

Synthesis, Structure and Solution Chemistry of (5,5'-Dimethyl-2,2'-bipyridine)(IDA)copper(II) and Structural Comparison With Aqua(IDA)(1,10-phenanthroline)copper(II) (IDA = iminodiacetato)

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Dedicated to Professor Bernt Krebs on the Occasion of his 65th Birthday

Abstract. The protolytic equilibria of copper(II), 5,5'-dimethyl-2,2'-bipyridine (bpy) and iminodiacetate (IDA) have been investigated by potentiometric titration between pH 2 and 8. Potentiometric titration suggests the presence of [Cu(IDA)(bpy)]⁰ at a fraction of 28 % of all copper species in solution at pH 8 with a stability constant $\log\beta = 13.9$. The crystal structures of [Cu(IDA)(bpy)] · 4H₂O (**1**) and [Cu(IDA)(H₂O)(phen)] · 4H₂O (**2**) show the IDA ligand coordinated in the *fac*-NO+O mode. The structure of **1** features “dimeric” entities of symmetry-independent five-coordinated Cu-complexes through a long Cu···O contact, hydrogen bonding

and π -stacking, including a “pyridyl–metal-chelate ring” π -contact as evidence for metalloaromaticity in aromatic α,α' -diimine-copper(II) chelates. The structure of **2** has the tetragonally six-coordinated molecular Cu-complexes arranged by hydrogen bonding and π -stacking. The crystal water in **2** forms infinite corrugated double chains composed of alternating four- and six-membered, edge-sharing rings of hydrogen-bonded water molecules.

Keywords: Copper; Iminodiacetate; Potentiometric titration; π -stacking; metalloaromaticity

Synthese, Struktur und Verhalten in Lösung von (5,5'-Dimethyl-2,2'-bipyridin)(IDA)kupfer(II) und Strukturvergleich mit Aqua(IDA)(1,10-phenanthrolin)kupfer(II) (IDA = iminodiacetato)

Inhaltsübersicht. Das Protolysegleichgewicht zwischen Kupfer(II), 5,5'-Dimethyl-2,2'-bipyridin (bpy) und Iminodiacetat (IDA) wurde mittels potentiometrischer Titration zwischen pH 2 und 8 untersucht. Die Ergebnisse der potentiometrischen Titration deuten das Vorhandensein der Verbindung [Cu(IDA)(bpy)]⁰ mit einem Anteil von 28 % an allen Kupferspezies in Lösung bei pH 8 mit einer Stabilitätskonstante von $\log\beta = 13.9$ an. Die Kristallstrukturen von [Cu(IDA)(bpy)]·4H₂O (**1**) und [Cu(IDA)(H₂O)(phen)]·4H₂O (**2**) zeigen den IDA-Liganden in der *fac*-NO+O Koordination. Die Struktur von **1** zeigt “dimere” Einheiten aus symmetrieunabhängigen

fünffach-koordinierten Kupferkomplexen, zusammengehalten durch langen Cu···O-Kontakt, H-Brücke und π -Stapelung, einschließlich eines “Pyridyl–Metall-Chelatring– π -Kontaktes als Hinweis auf Metalloaromatizität in aromatischen α,α' -Diimin-Kupfer(II)-Chelaten. Die Struktur von **2** weist tetragonale sechsfach-koordinierte molekulare Cu-Komplexe auf, die durch H-Brücken und π -Stapelung gepackt sind. Das Kristallwasser in **2** bildet unendliche, gewellte Doppelketten, die aus alternierenden vier- und sechsgliedrigen kantenverknüpften Ringen der H-Brücken-gebundenen Wassermoleküle aufgebaut sind.

Introduction

The chemistry of copper complexes is of interest owing to their importance in biological and industrial processes [1]. *Sigel* and co-workers have reported that electronic effects such as favorable interactions between π -systems, between hydrophobic systems, and between oppositely charged side groups contribute to the stability of the metal-complex structures [2]. 1,10-Phenanthroline (phen) and 2,2'-bipyri-

dine (2,2'-bipy) have extended π -systems and have been used in modeling complexes to mimic the non-covalent interactions in biological processes [3], e.g. the minor groove binding of [Cu(phen)₂]²⁺ ions [4] or the visible light induced nuclease activity of a Cu(phen) complex with 2-(methylthio)ethylsalicyldimine [5]. *Niclos-Gutiérrez* [6], *Solans* [7], *Srinivas* [8] and others [9, 10] have explored copper complexes with aromatic donor groups (L) and amino acid or related ligands (AA), such as [Cu(AA)(L)]ⁿ⁺ (L = 2,2'-bipy, phen or substituted derivatives thereof). In particular, structural comparisons of mixed-ligand copper(II) complexes having iminodiacetate (IDA) or IDA derivatives and imidazoles [11, 12, 13], nucleobases [14, 15, 16] or aromatic α,α' -diimines (bipyridine, phenanthroline) [6, 11, 17, 18, 19, 20] and related ligands (histamine and others) [6, 21, 22] serve as bioinorganic model compounds to illustrate con-

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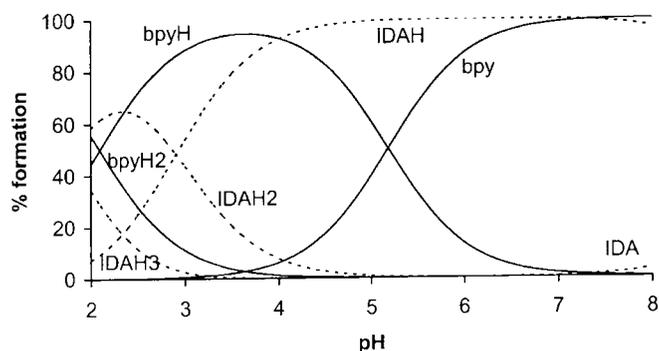
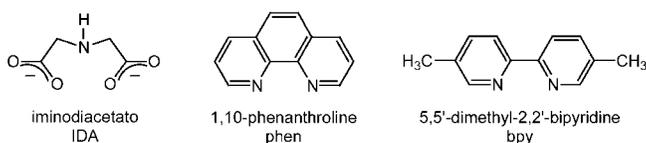


Fig. 1 Species distribution for 5,5'-dimethyl-2,2'-bipyridine (bpy, solid lines) and iminodiacetic acid (IDAH₂, dashed lines) in the range pH 2-8. $\log\beta$ values are given in the Experimental part; [IDA] = [bpy] = 1 mmol/L in 0.1 M KCl.

formational changes at the protein conformation for metal-protein centers in the absence or presence of appropriate substrates. IDA or an IDA-analog simulates the "protein moiety" and imidazole and different N-containing heterocycles play "substrate-like" roles [6].

We describe here the solution behavior of the ternary system Cu²⁺/5,5'-dimethyl-2,2'-bipyridine (bpy)/iminodiacetate (IDA) and report the crystal structures of [Cu(IDA)(bpy)] · 4H₂O (**1**) and [Cu(IDA)(H₂O)(phen)] · 4H₂O (**2**). In our structural investigations of the above compounds we expand on the supramolecular aromatic ringing π - π interactions [23, 24, 25, 26] between these ternary Cu^{II} complexes.



Results and Discussion

The potentiometric titrations were carried out at the 1:1:1 Cu:5,5'-dimethyl-2,2'-bipyridine (bpy) :iminodiacetic acid (IDAH₂) ratio. Variation of the metal:ligand ratio was not expected to yield extra information, and was not attempted. As part of the initial investigation, the ligands bpy and IDA were titrated separately to verify both ligand purity and the literature values for the acidity constants. The results of the individual titrations confirmed the literature values [27] or the accuracy of the experimental setup, respectively. As bpy and IDA(H₂) show only hydrogen-bonding interactions, the species distribution plot for the binary system bpy/IDAH₂ (Fig. 1) is a superposition of the individual species distributions (not shown here).

Results from the titrations of the ternary copper(II)/bpy/IDAH₂ system are shown in Fig. 2. The copper ions interact, that is form complexes with the ligands over the whole pH range. Thus, the presence of Cu²⁺ influences the pH-distribution and relative content of the ligands. We will only discuss here the metal-ligand species in the ternary system;

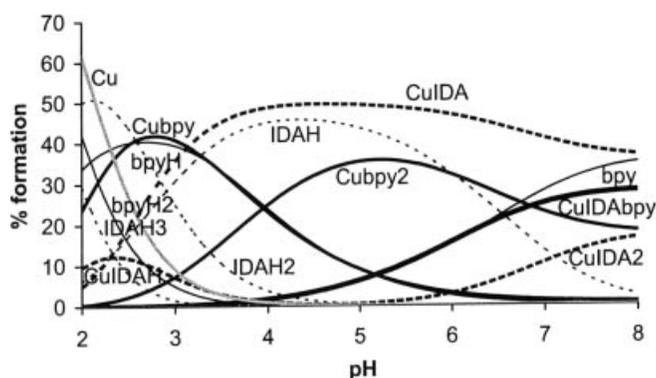


Fig. 2 Species distribution for the ternary copper(II)/bpy/IDAH₂ system in the range pH 2-8. $\log\beta$ values are given in the Experimental part; [IDA] = [bpy] = [Cu] = 1 mmol/L in 0.1 M KCl; bpy species = normal solid line, IDA species = normal dashed line, Cu²⁺ = grey solid line, Cu(bpy) species = bold solid line, Cu(IDA) species = bold dashed line, Cu(IDA)(bpy) species = very bold solid line; charges of the metal-ligand species are omitted for clarity (for charges see text and $\log\beta$ tabulation in the Experimental part).

water ligands are omitted for clarity in the description of the complexes. In the strongly acidic region at low pH between 2-3, the species [Cu(bpy)]²⁺ and [Cu(IDAH)]⁺ are present with their maximum relative percentage. There, [Cu(bpy)]²⁺ represents a sizable fraction of about 40 % of all ligated Cu species, while [Cu(IDAH)]⁺ is of minor overall percentage. Towards higher pH the content of these two species decreases as does the free Cu²⁺ concentration, with both [Cu(IDAH)]⁺ and Cu²⁺ negligible above a pH of 4. At strongly acidic pH the complexes [Cu(bpy)₂]²⁺ and [Cu(IDA)]⁰ are also present. Their percentage increases with pH, quickly exceeding the amount of [Cu(IDAH)]⁺ and reaching their relative maximum between pH 5-6 and pH 4-5, respectively. The species [Cu(IDA)]⁰ is the major copper-ligand complex with a fraction of 40-50 % over the pH range ~3.2 to 8. Its percentage decreases only slowly with increasing pH. Above a pH of ~3.5 the presence of complex [Cu(IDA)(bpy)]⁰ (**1**) can be noticed and its fraction increases steadily up to the final pH of 8. The complex [Cu(IDA)₂]²⁻ starts to form above a pH of 5. Still, at a pH of 8 [Cu(IDA)]⁰ comprises ~37 % of all copper atoms; 28 % are bonded in [Cu(IDA)(bpy)]⁰; 18 and 17 % are present as [Cu(bpy)₂]²⁺ and [Cu(IDA)₂]²⁻, respectively. From an equimolar 1:1:1 Cu²⁺/bpy/IDAH₂ solution at basic pH the complex [Cu(IDA)(bpy)]⁰ was found to crystallize. Among the species present, the complex [Cu(IDA)(bpy)]⁰ can be reasoned as the least soluble one because of its neutral character and a hydrophobic bpy ligand in the filled metal coordination sphere. The only other neutral complex [Cu(IDA)]⁰ still has aqua ligands in the first coordination sphere around the metal atom which increase the solubility because of hydrogen bond formation to water molecules. It is evident that the solid-state composition is primarily influenced by the solubility and not the solution composition [28].

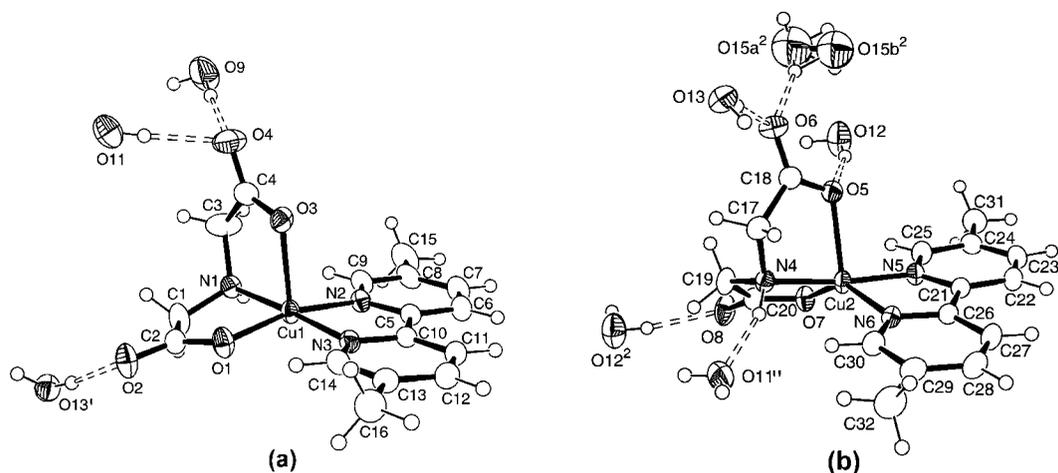
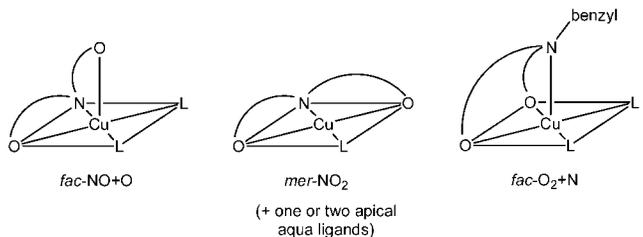


Fig. 3 The two symmetry-independent molecules in **1** with their hydrogen-bonded water molecules in the second coordination sphere. In (a) the second hydrogen atom on O11 is hidden behind its oxygen atom. The water molecule O15 is disordered. Selected distances and angles are given in Table 1. Symmetry transformations: ' = $x-1, y, z$; " = $x+1, y, z$; ² = $-x+2, -y+1, -z+1$.



L = N-heterocyclic donor, L-L = two heterocyclic donors or chelating aromatic α, α' -diimine

Fig. 4 Possible coordination modes of IDA in copper complexes [6].

The crystal structure of $[\text{Cu}(\text{IDA})(\text{bpy})]$ as the tetrahydrate (**1**) contains two symmetry-independent molecules in the unit cell (Fig. 3). Both are five-coordinated copper complexes. The coordination around Cu1 (Fig. 3a) shows a distorted square-pyramidal geometry ($\tau = 0.17$) [29]. The coordination around Cu2 (Fig. 3b) is exactly in-between a trigonal bi-pyramidal geometry and a square pyramid ($\tau = 0.50$) [29]. The IDA ligand is bonded in a *fac*-NO+O conformation (see Fig. 4) which is the typical coordination mode when either two aqua ligands or two N-heterocyclic donors (= one chelating aromatic α, α' -diimine) are present [6]. The possible IDA coordination modes are summarized in Fig. 4.

The *fac*-NO+O coordination of IDA gives rise to chiral complexes. The two symmetry-independent molecules of Cu1 and Cu2 in **1** are of opposite chirality. Albeit not centrosymmetrically related, they form a loosely bound "dimeric" entity by further contact of the O7 atom of the Cu2-molecule to the sixth vacant position of Cu1 with a distance $\text{Cu}\cdots\text{O7}$ of 2.972 Å (Fig. 5). In addition, there is a hydrogen bond from N1-H of the Cu1-molecule to O8 of Cu2 (Fig. 5) and π - π stacking between the pyridyl planes of N3 to N5 and N6 (Fig. 6a). Parameters for the π -interactions in **1** are collected in Table 2. The intra-,dimer" pyridyl- π -interaction is normal-to-weak with not much overlap between the pyridyl planes, that is long centroid-centroid distances (>3.9 Å),

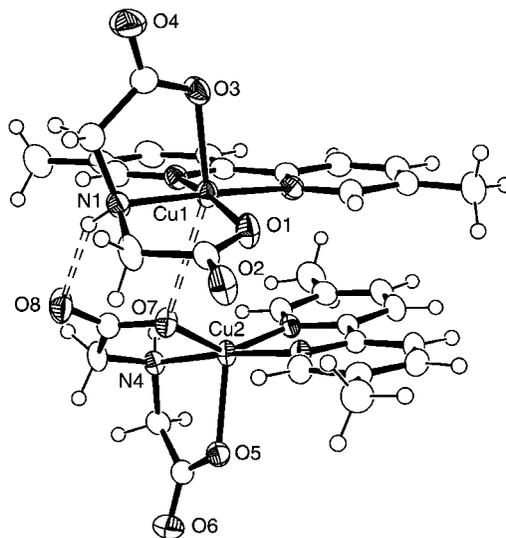


Fig. 5 Intermolecular interactions between the two symmetry-independent molecules in the "dimeric" entity in **1**, showing the intra-,dimer" $\text{Cu}\cdots\text{O7}$ contact and hydrogen bonding interaction.

large slip angles ($>30^\circ$) and vertical displacements (>2.0 Å) between the ring centroids [23, 24]. There is, however, substantial intra-,dimer" overlap between the pyridyl ring plane of N3 and the metal chelate ring built from Cu2-N5-C21-C26-N6 (Fig. 6a). Masui had suggested an active electron delocalization within the metal-N-heterocyclic chelate ring in such a way that it could exhibit some degree of "metalloaromaticity" [30, 31]. Stronger π -interactions in **1** are also observed between pyridyl planes from neighboring "dimers". These inter-,dimer" π -stackings exhibit rather short centroid-centroid contacts (<3.8 Å), small slip angles ($<25^\circ$) and vertical displacements (<1.5 Å) which translate into a sizable overlap of the pyridyl-plane areas (Fig. 6b).

The packing in **1** is different from the structure of $[\text{Cu}(\text{IDA})(2,2'\text{-bipy})]\cdot 6\text{H}_2\text{O}$ where only one molecule is found

Table 1 Selected bond distances/Å and angles/° in **1** and **2**.

1: Cu1 ^{a)}		1: Cu2 ^{a)}		2 ^{a)}	
Cu1-O1	1.953(2)	Cu2-O7	1.972(2)	Cu-O3	1.9730(13)
Cu1-O3	2.190(3)	Cu2-O5	2.159(3)	Cu-O1	2.3223(14)
Cu1-N1	2.042(3)	Cu2-N4	2.000(2)	Cu-N1	2.0303(16)
Cu1-N2	2.015(3)	Cu2-N6	2.028(2)	Cu-N3	2.0390(15)
Cu1-N3	1.995(3)	Cu2-N5	1.964(2)	Cu-N2	2.0043(15)
				Cu-O5	2.4240(15)
O1-Cu1-N1	84.76(8)	O7-Cu2-N4	86.39(11)	O3-Cu-N1	85.05(6)
O1-Cu1-N2	166.61(6)	O7-Cu2-N6	143.61(8)	O3-Cu-N3	174.43(6)
O1-Cu1-N3	92.61(8)	O7-Cu2-N5	94.20(11)	O3-Cu-N2	94.35(6)
N2-Cu1-N3	81.21(8)	N5-Cu2-N6	81.78(11)	N2-Cu-N3	82.13(6)
N1-Cu1-N2	101.06(8)	N4-Cu2-N6	101.36(11)	N1-Cu-N3	98.70(6)
N1-Cu1-N3	177.02(6)	N4-Cu2-N5	173.85(6)	N1-Cu-N2	176.74(6)
O1-Cu1-O3	96.04(12)	O5-Cu2-O7	104.95(8)	O3-Cu-O1	90.18(5)
O3-Cu1-N1	81.66(6)	O5-Cu2-N4	80.58(7)	O1-Cu-N1	78.96(6)
O3-Cu1-N2	96.73(11)	O5-Cu2-N6	111.37(6)	O1-Cu-N3	94.57(5)
O3-Cu1-N3	100.05(6)	O5-Cu2-N5	93.36(8)	O1-Cu-N2	97.84(5)
				N1-Cu-O5	88.17(6)
				N2-Cu-O5	95.01(6)
				N3-Cu-O5	88.87(5)
				O1-Cu-O5	167.03(5)
				O3-Cu-O5	87.13(5)

Selected hydrogen bonds in 1 ^{b)}				
D-H...A	D-H	H...A	D...A	D-H...A
N1-H1...O8	0.93	2.13	2.971(3)	149.6
N4-H4...O11"	0.93	1.92	2.821(3)	161.5
O9-H100...O4	0.87(2)	1.87(2)	2.737(4)	176(4)
O11-H104...O4	0.83(2)	1.97(2)	2.782(4)	168(3)
O12-H106...O82	0.83(2)	2.01(2)	2.820(3)	164(3)
O12-H107...O5	0.84(2)	2.09(2)	2.901(3)	160(3)
O13-H108...O2"	0.83(2)	1.96(2)	2.790(3)	173(3)
O13-H109...O6	0.83(2)	1.93(2)	2.765(4)	174(3)
O15a-H113...O6"	0.89(2)	1.91(3)	2.762(6)	160(6)

Selected hydrogen bonds in 2 ^{c)}				
D-H...A	D-H	H...A	D...A	D-H...A
O7-H107...O4	0.80(3)	1.94(3)	2.714(2)	165(3)
O6-H106...O2	0.89(3)	1.87(4)	2.759(2)	175(3)
O5-H105...O1"	0.76(3)	2.00(3)	2.759(2)	172(3)
O5-H205...O32	0.80(3)	2.14(3)	2.934(2)	169(3)
O6-H206...O22"	0.74(3)	2.01(3)	2.729(2)	163(3)
O9-H109...O7	0.72(3)	2.15(3)	2.845(3)	162(4)
O7-H207...O82'	0.70(3)	2.06(3)	2.739(2)	167(3)
O9-H209...O8	0.82(4)	2.14(4)	2.942(3)	165(4)
O8-H208...O7;m3	0.97(3)	1.84(3)	2.788(3)	167(3)
O8-H108...O6	0.75(3)	1.97(3)	2.716(2)	169(3)

^{a)} Comparative distances and angles for the two independent molecules of **1** and the molecule of **2** are listed side-by-side.

^{b)} Symmetry transformations: " = x+1, y, z; ² = -x+2, -y+1, -z+1.

^{c)} Symmetry transformations: ' = x-1, y, z; " = x+1, y, z; ² = -x+2, -y, -z+1; ^{2'} = -x+1, -y-1, -z+2; ^{2''} = -x, -y, -z+2.

in the unit cell of the same triclinic space group *P*-1 as in **1** [18]. The related structure of [Cu(IDA)(2,2'-bipy)]·6H₂O is built by "dimeric" species whose two halves are arranged around a center of symmetry through a Cu...O coordination and through hydrogen bonding to the water molecules of crystallization. The water molecules of crystallization in **1** do not form an extended motif [32] as in [Cu(IDA)(2,2'-bipy)]·6H₂O.

The crystal structure of [Cu(IDA)(H₂O)(phen)] as the tetrahydrate (**2**) contains one complex and four lattice water molecules in the asymmetric unit (Fig. 7). The copper atom shows a Jahn-Teller distorted, that is elongated-tetragonal, six-coordinated geometry with *fac*-NO+O coordination of the IDA ligand. The NO-donors from IDA and phen form

the basal plane. The remaining IDA-O-donor and an aqua ligand constitute the axial directions. The structure of **2** may be compared to the related structures of [Cu(L-aspartato)(H₂O)(phen)] · 4H₂O [10] and [Cu(glycinato)(NO₃)(H₂O)(phen)] · H₂O [7].

The intermolecular packing in **2** is controlled by hydrogen bonding from the aqua ligand to neighboring complexes along *a* and *b*, by π -stacking between the phen ligands along *a* (Fig. 9) and by hydrogen bonding to the water molecules of crystallization along *c*. The crystal water forms infinite double chains composed of alternating four- and six-membered, edge-sharing rings of hydrogen-bonded water molecules [32]. These corrugated double chains run along *a* above and below the [001]- (*ab*-) plane (Fig. 8).

Parameters for the π -interactions in **2** are collected in Table 2. The phen- π -contact is different to the adjacent molecules above and below (along *a*). A strong interaction in terms of short centroid-centroid contact (<3.8 Å), small slip angle (<25°) and vertical displacement (<1.5 Å), which translates into a sizable overlap of the aryl-plane areas, is found between a pyridyl and the central aryl ring from an adjacent molecule with symmetry relation 2666 = ² in Fig. 9a. The π -contacts to the opposite molecule of symmetry relation 2766 = ^{2'} in Fig. 9b are somewhat weaker but still in the normal π -stacking regime [23].

Experimental

5,5'-Dimethyl-2,2'-bipyridine (bpy) has been synthesized from 3-aminopyridine according to literature procedures [25, 33]. Elemental analyses were done on a VarioEL from Elementaranalysensysteme GmbH. 1,10-Phenanthroline (phen) and iminodiacetic acid (IDAH₂) were purchased from Aldrich. Deionized water was used as the solvent. In the potentiometric titrations KCl, KOH, HCl and potassium hydrogen phthalate (KHP, primary standard) were of high purity and used as received from Riedel-de-Haën, Roth, J. T. Backer and Aldrich, respectively.

(5,5'-Dimethyl-2,2'-bipyridine)(iminodiacetato)copper(II)-tetrahydrate, [Cu(IDA)(bpy)] · 4H₂O (1). A molar equivalent of IDAH₂ (1.33 g, 10.0 mmol) was added to a solution of Cu(NO₃)₂ · 3H₂O (2.42 g, 10.0 mmol) in 50 mL of water. A solution of 5,5'-dimethyl-2,2'-bipyridine (1.84 g, 10.0 mmol) in 40 mL of ethanol was added to the above solution. The mixture was then heated to 50 °C with stirring. An aqueous sodium hydroxide solution (1 mmol/L) was added dropwise with stirring (to neutralize the diacetic acid) until the solution started to turn cloudy [precipitation of Cu(OH)₂]. The resulting solution was filtered and blue, cubic crystals were obtained within a week through slow solvent evaporation from the filtrate (crystal yield 2.70 g, 60%). Calc. for C₁₆H₂₅CuN₃O₈ (450.93): C 42.62, H 5.59, N 9.32. Found: C 42.21, H 5.67, N 9.51 %.

Aqua(iminodiacetato)(1,10-phenanthroline)copper(II)-tetrahydrate, [Cu(IDA)(H₂O)(phen)] · 4H₂O (2). Equimolar amounts of phen (1.98 g, 10.0 mmol) and IDAH₂ (1.33 g, 10.0 mmol) were added to a solution of Cu(NO₃)₂ · 3H₂O (2.42 g, 10.0 mmol) in ethanol (40 mL). The mixture was then heated to 50 °C with stirring. An aqueous sodium hydroxide solution (1 mol/L) was added dropwise with stirring (to neutralize the diacetic acid) until the solution started to turn cloudy [precipitation of Cu(OH)₂]. The resulting

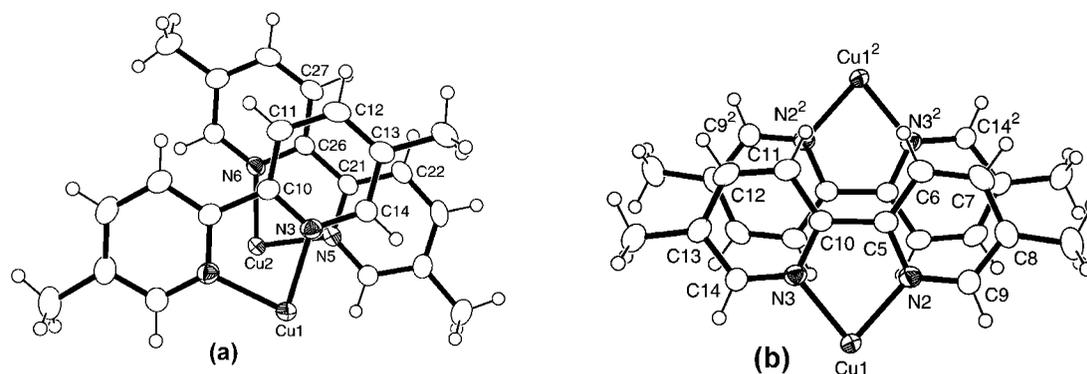
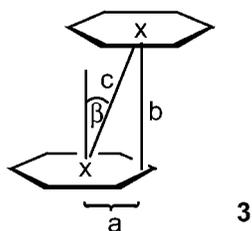


Fig. 6 π -Stacking interactions in **1**: (a) intra-,dimer“; (b) one of the two stronger inter-,dimer” interactions; see Table 2 for details. The π -stacking is viewed approximately perpendicular to the π planes with the IDA ligands omitted for clarity. Symmetry transformation $^2 = -x+2, -y+2, -z (= 2775$ in Table 2).

Table 2 Distances/ \AA and angles/ $^\circ$ for the π -contacts in **1** and **2**.^{a)}

	Centroid-centroid dist., c/ \AA	dihedral angle between planes $^\circ$ /degree	slip angle $^\circ$ β ^{b)}	vertical displacement between ring centroids, a $^\circ$ / \AA	interplanar distance, b/ \AA ^{d)}
1 intra-,dimer“					
ring N3–ring N5 ^{e)}	3.92	4.2	31.0 ^{d)}	2.02 ^{d)}	3.37 ^{d)}
ring N3–ring N6 ^{e)}	4.05	6.1	31.6 ^{d)}	2.12 ^{d)}	3.45 ^{d)}
aryl–metal chelate ring: ring N3–ring (Cu2–N5–C21–C26–N6) ^{e)}	3.63	7.3	18.4 ^{d)}	1.15 ^{d)}	3.44 ^{d)}
1 inter-,dimer“					
ring N2–ring N3 (2775) ^{e)}	3.59	1.9	15.9 ^{d)}	0.98 ^{d)}	3.45 ^{d)}
ring N5–ring N6 (2776) ^{e)}	3.71	4.7	22.3 ^{d)}	1.41 ^{d)}	3.43 ^{d)}
Symmetry transformation: 2775 = $-x+2, -y+2, -z$; 2776 = $-x+2, -y+2, -z+1$.					
2					
ring N3–ring (C8–C9–C10–C11–C15–C16) (2666) ^{e)}	3.542	0.43	19.9 ^{d)}	1.21	3.331 ^{d)}
ring (C8–C9–C10–C11–C15–C16)– ring (C8–C9–C10–C11–C15–C16) (2666)	3.989	0.00	33.25	2.19	3.336
ring N3–ring N3 (2766) ^{e)}	3.705	0.00	25.84	1.61	3.334
ring N3–ring (C8–C9–C10–C11–C15–C16) (2766) ^{e)}	3.759	0.43	27.3 ^{d)}	1.72	3.341 ^{d)}
Symmetry transformation: 2666 = $-x+1, -y+1, -z+1$; 2766 = $-x+2, -y+1, -z+1$.					

^{a)} For a graphical depiction of distances and angles in the assessment of π -stacking, see 3. – ^{b)} Angle between centroid-centroid vector and normal to plane. – ^{c)} Calculated according to $a = c \sin \beta$ or $a = (c^2 - b^2)^{1/2}$. – ^{d)} Normal from one ring plane onto the other. – ^{e)} Pyridyl ring is named by its nitrogen atom number. – ^{f)} Average values. Because the two ring planes are not exactly parallel there is a slight variation between the two normals to the planes and consequently the angle between the centroid-centroid vector to the ring normals.



3

solution was filtered and the filtrate was allowed to stand without solvent evaporation. Light-blue, plate-shaped crystals were obtained within 30 days (yield 3.0 g, 65%). Calc. for $\text{C}_{16}\text{H}_{23}\text{CuN}_3\text{O}_9$ (464.91): C 41.33, H 4.99, N 9.04. Found: C 41.67, H 4.87, 9.19%.

Potentiometric titrations

All titrations were carried out with a Metrohm 716DMS Titrimo (1 mL burette) using a Metrohm combined glass electrode with internal Ag/AgCl reference. Titration solutions were held at 25.0

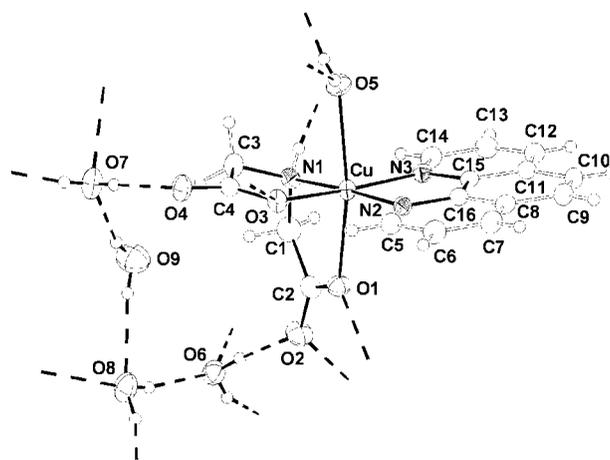


Fig. 7 The asymmetric unit of **2** with the hydrogen-bonded water molecules in the second coordination sphere. Selected distances and angles are given in Table 1.

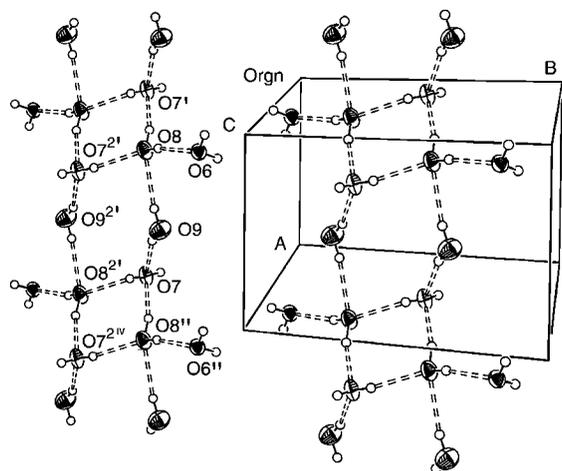


Fig. 8 Corrugated double chains of the hydrogen-bonded water molecules of crystallization in **2** running along *a* above and below the [001]- (*ab*-) plane. Symmetry transformations: ' = $x-1, y, z$; '' = $x+1, y, z$; 2' = $-x+1, -y-1, -z+2$; 21V = $-x+2, -y-1, -z+2$.

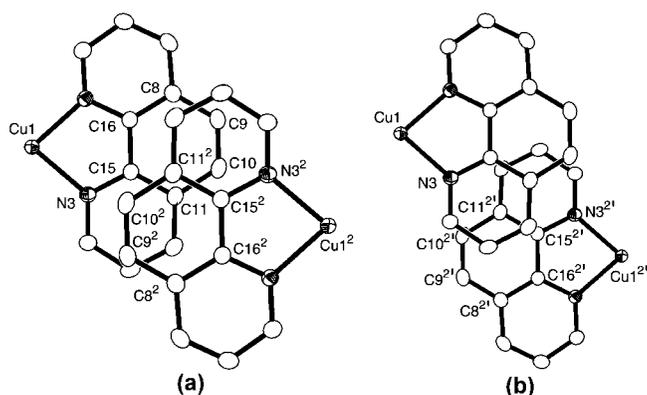


Fig. 9 π -stacking interactions in **2**: (a) to adjacent molecule of symmetry relation $^2 = -x+1, -y+1, -z+1$ (= 2666 in Table 2); (b) to adjacent molecule of symmetry relation $^{2'} = -x+2, -y+1, -z+1$ (= 2766 in Table 2); see Table 2 for details. The π -stacking is viewed approximately perpendicular to the π planes with the IDA and aqua ligands omitted for clarity.

(± 0.1) °C under a positive pressure of argon, to exclude air from the apparatus. The electrode was monitored using pH 4.01, 7.00 and 9.00 buffers from Merck. Calibration was done by titration against a strong acid (HCl) before and after each measurement, in order to calculate E° and pK_w values. A significant deviation of these values from the normal range (± 1.5 mV; 0.01 within 13.77–13.85) indicates instability of the electrode and these titrations results were not used. KOH concentration was confirmed by titrating pre-dried potassium hydrogen phthalate 5 times.

A solution of 0.1 mol/L KOH was used in all titrations, with 0.1 mol/L KCl as the inert electrolyte. Titration solutions were generally 50 mL, containing approximately 1 mmol/L ligand and 1 mmol/L metal. Ligand and ligand/metal solutions were acidified with HCl. 100 increments of the titrant were added slowly (0.030 mL/4min) with constant stirring. Titrations were repeated until at least 3 comparable titration curves were obtained.

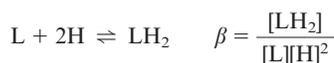
Data was collected using Vesuv Datalogger [34], stored in Vesuv Database [34] and manipulated using Microsoft Excel. Calibration information was calculated using the program Titkurve [35]. Speciation plots were compiled using the program SPEX [36]. Raw data (U /mV versus Vol_{OH} /mL) obtained from titrations were imported into the program HYPERQUAD [37] for calculation of stability constants in the form of concentration quotients ($\log\beta$ values, as defined below). Values calculated using HYPERQUAD were confirmed using BEST [38]. All stability constants quoted from experimental results are averages from HYPERQUAD; the errors in parentheses are the deviation in the averages. pH is defined as $-\log[H^+]$ and pK_w was taken as the average of the calibration values. Ligand constants (obtained from the literature [27] and verified as described below) were held constant for calculations involving metal and ligand. Metal and ligand concentrations were verified as below and held constant for the calculations.

The onset of hydroxide precipitation is usually visible in titration curves before becoming apparent in the vessel. Data points immediately before and all points after precipitation were eliminated from calculations. $\log\beta$ values for metal hydroxide species (from literature [27] and established from own metal titrations) were included in initial calculations to verify whether they would still influence the calculations. Points were eliminated until concentrations of metal hydroxide species were too low to influence the results. Refinement of a heterogeneous system is not possible at this stage. Speciation models were estimated using literature values and chemical knowledge. Constants were then refined by least squared regression minimizing the deviation between model and experimental results.

Metal and hydrogen concentrations of the metal stock solutions were established by weighing the appropriate amount of stock solution (densities determined experimentally) and titrating at various concentrations. Concentration and purity of 5,5'-dimethyl-2,2'-bipyridine and iminodiacetic acid in solution were assessed by potentiometric titration of ligand alone. As for metal and ligand titrations, all measurements were triplicate, and completed prior to further investigations. This stage also verified the ligand stability constants (as $\log\beta$ values) found in literature [27]. Initially the total amount (n /mmol) of ligand was verified by calculation using $\log\beta$ values from literature and refining both n_H and n_L . The new amounts were averaged and the data was re-calculated, this time holding n_H and n_L constant and refining the $\log\beta$ values. A significant deviation from the literature values ($> \pm 0.04$) prompted further investigation into the ligand before use.

The definition and values of the formation constants β (given as $\log\beta$ values) are as follows (L = bpy or IDA):

Acid formation constants



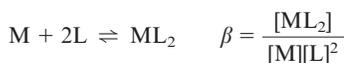
species	$\log\beta$
[bpyH] ⁺	5.1850
[bpyH ₂] ²⁺	7.2823
[IDA] ⁻	9.4560
IDA ₂	12.3670
[IDA ₃] ⁺	14.1370

Table 3 Crystal data for [Cu(IDA)(bpy)]·4H₂O (**1**) and [Cu(IDA)(H₂O)(phen)]·4H₂O (**2**).

	1	2
Empirical formula	C ₁₆ H ₂₅ CuN ₃ O ₈	C ₁₆ H ₂₃ CuN ₃ O ₉
Formula weight	450.93	464.91
Crystal size(mm)	0.54 x 0.50 x 0.35	0.6 x 0.30 x 0.10
θ range/°	1.57–30.80	1.72–30.88
h ; k ; l range	–16, 12; –19, 17; –21, 16	–9, 9; –13, 15; –17, 18
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
$a/\text{Å}$	11.491(14)	6.9101(11)
$b/\text{Å}$	13.729(16)	11.5867(19)
$c/\text{Å}$	14.855(18)	12.911(2)
$\alpha/^\circ$	66.43(2)	68.604(3)
$\beta/^\circ$	67.81(2)	80.321(3)
$\gamma/^\circ$	73.65(2)	89.186(3)
$V/\text{Å}^3$	1965(4)	947.5(3)
Z	4	2
$D/\text{g cm}^{-3}$	1.524	1.630
$F(000)$	940	482
μ/mm^{-1}	1.160	1.209
Max/min transmission	0.6870/0.5732	0.8886/0.5306
Measured reflections	16206	7795
Unique reflections (R_{int})	10820 (0.0184)	5233 (0.0218)
Observed reflections [$I > 2\sigma(I)$]	8471	4267
Parameters refined	587	354
Max/min $\Delta\rho/e \text{ Å}^{-3 \text{ a)}$	0.414/–0.561	0.518/–0.731
$R1/wR2$ [$I > 2\sigma(I)$] ^{b)}	0.0343/0.0946	0.0335/0.0826
$R1/wR2$ (all data) ^{b)}	0.0472/0.0998	0.0442/0.086
Goodness-of-fit on F^2 ^{c)}	1.068	0.997
Weighting scheme w ; alb ^{d)}	0.0575/0.1111	0.0505/0.0000

^{a)} Largest difference peak and hole – ^{b)} $R1 = [\sum(|F_o| - |F_c|)] / \sum F_o$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$ – ^{c)} Goodness-of-fit = $[\sum[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ – ^{d)} $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2 \text{ or } 0) + 2F_c^2) / 3$.

ML Complex formation Constants



species	$\log\beta$
[Cu(bpy)] ²⁺	6.2400
[Cu(bpy) ₂] ²⁺	11.0800
[Cu(IDA)] ⁰	*10.5600
[Cu(IDA) ₂] ²⁻	*16.3000
[Cu(IDAH)] ⁺	*12.8600
[Cu(IDA)(bpy)] ⁰	13.9000

In the $\log\beta$ tabulation * denotes direct literature values. All other values are refined constants based on literature values [27]. $\log\beta$ Cu(IDA)(bpy) is determined from titration only (not literature). Water ligands are omitted for clarity in the metal-ligand complexes.

Structure determinations

Data Collection: Bruker Smart with CCD area-detector, temperature 173(2) K, Mo-K α radiation ($\lambda = 0.71073 \text{ Å}$), graphite monochromator, ω -scan. Data collection with SMART [39], cell refinement with SAINT [39], data reduction with ABSSEN, empirical absorption correction with SADABS [40]. *Structure Analysis and Re-*

finement: The structure was solved by direct methods (SIR97 [41]); refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite [42]. All non-hydrogen positions were found and refined with anisotropic temperature factors. In **1** the C,N-hydrogen atoms were calculated with appropriate riding models (AFIX 43 for aromatic hydrogens on pyridine, AFIX 23 for CH₂ and AFIX 13 for NH, AFIX 137 for CH₃) and Ueq(H) = 1.2 Ueq(C) for CH, CH₂, and NH and Ueq(H) = 1.5 Ueq(C) for CH₃. The hydrogen atoms of the water molecules in **1** were found and refined with free temperature factors. In **2** all hydrogen atoms were found from the difference Fourier synthesis and refined isotropically with free temperature factors.

Graphics were obtained with ORTEP 3 for Windows [43]. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as spheres of arbitrary radii. Supramolecular interactions (π -contacts, hydrogen bonds) were computed with SHELXL or PLATON for Windows [44]. Crystal data and details on the structure refinement are given in Table 3. The structural data has been deposited with the Cambridge Crystallographic Data Center (No. CCDC-215455 for **1**, CCDC-215456 for **2**).

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