PERGAMON

Available online at www.sciencedirect.com

SCIENCE DIRECT

Polyhedron 22 (2003) 1039–1049

POLYHEDRON

www.elsevier.com/locate/poly

Ring–ring or nitro-ring π,π-interactions in *N*-(*p*-nitrobenzyl)iminodiacetic acid (H_2NBIDA) and mixed-ligand copper(II) complexes of NBIDA and imidazole (Him), 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen). Crystal structures of H_2NBIDA, [Cu(NBIDA)(Him)(H_2O)], [Cu(NBIDA)(bipy)]·3H_2O and [Cu(NBIDA)(phen)]·2H_2O

M.J. Sánchez-Moreno [a], Duane Choquesillo-Lazarte [a], Josefa M. González-Pérez [a], Rosa Carballo [b], José D. Martín-Ramos [c], Alfonso Castiñeiras [d], Juan Niclós-Gutiérrez [a,*]

[a] *Department of Inorganic Chemistry, Faculty of Pharmacy, University of Granada, Campus de Cartuja, s/n, E-18071 Granada, Spain*
[b] *Department of Inorganic Chemistry, Faculty of Sciences, University of Vigo, E-36200 Vigo, Spain*
[c] *Department of Mineralogy and Petrology, Faculty of Sciences, University of Granada, E-18071 Granada, Spain*
[d] *Department of Inorganic Chemistry, Faculty of Pharmacy, University of Santiago de Compostela, E-15706 Santiago de Compostela, Spain*

Received 4 October 2002; accepted 20 January 2003

Abstract

N-(*p*-nitrobenzyl)iminodiacetic acid (H_2NBIDA) and the mixed-ligand copper(II) complexes with NBIDA and imidazole (Him), 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) were prepared and characterised by thermal, spectral, magnetic and X-ray diffraction methods. Our aim is to study various possibilities of the *N*-(*p*-nitrobenzyl) arm in the iminodiacetate(2−) ion (IDA) skeleton to be involved in π,π-interactions which contribute to molecular recognition processes and crystal building. Analysis of the shortest aromatic ring–ring interactions were carried out with PLATON program and let us conclude that in free H_2NBIDA acid (**1**) and [Cu(NBIDA)(Him)(H_2O)] (**2**) only inter-molecular benzyl–benzyl π,π-stacks occur, whereas in [Cu(NBIDA)(bipy)]·3H_2O (**3**) and [Cu(NBIDA)(phen)]·2H_2O (**4**) there are both inter-molecular nitro-benzyl π,π-interactions (instead of benzyl–benzyl π,π-stacks) and α,α′-diimine-α,α′-diimine ring–ring π,π-interactions. In compound **2** NBIDA ligand has a typical *mer*-NO_2 tridentate conformation, whereas in **3** or **4** it exhibits an unusual *fac*-O_2+N(apical) conformation. The molecular recognition pathway in **3** and **4** is discussed on a structural basis, considering a variety of interligand interactions involved in molecular recognition processes to build these and closely related crystals. We conclude that both the presence of a non-coordinating N-substituent in the IDA-like ligand and the chelation of Cu(II) by an aromatic α,α′-diimine (bipy or phen) display active roles for promote a *fac*-O_2+N(apical) conformation and various modes of interligand π,π-stacking interactions.

Keywords: Copper(II); Mixed-ligand complexes; Crystal structures; π,π-Stacking; Nitro; Benzyl

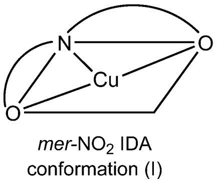
1. Introduction

Structural comparisons on the *catena*-poly-[diaqua(iminodiacetato)copper(II)], [Cu(IDA)(H_2O)$_2$]$_n$ [1] and a variety of mixed-ligand copper(II) complexes having IDA or IDA derivatives and imidazoles or aromatic α,α′-diimines (bipyridine, phenanthrolines) or related ligands (histamine and others) serve as bioinorganic

---

[*] Corresponding author. Tel.: +34-958-243-855; fax: +34-958-246-219.
E-mail address: jniclos@ugr.es (J. Niclós-Gutiérrez).

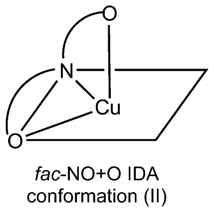
0277-5387/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0277-5387(03)00089-5



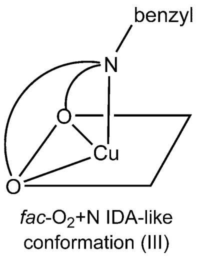
Scheme 1.

model compounds to illustrate conformational changes at the protein conformation for metal-protein centres in absence or presence of appropriate substrates [1–9]. To this purposes, IDA or IDA-analogues simulate the 'protein moiety' and imidazole (Him) and different N-containing heterocycles play 'substrate-like' roles. These experimental modelling possibilities arise from the changes of the *fac*-NO+O IDA conformation in the diaqua-copper(II) complex to a *mer*-NO_2 IDA or IDA-like (Scheme 1) in ternary complexes with equimolar ratio Cu(II)/(IDA or IDA-like)/N-heterocyclic donor, to go back for a *fac*-NO+O IDA conformation (Scheme 2) in compound with 1/1/2 Cu(II)/IDA or IDA-like/N-heterocyclic donor ratio [1,3–9]. Expanding these frontiers and on the knowledge of aromatic ring–ring π,π-interaction possibilities in various mixed-ligand copper(II) complexes with aromatic α-amino acids and N-heterocyclic secondary ligands [2] we considered of broad interest to introduce aromaticity and ligand conformational flexibility in the IDA skeleton to promote interligand π,π-stacking interactions in ternary Cu(II) complexes [3]. In this context we have proved that *N*-alkyl-, *N*-benzyl- or *N*-phenethyl-IDA copper(II) complexes display drastically different recognition modes with the non-substituted adenine, to such a point that these N-substituents of the IDA chelating ligand control selectively the metal chelate-nucleobase recognition process [4,5].

Several systems Cu(II)/NBzIDA/N-heterocyclic donor have been studied in our laboratories (NBzIDA = *N*-benzyliminodiacetate(2−) ion) [6–8]. An unique behaviour was found using 1,10-phenanthroline (phen) as secondary ligand, which affords $[Cu_4(phen)_4(OH)_4(H_2O)_2][Cu(NBzIDA)_2]_2 \cdot 20H_2O$ (**A**) and [Cu(NBzIDA) (phen)]$\cdot 2H_2O$ (**B**) [7]. Compound **A** is a salt with many π,π-stacking interactions whereas **B** is a typical mixed-ligand complex with molecules arranged in multi-π,π-stacked chains which involves alternating intra- and inter-ligand benzyl–phen π,π-interactions. An analogous of **B** is [Cu(NBzIDA)(TMphen)]$\cdot 5H_2O$ (compound **C**, TMphen = 3,4,7,8-tetramethylphenanthroline) [8]. In compounds **B** and **C** the NBzIDA acts as tridentate with an unusual *fac*-O_2+N(apical) conformation (Scheme 3) which has been explained as a consequence of the co-operation of intra- and intermolecular interligand benzyl–phen or phen-like π,π-stacks.



Scheme 2.



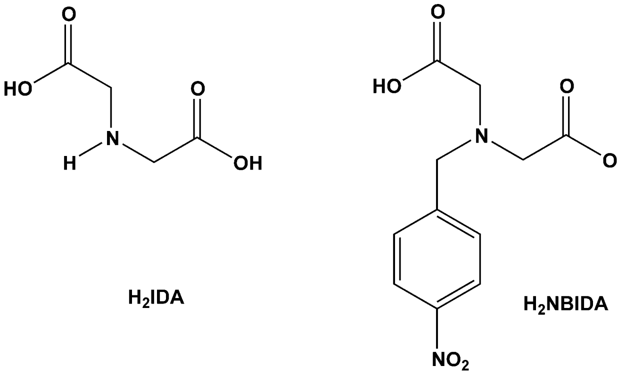
Scheme 3.

As a part of our program on this kind of copper(II) complexes [9] we report structural results concerning the possibilities of developing π,π-interactions in *N*-(*p*-nitrobenzyl)iminodiacetic acid (H_2NBIDA; see Scheme 4) and three new copper(II) derivatives with NBIDA and imidazole (Him) or 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen). The aim of this work is to study the influence on the π,π-stacking interactions of a *p*-nitro group in the *N*-benzyl-IDA skeleton.

2. Experimental

2.1. Synthesis of the acid H_2NBIDA and its copper(II) complexes

The acid H_2NBIDA (**1**) was prepared by reaction of 4-nitrobenzylamine hydrochloride (25 g, 132.5 mmol, Aldrich) and potassium chloroacetate in alkaline aqueous solution (KOH necessary for condensation plus 0.1 mol in excess, pH 11) at 90 °C approximately during 2 h. After cooling the reaction mixture was filtered and acidified with HCl 6 N to pH 2.5, which produces the



Scheme 4.

precipitation of a crude product. This was dissolved in water by a measured amount of $NaHCO_3$ and the acid H_2NBIDA was re-precipitated by addition of the equivalent amount of HCl 6 N. Single crystals of this amino acid were grown from water:ethanol or water:acetone 30:70. Yield: 18.78 g, 56.7%. *Anal*. Calc. for $C_{11}H_{12}N_2O_6$: C, 49.26; H, 4.51; N, 10.44. Found: C, 48.79; H, 4.88; N, 10.55. FT-IR relevant frequencies (cm^{-1}): 3448 of ν(O–H), 1711 and 1673 of ν(C=O), 1611 and 1382 of ν_{as} and ν_s(COO) in $-COO^-$... (HOOC–) or –COO...(H^+–N); 3082, 3067, 3027, 2977 for ν(C–H) modes, 2529 of $\nu(N^+-H)$, 1519 and 1346 as typical bands of ν_{as} and ν_s of $-NO_2$ group [10]. ^{1}H NMR (300 MHz, D_2O+KOD, δ ppm): broad singlets at 3.02 of NCH_2CO_2, 3.66 of ar–CH_2–N, 7.34 of H-2,6$_{ar}$ and 7.92 of H-3,5$_{ar}$. ^{13}C NMR (75 MHz, D_2O+d_6-acetone): 51.93 ar–CH_2–N, 57.44 of N–CH_2–carboxyl, 1232.81 of C-2,6$_{ar}$, 128.59 of C-3,5$_{ar}$, 146,81 C-1$_{ar}$, 147.68 of C-4$_{ar}$ and 178.86 of –COO. TG-analysis in two steps (190–370 and 370–625 °C) with production of CO_2, H_2O, CO, $N(CH_3)_3$ (only in first step), NH_3, and N_2O (first step) or NO_2 (only in second step).

Copper(II) complexes were obtained by reaction of $Cu_2CO_3(OH)_2$ (0.5 mmol, Aldrich) and H_2NBIDA (1 mmol) in 100 ml of water, under controlled vacuum, stirring and heating with addition of a N-heterocyclic ligand (Him, 2,2′-bipy or 1,10-phen). The resulting solution was filtered without vacuum on a crystallisation device and evaporated at room temperature. When precipitation initiated, the solution was filtered once more on an appropriate crystallisation device to obtain by evaporation many well shaped crystals for diffractrometric purposes. Successive samples of these compounds were collected to a final yield >70%. For $[Cu(NBIDA)(Him)(H_2O)]$ ($C_{14}H_{16}CuN_2O_7$, compound **2**, yield: 314.4 mg, 75.6%): Calc.: C 40.44, H 3.88, N 13.47. Found: 40.25, H 3.82, N 13.47. For $[Cu(NBIDA)(bipy)]\cdot 3H_2O$, ($C_{21}H_{24}CuN_4O_9$, compound **3**, yield: 390.9 mg, 72.4%): Calc.: C 46.71, H 4.48, N 10.38. Found: C 47.12, H 4.84, N 10.57. For $[Cu(NBIDA)(phen)]\cdot 2H_2O$ ($C_{23}H_{22}CuN_4O_8$, compound **4**, yield: 432.4 mg, 79.2%), Calc.: C 50.60, H 4.06, N 10.26. Found: C 50.67, H 4.24, N 10.36.

2.2. Crystal structure determination

A prismatic crystal of each studied compound was mounted on a glass fibre and used for data collection. Crystal data were collected at 233 (compound **2**) or 293 K (compounds **1**, **3** and **4**) using a Bruker SMART CCD 1000 or an Enraf Nonius CAD4 automatic diffractometer. Graphite monochromated Mo Kα ($\lambda = 0.71073$ Å, compounds **1**, **3** and **4**) or CuKα ($\lambda = 1.54184$ Å, compound **2**) radiation was used. The data were corrected for Lorentz and polarization effects. Absorption corrections were made with SADABS [11] or using a semi-empirical method [12]. The structures were solved by direct methods (compounds **1**, **3** and **4**) or by the Patterson method (compound **2**) using the program SHELXS-97 [13] and refined by full-matrix least-square techniques (FMLS below in Table 1) on F^2 using SHELXL-97 [14]. Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. For compounds **1**, **3** and **4**, hydrogen atoms were placed geometrically and positional parameters were refined using a riding model. For compound **2** all hydrogen atoms were located from difference Fourier maps and included as fixed contributions riding on attached C atoms with isotropic thermal parameters 1.3 times those of the respective C atoms. Atomic scattering factors were obtained from 'International Tables for X-ray Crystallography' [15]. Molecular graphics and geometrical calculations have been obtained from SHELXTL [16] or PLATON [17]. A summary of the crystal data, experimental details and refinement results for studied compounds are listed in Table 1.

2.3. Physical measurements

All physical measurements were carried out as described in a previous paper [4] except for susceptibility measurement, which were only made at room temperature for compounds **2** and **3**.

3. Results and discussion

In addition to the data reported in Table 1, bond distances and angles for H_2NBIDA could be obtained from deposited files or from the authors. This amino diacid exists as zwitterions (Fig. 1(a)) stabilised by one intra-molecular hydrogen bond (N9–H9A...O11, 2.66(1) Å, 114(1)°) between the ammonium proton and the H-free O(11) atom of the unionised –C(11)O(11)O(12)H group. These zwitterions form zig–zag chains along the *b* axis of the crystal by a rather linear inter-molecular H-bond (O(12)–H(12)...O(13^i), 2.50 Å, 172°, $i = -x+1$, $y-1/2$, $-z+1/2$) linking carboxyl-adjacent carboxylate groups. These chains build up a 2D framework (Fig. 1(b)) by inter-molecular π,π-stacking interactions (see below, and Table 3). Such layers fall parallel to the *bc* plane of the crystal connected by van der Waals forces. Stacking parameters hereafter taken into account are d_{c-c} (centroid–centroid distance), α (angle between planes containing aromatic rings), slipping angles β and γ (defined by the vector c1–c2 and the normal to plane P(1) or P(2) from C1 and C2, respectively).

Compound **2** (Fig. 2(a)) forms molecules which exhibits a typical 4+1 copper(II) coordination (see τ data in Table 2), a *mer*-NO_2 tridentate conformation of NBIDA, with Him in the *trans*-site to the Cu–

Table 1
Crystal data and structure refinement for H_2NBIDA acid (compounds **1**) and copper(II) compounds **2**–**4**

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{11}H_{12}N_2O_6$	$C_{14}H_{16}CuN_4O_7$	$C_{21}H_{24}CuN_4O_9$	$C_{23}H_{22}CuN_4O_8$
Formula weight	268.23	415.85	539.98	545.99
Temperature (K)	293(2)	233(2)	293(2)	293(2)
Wavelength (Å)	0.71073	1.54184	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Triclinic	Triclinic
Space group	$P2_1/n$	Pbca	P-1	P-1
Unit cell dimensions				
a(Å)	7.225(6)	12.110(1)	7.063(7)	7.199(1)
b(Å)	14.788(1)	23.160(1)	12.364(1)	12.054(2)
c(Å)	10.809(9)	12.017(1)	14.087(1)	14.064(2)
α(°)	90	90	105.745(2)	102.180(3)
β(°)	94.968(2)	90	100.003(2)	102.938(3)
γ(°)	90	90	101.550(2)	101.331(3)
V (Å^3)	1150.50(2)	3370.4(4)	1125.64(2)	1124.00(3)
Z	4	8	2	2
Calculated density (Mg m^{-3})	1.549	1.639	1.593	1.613
Absorption Coefficient (mm^{-1})	0.128	2.269	1.032	1.031
F(0 0 0)	560	1704	558	562
Crystal size (mm)	0.17 × 0.43 × 0.97	0.15 × 0.15 × 0.10	0.08 × 0.10 × 0.18	0.24 × 0.10 × 0.10
θ Range data collected (°)	2.34–28.03	5.30–64.97	1.55–28.05	1.54–28.08
Index ranges	$-9 \leqslant h \leqslant 6$, $-19 \leqslant k \leqslant 19$, $-14 \leqslant l \leqslant 13$	$0 \leqslant h \leqslant 14$, $-27 \leqslant k \leqslant 0$, $-14 \leqslant l \leqslant 1$	$-8 \leqslant h \leqslant 9$, $-16 \leqslant k \leqslant 14$, $-18 \leqslant l \leqslant 15$	$-9 \leqslant h \leqslant 8$, $-15 \leqslant k \leqslant 15$, $-14 \leqslant l \leqslant 18$
Reflections collected/unique	6867/2674 R(int) = 0.073	3152/2855 R(int) = 0.0426	6714/4662 R(int) = 0.048	6734/4689 R(int) = 0.054
Absorption correction	SADABS	Semi-empirical	SADABS	SADABS
Max/min transmission	1.000/0.505	0.805/0.727	1.000/0.762	1.000/0.8339
Refinement method	FMLS [a] on F^2	FMLS [a] on F^2	FMLS [a] on F^2	FMLS [a] on F^2
Data/restraints/parameters	2674/0/177	2855/0/236	4662/0/340	4689/0/325
Goodness-of-fit on F^2	1.067	1.006	0.752	0.813
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.049$, $wR_2 = 0.132$	$R_1 = 0.051$, $wR_2 = 0.119$	$R_1 = 0.048$, $wR_2 = 0.087$	$R_1 = 0.059$, $wR_2 = 0.105$
R indices (all data)	$R_1 = 0.064$, $wR_2 = 0.140$	$R_1 = 0.102$, $wR_2 = 0.141$	$R_1 = 0.112$, $wR_2 = 0.101$	$R_1 = 0.160$, $wR_2 = 0.126$
Large difference peak/hole (e Å^{-3})	0.267/−0.189	0.331/−0.641	0.346/−0.302	0.378/−0.297

[a] FMLS = Full-matrix least-squares.

N(NBIDA) bond and an apical/distal aqua ligand. These structural features are mostly common in mixed-ligand complexes with equimolar ratio Cu(II)/IDA or derivative/N-heterocyclic donor [1,3–9]. Compound **2** has a very low distortion toward the trigonal bipyramid, but a remarkable tetragonality (see Table 2). The metal atom is at 0.112(2) Å from the mean basal plane P1, and both N and O pairs of donors deviate 0.10(1) Å in opposite sense (O donor toward aqua ligand). The Him plane defines a dihedral angle of 17.4(2)° with P1 and the Cu(II) atom is 0.21(1) from the Him plane, in accordance with the σ nature of the Cu–N(Him) bond. The analysis of the shortest ring–ring interactions in compound **2** reveals again that side-on π,π-interactions participate in the molecular recognition process. That occurs in such a way that two NBIDA benzyl aromatic rings lie parallel ($\alpha = 0.00°$) at 3.39 Å and are involved in a 'complex pair formation' (Fig. 2(b)). Pairs of stacked molecules build the crystal by hydrogen bonds, which link O–H bonds of aqua ligands, imidazole N–H groups with O-carboxylate acceptors from six adjacent complex molecules. A comprehensive and critical account of these π,π-interactions in metal complexes with N-aromatic heterocycles has been recently reported by Janiak [18].

Table 2
Coordination bond distances (Å) in compounds **2**–**4** and parameters for the distortion of 4+1 polyhedron

Compound	**2**	**3**	**4**
Cu–N(NBIDA)	1.984(3)	2.343(3)	2.252(4)
Cu–O(NBIDA)	1.962(3)	1.949(3)	1.945(4)
Cu–O(NBIDA)	1.982(3)	1.986(3)	1.958(4)
Cu–O(aqua)	2.349(3)		
Cu–N(Him)	1.936(4)		
Cu–N(bipy or phen)		2.012(3)	2.003(4)
Cu–N(bipy or phen)		2.016(3)	2.021(4)
T (tetragonality)	0.184	0.85	0.88
τ (%)	1.60	7.33	9.98
ϕ Chelate rings (°)	14.34	99.65/80.35	75.6
NBIDA Conformation	*mer*-NO_2	*fac*-O_2+N(apical)	*fac*-O_2+N(apical)

$\tau = 100(\theta - \phi)/60$, where $\theta > \phi$ are the *trans*-donor-Cu-donor angles for the four closest donor atoms. τ is 0 or 100 for ideal SBP or BPT coordination, respectively [19].

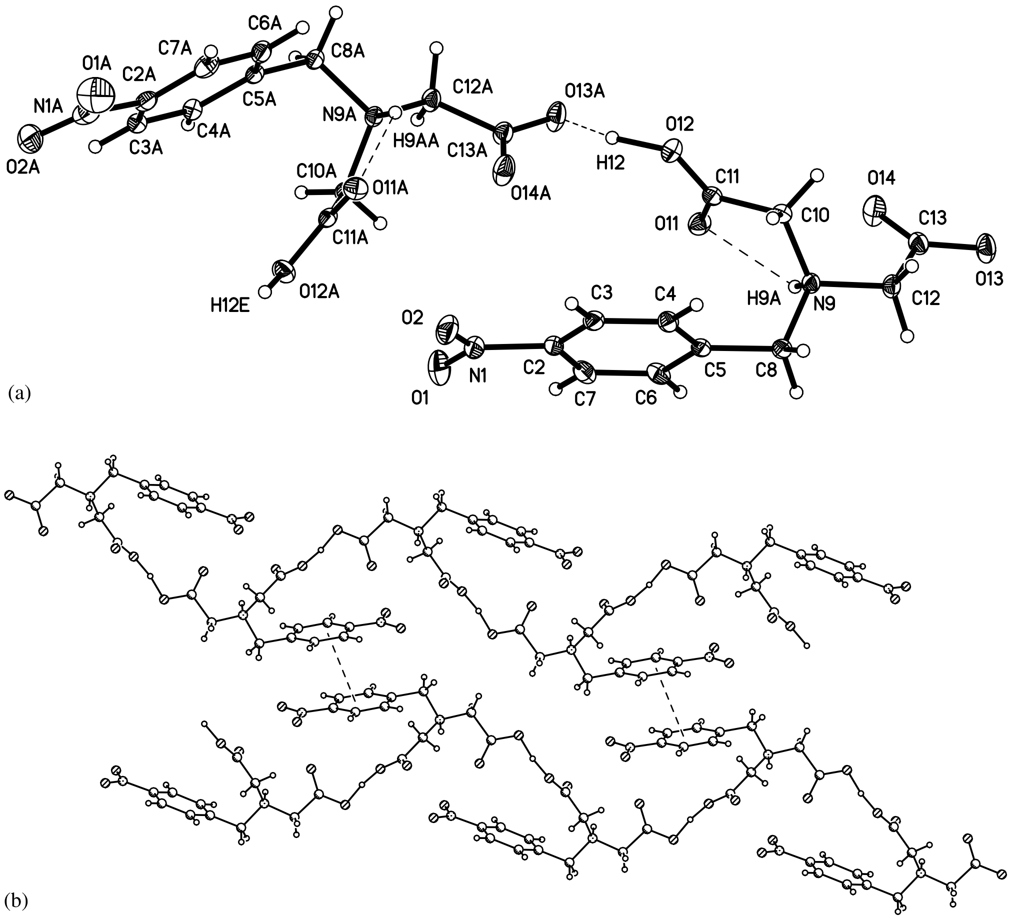


Fig. 1. (a) Two zwitterions of H_2NBIDA acid showing the intra- and inter-molecular H-bonds. (b) Inter-molecular benzyl–benzyl π,π-interaction (dashed lines) connecting H-bonded chains of H_2NBIDA acid into 2D layers extending parallel to the *bc* plane of the crystal (stacked rings are related by the symmetry code $i = -x,\ 1-y,\ -z$).

Compounds **3** and **4** also exhibit a square base pyramidal coordination (see Fig. 3 and τ data in Table 2). The four closest donors of the metal atoms are both N atom of aromatic α,α′-diamine (bipy or phen) and two O carboxylate atoms from NBIDA acetate arms, whereas the N amino donor of this chelate ligand lies at the apical/distal coordination site. That represents an unusual *fac*-O_2+N(apical) conformation for NBIDA in compounds **3** and **4** (Table 2). As far as concerns to molecular recognition processes and building of crystals, data of Table 3 reveal that *p*-nitro-benzyl rings fall parallel ($\alpha = 0.00°$) and at 3.56±0.03 Å. However they are too slipped (angles β and γ ~45°) to enable effective ring–ring π,π-stacking interactions between the 'benzyl ring moieties' of compound **3** and **4** (see below). On the other hand, data of Table 4 reveal possibilities for such π,π-stacking interactions between aromatic rings of α,α′-diimines. In compound **3** that indeed represents the formation of 'pairs of complex molecules' with 2,2′-bipy planes defining a dihedral angle $\alpha = 4.43°$. In this case both pyridyl rings of each bipy ligand are involved in the stack for complex pair formation (Fig. 4(a)) and, in addition, inter-molecular interligand nitro-benzyl π,π-interactions (Fig. 4(b)) are used to give infinitive chains of pairs of complex molecules (Fig. 4(c)). The molecular recognition pattern in compound **4** is very different. Data of Table 4 and Fig. 5(a) show that phen ligands lie parallel ($\alpha = 0.00$) and are involved in both complex pairs (stacked at 3.41 Å) and in the formation of an infinite chain (stacked at 3.46 Å) by means of inter-molecular π,π-stacking interactions between C_6-phen ring (Table 4). Moreover these inter-molecular stacks are still unequally slipped for base pairing ($\beta = \gamma = 15.0°$) and for chain ($\beta = \gamma = 23.8°$) formation. In addition infinite chains are involved to each other side in 'nitro-adjacent benzyl' π,π-interactions (Fig. 5(b)) giving a supramolecular 2D framework (Fig. 5(c)). These layers are connected by H-bonding interactions involving non-coordinated water molecules.

The *fac*-O_2+N(apical) NBIDA conformation in compounds **3** and **4** cannot be attributed to the contribution of intra-molecular π,π-stacking interligand interactions, as has been argued in compounds $[Cu(NBzIDA)(phen)]\cdot 2H_2O$ [7] and $[Cu(NBzIDA)(TMphen)]\cdot 5H_2O$ [8] where both intra- and inter-molecular π,π-stacks seem to co-operate in

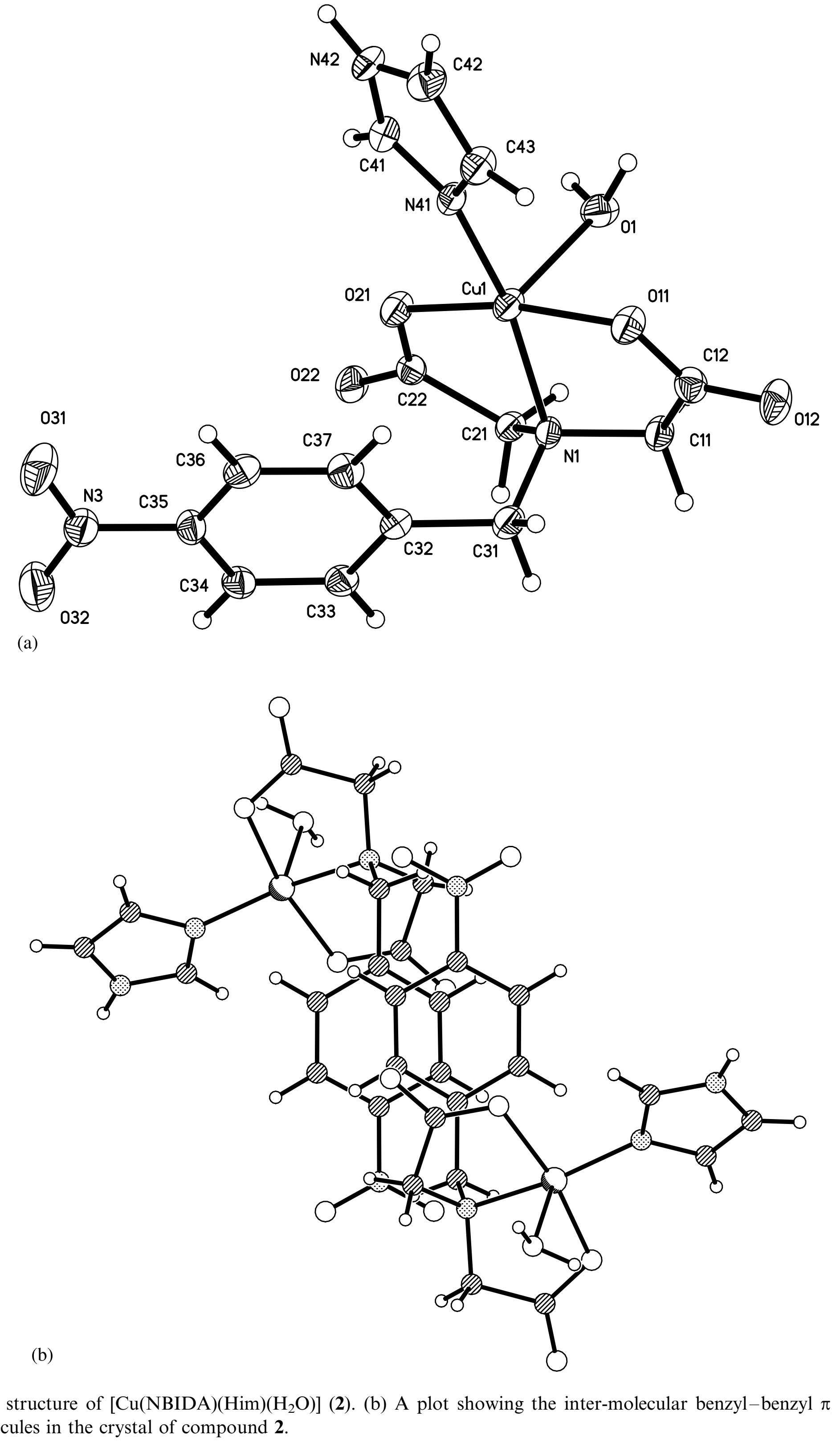


Fig. 2. (a) Molecular structure of [Cu(NBIDA)(Him)(H_2O)] (**2**). (b) A plot showing the inter-molecular benzyl–benzyl π,π-stacking interaction forming pairs of molecules in the crystal of compound **2**.

multi-stacked chains. On the basis of the present knowledge we could consider that the lack of π,π-stacking interactions in [Cu(IDA)(bipy)]·$6H_2O$ [20] (where the non-N-substituted IDA ligand exhibits a *fac*-NO+O(apical) conformation) as well as the structure of [Cu(TEBIDA)(bipy)]·$4.5H_2O$ [21] where in contrast the *N*-(*tert*-butyl)-iminodiacetato ligand (TEBIDA) adopts a *fac*-O_2+N(apical) conformation and

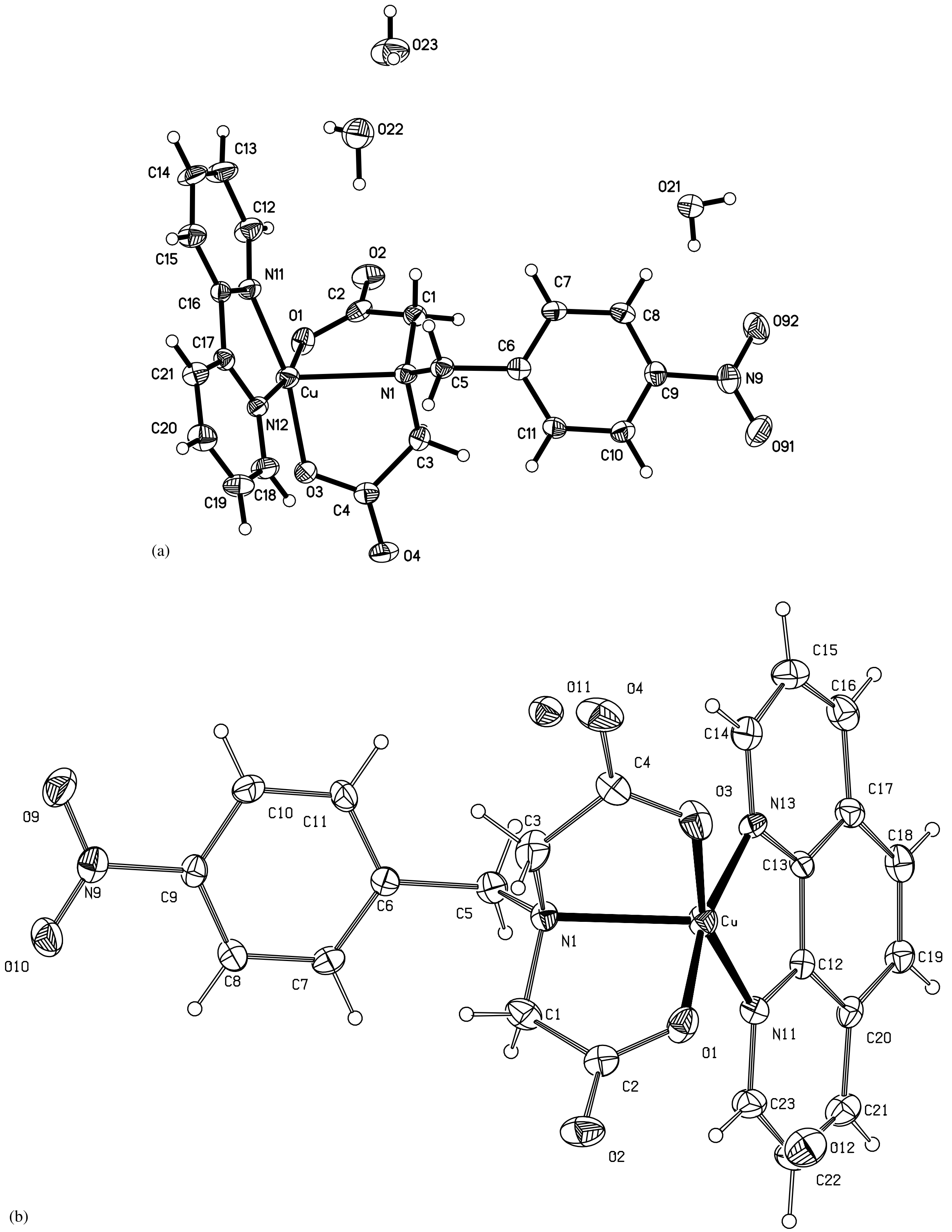


Fig. 3. (a) Asymmetric unit of [Cu(NBIDA)(bipy)]·$3H_2O$ (**3**). (b) Asymmetric unit of [Cu(NBIDA)(phen)]·$2H_2O$ (**4**).

once more 'pairs of complex molecules are formed by a π,π-stacking interaction between bipy ligands (d_{c-c} = 3.78 Å, $d_{\pi-\pi} = 3.41$ Å, $\alpha = 4.74°$, $\beta = 20.27°$, $\gamma =$ 24.95°). Indeed the structure of the latter compound has significant similarities with that now reported for compound **3**. Consequently, it seems clear that two features are required to promote a change from *fac*-NO+O(apical) to *fac*-O_2+N(apical) in IDA-like li-

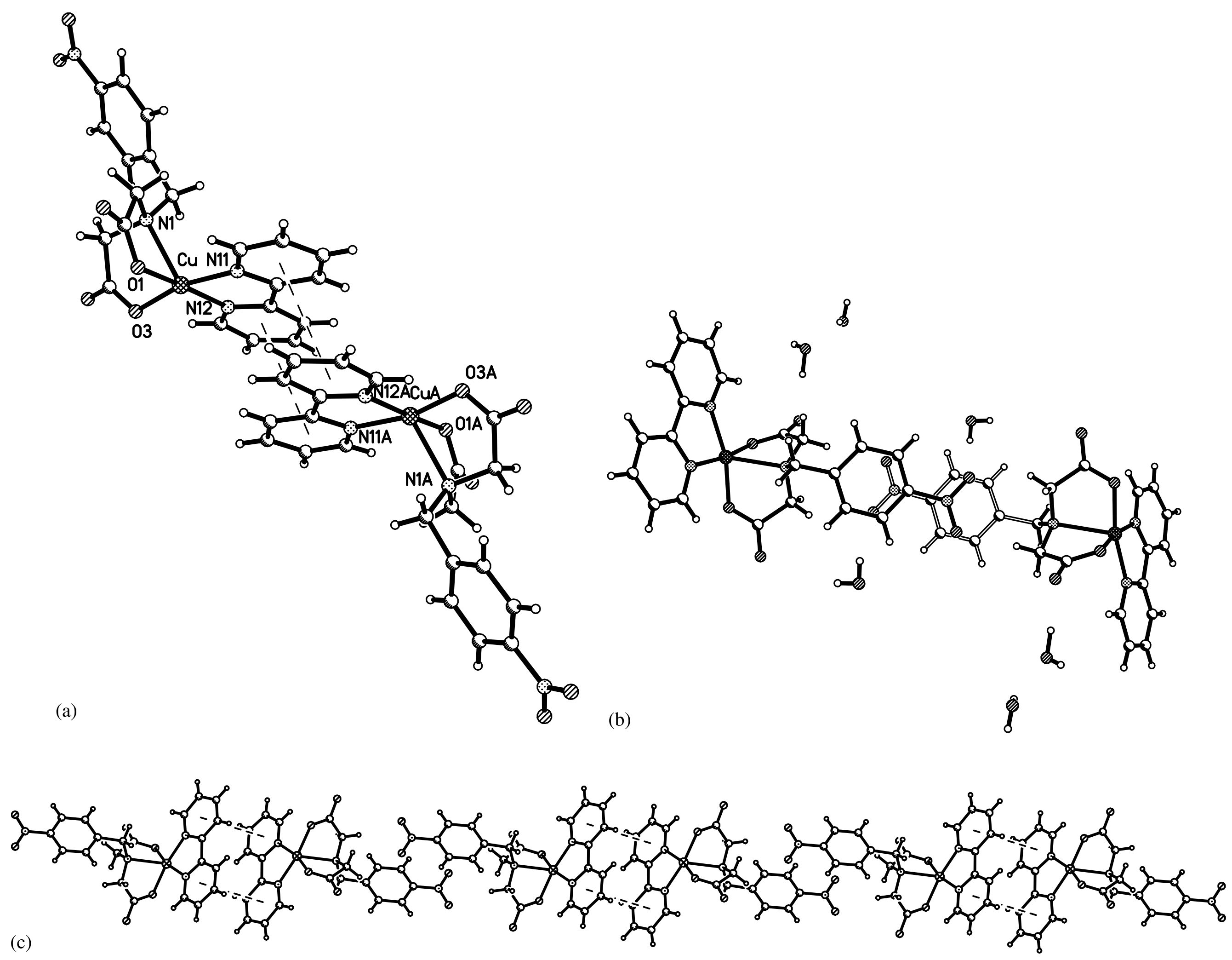


Fig. 4. (a) Inter-molecular π,π-stacking interaction between bipy ligands forming a pair of complex molecules in **3**. (b) π,π-Interactions between adjacent *p*-nitro groups and benzyl rings of NBIDA ligands in **3**. (c) Fragment of a chain of **3** formed by alternating bipy–bipy and nitro-benzyl π,π-interactions.

gands. These are the presence of non-coordinating N-substituent in the IDA skeleton and the binding of an aromatic and chelating α,α′-diimine (such as 2,2′-bipy or 1,10-phen). We can note that if the N-substituent of IDA skeleton has appropriate conformational flexibility (as the benzyl arm), a π-electron rich group (as nitro) and/or an aromatic ring (as the phenyl moiety in the benzyl substituent), a variety of interligand π,π-stacking interactions could be displayed. Then such interactions take part of molecular recognition processes involved in crystal building. In this connection, we can appreciate that the binding of copper(II) to an aromatic chelating α,α′-diimine modifies the π,π-stacking pattern of the NBIDA *p*-nitro-benzyl arm. In fact, H_2NBIDA acid and [Cu(NBIDA)(Him)(H_2O)] (compound **2**) gives ‘benzyl–benzyl’ inter-molecular stacks, whereas compounds **3** and **4** produces ‘nitro-benzyl’ inter-molecular π,π-interactions. Finally it is also interesting to note that the own skeleton of the aromatic α,α′-diimine influences its implication in inter-molecular recognition processes. Both Cu-bipy derivatives with TEBIDA or NBIDA display very similar bipy–bipy stacks, but they are clearly different to those observed in Cu-phen derivatives with NBzIDA [7,8] or NBIDA (compound **4**). Unfortunately, until the present the crystal structure of other hypothetical ternary complexes (such as Cu(II)+IDA+phen or Cu(II)+TEBIDA+phen) remain unknown. Additional researches should be carried out to accomplish fundamental structural co-relations and increase our present knowledge on the molecular recognition processes in these mixed-ligand copper(II) complexes.

As it is show in Table 5, the studied compounds have thermal, spectral and magnetic properties in accordance with the reported structures. Its should be outlined that in dry-air atmosphere the compound **2** loosely retains the aqua apical ligand in a molar H_2O:Cu ratio 0.94/1, but compounds **3** and **4** loss a significant amount of

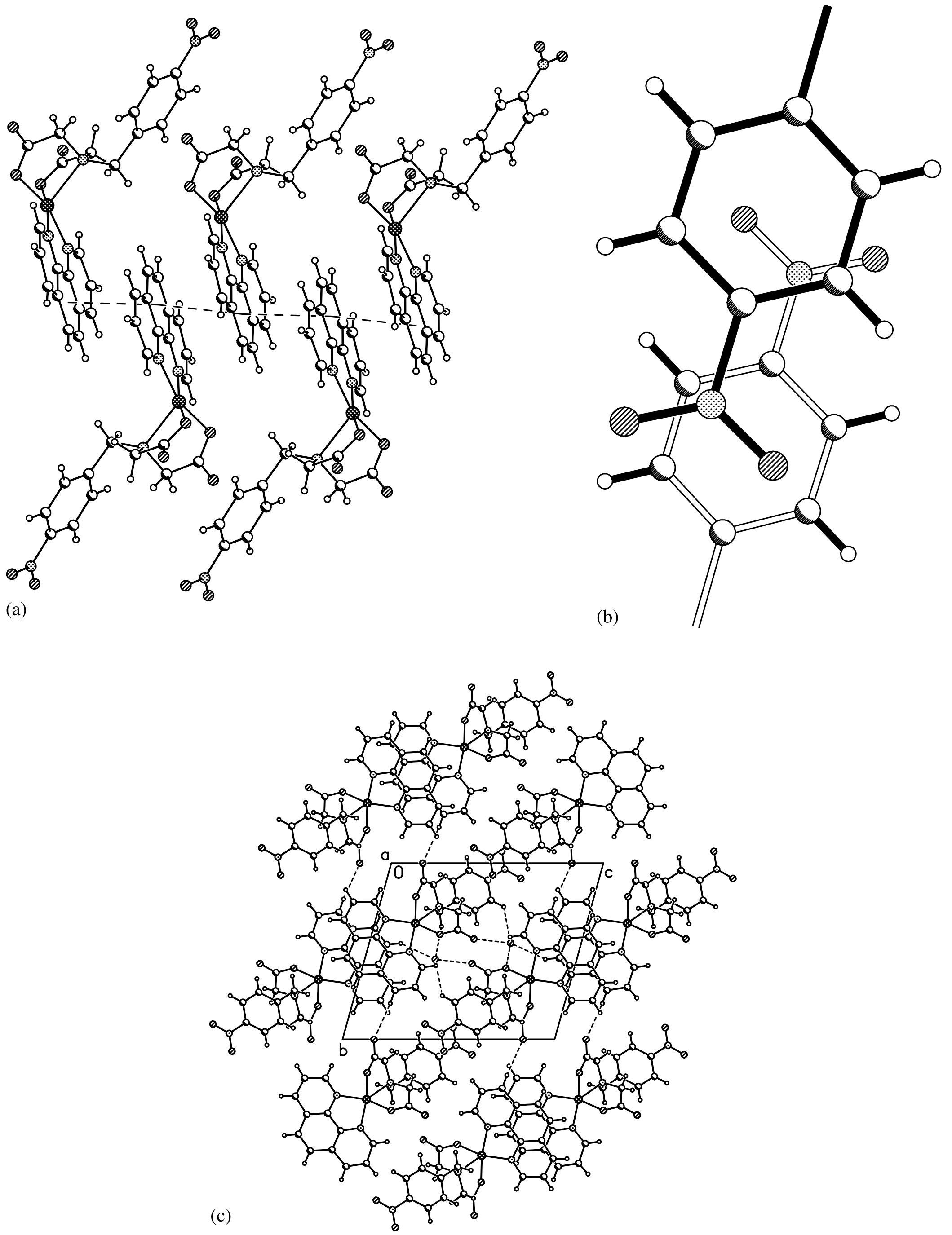


Fig. 5. (a) Fragment of a multi-stacked chain by inter-molecular π,π-interaction between phen ligands of **4** (see text). (b) Detail of the overlapping between pairs of *p*-nitrobenzyl groups in **4**. (c) 2D framework in the crystal of **4** build up by both phen–phen and (*p*-nitrobenzyl)-(*p*-nitrobenzyl) π,π-interactions.

Table 3
Analysis of short benzyl–benzyl interaction between molecules of H_2NBIDA and ternary Cu(II) complexes with NBIDA and N-heterocyclic donors

Compound	d_{c-c}(Å)	α(°)	β(°)	γ(°)	$d_{\pi,\pi}$ (Å)	Angle NO_2/Bz-ring (°)
1	3.68	0.03	25.3	25.3	3.33	5.3
2	3.72	0.00	24.3	24.3	3.39	9.1
3	5.10	0.00	45.3	45.3	3.59	6.5
4	5.01	0.00	45.2	45.2	3.53	3.7

Table 4
Analysis of short ring–ring inter-molecular π,π-interactions between bipy or phen ligands in [Cu(NBIDA)(bipy)]·$3H_2O$ (**3**) and [Cu(NBIDA)(phen)]·$2H_2O$ (**4**)

Compound	d_{c-c} (Å)	α(°)	β(°)	γ(°)	$d_{\pi,\pi}$ (Å)	Comment
3 (both pyridyl rings)	3.98	4.43	28.6	24.4	3.56	Pairs of molecules
	3.98	4.43	24.4	28.6	3.56	Stacking the two rings of bipy
4 (C_6-rings)	3.53	0.00	15.0	15.0	3.41	Forming pairs
	3.78	0.00	23.8	23.8	3.46	Linking pairs

Table 5
Summary of thermal, spectral and magnetic properties of Cu(II) compounds **2**–**4**

Copper(II) compound	**2**	**3**	**4**
TG analysis			
H_2O in formula	1	3	2
H_2O on starting TG	0.94	0.88	1.60
N° Steps	4	3	2
Temperature (°C)	108–490	50–500	40–490
Loss in 1st step	H_2O	H_2O	H_2O
Other steps loss [a]	CH_4		
Final residue	CuO	CuO	CuO
IR spectrum (cm^{-1})			
H_2O ν_{as}	3419	3486, 3403	3485
δ	1621	1625	1617
ImH ν_{as}(NH)	3145		
δ(N–H)	~1500		
Carboxylate ν_{as}	~1600	~1600	1592
ν_s [b]	1397	1381	1383
Electronic spectrum			
ν_{max} (cm^{-1})	14 165	15 550, 10 050 (shoulder)	16 050, 10 000 (shoulder)
$\nu_{baricenter}$ (cm^{-1})	12 920	~12 000	~12 500
ESR spectrum			
Type	Axial	Axial	Axial
$g_{\parallel}$	2.24	~2.30	~2.25
$g_{\perp}$	2.06	2.05	2.05
Magnetic properties (293 K)			
μ (B.M.)	1.78	1.81	1.98 [c]

[a] In addition to H_2O, CO_2, CO, N_2O and NO.
[b] Difference between experimental and calculated residue within 1.0%.
[c] Curie–Weiss behaviour ($\chi = C/(T-\theta)$; 80–300 K): $C = 0.49$ K emu mol^{-1}, $\theta = -5.63$ K.

non-coordinated water before starting the TG-analysis. The three copper(II) compounds produce abundant N_2O and NO oxides, upon the oxidative pyrolysis (but not $N(CH_3)_3$ and NH_3 as for H_2NBIDA acid) and give a residue of CuO.

4. Concluding remarks

The results of the present study show different modes of the N-(nitrobenzyl) group to be involved in π,π-stacking interactions as a N-substituent of IDA chelating ligand. These modes represent inter-molecular benzyl–benzyl or nitro-benzyl stacks. This latter pattern is found in ternary Cu(II) complexes of NBIDA and aromatic α,α′-diimines which exhibits a *fac*-O_2+N(apical) IDA-like conformation. A comparison with other structural findings reported in previous works reveal that both the presence of non-coordinating N-substituent in the IDA skeleton and the chelation of the copper(II) atom by an aromatic α,α′-diimine contribute actively to the molecular recognition processes and the crystal building in compounds with NBIDA in *fac*-O_2+N(apical) conformation.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Centre CCDC No. 189626 for H_2NBIDA acid (compound **1**), CCDC No. 189627 for [Cu(NBIDA)(Him)(H_2O)] (compound **2**), CCDC No. 189628 for [Cu(NBIDA)(2,2′-bipy)]·$3H_2O$ (compound **3**) and CCDC No. 189629 for [Cu(NBIDA)(1,10-phen)]·$2H_2O$ (compound **4**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors are gratefully indebted to the Dirección de Investigación, MCYT, Spain for financial support (Research Projects: BQU2002-04523-C02-01/02 and BQU2002-03543). Doctoral research grants from the MCYT (Spain) or from the AECI (MAE, Spain) are grateful acknowledged by M.J.S.M. and D.Ch.-L., respectively.

References

[1] (a) A. Podder, J.K. Dattagupta, N.N. Saha, N. Saenger, Acta Crystallogr. Sect. B 35 (1979) 53;
(b) F.G. Kramanenco, T.N. Polynova, M.A. Porai-Koshits, V.P. Chalvi, G.N. Kumivanova, L.I. Martynenko, Zh. Strukt. Khim. 14 (1973) 744;
(c) M.J. Román-Alpiste, J.D. Martín-Ramos, A. Castiñeiras-Campos, E. Bugella-Altamirano, A.G. Sicilia-Zafra, J.M. González-Pérez, J. Niclós-Gutiérrez, Polyhedron 15 (1999) 439 (and references therein).

[2] (a) F. Zhang, A. Odani, H. Masuda, O. Yamauchi, Inorg. Chem. 35 (1996) 7148;
(b) T. Sugimori, H. Masuda, N. Ohata, K. Koiwai, A. Odani, O. Yamauchi, Inorg. Chem. 36 (1997) 576;
(c) F. Zhang, T. Yajima, H. Masuda, A. Odani, O. Yamauchi, Inorg. Chem. 36 (1997) 5777.

[3] J. Niclós-Gutiérrez, Double intra-molecular inter-ligand π,π-interactions in dinuclear copper(II) complexes, XIII Spanish-Italian and Mediterranean Congress on Thermodynamics of Metal Complexes, Santiago de Compostela, Spain, 2002, Plenary lecture C4 (and references therein).

[4] E. Bugella-Altamirano, D. Choquesillo-Lazarte, J.M. González-Pérez, M.J. Sánchez-Moreno, R. Marín-Sánchez, J.D. Martín-Ramos, B. Covelo, R. Carballo, A. Castiñeiras, J. Niclós-Gutiérrez, Inorg. Chim. Acta 339 (2002) 160 (and references therein).

[5] M.J. Sánchez-Moreno, D. Choquesillo-Lazarte, J.M. González-Pérez, R. Carballo, A. Castiñeiras, J. Niclós-Gutiérrez, Inorg. Chem. Commun. 5 (2002) 800.

[6] (a) A.G. Sicilia Zafra, E. Bugella Altamirano, J.M. González Pérez, J.D. Martín Ramos, J. Niclós Gutiérrez, VIII Italian-Spanish Congress on Thermodynamics of Metal Complexes, Cagliari, Italy, 1997, p. 56.;
(b) E. Bugella, A.G. Sicilia, J.M. González, A. Castiñeiras, J. Niclós, IX Spanish-Italian Congress on Thermodynamics of Metal Complexes, Girona, Spain, 1998, Report P-2.;
(c) E. Bugella-Altamirano, J.M. González-Pérez, A.G. Sicilia-Zafra, A. Castiñeiras-Campos, J. Niclós-Gutiérrez, XI Spanish-Italian Congress on Thermodynamics of Metal Complexes, Valencia, Spain, 2000, Report P-18.

[7] A. Castiñeiras Campos, J.D. Martín Ramos, E. Bugella Altamirano, J.M. González Pérez, D. Choquesillo Lazarte, J. Niclós Gutiérrez, X Italian-Spanish Congress on Thermodynamics of Metal Complexes, S. Martino al Cimino, Italy, 1999, Report C-18.

[8] A. Castiñeiras, E. Bugella Altamirano, J.M. González Pérez, J. Niclós Gutiérrez, Reunión Científica de Bioinorgánica 2001, University of Granada, Granada, 2001. Report P35.

[9] M.J. Sánchez Moreno, Ph.D. dissertation, University of Granada, Granada, 2002.

[10] L.J. Bellamy, The Infrared Spectra of Complex Molecules, vol. 1, third ed., Chapman and Hall, London, 1975.

[11] G.M. Sheldrick, SADABS: Program for Absorption Corrections, University of Göttingen, Göttingen, Germany, 1996.

[12] A.C.T. North, D.C. Phillips, F.S. Mathews, Acta Crystallogr. Sect. A 24 (1968) 351.

[13] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.

[14] G.M. Sheldrick, SHELXL-97. Program for the Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

[15] International Tables for X-ray Crystallography, vol. C, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1995.

[16] SHELXTL: Integrated System for the Determination of Crystal Structures, Bruker AXS Inc., Madison, WI, USA, 2000.

[17] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, The Netherlands, 2001.

[18] C. Janiak, J. Chem. Soc., Dalton Trans. (2000) 3885.

[19] B.J. Hathaway, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 5 (Chapter 53), Pergamon, Oxford, 1987.

[20] (a) G. Nardin, L. Randaccio, R.P. Bonomo, E. Rizzareli, J. Chem. Soc., Dalton Trans. (1980) 369;
(b) A. Castiñeiras, M.E. Abarca, I. de la Cueva, J.M. González, J. Niclós, J. Coord. Chem. 30 (1993) 273.

[21] P.X. Rojas-Gonzalez, D. Choquesillo-Lazarte, J.M. González-Pérez, S.A. Ruíz-García, R. Carballo, A. Castiñeiras, J. Niclós-Gutiérrez, Polyhedron., 22 (2003) X-ref: 10.1016/S0277-5387(03)00088-3