




## DESIGN, SYNTHESIS, AND STRUCTURAL STUDY OF MONO- AND POLYNUCLEAR Cu(II) IMINODIACETATE COMPLEXES

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**Abstract.** The synthesis of three structurally distinct copper(II) coordination compounds was conducted under different pH conditions, employing iminodiacetic acid (IDAH<sub>2</sub>) as the ligand. In a neutral medium, compound **1** was obtained as a two-dimensional ionic coordination polymer with the formula  $\{(\text{NH}_2(\text{CH}_3)_2)_2[\text{Cu}_3(\text{IDA})_4] \cdot 1.75\text{H}_2\text{O}\}_n$ , featuring layered  $[\text{Cu}_3(\text{IDA})_4]_n^{2n-}$  anions stabilized by hydrogen bonding networks (pH= 6–6.5). In a basic medium (pH= 8–8.5), compound **2** was isolated as a neutral 2D molecular coordination polymer,  $\{[\text{Cu}_3(\text{IDA})_2(\text{IDAH})_2] \cdot 5\text{H}_2\text{O}\}_n$ , based on trinuclear copper units bridged by bi- and monodeprotonated ligands. Acidic conditions (pH= 3) led to the formation of compound **3**,  $((\text{CH}_3)_2\text{OH})_2[\text{Cu}(\text{IDA})_2] \cdot [\text{Cu}(\text{IDAH})_2]$ . The compound exhibits an ionic structure composed of a neutral and anionic mononuclear complexes, charge-balanced by protonated dimethylether cations. The observed structural diversity is attributable to the various deprotonation states of the ligand, in association with the nature of the outer-sphere components. A detailed investigation into the infrared (IR) spectra of the compounds provided substantial evidence supporting the proposed coordination modes and hydrogen-bonding interactions. These interactions have been demonstrated to play a pivotal role in the formation of extended supramolecular architectures in all three compounds.

**Keywords:** coordination compound, Cu(II), iminodiacetic acid, dioxime, X-ray study.

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### Introduction

Iminodiacetic acid (IDAH<sub>2</sub>) is an organic compound with a simple structure, but its chemical and biological properties make it important in numerous fields of chemistry and biology. Iminodiacetic acid is a tridentate ligand, coordinating to metal atoms through ONO donor atoms, forming two conjugated five-membered chelate rings in its complexes [1,2]. The iminodiacetate dianion and trianion already exhibit structural diversity, involving not only coordination through the ONO donor atoms but also the participation of peripheral oxygen atoms in bridging adjacent metal atoms, thereby generating coordination polymers of different dimensionalities [3–8]. A known case shows that this bideprotonated ligand coordinates to copper atoms solely as an exo-bidentate ligand [9].

In aqueous biological pH ranges (pH= 6–7), the carboxylic groups of IDAH<sub>2</sub> dissociate to form the iminodiacetate dianion (IDA<sup>2-</sup>), which actively interacts with transition metal ions to form metal iminodiacetate complexes. Complex formation of Co(II), Ni(II), Cu(II), and Cr(III) with IDAH<sub>2</sub> in combination with *N,N*-donor ligands such as

1,10-phenanthroline (phen) or 2,2'-bipyridine (bpy) yields mononuclear complexes [10,11]. When additional bridging ligands are introduced, both bi- and polynuclear compounds are obtained [12,13]. Iminodiacetic acid or its derivatives also form complexes with Ca(II), Fe(III), Zn(II) [14–16], as well as with rare earth metals [17] or mixed systems such as rare earth metal-Cu(II) [18–21].

A review of the literature has shown that the pH of the reaction plays a crucial role in the formation of copper(II) complexes with IDAH<sub>2</sub>, while the temperature of the reaction has a less significant effect. Nevertheless, several Cu(II) complexes with a ligand mixture of IDAH<sub>2</sub>:2-mim (2-methylimidazole) were synthesized at different temperature ranges, and their catalytic activity in cyclohexane oxidation was investigated [22]. Cu(II) ion complexes with a *d*<sup>9</sup> configuration exhibit various coordination geometries, such as square planar with a tetracoordinated metal centre, square pyramidal with a pentacoordinated centre, and octahedral with a hexacoordinated metal. The high potential of this ion to readily form complex compounds allows for greater flexibility in selecting ligands

with different donor atoms such as N, O, S, and halides [23].

Although numerous iminodiacetic acid complexes with various metal ions - especially transition metals - are reported in the literature, copper(II) complexes are the most frequently encountered. These often involve additional *N,N*- or *N,O*-donor ligands in their formation using the mixed-ligand method [12,24–26].

The aim of this work is to develop synthesis methodologies for a series of Cu(II) complexes derived from iminodiacetic acid (IDAH<sub>2</sub>) and dianilineglyoxime (DAnH<sub>2</sub>) under variable pH conditions, to explore ligand competition, and to elucidate their crystal structures, coordination modes, and molecular architectures using FT-IR spectroscopy and single-crystal X-ray diffraction.

## Experimental

### Materials

All reagents were purchased from commercial sources. The starting materials: methanol, dimethylformamide (DMF), iminodiacetic acid (IDAH<sub>2</sub>), dianilineglyoxime (DAnH<sub>2</sub>) and copper(II) acetate monohydrate - were all purchased from Sigma Aldrich.

### Synthesis of $\{(NH_2(CH_3)_2)_2[Cu_3(IDA)_4] \cdot 1.5H_2O\}_n$ (1)

In 6 mL of DMF, 0.054 g (0.2 mmol) of DAnH<sub>2</sub> was dissolved, forming a yellowish solution which was stirred. Separately, in 6 mL of methanol, 0.02 g (0.1 mmol) of Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O was dissolved, yielding a second, intensely blue solution. Solution 2 was added dropwise to solution 1 under continuous stirring, resulting in a brownish-black mixture. After 5 minutes, with continued stirring, a third solution was added - a colourless solution obtained by dissolving 0.02 g (0.2 mmol) of iminodiacetic acid in 3 mL of water. Upon addition, the mixture gradually changes colour to dark blue, and the reaction medium reaches near-neutral conditions (pH= 6–6.5). The entire mixture was stirred for an additional 10 minutes, then filtered and left to crystallise at room temperature. After 23 days, two types of crystals were observed in the crystallisation vessel: light-blue crystals with a rhombic shape (mononuclear complex) [27], and dark-blue cubic crystals - the latter being the crystals of compound **1**. All cubic crystals were collected and weighed. Yield: 11.13% (0.01 g).

### Synthesis of $\{[Cu_3(IDA)_2(IDAH)_2] \cdot 4.5H_2O\}_n$ (2)

The synthesis of compound **2** was carried out using the same procedure as described for compound **1**, with the only modification being the addition of 13 drops of NH<sub>4</sub>OH to create a basic

medium (pH= 8–8.5). Upon the addition of the base, the reaction mixture turned an intense blue colour. The entire mixture was stirred for an additional 10 minutes, then filtered and left to crystallize at room temperature. After 18 days, dark-blue rectangular plate-shaped crystals were obtained. Yield: 32% (0.019 g).

Anal. Calcd. for C<sub>16</sub>H<sub>31</sub>Cu<sub>3</sub>N<sub>4</sub>O<sub>20.5</sub>: Calcd., %: C 24.08; H 3.91; Cu 23.88; N 7.02; Found, %: C 24.11; H 3.99; Cu 23.85; N 7.08. The IR spectra ( $\nu$ , cm<sup>-1</sup>): 3369 w, 3246 w, 3168 w, 3053 vw, 2956 w, 2929 w, 2887 w, 1651 vs, 1618 vw, 1599 vs, 1578 w, 1498 m, 1436 w, 1419 w, 1387 vs, 1308 m, 1252 m, 1217 w, 1133 w, 1101 m, 1063 w, 1033 vw, 1016 w, 954 w, 925 w, 913 w, 907 w, 886 w, 752 w, 717 w, 696 w, 661 w, 625 w, 608 w, 588 w, 547 w, 520 w, 493 w, 437 vw, 418 vw.

### Synthesis of

### $((CH_3)_2OH)_2[Cu(IDA)_2] \cdot [Cu(IDAH)_2]$ (3)

The synthesis of compound **3** followed the same procedure as described for compound **1**, with the exception that dianilineglyoxime was omitted in order to create an acidic medium (pH= 3). A light-blue solution was formed. The reaction mixture was stirred for an additional 10 minutes, then filtered and left to crystallize at room temperature. After 20 days, blue square plate-shaped crystals were obtained. Yield: 36% (0.02 g).

Anal. Calcd. for C<sub>20</sub>H<sub>36</sub>Cu<sub>2</sub>N<sub>4</sub>O<sub>18</sub>: Calcd., %: C 32.13; H 4.85; Cu 17.00; N 7.49; Found, %: C 32.18; H 4.95; Cu 17.18; N 7.45. The IR spectra ( $\nu$ , cm<sup>-1</sup>): 3384 w, 3233 w, 3055 w, 2967 vw, 2952 vw, 2930 w, 2776 m, 2491 w, 1608 vs, 1574 vs, 1478 w, 1461 w, 1434 w, 1391 s, 1373 s, 1327 m, 1245 w, 1227 w, 1102 vw, 1089 m, 1041 w, 1024 m, 965 w, 941 w, 924 w, 913 m, 872 w, 738 w, 705 vw, 684 w, 599 w, 573 w, 543 m, 499 w, 417 vw.

### Physical measurements

*Elemental analysis* of the complexes for C, H, S and N, was performed on a Vario EL (III) Elemental Analyzer and on an AAS-IN atomic absorption spectrometer (Carl Zeiss) for metals.

*Infrared spectra* (IR) were recorded on a FT-IR Spectrum-100 Perkin Elmer spectrometer using ATR technique (650–4000 cm<sup>-1</sup>). Intensities are given as: vs - very strong, s - strong, m - medium, w - weak, vw - very weak.

*Crystallographic studies.* X-ray diffraction data of **1**–**3** were collected at room temperature on a Xcalibur E diffractometer with a CCD area detector and a graphite monochromator using MoK<sub>α</sub> radiation. Determination of the unit cell parameters and processing of experimental data

were performed using the CrysAlis Oxford Diffraction Ltd. [28]. The programs SHELXS97 and SHELXL2014 [29,30] were used for structure solution and refinement of the proposed models. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon were positioned geometrically and treated as riding atoms, while water molecules hydrogen atoms were calculated based on the formation of a hydrogen bond. Full crystallographic details are given in Table 1. The resulting structures were deposited with the CCDC deposition numbers 2473663-2473665. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

## Results and discussion

According to the reaction scheme (Figure 1), three different copper(II) compounds were obtained. Compound **1** was obtained in a slightly acidic medium (pH= 6–6.5) as a result of a mixture of two structurally distinct compounds: a monomeric complex [27] and a two-dimensional polymer **1**. Compound **2** was obtained in

the reaction carried out in a basic medium (pH= 8–8.5), and was found to be a two-dimensional polymer similar to the one identified in **1**. It is important to note that, although the same mixture of DAnH<sub>2</sub> and IDAH<sub>2</sub> ligands was used in both reactions, the resulting compounds did not incorporate the dioxime ligand, which reflects the competitive behaviour of the ligands.

The synthesis of compound **3** was carried out in the absence of dianilinyloxime, under acidic conditions (pH= 3), which led to the formation of a single mononuclear ionic compound.

The IR spectrum of the coordinating agent (HOOC-CH<sub>2</sub>-NH-CH<sub>2</sub>-COOH) is characterized by the presence of absorption bands corresponding to associated  $\nu(\text{NH})$  at 3086 cm<sup>-1</sup> [31] and  $\nu(\text{C}=\text{O})$  at 1704 cm<sup>-1</sup>. The CH<sub>2</sub> group vibrations are observed as absorption bands at 2973 cm<sup>-1</sup> -  $\nu_{\text{as}}(\text{CH}_2)$  and 2840 cm<sup>-1</sup> -  $\nu_{\text{s}}(\text{CH}_2)$ . Absorption bands at 2597, 2428, 2290, and 1870 cm<sup>-1</sup> are attributed to  $\nu(\text{OH})$  vibrations with varying degrees of association, while the band at 1387 cm<sup>-1</sup> corresponds to associated  $\delta_{\text{pl}}(\text{OH})$  vibrations. The presence of  $\nu(\text{C}=\text{O})$  vibrations is further confirmed by the 1704 cm<sup>-1</sup> band, and the strong absorption band at 1577 cm<sup>-1</sup> can be assigned to associated  $\delta_{\text{pl}}(\text{OH})$  vibrations [32].

Table 1

Crystallographic data and structure refinement details for compounds 1-3.

	1	2	3
Empirical formula	C <sub>20</sub> H <sub>39</sub> Cu <sub>3</sub> N <sub>6</sub> O <sub>17.5</sub>	C <sub>16</sub> H <sub>31</sub> Cu <sub>3</sub> N <sub>4</sub> O <sub>20.5</sub>	C <sub>20</sub> H <sub>36</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>18</sub>
Formula weight	834.19	798.07	747.61
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	I2/c	P2 <sub>1</sub> /c
<i>a</i> (Å)	40.128(3)	18.8476(8)	16.7093(14)
<i>b</i> (Å)	9.9510(6)	9.8982(4)	5.5770(4)
<i>c</i> (Å)	15.9211(9)	15.8562(6)	17.7236(15)
$\alpha$ (deg)	90	90	90
$\beta$ (deg)	105.245(6)	106.166(4)	117.592(11)
$\gamma$ (deg)	90	90	90
<i>V</i> (Å <sup>3</sup> )	6133.8(7)	2841.1(2)	1463.8(2)
<i>Z</i>	8	4	2
<i>D<sub>c</sub></i> (g/cm <sup>-3</sup> )	1.807	1.866	1.696
$\mu$ (mm <sup>-1</sup> )	2.149	2.321	1.541
<i>F</i> (000)	3424	1624	772
Crystal size (mm <sup>3</sup> )	0.20x0.18x0.04	0.40x0.12x0.04	0.26x0.20x0.03
Reflections collected /unique	11227/5407	5018/2492	5039/2716
	[R(int)= 0.0852]	[R(int)= 0.0219]	[R(int)= 0.0311]
Reflections with [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	2604	2129	1884
Completeness, $\theta$ = 25.05°	99.4	98.9	99.4
Parameters	446	203	206
GOF on <i>F</i> <sup>2</sup>	1.000	1.002	1.004
<i>R</i> <sub>1</sub> , w <i>R</i> <sub>2</sub> [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	0.0730, 0.1096	0.0346, 0.0849	0.0449, 0.1150
<i>R</i> <sub>1</sub> , w <i>R</i> <sub>2</sub> (all data)	0.1595, 0.1381	0.0429, 0.0900	0.0689, 0.1299

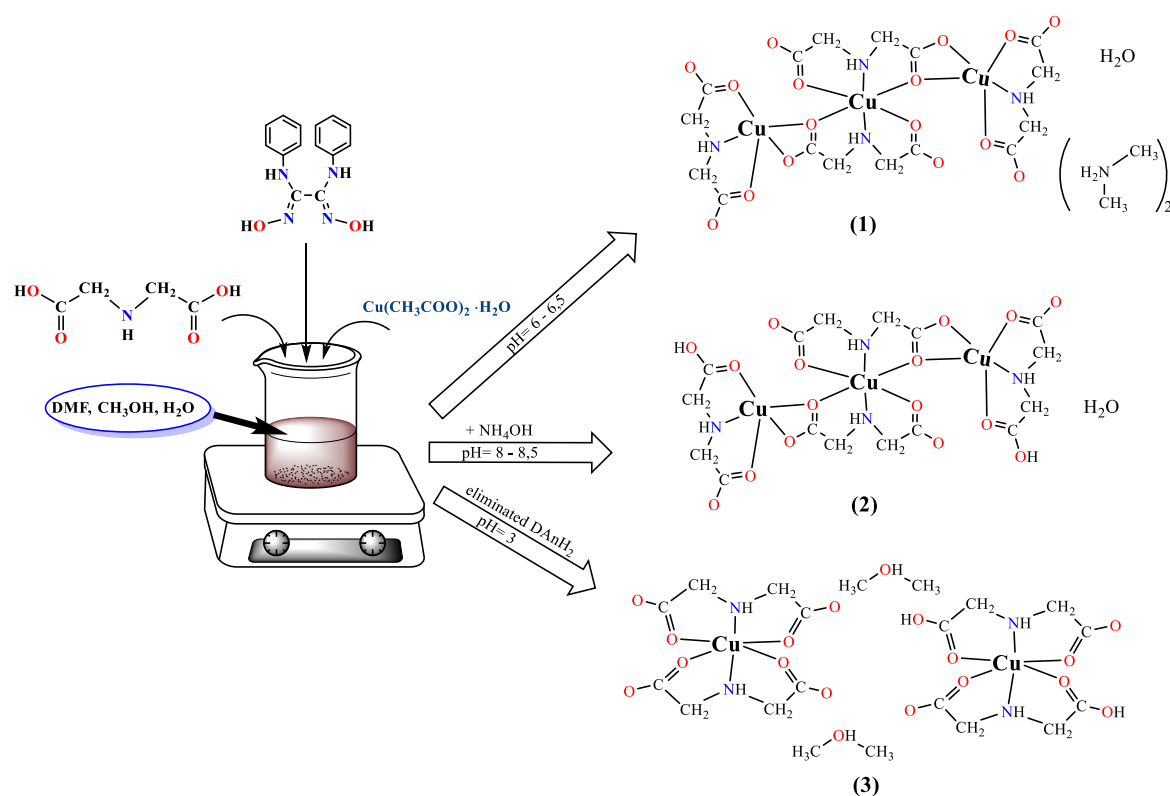


Figure 1. Scheme of the synthesis reactions of complexes 1-3.

In the IR spectrum of compound **2**, absorption bands at 3444, 3369, 3168, and 3053  $\text{cm}^{-1}$  are attributed to associated  $\nu(\text{OH})$  stretching vibrations, including contributions from crystallization water molecules. The band at 3246  $\text{cm}^{-1}$  corresponds to associated  $\nu(\text{NH})$  vibrations. The  $\text{CH}_2$  valence vibrations are observed at 2928  $\text{cm}^{-1}$  ( $\nu_{\text{as}}$ ) and 2820  $\text{cm}^{-1}$  ( $\nu_{\text{s}}$ ). The absorption band at 1651  $\text{cm}^{-1}$  is assigned to coordinated  $\nu(\text{C}=\text{O})$  stretching, while the band at 1599  $\text{cm}^{-1}$ , with similar intensity, is attributed to  $\delta(\text{NH})$  bending vibrations. The most intense band in the spectrum, at 1387  $\text{cm}^{-1}$ , is assigned to associated  $\delta_{\text{pl}}(\text{OH})$  vibrations [32].

In the IR spectrum of compound **3**, the broad absorption band at 3384  $\text{cm}^{-1}$  corresponds to weakly associated  $\nu(\text{OH})$  vibrations. The bands at 3233  $\text{cm}^{-1}$  and the shoulder at 3200  $\text{cm}^{-1}$  are assigned to  $\nu(\text{NH})$  stretching vibrations. Absorption bands at 2967, 2952, and 2930  $\text{cm}^{-1}$  are attributed to overlapping  $\nu(\text{CH}_3) + \nu(\text{CH}_2)$  vibrations. The bands at 2776 and 2491  $\text{cm}^{-1}$  correspond to strongly associated  $\nu(\text{OH})$  vibrations, predominantly from the  $(\text{CH}_3)_3\text{OH}$  groups. High-intensity bands at 1608 and 1574  $\text{cm}^{-1}$  are assigned to coordinated  $\nu(\text{C}=\text{O})$  and  $\delta(\text{NH})$  vibrations, respectively. The band at 1373  $\text{cm}^{-1}$  is attributed to associated  $\delta_{\text{pl}}(\text{OH})$  bending vibrations [32,33].

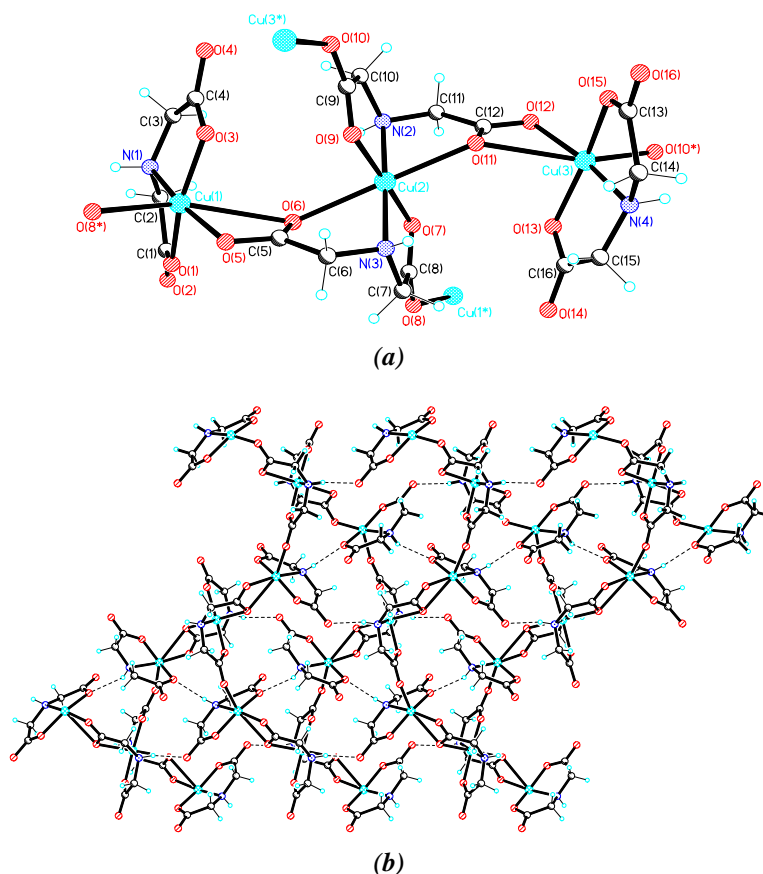
The ionic compound **1**, with the formula  $\{(\text{NH}_2(\text{CH}_3)_3)_2[\text{Cu}_3(\text{IDA})_4] \cdot 1.5\text{H}_2\text{O}\}_n$ , crystallizes in the monoclinic space group  $C2/c$  (Table 1). The structure consists of organic dimethylammonium cations  $(\text{NH}_2(\text{CH}_3)_2)^+$  - resulted from the dimethylformamide hydrolysis in slightly acidic medium, two-dimensional polymeric anions  $[\text{Cu}_3(\text{IDA})_4]_n^{2n-}$ , arranged in parallel layers, and solvate water molecules. The polymeric anions are based on three copper atoms and four crystallographically independent bideprotonated  $\text{IDA}^{2-}$  ligands (Figure 2(a) and (b)). The coordination polyhedra surrounding the Cu(1), Cu(2), and Cu(3) atoms adopt the geometry of tetragonal bipyramids. The coordination environment of Cu(2) is formed by  $\text{N}_2\text{O}_4$  donor atoms from two tridentate ligands coordination *via*  $\text{NO}_2$  donor sets and is nearly regular, whereas the environments of Cu(1) and Cu(3) consist of  $\text{NO}_5$  donor sets derived from three ligands: one tridentate through  $\text{NO}_2$ , one bidentate-chelating through two oxygen atoms, and one monodentate *via* a single oxygen atom (Figure 2 and Table S1, see supplementary information). The coordination polyhedra surrounding Cu(1) and Cu(3) are significantly distorted.

Thus, two peripheral  $\text{IDA}^{2-}$  ligands coordinate in a tridentate fashion through  $\text{NO}_2$  donor atoms to a single metal centre,

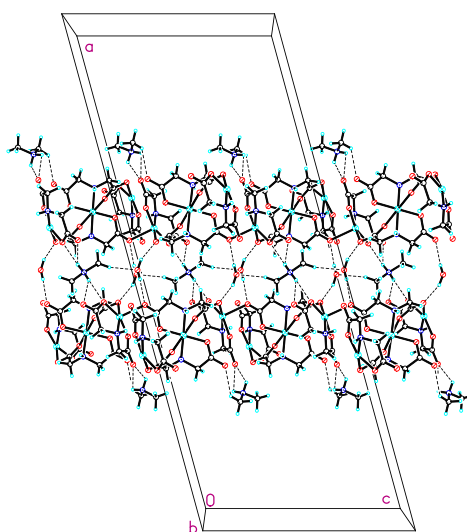
while the two central ligands each act as bridging hexadentate ligands, coordinating to three metal atoms. The polymeric anion is stabilized by a network of N–H···O and C–H···O hydrogen bonds (Figure 2(b) and Table S2, see supplementary information).

The outer-sphere components, namely the organic cations and water molecules, are involved in the formation of N–H···O and O(w)–H···O

hydrogen bonds, as well as C–H···O and C–H···O(w) interactions, which connect the layers (Figure 3, Table S2, see supplementary information). Crystallographically independent water molecules occupy four positions, with the occupancy coefficient ranging from 0.2 to 0.8. Consequently, stable supramolecular networks do not form within the crystal.



**Figure 2.** Structure of the trinuclear core fragment from the anionic polymer of compound 1 (a) and the formation mode of the 2D coordination polymer (b).

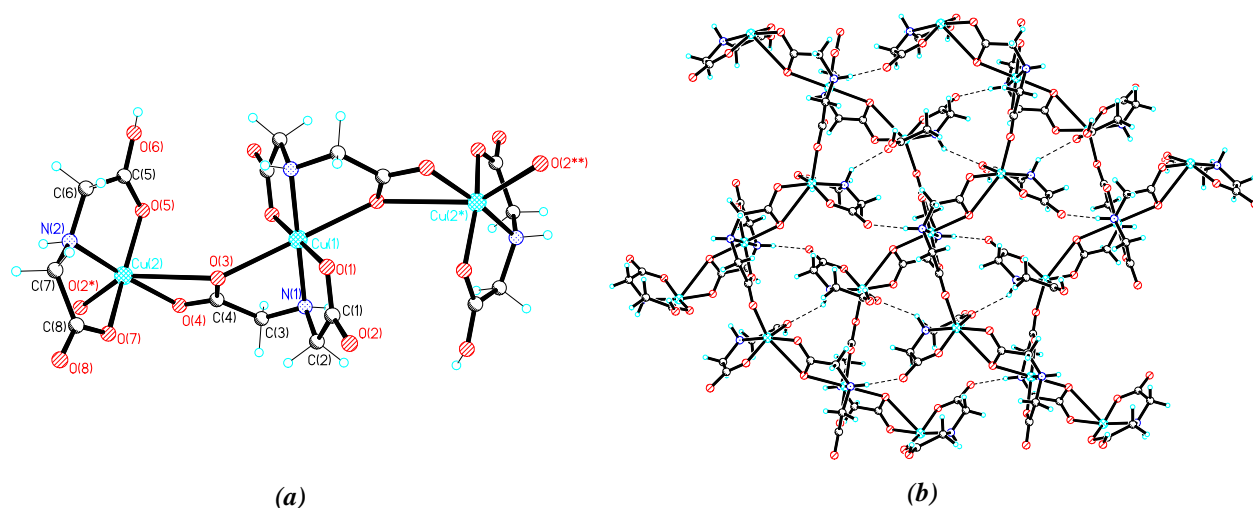


**Figure 3.** Crystal packing of the 2D anionic polymeric networks mediated by the outer-sphere components in compound 1.

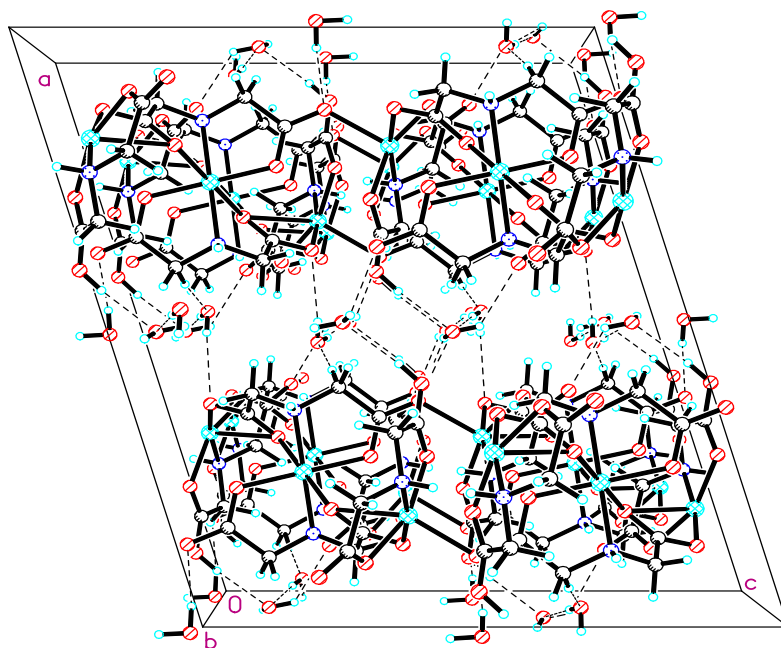
The 2D molecular polymeric compound with the formula  $\{[\text{Cu}_3(\text{IDA})_2(\text{IDAH})_2] \cdot 4.5\text{H}_2\text{O}\}_n$  (**2**), constructed in a manner similar to the polymeric anion in compound **1**, was obtained through the same reaction, but with the addition of an ammonia solution. It crystallizes in the monoclinic space group  $I2/c$  (Table 1). The coordination polymer in compound **2** is based on a centrosymmetric fragment composed of three copper atoms and pairs of bi- and monodeprotonated ligands (Figure 4). The coordination polyhedra of the Cu(1) and Cu(2) atoms adopt tetragonal bipyramidal geometries, formed by  $\text{N}_2\text{O}_4$  and  $\text{NO}_5$  donor atom sets, respectively (Figure 4 and Table S1, see supplementary information). The monodeprotonated ligand  $\text{IDAH}^-$  coordinates

tridentately through  $\text{NO}_2$  donor atoms to a single metal centre (Cu(2)), while the doubly deprotonated ligand acts as a hexadentate bridging ligand, linking three metal atoms.

In the crystal, the coordination polymer is stabilized by a system of  $\text{N-H}\cdots\text{O}$  and  $\text{C-H}\cdots\text{O}$  hydrogen bonds, while the polymeric layers are interconnected through  $\text{O-H}\cdots\text{O}(w)$ ,  $\text{O}(w)\cdots\text{H}$ , and  $\text{C-H}\cdots\text{O}(w)$  hydrogen bonds involving solvate water molecules (Figure 5 and Table S2, see supplementary information). Crystallographically independent 2.25 water molecules occupy five positions, with the occupancy coefficient ranging from 0.25 to 1.0. Consequently, stable supramolecular networks cannot be evident in the crystal.



**Figure 4.** Structure of the trinuclear core fragment in the molecular polymer of compound **2** (a) and the formation mode of the 2D polymer (b).



**Figure 5.** Crystal packing of the 2D polymeric networks mediated by hydrogen bonds involving water molecules in compound **2**.



By modifying the synthesis conditions, the pure compound  $((\text{CH}_3)_2\text{OH})_2[\text{Cu}(\text{IDA})_2] \cdot [\text{Cu}(\text{IDAH})_2]$  (**3**) was successfully obtained, previously reported only as part of a mixture [27]. Unlike compounds **1** and **2**, compound **3** is ionic, comprising two centrosymmetric mononuclear complexes - one a neutral molecular complex, the other an anionic complex - whose charge is balanced by a protonated dimethylether organic cation  $((\text{CH}_3)_2\text{OH})^+$  - generated through the intermolecular dehydration of methanol present in the solvent system (Figure 6). Compound **3**

crystallizes in the monoclinic space group  $P2_1/c$  (Table 1). The coordination polyhedra surrounding Cu(1) and Cu(2) are similarly formed by four oxygen atoms and two nitrogen atoms belonging to either two monodeprotonated IDAH<sup>-</sup> ligands or two doubly deprotonated IDA<sup>2-</sup> ligands, respectively. Consequently, a coordination environment of  $\text{N}_2\text{O}_4$  is established. Each metal centre exhibits hexacoordinate surrounding. The Cu–N bond lengths in the complexes of compound **3** are 2.001(3) and 2.012(3) Å, while the Cu–O distances range from 1.937(2) to 2.622(1) Å (Table S1, see supplementary information).

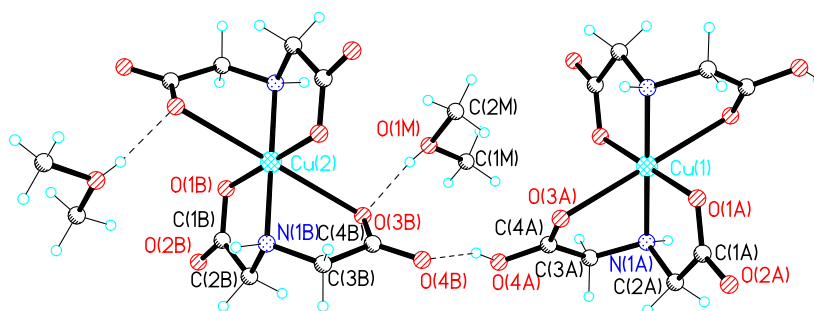


Figure 6. Structure of the mononuclear Cu(II) complexes in compound **3**.

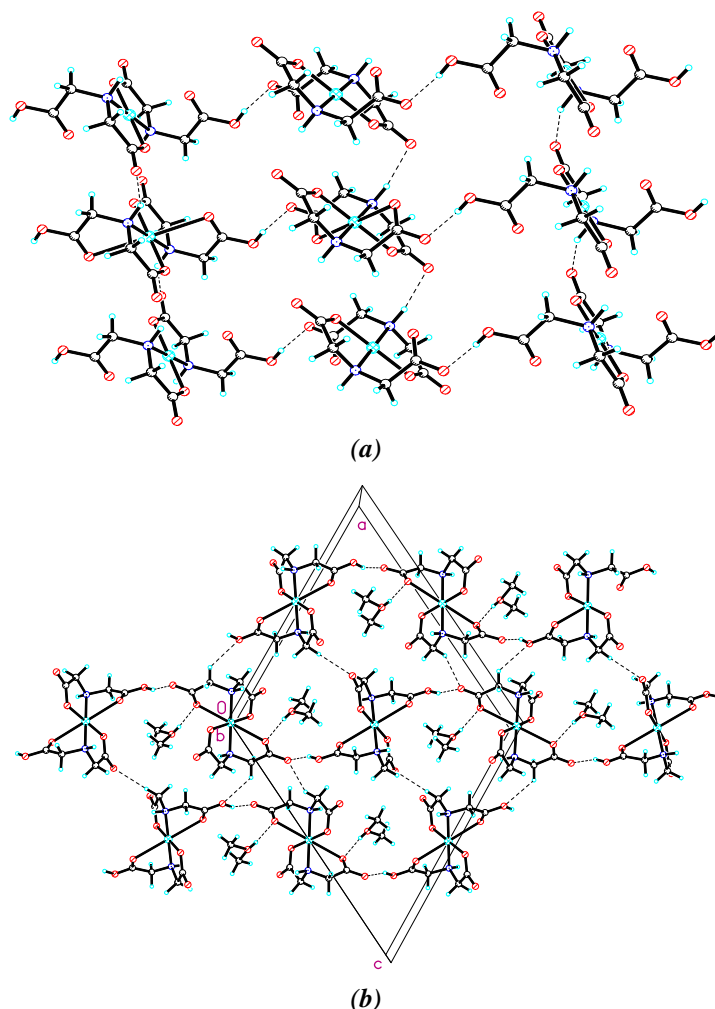


Figure 7. Formation of layers from the mononuclear Cu(II) complexes in the crystal structure of compound **3** (a,b), and the binding mode of the organic cation to the supramolecular network.

In the crystal, the anionic and neutral complexes are connected *via* intermolecular O–H...O and N–H...O hydrogen bonds, forming a layer (Figure 7(a)), while these layers are further linked by weak C–H...O hydrogen bonds (Figure 7(b)). The outer-sphere organic cations ((CH<sub>3</sub>)<sub>2</sub>OH)<sup>+</sup> are connected to the supramolecular network through O–H...O hydrogen bonds, in which the oxygen atoms of the bideprotonated IDA<sup>2-</sup> ligands act as acceptors. As a result, the crystal components assemble into a three-dimensional supramolecular network through the hydrogen-bonding system (Figure 7(b), Table S2, see supplementary information).

### Conclusions

Depending on the pH of the solution, the reaction between Cu(II) acetate and iminodiacetic acid led to the formation of three compounds with distinct structural topologies: an ionic compound featuring a coordination polymer anion ((NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>[Cu<sub>3</sub>(IDA)<sub>4</sub>]·1.5H<sub>2</sub>O)<sub>n</sub> (**1**); a molecular coordination polymer ([Cu<sub>3</sub>(IDA)<sub>2</sub>(IDAH)<sub>2</sub>]·4.5H<sub>2</sub>O)<sub>n</sub> (**2**) - these two differing primarily in their outer-sphere components; and a third ionic compound consisting of two mononuclear complexes of different natures - one anionic and the other neutral - resulting from the different degrees of ligand deprotonation (((CH<sub>3</sub>)<sub>2</sub>OH)<sub>2</sub>[Cu(IDA)<sub>2</sub>]·[Cu(IDAH)<sub>2</sub>] (**3**)).

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### Supplementary information

Supplementary data are available free of charge at <http://cjm.asm.md> as a PDF file.

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