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Structural Evidence for an Unusual Conformation and Weak Interligand Interactions in Two Copper Chelates with (*o*-Nitrophenyl)-ethylenediaminediacetic Acid

Mustapha Allali,[a,b] Joël Jaud,[c] Nouzha Habbadi,[b] Michèle Dartiguenave,[a] André L. Beauchamp,[d] and Eric Benoist*[a][‡]

In memory of Prof. Yves Dartiguenave

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Two mixed-ligand copper(II) complexes, $[Cu(L_1)(H_2O)]\cdot H_2O$ (**1**) and $[Cu(L_1)(bipy)]\cdot 2H_2O$ (**2**), containing the title *N*-substituted iminodiacetate (IDA) derivative (L_1^{2-}) as primary ligand with and without 2,2′-bipyridine as auxiliary ligand, have been synthesised. Both have been fully characterised by means of IR spectroscopy, mass spectrometry, elemental analysis and conductimetry, as well as X-ray crystallography. The dominant structural feature of these complexes is the presence of a flexible coordinating arm on the IDA skeleton which controls the conformation of the resulting complexes. The Cu^{II} centre in complex **1** exhibits a distorted square-pyramidal [4+1] coordination in which the apical site is unexpectedly occupied by the N(2) atom of the coordinating arm instead of a water molecule. The IDA skeleton adopts a tridentate *mer*-O_2N arrangement in **1**, whereas in **2** it exhibits an unusual *fac*-O_2N(apical) configuration, which is observed for the first time for a tridentate IDA unit bearing a flexible arm containing a coordinating atom. The *o*-nitro aromatic group in the flexible arm gives rise to different inter- and/or intramolecular stacking interactions. Classic intermolecular "nitrophenyl-nitrophenyl" π-π stacking interactions are observed between pairs of complex molecules in crystals of **1**, whereas intramolecular "nitrophenyl-pyridyl" interactions alternate with unprecedented interligand π-π "nitrophenyl–metal chelate ring" interactions in crystals of **2**.

1. Introduction

Non-covalent interactions involving aromatic rings play a vital role in certain biological reactions and are key processes in both chemical and biological molecular recognition.[1] Self-assembly and specific binding between molecules are achieved by a combination of weak interactions, such as hydrogen and electrostatic bonding and aromatic ring stacking.[2] In this broad context, structural studies on ternary mixed-ligand metal complexes containing one or more aromatic ligands have shown the existence of intra- and/or intermolecular π-π interactions and have established that both hydrogen-bonding and stacking interactions contribute to crystal building.

Mixed-ligand metal complexes, such as ternary copper(II) complexes containing iminodiacetate (IDA) and N-heterocyclic amines, or closely related ligands, may therefore serve as bioinorganic model compounds. These ternary complexes are a source of inorganic structural correlations for mono- or dinuclear copper proteins. Because of their biological significance, numerous model IDA- or IDA-derivative-containing copper(II) chromophores have been studied: the copper(II) chelate is regarded as a metal centre, while the IDA or IDA derivative (primary ligand) and different N-heterocyclic amine compounds (secondary ligand) act as "protein-like" and "substrate-like" moieties, respectively.[3–7] The IDA ligand exhibits a *fac*-chelating arrangement in diaqua(iminodiacetato)copper(II), which is considered as the reference compound for all mixed-ligand copper(II) complexes containing IDA or IDA derivatives.[8] This *fac*-chelating structure is retained in all known mixed-ligand copper(II) complexes with a 1:1:2 Cu^{II}/IDA/N-heterocyclic amine ratio.[3,9] In contrast, when the ratio is

[a] Laboratoire de Chimie Inorganique, Université Paul Sabatier, Bat. IIR1, 118, route de Narbonne, 31062 Toulouse, France
E-mail: benoist@chimie.ups-tlse.fr
[b] Laboratoire de Chimie Organique et d'Agrochimie, Université Ibn Tofail, Faculté des Sciences, Kénitra, Maroc
[c] CEMES-CNRS, 29, rue Jeanne Marvig, B. P. 4347, 31055 Toulouse, France
[d] Département de Chimie, Université de Montréal, CP 6128, Succ. Centre-ville, Montréal, QC H3C 3J7, Canada
[‡] Present address: Laboratoire de Synthèse et Physicochimie de Molécules d'Intérêt Biologique (SPCMIB), UMR 5068, Université Paul Sabatier, 118, route de Narbonne, 31062 Toulouse, France

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1:1:1, the IDA units exhibit a *mer*-chelating arrangement.[4,10] X-ray structures of these compounds have shown that both the nature of the side chain in *N*-substituted IDA derivatives and the secondary ligand have a tremendous impact on the conformational and structural changes. For example, Sánchez-Moreno and co-workers have reported recently that introducing a benzyl or nitrobenzyl group in the IDA skeleton gives rise to a variety of interligand π-π stacking interactions.[11] The mixed-ligand copper(II) complexes [Cu(NBzIDA)(phen)]·2H_2O (NBzIDA = *N*-benzyliminodiacetate) and [Cu(NBIDA)(bipy)]·3H_2O [NBIDA = *N*-(4-nitrobenzyl)iminodiacetate] present alternating intra- and intermolecular benzyl-phen π-π stacking interactions and alternating intermolecular bipy-bipy and nitrobenzyl-nitrobenzyl π-π stacking interactions, respectively. The authors explained the variety of interligand π-π stacking interactions by the conformational flexibility of the benzyl or nitrobenzyl arm of the IDA derivatives.

With these points in mind, we became interested in studying copper(II) complexes containing (*o*-nitrophenyl)-ethylenediaminediacetic acid (*o*-NO_2Ph-EDDA) as primary ligand, with or without the presence of 2,2′-bipyridine as auxiliary ligand. This *o*-NO_2Ph-EDDA ligand, which was synthesised as its hydrochloride salt (H_2L_1·HCl), may be considered as an *N*-substituted IDA derivative[12] and comprises an IDA unit for tridentate coordination to copper(II) ions, an aromatic ring system bearing a π-electron-rich group (nitro group) and a secondary amino function, and a flexible tethering moiety (ethylene bridge) between the aromatic ring and the tridentate chelating site. Considering these structural features, it was anticipated that the coordinating *N*-(*o*-nitrophenyl)aminoethyl arm in the IDA skeleton should participate in inter- and/or intramolecular aromatic π-π stacking interactions and consequently influence the conformation of the resulting copper(II) complexes. This expectation materialized in the isolation and X-ray characterisation of the two copper complexes [Cu(L_1)(H_2O)]·H_2O (**1**) and [Cu(L_1)(bipy)]·2H_2O (**2**). The former presents an unusual *mer*-configuration, whereas the latter displays intramolecular ring-ring and unprecedented interligand π-π "nitrophenyl–metal chelate ring" interactions. The syntheses and structures of both complexes, as well as a study of their spectroscopic and magnetic properties, are reported herein.

2. Results and Discussion

2.1. Ligand Synthesis

The chelating *o*-NO_2Ph-EDDA ligand (H_2L_1·HCl) used in the present work was synthesised in good yield via a multi-step reaction, as described previously.[12] The coordinating iminodiacetic acid unit acts as a tridentate dianionic ligand by coordination via the two negatively charged monodentate carboxylate functions and the tertiary nitrogen bearing these two carboxylate groups.

2.2. Syntheses and Spectroscopic Properties of the Copper Complexes

The copper complexes **1** and **2** were prepared in excellent yields (75–85%) by mixing equimolar amounts of ligand H_2L_1·HCl and copper(II) chloride dihydrate in methanol in the presence of triethylamine as deprotonating agent for **1**, and by mixing copper(II) hydroxycarbonate $Cu_2(CO_3)(OH)_2$, the ligand L_1H_2·HCl and 2,2′-bipyridine in a 1:2:2 molar ratio in water for **2**. Coordination took place in 2 h in both cases and led, after crystallisation, to a single copper complex of general formula [Cu(L_1)(H_2O)]·H_2O for **1** and [Cu(L_1)(bipy)]·2H_2O for **2**, as evidenced from the elemental analyses. Both complexes exhibit good solubility in polar organic solvents, and **2** is also soluble in water. They were characterised by standard analytical techniques including X-ray diffraction analysis. The positive-ion ESI mass spectra show the parent peak with the correct isotope distribution pattern, consistent with the presence of a neutral mononuclear complex ([M – H_2O + H^+] for **1** and [M + H^+] for **2**) without significant fragmentation. The low electrical conductance values (Λ_m = 30–45 $\Omega^{-1}cm^2mol^{-1}$) for both complexes in methanol are consistent with neutral species.[13]

The IR spectra of compounds **1** and **2** clearly show the presence of water, with several peaks at 3200–3550 cm^{-1} and a smooth shoulder near 1620 cm^{-1} corresponding to the stretching and bending modes, respectively. Non-deprotonation of the secondary aromatic amine of the side chain was confirmed by the stretching absorption of the N–H bond at 3342 cm^{-1} for **1** and 3240 cm^{-1} for **2**. In contrast, the δ(N–H) mode near 1500 cm^{-1} was blurred by the stretching mode of the nitro group. In addition, two strong absorptions in the regions 1613–1628 and 1388–1393 cm^{-1}, which correspond to the ν_{as}(C=O) and ν_s(O–C–O) vibrations of the carboxylate functionalities, respectively, were observed in both cases. The large ν_{as}(C=O) band, which probably overlaps with the ν(C=C) skeletal in-plane vibration of the aromatic ring, exhibits a significant blue shift due to metal coordination. As the value of Δ [Δ = ν_{as}(C=O) – ν_s(O–C–O)] is greater than 200 cm^{-1}, bidentate coordination can be ruled out since this usually gives a Δ value of 40–80 cm^{-1}.[14]

The electronic spectra in methanol show an unsymmetrical d-d band with λ_{max} = 13793 cm^{-1} for **1** and 16420 and 13755 (shoulder) cm^{-1} for **2**. These values are in accordance with those reported for closely related compounds with distorted square-pyramidal or elongated octahedral copper(II) coordinations.[5,7c,11] These transitions were attributed to the $d_{z^2} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions.[15]

The EPR spectra of polycrystalline samples recorded at room temperature for **2** and 77 K for **1** are typical of an axially symmetrical complex with $g_\parallel > g_\perp$ ($g_\parallel$ = 2.29 > $g_\perp$ = 2.07 for **1** and $g_\parallel$ = 2.27 > $g_\perp$ = 2.06 for **2**) and a $d_{x^2-y^2}$ ground state for the copper(II) atom, as expected for elongated square-pyramidal or octahedral coordination polyhedra. These data are typical for powdered monomeric copper(II) complexes and in accordance with a misalignment of the chromophores in their crystal lattice. The estimated

values of μ_{eff} for Cu^{II} at room temperature are 1.65 and 1.79 BM for complexes **1** and **2**, respectively. These values are consistent with dilute magnetic copper(II) complexes with large Cu^{II}–Cu^{II} separations.

2.3. Crystallographic Studies

Crystals of $[Cu(L_1)(H_2O)]\cdot H_2O$ (**1**) and $[Cu(L_1)(bipy)]\cdot 2H_2O$ (**2**) were obtained by slow evaporation of a dichloromethane/methanol and a water solution, respectively. Crystallographic data and selected bond lengths and angles are summarised in Tables 4 and 1, respectively.

Table 1. Selected bonds lengths [Å] and angles [°] in $[Cu(L_1)H_2O]\cdot H_2O$ (**1**) and $[Cu(L_1)(bipy)]\cdot 2H_2O$ (**2**).

Complex 1		Complex **2**	
Cu(1)–O(1)	1.922(2)	Cu(1)–O(1)	1.950(4)
Cu(1)–O(2)	1.940(2)	Cu(1)–O(3)	1.958(4)
Cu(1)–O(3)	1.940(2)	Cu(1)–N(1)	2.302(4)
Cu(1)–N(1)	1.993(3)	Cu(1)–N(4)	1.987(4)
Cu(1)–N(2)	2.627(3)	Cu(1)–N(5)	1.998(5)
O(1)–Cu(1)–O(2)	92.40(10)	O(1)–Cu(1)–O(3)	89.4(2)
O(1)–Cu(1)–O(3)	164.43(11)	O(1)–Cu(1)–N(1)	81.5(2)
O(1)–Cu(1)–N(1)	85.45(10)	O(1)–Cu(1)–N(4)	165.2(2)
O(2)–Cu(1)–O(3)	96.58(10)	O(1)–Cu(1)–N(5)	91.7(2)
O(2)–Cu(1)–N(1)	177.58(11)	O(3)–Cu(1)–N(1)	81.3(2)
O(3)–Cu(1)–N(1)	85.77(10)	O(3)–Cu(1)–N(4)	93.7(2)
N(2)–Cu(1)–N(1)	92.26(11)	O(3)–Cu(1)–N(5)	160.6(2)
N(2)–Cu(1)–O(1)	109.70(10)	N(1)–Cu(1)–N(4)	113.2(2)
N(2)–Cu(1)–O(2)	99.18(10)	N(1)–Cu(1)–N(5)	118.0(2)
N(2)–Cu(1)–O(3)	81.41(10)	N(4)–Cu(1)–N(5)	80.7(2)

The binary mixed-ligand copper(II) complex $[Cu(L_1)(H_2O)]\cdot H_2O$ (**1**) crystallises as the neutral molecular complex shown in Figure 1. As suggested by the spectroscopic data, this complex exhibits a distorted square-pyramidal coordination in which the apical position is occupied by the N(2) nitrogen of the flexible arm. The square plane is defined by the N(1), O(1) and O(3) atoms of the *mer*-tridentate IDA unit and the O(2) atom of the coordinated water molecule. The N–Cu–O angles in the chelate rings are reduced to around 85.5° by the bite of the ligand, which is balanced by an increase in the O–Cu–O(water) angles to 92.4(1)° and 96.6(1)°. Except for these small angular deviations from ideality, the basal plane is only slightly distorted, the Cu atom being displaced only around 0.10 Å from the plane on the side of the apical donor atom N(2). The trans angles of 164.4(1)° and 177.6(1)° lead to a trigonality index, τ,[16] of 0.22, which definitely supports the description of the coordination as square-pyramidal. Nevertheless, the apical Cu–N(2) bond deviates appreciably from the ideal direction along the pseudo-C_4 axis, as evidenced by the broad range of N(2)–Cu(1)–L angles [81.4(1)–109.7(1)°]. The tilt of the apical bond on the O(3) side likely reflects conformational constraints in the connecting arm. It is noteworthy that the nitrophenyl ring is oriented so as to form an intramolecular hydrogen bond between the nitro O(6) atom and the nearby amino group (Table 2).

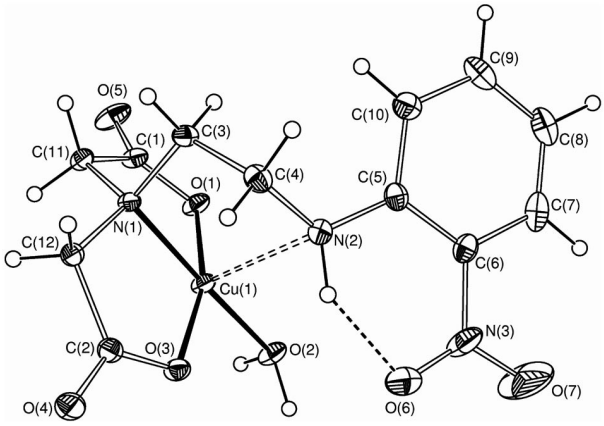

Figure 1. ORTEP drawing of $[Cu(L_1)H_2O]$ (**1**) with numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. The dashed line corresponds to a hydrogen bond.

Table 2. Geometry of the hydrogen bonds for complexes **1** and **2**.

D–H···A	*d*(D–A) [Å]	angle (D–H–A) [°]
Compound **1**		
N(2)–H(2)···O(6)	2.613(4)	135
O(13)–H(13A)···O(4)	2.790(3)	177
O(13)–H(13B)···O(4)′	2.809(4)	163
O(2)–H(2A)···O(5)	2.685(3)	166
O(2)–H(2B)···O(13)	2.672(4)	178
Compound **2**		
N(2)–H···O(5)	2.168(7)	125
O(30)–H(30A)···O(2)	2.915(7)	180
O(30)–H(30B)···O(40)	2.860(7)	173
O(40)–H(40B)···O(4)	2.786(8)	154
O(40)–H(40A)···O(30)	2.895(7)	129

The bond lengths between the metal and the four closest donor atoms [Cu(1)–O(1) 1.922(2), Cu(1)–O(2) 1.940(2), Cu(1)–O(3) 1.940(2), Cu(1)–N(1) 1.993(3) Å] are within the ranges observed for similar mixed-ligand copper(II) complexes. In contrast, the Cu(1)–N(2) distance [2.627(3) Å] is one of the largest known for an axial bond in this kind of complex, the apical position generally being occupied by a water molecule with a Cu–O distance in the range 2.20–2.45 Å.[7c,11,17]

The chelating tridentate IDA unit in this distorted [4+1] square pyramid adopts a *mer*-NO_2 configuration with a dihedral angle of 15.6° between the mean planes through the Cu-glycinato five-membered rings. This unexpected *mer*-NO_2 arrangement instead of the *fac*-NO+O tridentate configuration observed in diaqua(iminodiacetato)copper(II)[8] has been found in several copper(II) chelates with *N*-(phenyl-like)iminodiacetate ions (devoid of coordinating atoms on the phenyl substituent) and, more recently, in the mixed-ligand copper(II) complex $[Cu(TEBIDA)(H_2O)_2]$ (TEBIDA = *N*-*tert*-butyliminodiacetate).[7c] Steric factors have been invoked to explain this unexpected structure in the latter case. Two main structural features could, in our opinion, explain the *mer*-configuration observed in **1**: the length and conformational flexibility of the *N*-(*o*-nitrophenyl)aminoethyl arm on the IDA skeleton and the

presence of a coordinating atom [N(2) of the aromatic amino group] in this arm to occupy the apical position. To the best of our knowledge, this is the first mixed-ligand copper(II) complex where the apical position is occupied by a coordinating atom belonging to the IDA ligand.

The crystal consists of double layers centred on the *ac* face of the unit cell in which the molecules participate in a series of hydrogen bonds. The space between these layers is occupied by nitrophenyl groups of IDA side chains (Figure S1 in the Supporting Information) to form pairs via aromatic ring-ring interactions. A detailed view of this π-π stacking interaction is given in Figure 2 and the corresponding parameters, as calculated by PLATON,[18] are summarised in Table 3. This π-π interaction is actually a slipped stacking, that is, the rings are parallel displaced with respect to one another. The nitrophenyl rings, which are perfectly parallel because they are related by a crystallographic inversion centre, show a centroid–centroid distance of 3.63 Å. The value of 25.6° for the slipping angle allows effective π-π overlap between aromatic moieties of adjacent complexes. Such a parallel-displaced arrangement also involves a contribution from a π-σ attraction, as described recently by Janiak.[2] An additional contribution to crystal cohesion is provided by a network of intra-layer hydrogen bonds in which the complex molecules and lattice water participate (Table 2). The lattice water molecule forms O(13)–H···O bonds with free carboxylate oxygens O(4) of two different molecules. At the same time, it acts as the acceptor in O–H···O hydrogen bonds from the coordinated water molecule O(2), and this latter water molecule makes another O–H···O hydrogen bond with the second free carbonyl atom O(5).

Figure 3 shows a perspective view of the ternary mixed-ligand copper(II) complex **2**. Selected bond lengths and angles are listed in Table 1. The copper(II) centre presents a distorted [4+1] square-pyramidal geometry (τ = 0.077), with the two bipyridine nitrogens and the two carboxylate oxygens of the IDA residue in the basal plane, while the tertiary nitrogen atom of the IDA unit fills the axial position. The bond lengths in the basal plane [Cu(1)–O(1) 1.950(4), Cu(1)–O(3) 1.958(4), Cu(1)–N(4) 1.987(4), Cu(1)–N(5) 1.998(5) Å] and the apical Cu–N bond length [Cu(1)–N(1) 2.302(4) Å] are unexceptional and agree well with those reported previously for five-coordinate copper(II) complexes.[11,19] The Cu(1) atom lies 0.282 Å from the basal plane on the N(1) side. As above, the apical bond does not lie along the pseudo-C_4 axis but is tilted away from the bipy ligand, leading to N(1)–Cu–N angles around 34° greater than the N(1)–Cu–O angles. The Cu atom might be considered to interact very weakly with the side-arm N(2) nitrogen at 3.561(5) Å. By including this interaction, the copper co-

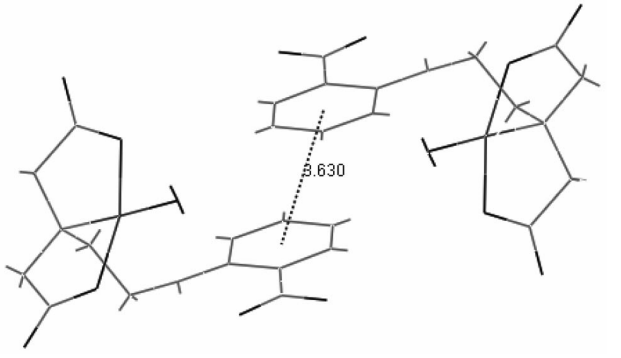

Figure 2. Intermolecular "nitrophenyl–nitrophenyl" π-π stacking interactions in complex **1**. The dotted line links the centroids of the two rings involved in the stacking interaction.

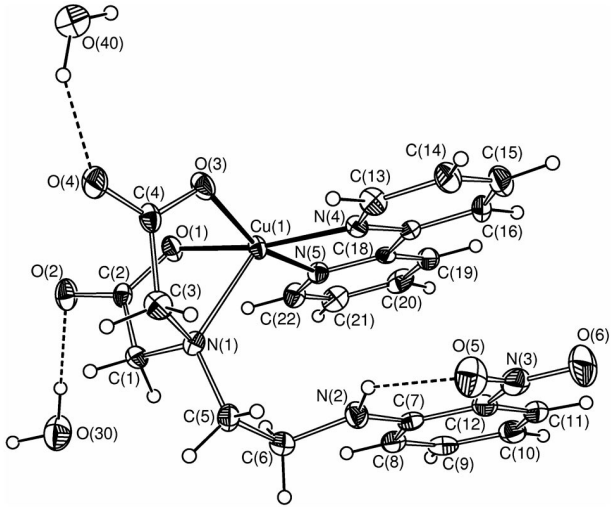

Figure 3. ORTEP drawing of $[Cu(L_1)(bipy)]\cdot 2H_2O$ (**2**) with numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. Dashed lines represent hydrogen bonds.

Table 3. Intramolecular and intermolecular π-π stacking parameters for complexes **1** and **2**.[a]

Stacking parameters	**1** Nitrophenyl/nitrophenyl (intermolecular)	**2** Pyridyl/nitrophenyl (intramolecular)	**2** Nitrophenyl/metal chelate (intermolecular)
Ring A (R_A)	C(5)–C(6)–C(7)–C(8)–C(9)–C(10)	N(5)–C(18)–C(19)–C(20)–C(21)–C(22)	Cu(1)–N(4)–C(17)–C(18)–N(5)
Ring B (R_B)	C(5)–C(6)–C(7)–C(8)–C(9)–C(10)[b]	C(7)–C(8)–C(9)–C(10)–C(11)–C(12)	C(7)–C(8)–C(9)–C(10)–C(11)–C(12)
$d(C_A–C_B)$ [Å]	3.63	3.70	3.41
$d(C_A–R_B)$ [Å]	3.27	3.37	3.23
$d(C_B–R_A)$ [Å]	3.27	3.45	3.35
Dihedral angle R_A/R_B [°]	0.0	6.8	7.7
Angle $V(C_A\rightarrow C_B)/\perp C_A$ [°]	25.6	21.3	10.9
Angle $V(C_B\rightarrow C_A)/\perp C_B$ [°]	25.6	24.6	18.5

[a] R_I = least-squares plane defining Ring I; C_I = centroid of Ring I; $V(C_I\rightarrow C_J)$ is the vector between ring centroids; $\perp C_I$ = line perpendicular to Ring I. [b] Symmetry equivalent ring related by a crystallographic inversion centre.

ordination could be described as a distorted capped square pyramid of type [4+2], although a [(4+1)+1] description would be more appropriate considering that the Cu–N(2) distance is very large.[20]

The nitrophenyl ring again adopts an orientation leading to an intramolecular N(2)–H···O(5) hydrogen bond (Table 2). The compound crystallises in a non-centric space group, but the chirality around the Cu centre is imposed by crystal packing, since it is due only to the conformation of the flexible arm. The lattice contains two water molecules per complex unit, which both form strong O–H···O hydrogen bonds with a free carbonyl oxygen, as shown in Figure 3.

The eight-membered copper iminodiacetato ring exhibits a boat conformation due to the unusual *fac*-O_2+N(apical) coordination of the IDA moiety, a binding mode which has been reported to date for the two 1:1:1 mixed-ligand copper(II) complexes Cu^{II}/TEBIDA/bipy[7c] and Cu^{II}/NBIDA/bipy.[11] To explain their results, the Niclós-Gutiérrez group proposed that both the complexation of the copper ion by an aromatic α,α′-diimine (like bipyridine) and the presence of a non-coordinating N-substituent in the IDA-like ligand are required to promote a change from a *fac*-NO+O(apical) to a *fac*-O_2+N(apical) arrangement. Our compound **2**, which possesses a coordinating atom in the IDA side-arm, obviously demonstrates that the latter structural feature is not a requirement and suggests that the length of the N-substituted flexible arm on the IDA skeleton is an extra important structural parameter to explain the unusual *fac*-O_2+N(apical) configuration. We can therefore conclude that if the *N*-(nitrophenyl)-substituted arm has appropriate length and conformational flexibility, intramolecular π-π stacking interactions can take place. Thus, contrary to the [Cu^{II}(NBIDA)(bipy)] complex, compound **2** exhibits an intramolecular π-π stacking interaction involving a bipyridine six-membered ring [N(5)–C(18)–C(19)–C(20)–C(21)–C(22)] and the nitrophenyl ring, as illustrated in Figure 4. The structural parameters (see Table 3) give a centroid-centroid distance of 3.70 Å and reasonable values for the dihedral angle (6.8°) and the slipping angles (21.3° and 24.6°).

In addition to this intramolecular interaction, the aryl ring of one complex is stacked with the metal chelate ring of the neighbouring complex in the crystal to give unprecedented interligand π-π "nitrophenyl–metal chelate ring" interactions, as illustrated in Figure 4. This structural feature is a most interesting result because, to the best of our knowledge, this kind of interaction has never been observed for similar ternary complexes with a 1:1:1 Cu^{II}/bipy/N-substituted IDA derivative ratio (such complexes usually display intermolecular "bipy-bipy" and/or "aryl-aryl" π-π stacking interactions instead),[7,11] and these interligand π-π "nitrophenyl–metal chelate ring" interactions represent a new example of the metalloaromaticity concept developed by Calvin and Wilson and improved by Matsui.[21] Several studies involving non-covalent interactions with a chelate ring as a π-system have been reported.[22] In our case, similar interactions have been described previously with [Cu(Bzmal)(aromatic α,α′-diimine)(H_2O)] (Bzmal = 2-benzylmalonate and α,α′-diimine = phen or bipy).[22a] It is noteworthy that the values of the stacking parameters for the intramolecular π-π "aryl–metal chelate ring" interaction in [Cu(Bzmal)(bipy)(H_2O)] and the intermolecular π-π "aryl–metal chelate ring" interaction in our complex are similar. The alternation of intra- and intermolecular stacking interactions leads to an infinite chain of complexes **2** along the *b* axis (Figure S2 in the Supporting Information). Cohesion between theses columns is provided to a large extent by hydrogen bonds involving the water molecules already connected to the carbonyl oxygens. These water molecules pendant from the columns of complexes form O–H···O hydrogen bonds between one another (Table 2) and create chains of hydrogen bonds along the *a* direction. Thus, all O–H and N–H polar bonds are involved in inter- and intramolecular hydrogen-bond formation.

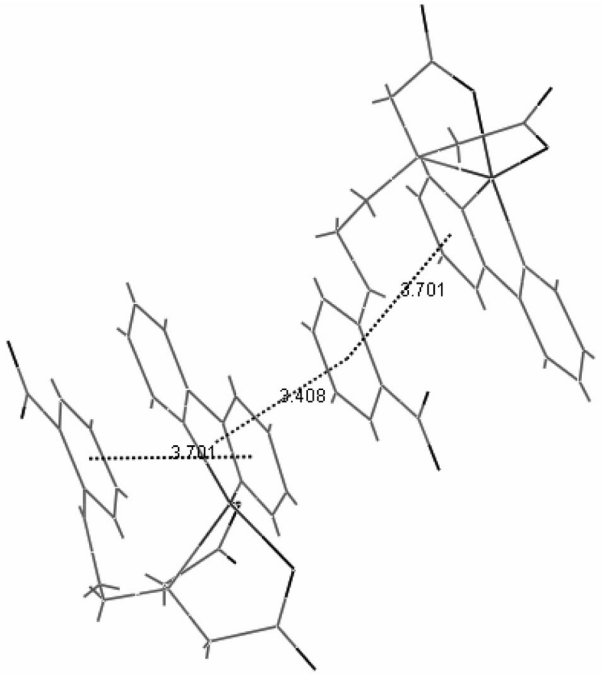

Figure 4. Details of the intramolecular "pyridyl–nitrophenyl" and intermolecular "nitrophenyl–metal chelate ring" π-π stacking interactions for a pair of complex molecules in **2**. Dotted lines represent centroid–centroid segments of the inter- (3.408 Å) and intra-molecular (3.701 Å) stacking interactions.

3. Conclusion

Two novel mixed-ligand copper(II) complexes containing a flexible *N*-(*o*-nitrophenyl)aminoethyl arm linked to the IDA skeleton have been synthesised and fully characterised. The main objective of this work was to evaluate the impact of this flexible coordinating arm on the structural features of the resulting copper(II) complexes, such as their conformation, geometry, stacking interactions, and so on. Complex **1** exhibits a distorted square-pyramidal Cu^{II} coordination of type [4+1] with an unexpected apical bond between the coordinating N(2) nitrogen and the metal; the apical position is generally occupied by a coordinated water mole-

cule in binary mixed-ligand copper(II) complexes with a similar geometry. This results in a *mer*-NO_2 configuration of the tridentate IDA unit here. In complex **2**, an unexpected *fac*-O_2+N(apical) configuration is observed for the first time for a tridentate IDA unit bearing a coordinating atom in the IDA skeleton. In addition, with such a flexible coordinating arm, compounds **1** and **2** display different inter- and/or intramolecular π-π stacking interactions, which take part in molecular-recognition processes involved in crystal building. Interestingly, the unprecedented interligand π-π "aryl–metal chelate ring" interactions observed in complex **2** provide new structural evidence for the metalloaromaticity concept.

Experimental Section

General Methods: All reagents and organic solvents used in this study were reagent grade and were used without further purification. The ligand H_2L_1·HCl was prepared as described previously.[12] TLC was performed on precoated Kieselgel 60 plates F_{254} (TLC plates, Merck) and was visualised by UV. Column chromatography was carried out using "gravity" silica (Merck). Infrared spectra (4000–400 cm^{-1}) were recorded as KBr pellets with a Vector 22 Bruker spectrophotometer. Positive electrospray mass spectra were obtained with a NERMAG R10–10 mass spectrometer. Carbon, hydrogen and nitrogen analyses were carried out by the microanalytical department of the École Nationale Supérieure de Chimie de Toulouse.

Synthesis of Complexes

$[Cu(L_1)(H_2O)]·H_2O$ (1): A solution of copper(II) chloride dihydrate (127.9 mg, 0.75 mmol) in methanol (15 mL) was added dropwise to a suspension of H_2L_1·HCl (250 mg, 0.75 mmol) and Et_3N (0.34 mL, 2.4 mmol) in methanol (25 mL). After two hours at room temperature, the solution was evaporated to dryness and the residue dissolved in CH_2Cl_2 (40 mL). After filtration, the filtrate was concentrated to dryness under reduced pressure to give **1** as a blue-green powder (220 mg, 75%). Dark blue crystals of **1** suitable for X-ray crystal structure determination were grown by slow evaporation of a methanol/dichloromethane solution (70:30, v/v). IR (KBr): ν_{O-H} = 3546, ν_{N-H} = 3342, $\nu_{C=O}$ = 1613 cm^{-1}. MS (ESI^+): *m*/*z* 359/361 [M – H_2O + H^+], 381/383 [M – H_2O + Na^+], 397/399 [M – H_2O + K^+]. $C_{12}H_{15}CuN_3O_7·H_2O$ (394.82): calcd. C 36.5, H 4.3, N 10.6; found C 37.3, H 4.3, N 10.5.

$[Cu(L_1)(bipy)]·2H_2O$ (2): A solution of $Cu_2(CO_3)(OH)_2$ (66.3 mg, 0.3 mmol) and H_2L_1·HCl (200 mg, 0.6 mmol) in water (40 mL) was heated at 50 °C for 15 min (to remove the CO_2 produced). The resulting solution was cooled before adding 2,2′-bipyridine (93 mg, 0.6 mmol). The reaction mixture was stirred for two hours at room temperature and then filtered. Dark green crystals of **2** suitable for X-ray crystal structure determination were obtained by slow evaporation of the filtrate (280 mg, 85%). IR (KBr): ν_{O-H} = 3472, ν_{N-H} = 3240, $\nu_{C=O}$ = 1628 cm^{-1}. MS (ESI^+): *m*/*z* 515/517 [M + H^+], 537/539 [M + Na^+], 553/555 [M + K^+]. $C_{22}H_{21}CuN_5O_6·2H_2O$ (551.01): calcd. C 48.0, H 4.6, N 12.7; found C 47.9, H 4.3, N 12.9.

X-ray Crystal Structure Determination of Complexes 1 and 2

$[Cu(L_1)(H_2O)]H_2O$ (**1**) and $[Cu(L_1)(bipy)]·2H_2O$ (**2**) were crystallised by slow evaporation of a dichloromethane/methanol and a water solution, respectively. The data were collected with a Nonius Kappa CCD diffractometer equipped with a CCD detector. X-ray intensity data were collected with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at a temperature of 298 K. Further details of the crystallographic study are reported in Table 4. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically using the full-matrix least-squares procedure based on F^2. Structure determination and refinement were performed with SIR97, Maxus and SHELX-97.[23] Sets of 4369 and 6096 independent reflections with $I \geq 3\sigma(I)$ were used for refinement.

CCDC-713133 (for **1**) and -713134 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Supporting Information (see also the footnote on the first page of this article): Selected PLATON parameters and packing diagrams for complexes **1** and **2**.

Table 4. Crystal data and structure refinement for complexes $[Cu(L_1)H_2O]·H_2O$ (**1**) and $[Cu(L_1)(bipy)]·2H_2O$ (**2**).

	Complex **1**	Complex **2**
Formula	$C_{12}H_{17}CuN_3O_8$	$C_{22}H_{25}CuN_5O_8$
M	394.83	551.01
Crystal system	monoclinic	orthorhombic
Colour	dark blue	dark green
Space group	$P2_1/c$	$P2_12_12_1$
a [Å]	14.9690(8)	10.1919(3)
b [Å]	7.5584(7)	13.457(3)
c [Å]	13.8321(7)	16.6086(8)
α [°]	90	90
β [°]	106.039(5)	90
γ [°]	90	90
V [Å^3]	1504.0(2)	2277.9(5)
Z	4	4
T [K]	298(2)	298(2)
d [g cm^{-3}]	1.744	1.607
F(000)	812	1140
Total reflections	29511	33549
Independent reflections	4369	6096
Observed reflections [$I > 3\sigma(I)$]	2741	3389
Data/restraints/parameters	2741/0/227	3389/0/326
Final *R* indices [$I > 2\sigma(I)$][a]	R_1 = 0.054, wR_2 = 0.099	R_1 = 0.062, wR_2 = 0.182
R indices (all data)[a]	R_1 = 0.127, wR_2 = 0.123	R_1 = 0.121, wR_2 = 0.196
S[a]	1.695	1.285

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$; $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{param})\}^{1/2}$.

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