90	81.694(7)	82.2480(10)
$V(Å^3)$	759(3)	789.33(6)	1214.6(4)	1231.96(9)
Ζ	2	2	1	1
$ ho_{\rm calc} ({ m g}{ m cm}^{-3})$	1.523	1.607	1.461	1.483
F(000)	364	400	560	576
Crystal size (mm)	$0.45 \times 0.22 \times 0.13$	$0.15 \times 0.15 \times 0.04$	$0.35\times0.30\times0.12$	$0.30 \times 0.27 \times 0.20$
θ Range (°)	2.85-26.36	2.71-25.65	3.54-66.13	3.56-66.49
Reflections collected	8705	13383	15616	16685
Independent reflections	3084	3002	3985	3903
Maximum/minimum transmission	0.8483-0.5904	0.9508-0.8317	0.8314-0.6048	0.7374-0.6419
Goodness-of-fit on $F^2$	1.458	1.035	1.063	1.023
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0305$	$R_1 = 0.0225$	$R_1 = 0.0544$	$R_1 = 0.0496$
	$wR_2 = 0.0735$	$wR_2 = 0.0455$	$wR_2 = 0.1488$	$wR_2 = 0.1313$

#### Table 2

Selected interatomic bonds lengths (Å) and trans angles (°) in compounds 1-4.

	Lengths (Å)			Angles (°)	
1					
Ni1-011	2.024(2)			011-Ni1-03	175.38(9)
Ni1-021	2.032(2)			01-Ni1-N1	172.21(12)
Ni1-03	2.033(2)			021-Ni1-02	175.74(9)
Ni1-02	2.046(2)				
Ni1-01	2.0682(18)				
Ni1-N1	2.137(2)				
2					
Ni1-011	2.0099(15)			011-Ni1-03	177.50(6)
Ni1-03	2.0467(15)			021-Ni1-02	175.53(6)
Ni1-021	2.0526(14)			01-Ni1-N10	170.27(7)
Ni1-02	2.0598(15)				
Ni1-01	2.0646(13)				
Ni1-N10	2.1375(15)				
3					
Ni1-04#1	2.043(2)	Ni2-N18#2	2.121(2)	04#1-Ni1-04	180.0
Ni1-04	2.043(2)	Ni2-N18	2.121(2)	N1-Ni1-N1#1	180.0
Ni1-08#1	2.0745(19)	Ni2-N23#2	2.138(2)	08#1-Ni1-08	180.0
Ni1-08	2.0745(19)	Ni2-N23	2.138(2)	N28-Ni2-N28#2	180.0
Ni1–N1	2.108(2)	Ni2-N28	2.149(2)	N23#2-Ni2-N23	179.998(1)
Ni1-N1#1	2.108(2)	Ni2-N28#2	2.149(2)	N18#2-Ni2-N18	180.0
#1 - x + 1, -y, -z; #2 - x,	-y + 1, -z + 1				
4					
Ni1-04#1	2.0470(16)	Ni2-N29#2	2.128(2)	04#1-Ni1-04	180.00(6)
Ni1-04	2.0470(16)	Ni2-N29	2.128(2)	08-Ni1-08#1	179.999(1)
Ni1-08	2.0682(16)	Ni2-N19#2	2.1396(19)	N1-Ni1-N1#1	179.999(1)
Ni1-08#1	2.0683(16)	Ni2-N19	2.1396(19)	N29#2-Ni2-N29	180.0
Ni1-N1	2.1073(17)	Ni2-N24#2	2.1428(18)	N19#2-Ni2-N19	180.0
Ni1-N1#1	2.1073(17)	Ni2-N24	2.1428(18)	N24#2-Ni2-N24	180.0
#1 - x + 1, -y + 1, -z + 1; =	#2 - x, -y, -z				

faces (Fig. 2, right). However, these layers are connected by C–H/ $\pi$  interactions [C(33)–H(33)···(Cg, centroid of the involved ring) 154.0°, C(33)···Cg 3.70 Å; symmetry code 1–x, 1/2 + y, –z] (see detail in Fig. 2, right). It is noteworthy that in this way the O-methoxy atom of the MOBIDA ligand cannot participate in H-bonding interactions.

Compound **1** is stable up to  $\sim$ 100 °C and then shows the loss of the three aqua ligands (100–200 °C, exp. 14.907%, calc. 15.532%). Anhydrous Ni(MEBIDA) exhibits a pyrolytic process (300–400 °C)

with the production of H<sub>2</sub>O, CO<sub>2</sub>, CO, CH<sub>3</sub>OH, CH<sub>4</sub> and probably N<sub>2</sub>O, to give a residue of NiO (exp. 22.480%, calc. 21.461%). Compound **2** seems to be less stable under dry-air flow, and loses water before the start of the TG analysis to give Ni(MOBIDA)·3.16H<sub>2</sub>O. This hydrate loses all remaining water in two overlapping steps (75–170 and 170–265 °C, exp. 15.539%, calc. for 3.16H<sub>2</sub>O 15.519%). Two pyrolytic steps (265–410 °C and 410–490 °C) of Ni(MOBIDA) give H<sub>2</sub>O, CO<sub>2</sub>, CO, CH<sub>3</sub>OH, CH<sub>4</sub>, N<sub>2</sub>O and NO, leaving a residue of NiO (exp. 19.228%, calc. 20.360%).



**Fig. 1.** Structure of [Ni(MEBIDA)(H<sub>2</sub>O)<sub>3</sub>] (1). Left: asymmetric unit, with the numbering of the coordination atoms. Right: fragment of a H-bonded layer, parallel to the *ab* plane, with the benzyl arms of MEBIDA towards its external faces.



**Fig. 2.** Structure of  $[Ni(MOBIDA)(H_2O)_3]$ - $H_2O$  (2). Left: asymmetric unit, with the numbering of the coordination atoms. Right: fragment of two H-bonded layers, parallel to the *ab* plane, with the benzyl arms of MOBIDA towards its external faces. Detail of one of the C-H/ $\pi$  interactions connecting the MOBIDA ligands of the external faces from two layers.

The FT-IR spectra of compounds **1** and **2** show a broad band near 3350 cm<sup>-1</sup> due to the stretching absorption of water and/aqua ligands. In the range 3000–2800 cm<sup>-1</sup>, several peaks are assignable to stretching modes of the chromophores C–H<sub>arom</sub>, –CH<sub>2</sub>– and – CH<sub>3</sub>. An skeletal absorption is recorded near 1675 cm<sup>-1</sup> followed by a broad band at ~1595 cm<sup>-1</sup>, due to overlapped contributions

of  $\delta$ (H<sub>2</sub>O) and  $v_{as}$ (COO) modes. The band of  $v_s$ (COO) is clearly recognized at 1414 (**1**) or 1412 cm<sup>-1</sup> (**2**). A comparison of both spectra enables the valuable assignation of a defined and intense band at 1182 cm<sup>-1</sup> corresponding to  $v_{as}$ (C–O–C) due to the alkyl–aryl ether chromophores in the spectrum of (**2**). This band is also observed in the spectrum of **4** (see below). FT-IR spectra of both binary com-

pounds also show a defined band for the 'out-of-plane' deformation mode,  $\pi$ (C-H<sub>arom</sub>), at 741 (**1**) or 742 cm<sup>-1</sup> (**2**).

Octahedral symmetry is well reflected in the shape of electronic spectra of the compounds with the  $v_1$  band at 1050 or 1060 nm ( $\sim\Delta_o$  9535 cm<sup>-1</sup>). As expected for a NiNO<sub>5</sub> chromophore, the estimated  $\Delta_o$  values of these compounds exceed that of the [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> ion (8500 cm<sup>-1</sup>).

## 3.2. Structure and properties of salts **3** and **4** with the hexakis(imidazole)nickel(II) ion

The attempt to obtain ternary compounds have yielded two isotype salts  $[Ni(Him)_6][Ni(MEBIDA or MOBIDA)_2]\cdot4H_2O$ . They consist of centro-symmetric anions and cations, and non-coordinated water molecules (see Fig. 3 for the MOBIDA salt). The Ni–N(Him) bond lengths are similar both within each cation and between the compounds (~2.14 Å), with average values of 2.136 and 2.139 Å for compounds **3** and **4**, respectively. Again, the bond distances in the bis-chelate anions are rather similar and have values for Ni–O of 2.05 and 2.07 Å, shorter than the Ni–N distance of 2.11 Å. There are no important differences in the corresponding bond lengths of the neutral binary compounds and the bis-chelate anions of the studied salts, and all IDA moieties revealed a *fac*-NO<sub>2</sub> conformation.

In these crystals,  $\pi,\pi$ -stacking interactions between the aromatic rings of MEBIDA or MOBIDA are missing. These crystals consist of 2D layers parallel to the *ab* plane where four Him ligands of each cation acts as H-donors to four N-H···O(carboxylate) acceptors of four different neighboring anions. This builds two kinds of channels (I and II, in Fig. 4, top). These layers are connected along the *c*-axis by additional H-bonding interactions involving N-H bonds of the remaining Him ligands and the water molecules, in a H-bonding 3D framework (Fig. 4, bottom). Interestingly, the *p*-methoxy-benzyl arms of the MOBIDA ligands in **4** only participate in hydrophobic interactions. This role is also displayed by the *p*-methyl-benzyl arms of the MEBIDA ligand in **3**. The hydrophobic behavior of the benzyl-like arms of MEBIDA and MOBIDA in these salts is consistent with the iso-type structures of their crystals.

These compounds lose water rather easily under dry-air flow, giving TG-formulas of [Ni(Him)<sub>6</sub>][Ni(MEBIDA)<sub>2</sub>]·3.68H<sub>2</sub>O (exp.

6.244%, calc. 6.239%) and  $[Ni(Him)_6]$   $[Ni(MOBIDA)_2]$ ·3.13H<sub>2</sub>O (exp. 5.209%, calc. 5.198%) and the corresponding pyrolyses give a residue of NiO (exp. 13.800% at 430 °C, calc. 14.058% for **3**; exp. 14.464% at 450 °C, calc. 13.810% for **4**). If the beginning of the TG experiment is retarded until the sample weight remains stable, the water content (*n*) of the compounds decreases to *n* = 1.35 and 0 for **3** and **4**, respectively. The anhydrous salt  $[Ni(Him)_6]$ - $[Ni(MEBIDA or MOBIDA)_2]$  decomposes (>250 °C) in three overlapped steps to give NiO as the residue at *ca.* 450 °C. After the loss of the non coordinated water, pyrolysis of the organic ligands from **3** yields CO<sub>2</sub>, H<sub>2</sub>O, CO, CH<sub>4</sub>, NH<sub>3</sub> and probably N<sub>2</sub>O, and trace amounts of NO. The three pyrolytic steps (a–c) of **4** enable the FT-IR identification of CO<sub>2</sub> and H<sub>2</sub>O (a), CO<sub>2</sub>, H<sub>2</sub>O, CO, CH<sub>4</sub> and CH<sub>3</sub>OH (b) or CO<sub>2</sub>, H<sub>2</sub>O, CO, CH<sub>4</sub>, NH<sub>3</sub>, N<sub>2</sub>O, NO and trace amounts of NO<sub>2</sub> (c).

The FT-IR spectra for solid samples of **3** and **4** are remarkably similar, according to the iso-type nature of these crystals and the small structural differences between the MEBIDA and MOBIDA ligands. It is easy to identify bands due to the chromophores of H<sub>2</sub>O ( $v_{as} \sim 3450$ , δ 1615 cm<sup>-1</sup>), MEBIDA or MOBIDA ( $v_{as}$ (COO) 1588 cm<sup>-1</sup>,  $v_s$ (COO) 1382 cm<sup>-1</sup>,  $\pi$ (C–H)<sub>arom</sub> 747 or 745 cm<sup>-1</sup>) and Him ( $\nu$ (N–H) 3133 cm<sup>-1</sup>,  $\delta$ (N–H) 1542 or 1515 cm<sup>-1</sup>,  $\pi$ (C–H)<sub>arom</sub> 668 cm<sup>-1</sup>). It is interesting to point out that the stretching band of C–O(ether)– $C_{arom}$  at 1181 cm<sup>-1</sup> (defined absorption of medium intensity) is present in the spectrum of 4, but not in that of 3. The electronic spectra of these compounds exhibit the typical bands of octahedral nickel(II) complexes, which represent the averaged contribution of NiN<sub>6</sub> and NiN<sub>2</sub>O<sub>4</sub> chromophores of the cation and anion, respectively. However, the maximum of the  $v_1$ band ( $\sim \Delta_0$  10417 cm<sup>-1</sup>) has a higher value than that observed for the corresponding binary compounds ( $\sim$ 9500 cm<sup>-1</sup>) and the corresponding hexaaqua-cation (8500 cm<sup>-1</sup>), according to the strength of the ligand field from the chromophores: NiN<sub>2</sub>O<sub>4</sub>  $(averaged) > NiNO_5 > NiO_6$ .

## 3.3. Ni(II) and Cu(II) iminodiacetates: a structural and conformational comparison

We found it instructive to make a comparison of the structural and ligand conformational information available for the copper(II)



Fig. 3. Asymmetric unit of [Ni(Him)<sub>6</sub>][Ni(MEBIDA)<sub>2</sub>]-4H<sub>2</sub>O (3), with the numbering of the coordination atoms.



**Fig. 4.** Crystal packing of [Ni(Him)<sub>6</sub>][Ni(MOBIDA)<sub>2</sub>]-4H<sub>2</sub>O (**4**). Top: H-bonded layer parallel to the *ab* plane, with two sizes of channels (I and II). Bottom: H-bonded layers of **4** along the *c*-axis, building the 3D crystal. Note that the O-methoxy atom of the MOBIDA ligands is not involved in H-bonding interactions.

#### Table 3

Iminodiacetate moiety conformation in copper(II) complexes. Selected references are given in brackets. Most complexes exhibit a 4 + 1 coordination polyhedron, whereas the others exhibit an elongated octahedral coordination, type ~4 + 2.

Type of complex	IDA-moiety conformation	IDA-like ligands <sup>a</sup>	N-heterocyclic ligands	Denticity of the N-heterocycle
Binary	fac-NO + O(apical) mer-NO <sub>2</sub>	IDA [17] μ <sub>2</sub> -1,6-HDTA [18] TEBIDA [21], BCAA [22], N- phenyl-IDA-like [19], μ <sub>2</sub> - EDTA [20]	None None	
Ternary	mer-NO <sub>2</sub>	All used tridentate IDA-like ligands [17,21–28]	Imidazole (various). Also NH <sub>3</sub> . 4,4'- Bipyridine (in µ <sub>2</sub> -bridging mode), 2,4'-bipyridine (as N <sub>4</sub> -monodentate), pyrazine (as µ <sub>2</sub> -bridge), creatinine adenine (as N <sub>3</sub> or N <sub>7</sub> -monodentate) or as µ <sub>2</sub> -N <sub>3</sub> , N <sub>7</sub> - and µ <sub>2</sub> -N <sub>7</sub> , N <sub>9</sub> -bridge	Monodentate
	fac-NO + O (apical)	All used IDA-like [21,22,29- 32] excepting those with a bulky N-substituent (cited below)	Aromatic α,α'-diimines (such as 2,2'- bipyridine or 1,10-phenanthroline and related ligands), 2-aminomethyl- benzimidazole, 2-pyridine- carboxamide imidazole (two per Cu <sup>II</sup> atom)	Bidentate (or two monodentate Him)
	fac-O <sub>2</sub> + N(apical)	TEBIDA [21], BCAA [22], N- (benzyl-like)-IDA [28]	Aromatic $\alpha, \alpha'$ -diimines (such as 2,2'- bipyridine or 1,10-phenanthroline)	Bidentate

<sup>a</sup> Chelating ligands: IDA = iminodiacetate(2-), IDA-like = any tridentate N-substituted-IDA(2-), 1,6-HDTA = hexamethylene-1,6-diamino tetraacetate(4-), TEBIDA = Ntert-butyl-IDA(2-), BCAA = N-(1-adamantyl)-IDA(2-), N-phenyl-IDA-like = several ligands with one or two IDA groups directly linked to a benzene ring (2- or 4- charged), EDTA = ethylenediaminotetraacetate(4-), N-(benzyl-like)-IDA = the own N-benzyl-IDA(2-) or various N-(*p*-substituted-benzyl)-IDA(2-).

and nickel(II) complexes. With this purpose in mind, Table 3 summarized the data concerning Cu(II) iminodiacetates. Binary compounds can be mononuclear or binuclear (1,6-HDTA [18] or EDTA [20]). In both kinds of complex, the IDA moiety group exhibits a fac-NO + O(apical) conformation, as seen for the polymeric compound  $[Cu(IDA)(H_2O)_2]$  [17] and the binuclear compound with a bridging 1,6-HDTA ligand [18]; therefore fac-NO + O(apical) conformation seem to be proved for iminodiacetate-chelating groups where the N-amino atom is linked to a hydrogen atom (IDA) or a long hexamethylene chain (1,6-HDTA). In contrast, when N-R-IDA has a bulky R-group, such as *tert*-butyl, adamantyl or phenyl, the binary complex exhibits a mer-NO<sub>2</sub> conformation for the IDA chelating group. This latter conformation is also observed in the binuclear binary complex of EDTA, with a short ethylene chain bridging the two IDA-like chelating groups [20]. Three kinds of ternary Cu(II)-iminodiacetates are known, the most numerous group refers to all ternary complexes where the Cu(IDA-like) chelate binds one monodentate N-heterocyclic donor ligand (or one NH<sub>3</sub> ligand). All these complexes exhibit a *mer*-NO<sub>2</sub> conformation for the IDA moiety group in a five-coordination polyhedron. In ternary complexes where the Cu(IDA-like) chelate binds two Him ligands per copper(II), atom or one aromatic  $\alpha, \alpha'$ -diimine or closely related bidentate ligand, the IDA chelating conformation is *fac*-NO + O(apical), except for those compounds where the IDA moiety has a bulky N-R arm. In these latter cases, the IDA moiety exhibits a less common conformation, *fac*-O<sub>2</sub> + N(apical). Thus, two main features should be observed in Cu(II) iminodiacetates. First, the IDA moiety conformation is different in ternary compounds where the auxiliary ligand is monodentate (ammonia, imidazoles, etc.) or bidentate (aromatic  $\alpha, \alpha'$ -diimines and related bidentate ligands or two Him ligands). Second, all the ternary systems reported in Table 3 are mixed ligand complexes; it means that none of these systems yield the corresponding salts.

The available information concerning Ni(II) iminodiacetates is summarized in Table 4, including the compounds reported in this paper. In this context, we found binary and ternary complexes as

Table 4
---------

C C + '	- C + 1	the second s	-1						D - f	a sea and a sea a sea the term	
ODIOPEDITION	οτ τηρ	iminodiacerare	cheisting	molerv	n c	ICTINEATI	DICKER III	compleyes	References	are given in $ni$	'ackers
comornation		mmounacctate	chiciating	monety	III C	Jetaneurai	merce in j	complexes.	References	are given in Di	achets.

Type of compound	IDA moiety conformation	IDA-like ligands <sup>a</sup>	N-heterocyclic ligands	Denticity of N- heterocyclic ligand
Binary	fac-NO <sub>2</sub>	IDA [1–3], MIDA [14], HNTA (as tridentate!) [15], p-Cph-IDA [9], MEBIDA or MOBIDA (this work)	None	
Ternary	fac-NO <sub>2</sub>	IDA [4-6], N-ph-IDA, <i>p</i> -PhDTA [11,12], ADA (as tridentate!) [15]	3 Him or 3 benzimidazole or one bis-thiazole ligands per Ni <sup>II</sup> atom 2,2'-bipyridine, 2,2'-bipyridine or 1,10-phenanthroline, 2,2'-bipypiridine	Monodentate or bidentate Bidentate
Salt	mer-NO <sub>2</sub> fac-NO <sub>2</sub>	p-Cph-IDA [9] MIDA [4], NB2IDA [3], MEBIDA or MOBIDA (this work)	$\begin{array}{l} \mu_2\text{4,4}^{-1}\text{-bipyridine (thus, one N donor per Ni^{II}) atom \\ Imidazole in [Ni(Him)_6]^{2*} [4,this work] or \\ [Ni(Him)_2(H_2O)_4]^{2*} [3] cations \end{array}$	Monodentate Monodentate

<sup>a</sup> Chelating ligands: IDA = iminodiacetate(2–), MIDA = N-methyl-IDA(2–), HNTA = hydrogen-nitrilotriacetate(2–) or N-carboxymethyl-IDA(2–), *p*-Cph-IDA = N-(*p*-carboxyphenyl)-IDA(2–), N-ph-IDA = N-phenyl-IDA(2–), *p*-PhDTA = *p*-phenylenediaminotetraacetate(4–), ADA = N-(2-amidomethyl)-IDA(2–), NBzIDA = N-benzyl-IDA(2–).

well as some salts. All these complexes exhibit octahedral coordination polyhedra, as is always found for the structures of Ni(II) derivatives with amino-polycarboxylate ligands. The limited information available for Ni(IDA-like) complexes shows remarkable differences with regard to that which is observed for the Cu(II) complexes. First, all binary Ni(IDA-like) compounds have the IDA-like moiety in a *fac*-NO<sub>2</sub> conformation (including the HNTA<sup>2-</sup> ligand acting only as a tridentate ligand [15]). Second, with just one exception [9], the ternary Ni(II) complexes also have a fac-NO<sub>2</sub> conformation for the IDA chelating group. It is interesting to note that this exception, with the mer-NO<sub>2</sub> IDA moiety conformation, corresponds to a compound where the bridging 4,4'-bipyridine ligand supplies only one heterocyclic donor atom to each Ni(II) centre. In contrast, all other ternary compounds referred to in Table 4 correspond to examples where each Ni(IDA-like) chelate adds two or three N-heterocyclic donor atoms. A few Ni(II) iminodiacetates are salts where the bis-chelate anion (IDA moiety) exhibits a fac-NO<sub>2</sub> conformation. These compounds have one methyl or benzyl-like non-coordinating arm in the IDA-like chelating agent. Moreover, although with one exception, these salts contain the  $[Ni(Him)_6]^{2+}$ counter-cation. It is interesting to point out that the salt [Ni(Him)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>][Ni(NBzIDA)<sub>2</sub>] [4] has a Ni/Him/NBzIDA equimolar ratio. Thus, we can observe that Ni(II) iminodiacetates where the IDA-like ligand has a methyl or benzyl-like non-coordinating arm are salts and not ternary complexes, irrespectively of the number of N-heterocyclic donor atoms (one or three) per nickel(II) centre.

#### 4. Concluding remark

Summarizing, we have reported the structure of two novel nickel(II)-(NBzIDA-like) complexes, where the IDA moiety exhibits a *fac*-NO<sub>2</sub> conformation. We also verified that the equimolar (1:1:1) ternary systems Ni/(NBzIDA-like)/3Him yield salts of the Ni-(bis-chelate) and the hexakis(imidazole)nickel(II) ion. Therefore, perhaps this work should be followed by the study of ternary systems such as Ni/IDA or HNTA/Him (or a half of 4,4'-bipyridine), in order to see if ternary complexes or the related salts will be crystallized.

#### Acknowledgements

Financial support from ERDF-EC, MEC-Spain (Project CTQ2006-15329-C02/BQU) is acknowledged. DKP thanks MAE-AECID (Spain) for a PhD Grant. DChL thanks SIC-EU for a I3P postdoctoral research contract. The Project "Factoría de Cristalización, CONSOLIDER INGENIO-2010" provided X-ray structural facilities for this work. ADM thanks ME for a PhD fellowship (FPU Program).

#### Appendix A. Supplementary data

CCDC 732816, 732817, 732818 and 732819 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.09.034.

#### References

- Yan-Rong Wu, La-Sheng Long, Rong-Bin Huang, Lan-Sun Zheng, Seik Weng Ng, Acta Crystllogr., Sect. E 59 (2003) m390.
- [2] P.M. Forster, A.K. Cheetham, Micropor. Mesopor. Mater. 73 (2004) 57.
- [3] V.M. Agre, T.F. Sisoeva, V.K. Trunov, N.M. Dyatlova, A.Ya. Fridman, Zh. Strukt. Khim. 25 (1984) 141.
- [4] I.N. Polyakova, A.L. Poznyak, V.S. Sergienko, Kristallografiya 45 (2000) 833.
- [5] Jian-Rong Su, Kai-Liang Yin, Duan-Jun Xu, Acta Crystllogr., Sect. E 60 (2004) m1020.
- [6] Jia-Geng Liu, Duan-Jun Xu, J. Coord. Chem. 58 (2005) 735.
- [7] F.G. Kramarenko, T.N. Polynova, M.A. Porai-Koshits, V.P. Chalyi, N.D. Mitrofanova, Zh. Strukt. Khim. 15 (1974) 161.
- [8] N.J. Mammano, D.H. Templeton, A. Zalkin, Acta Crystllogr., Sect. B 33 (1977) 1251.
- [9] Guoping Yong, Zhiyong Wang, Jiutong Chen, J. Mol. Struct. 707 (2004) 223.
- [10] Zhi-Feng Hao, Yao-Fang Zhang, Yao-Wen Chen, Jian Yu, Lin Yu, Wuji Huaxue Xuebao 21 (2005) 573.
- [11] Zhi-Feng Hao, Hai-Feng Li, Yao-Wen Chen, Yao-Fang Zhang, Jian Yu, Lin Yu, Wuji Huaxue Xuebao 22 (2006) 1090.
- [12] Xiang-Dong Zhang, Chun-Hua Ge, Fang Yu, Qi-Tao Liu, Mio-Li Zhu, Acta Crystallogr., Sect. C 63 (2007) m519.
- [13] S. Dominguez, A. Mederos, P. Gili, A. Rancel, A.E. Rivero, F. Brito, F. Lloret, X. Solans, C. Ruíz-Pérez, M.L. Rodríguez, I. Brito, Inorg. Chim. Acta 255 (1997) 367.
- [14] M.R. Wagner, D.B. Beach, Acta Crystallogr., Sect. C 41 (1985) 669.
   [15] P.A. Petrenko, M. Gdaniec, Yu.A. Simonov, V.G. Stavile, A.P. Gulya, Koord. Khim.
- 30 (2004) 862.
   [16] E. Bugella-Altamirano, J.M. González-Pérez, D. Choquesillo-Lazarte, R. Carballo, A. Castiñeiras, J. Niclós-Gutiérrez, Inorg. Chem. Commun. 5 (2002) 727.
- [17] M.J. Román-Alpiste, J.D. Martin-Ramos, A. Castiñeiras, E. Bugella-Altamirano, A.G. Sicilia-Zafra, J.M. González-Pérez, J. Niclós-Gutiérrez, Polyhedron 18 (1999) 3341.
- [18] G.V. Khvorykh, L.I. Martynenko, Koord. Khim. 20 (1994) 624.
- [19] C. Ruiz-Pérez, M.L. Rodríguez, F.V. Rodríguez-Romero, A. Mederos, P. Gili, P. Martín-Zarza, Acta Crystallogr., Sect. C 46 (1990) 1405.
- [20] T.V. Filippova, T.N. Polynova, M.A. Porai-Koshits, N.V. Novozhilova, L.I. Martynenko, Zh. Stukt. Khim. 14 (1973) 280.
- [21] P.X. Rojas-González, D. Chquesillo-Lazarte, J.M. González-Pérez, S.A. Ruiz-García, R. Carballo, A. Castiñeiras, J. Niclós-Gutiérrez, Polyhedron 22 (2003) 1037.
- [22] R. Fernández-Piñar, C. Sánchez de Medina-Revilla, A. Domínguez-Martín, M.P. Brandí-Blanco, D. Choquesillo-Lazarte, J.M. González-Pérez, J. Niclós-Gutiérrez, Z. Anorg. Allg. Chem. 633 (2007) 2658.
- [23] Erpeng Zhang, Hongwei Hou, Huayun Han, Yaoting Fan, J. Organomet. Chem. 693 (2008) 1927.
- [24] Dong-Zhao Gao, Jing Chen, Shu-Ping Wang, You Song, Dai-Zheng Liao, Zong-Hui Jiang, Shi-Ping Yan, Inorg. Chem. Commun. 9 (2006) 132.

- [25] S. Mukhopadhyay, P.B. Chatterjee, D. Mandal, G. Mostafa, A. Caneschi, J. Van Slageren, T.J.R. Weakley, M. Chaudhury, Inorg. Chem. 43 (2004) 3413.
- [26] E. Bugella-Altamirano, D. Choquesillo-Lazarte, J.M. González-Pérez, M.J. Sánchez-Moreno, R. Marín-Sánchez, J.D. Martin-Ramos, B. Covelo, R. Carballo, A. Castiñeiras, J. Niclós-Gutiérrez, Inorg. Chim. Acta 339 (2002) 160.
- [27] P.X. Rojas-González, A. Castiñeiras, J.M. González-Pérez, D. Choquesillo-Lazarte, J. Niclós-Gutiérrez, Inorg. Chem. 41 (2002) 6190.
- [28] M.J. Sánchez-Moreno, D. Choquesillo-Lazarte, J.M. González-Pérez, R. Carballo, J.D. Martin-Ramos, A. Castiñeiras, J. Niclós-Gutiérrez, Polyhedron 22 (2003) 1039.
- [29] E. Craven, Cungen Zhang, C. Janiak, G. Rheinwald, H. Lang, Z. Anorg. Allg. Chem. 629 (2003) 2282.
- [30] B. Selvakumar, V. Rajendiran, P.U. Maheswari, H. Stoeckli-Evans, M. Palaniandavar, J. Inorg. Biochem. 100 (2006) 316.
- [31] Nguyen-Huy Dung, B. Viossat, A. Busnot, A.G. Sicilia-Zafra, J.M. González-Pérez, J. Niclós-Gutiérrez, Inorg. Chim. Acta 169 (1990) 9.

- [32] M.P. Brandi-Blanco, M.M. de Benavides-Giménez, J.M. González-Pérez, D. Choquesillo-Lazarte, Acta Crystallogr., Sect. E 63 (2007) m1678.
- [33] BRUKER, SMART and SAINT. Area Detector Control Integration Software, Bruker.
- [34] BRUKER, APEX2 Software, Bruker AXS Inc., V2008.1, Madison, Wisconsin, USA, 2008.
- [35] G.M. Sheldrick, saDABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1997.
- [36] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.
- [37] G.M. Sheldrick, SHEIXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
- [38] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2003.
- [39] C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock, L. Rodríguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, J. Appl. Cryst. 41 (2008) 466.