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New Polynuclear Coordination Compounds Based on 2–(Carboxyphenyl)iminodiacetate Anion: Synthesis and X-rays Crystal Structures

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Abstract: In the present work, novel polymeric copper(II) coordination compounds, namely $[Cu_2(cpida)(H_2O)_4][Cu(cpida)]\cdot 3H_2O$ (**1**) ($cpida^{3-}$ = 2-(carboxyphenyl)iminodiacetate anion) and $Na[Cu(cpida)]$ (**3**), were synthesized and characterized using infrared spectroscopy, thermogravimetric analysis, elemental analysis, and single-crystal X-ray diffraction. Compound **1** was obtained by slowly evaporating an aqueous solution of H_3cpida, copper(II) sulfate, and NaOH at room temperature. The structural characterization revealed that **1** is an ionic entity formed by the $[Cu(cpida)]^-$ anion and the $[Cu_2(cpida)(H_2O)_4]^+$ cation, both of polymeric 1D structure. Compound **3** was prepared under similar conditions from copper perchlorate and crystallized via acetone diffusion. It is a coordination polymer formed by the $[Cu(cpida)]^-$ units, and the sodium cation is present in the structure, counterbalancing the anion charge. Depending on the crystallization conditions, it was possible to obtain other solvation forms of these structures. Starting from the conditions of compound **1**, via the diffusion of ethanol, $[Cu_2(cpida)(H_2O)_4][Cu(cpida)]\cdot H_2O\cdot 1/2EtOH$ (**2**) was precipitated, while a hydrate form of compound **3** with the formula $Na[Cu(cpida)]\cdot 2H_2O$ (**4**) was obtained via methanol diffusion.

Keywords: polynuclear complexes; X-ray crystal structures; Cu(II); 2-carboxyphenyliminodiacetic acid

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1. Introduction

Over the past few decades, there has been substantial development in the research on polynuclear coordination compounds and coordination polymers, which is particularly fueled by their potential applications as materials for gas storage, catalysis, environmental remediation, drug delivery, and in magnetochemistry or semiochemistry [1–13].

According to the IUPAC recommendations, coordination polymers are "coordination compounds with repeating coordination entities extending in 1, 2, or 3 dimensions" [14,15]. In the structures of these compounds, there are inorganic nodes (metal-containing clusters or metal ions) connected by organic divergent molecules (called linkers or connectors) [1,16,17]. Rigid ligands with a high degree of directionality were originally used as linkers in order to obtain specific crystal motifs [18]. However, the employment of more flexible ligands in the development of coordination polymers has lately been explored by numerous research groups [19–33]. The flexibility arises from the rotation of single bonds in carbon chains [22], allowing for various conformations that can result in distinct final structures [24].

The employment of flexible ligands as linkers in coordination polymers has encountered some hurdles when compared with the use of less flexible or rigid connectors [24].

This is due to the fact that the process of self-assembling is dependent on the reaction conditions, particularly the solution pH value, the type of metal cation, the concentrations of the different reactants, and the solvent employed. What is more, flexible polydentate ligands are also able to form mononuclear coordination compounds in competitive processes or adopt different conformations that are difficult to control.

Flexible molecules containing carboxylic acid groups are often chosen for the assembly of polynuclear coordination compounds. This preference is supported by the fact that this type of ligand can coordinate in different ways due to the possibility of fully or partially deprotonating the carboxylate groups, resulting in different topologies of the final structure [34]. These flexible molecules can act as bridging bidentate or tridentate ligands or chelating agents and even coordinate in a unidentate mode [35]. They are also good hydrogen bond acceptors capable of assembling supramolecular structures [36].

For several years now, we have focused our work on the development of polynuclear coordination compounds using polytopic flexible ligands. When working with aqueous solutions at mild acidic pH values, we reported the obtention of four capsule-like trinuclear copper(II) complexes assembled with nitrilotripropionic acid (H_3ntp) [37,38] and three new metal polynuclear compounds (containing nickel(II) or copper (II)) with *N*-benzyliminodipropionic acid (H_2bzlidp) [39]. In the case of the ntp complexes, the anion of copper salt had a significant influence on the obtained structure, defining the connectivity between the capsules [37]. When bzlidp^{2-} was employed as a ligand, it was possible to obtain Cu(II) complexes whose structures were significantly different (dinuclear complex vs. 2D layered structure) depending on the starting conditions [39].

We then turned our attention to the tricarboxylic acid compound 2-(carboxyphenyl) iminodiacetic acid (H_3cpida, Figure 1) as a connector of the metal ions. This is a multidentate ligand with the ability to form five-membered chelate rings. It presents flexible iminodiacetate groups and an aromatic ring that can initiate π–π interactions to stabilize the crystal packing.

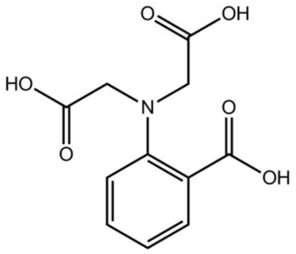


Figure 1. Structure of 2-carboxyphenyliminodiacetic acid.

This ligand has already been employed in the preparation of mononuclear [40–43] and trinuclear coordination compounds [44] and high-nuclearity metal aggregates [45–49]. However, the employment of this tricarboxylic molecule to connect metal centers in a 1D structure has been scarcely studied [44,50,51]. Bandyopadhyay and collaborators reported two polymeric copper (II) compounds, $\{[Cu(Hcpida)]\cdot H_2O\}_n$ and $\{[Cu(Hcpida)(H_2O)]\cdot H_2O\}_n$ [50]. In the first compound, the copper centers are pentacoordinated, showing a square pyramid geometry with the Hcpida^{2-} anion bridging the metal ions through the carboxylate groups attached to the phenyl ring. In this complex, one of the carboxylate groups remains protonated, stabilizing the chains through hydrogen bonds. In the second compound, the Cu(II) center is hexacoordinated, presenting a distorted octahedral geometry. The protonated carboxylate group is connected to the coordinated water molecule of a $[Cu(Hcpida)(H_2O)]$ unit of an adjacent chain through a hydrogen bond. In this way, cylindrical channels are formed in the structure that hosts the water crystallization molecule. Yong and coworkers described a Cd(II) coordination polymer, $[Cd_3(cpida)_2(H_2O)]\cdot H_2O$, which contains three crystallographically independent Cd(II) centers and forms infinite helical chains [51]. Heteroleptic Cu(II) chain-like structures can also be found in the literature. Ma and coworkers characterized a Cu(II) coordination polymer containing the cpida^{3-} anion and 1,10-phenantroline (phen) with a $\{[Cu_2(cpida)(phen)(NO_3)]\cdot 2H_2O\}_n$ formula. The complex contains two five-coordinated copper(II) centers with a square pyramid geometry. Two cpida^{3-} anions bridge three copper ions, forming a trinuclear triangular cluster that, in turn, is connected by their vertices, forming a 1D structure [44]. Polymeric coordination compounds based on the meta and para isomers of the 2-(carboxyphenyl)iminodiacetate anion have also been reported [35,52–54].

We decided to further explore the potential of H_3cpida to form polynuclear systems, in conditions analogous to those employed in the preparation of the H_2bzlidp or H_3ntp compounds mentioned above. Copper(II) was used as a metal ion and we report the preparation of four new copper(II) polynuclear compounds, $[Cu_2(cpida)(H_2O)_4][Cu(cpida)]\cdot 3H_2O$ (**1**), $[Cu_2(cpida)(H_2O)_4][Cu(cpida)]\cdot H_2O\cdot 1/2EtOH$ (**2**), Na[Cu(cpida)] (**3**), and $Na[Cu(cpida)]\cdot 2H_2O$ (**4**), obtained under different crystallization conditions.

2. Materials and Methods

2.1. General Information

All common laboratory chemicals were reagent grade, acquired from commercial suppliers, and employed without additional purification. Elemental analysis (C, H, N, S) was carried out on a Flash 2000 instrument (Thermo Fisher Scientific, USA). The infrared spectra, as KBr pellets, were obtained on an FTIR Shimadzu IR-Prestige-21 spectrophotometer (Shimadzu, Kyoto, Japan) in the 4000–400 cm^{-1} range. Thermogravimetric analyses (TGAs) were executed in a Shimadzu TGA-50 instrument with a TA 50 l interface (Shimadzu, Kyoto, Japan), using platinum cells. TGAs were recorded under a nitrogen stream (50 mL min^{-1}) at 1.0 °C min^{-1} up to 300 °C and 30 °C min^{-1} from 300 to 700 °C.

CAUTION! Perchlorate salts of metal coordination compounds containing organic ligands have the potential to be explosive. Only small quantities of material should be prepared and it should be handled with caution.

2.2. Synthesis of the Complexes

2.2.1. Synthesis of $[Cu_2(cpida)(H_2O)_4][Cu(cpida)]\cdot 3H_2O$ (**1**)

H_3cpida (0.167 g, 0.66 mmol) was dissolved in distilled water (12 mL) and copper sulfate (0.159 g, 1.00 mmol) was added. The solution was magnetically stirred at room temperature and adjusted to pH 4.1 with 5 mol L^{-1} NaOH solution. The blue solution was filtered and the solvent was slowly evaporated at room temperature. After four months, **1** precipitated as green crystals. The crystals were filtered through paper and washed with cold distilled water (0 °C). The solid material was dried in open air, and 0.084 g of the product was obtained. The yield was 31% (based on copper(II)). Anal. Calc. for $C_{22}H_{30}Cu_3N_2O_{19}$; C, 32.34; H, 3.70; N, 3.43. Found: C, 31.90; H, 3.45; N 3.39%. Selected IR data (ν_{max}/cm^{-1}): 3447, 3178, 2968 (sh), 2929 (sh), 1599, 1549, 1481, 1454, 1410, 1306, 1259, 1175, 1117, 1084, 1032, 1001, 990, 957, 932, 880, 812, 763, 723, 710, 646,594, 527, 446. TGA (30–700 °C, N_2), % weight loss: 11.29 (left limit 19 °C–right limit 63 °C), 4.95 (left limit 63 °C–right limit 139 °C), 38.95 (left limit 170 °C –right limit 328 °C), 7.26% (left limit 328 °C–right limit 700 °C).

2.2.2. Synthesis of $[Cu_2(cpida)(H_2O)_4][Cu(cpida)]\cdot H_2O\cdot 1/2EtOH$ (**2**)

H_3cpida (0.253 g, 1.0 mmol) was dissolved in distilled water (6 mL) and the pH was set to 7 through addition of 5 mol L^{-1} NaOH. This solution was added to a 2 mL aqueous solution of copper trifluoromethanesulfonate (0.543 g, 1.5 mmol). The solution was stirred at room temperature and its pH adjusted to 5.2 with aqueous 5 mol L^{-1} NaOH solution. This solution was subsequently divided into two portions of 4 mL each, which were set to crystalize either by diffusion of ethanol or methanol vapors. After 21 d, green crystals were obtained from the first (ethanol vapors). The crystals were filtered through paper and washed with cold distilled water (0 °C). After allowing the crystals to dry in open air, 0.070 g of **2** was obtained. The yield was 35% (based on copper(II)). Anal. Calc. for $C_{46}H_{58}Cu_6N_4O_{35}$: C, 34.35; H, 3.64; N, 3.48. Found: C, 33.54; H, 3.61; N 3.34%. Selected IR data (ν_{max}/cm^{-1}): 3447, 3145 (sh), 2972, 2928, 2855, 1609, 1564, 1547, 1479, 1454, 1408, 1373, 1304, 1258, 1173, 1121, 1086, 1040, 999, 957, 934, 876, 808,766, 721, 712, 646, 590, 525.

Blue needle-shaped crystals of a different compositions were obtained from the diffusion of methanol (see below).

2.2.3. Synthesis of Na[Cu(cpida)] (**3**)

H_3cpida (0.253 g, 1.0 mmol) was dissolved in 6 mL of distilled water and the pH value of the resulting solution was set to 7 by adding NaOH (5 mol L^{-1} solution). This ligand solution was added to a 2 mL aqueous solution of copper perchlorate hexahydrate (0.556 g, 1.5 mmol). The solution was stirred at room temperature and its pH was set to 5.2, again with 5 mol L^{-1} NaOH solution. Blue needle-shaped crystals were obtained after 60 days, produced from 2 mL of this solution via diffusion of acetone vapors. These crystals were filtered, washed with cold distilled water (0 °C), and allowed to dry in open air. Following this procedure, 0.034 g of the product was obtained. The yield was 40% (based on H_3cpida). Anal. Calc. for $C_{11}H_8CuNNaO_6$; C, 39.24; H, 2.39; N, 4.16. Found: % C, 38.82; H, 2.42; N 4.06%. Selected IR data (ν_{max}/cm^{-1}): 3441, 2979, 2939, 1674, 1638, 1616, 1483, 1450, 1396, 1385, 1339, 1219, 1171, 1152, 1103, 1061, 1045, 961, 941, 908, 881, 853, 777, 752, 669, 617, 575, 550, 523, 442.

2.2.4. Synthesis of Na[Cu(cpida)]·2H_2O (**4**)

H_3cpida (0.253 g, 1.0 mmol) was dissolved in 6 mL of distilled water and the pH was set to 7 with the addition of NaOH (5 mol L^{-1} solution), drop by drop. This solution was added to 2 mL of aqueous copper perchlorate hexahydrate solution (0.556 g, 1.5 mmol). The mixture was magnetically stirred at room temperature and the pH was set to 5.2 with aqueous NaOH solution. Blue needle-shaped crystals of compound **4** were obtained after 50 days, produced from 2 mL of the resulting solution via diffusion of methanol vapors. The crystals were separated by filtration, washed with cold water (0 °C), and dried in open air. Following this procedure, 0.035 g of the product was obtained. The yield was 38% (based on H_3cpida) Anal. Calc. for $C_{11}H_{12}CuNNaO_8$, C, 35.44; H, 3.25; N, 3.76. Found: C, 35.05; H, 3.12; N, 3.54%. Selected IR data (ν_{max}/cm^{-1}): 3423, 2970, 2932, 1657, 1634, 1481, 1447, 1402, 1369, 1346, 1317, 1228, 1182, 1163, 1148, 1099, 1063, 1049, 982, 959, 941, 910, 880, 853, 766, 752, 708, 671, 652, 617, 578, 552, 529, 492, 447. TGA (30–700 °C, N_2) % weight loss: 8.00 (left limit 19 °C–right limit 120 °C), 34.66 (left limit 100 °C–right limit 305 °C), 20.96 (left limit 305 °C–right limit 700 °C).

Compound **4** could also be obtained from copper trifluoromethanesulfonate, in a similar manner as compound **2** but using methanol for the diffusion (0.0315 g).

2.3. X-ray Crystallography

The X-ray diffraction data for all compounds were collected with a Rigaku SuperNOVA diffractometer with microfocus X-ray using Cu/Mo Kα radiation (λ = 1.54184/0.71073 Å). CrysAlisPro 1.171.39.46 [55] software was employed to collect, index, scale, and apply analytical absorption correction based on the faces of the crystal. The SHELXT program was used to solve the structure with a dual-space algorithm [56]. Fourier recycling and least-squares refinement were used for the model completion with SHELXL-2019 [57]. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in geometrically suitable positions and refined through riding with the isotropic thermal parameter related to the equivalent isotropic thermal parameter of the parent atom. The hydrogen atoms were geometrically positioned with C-H = 0.93 Å and Uiso(H) = 1.2 Ueq(C). The geometrical analysis of interactions in the structure was performed with the Olex2 [58] program (version 1.5).

The crystal data, collection procedures, and refinements results are summarized in Table 1.

Table 1. Crystallographic data for compounds **1**–**4**.

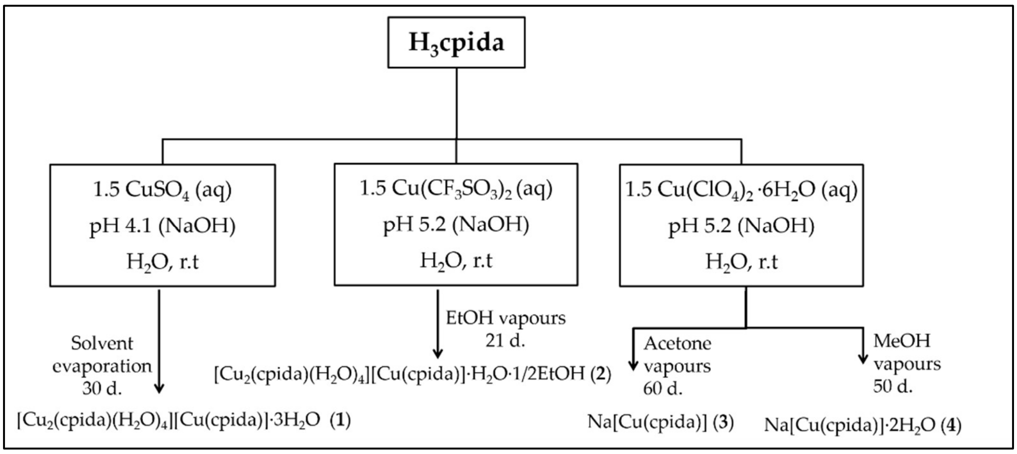
Compound	1	2	3	4
CCDC number	2304883	2304881	2304880	2304882
Empirical formula	$C_{22}H_{30}Cu_3N_2O_{19}$	$C_{23}H_{29}Cu_3N_2O_{17\cdot5}$	$C_{11}H_8CuNNaO_6$	$C_{11}H_{12}CuNNaO_8$
Formula weight	817.10	804.10	336.71	372.75
Temperature (K)	293(2)	293(2)	150(2)	150(2)
Wavelength	0.71073 Å	1.54184 Å	1.54184 Å	1.54184 Å
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P\ 2_1/n$	$P\ 2_1/n$	Pbca	Iba2
a (Å)	18.0990 (7)	18.1311 (4)	14.4270 (8)	28.1538 (16)
b (Å)	9.7523 (3)	9.7972 (2)	6.4340 (4)	14.5726 (7)
c (Å)	18.2152 (6)	18.1195 (5)	23.3780 (16)	6.2930 (3)
α (°)	90	90	90	90
β (°)	93.438 (3)	94.229(2)	90	90
γ (°)	90	90	90	90
Volume (Å^3)	3209.32 (19)	3209.88 (13)	2170.0 (2)	2581.9 (2)
Z	4	4	8	8
D_{calc}(g·cm^{-3})	1.691	1.664	2.061	1.918
Absorption coefficient (mm^{-1})	2.053	3.011	3.540	3.164
F(000)	1660	1632	1352	1512
Crystal dimensions (mm)	0.22 × 0.17 × 0.11	0.43 × 0.30 × 0.22	0.19 × 0.07 × 0.03	0.33 × 0.11 × 0.05
Theta range for data collection (°)	1.636 to 26.372	5.135 to 66.585	4.869 to 67.033	5.607 to 66.556
Index ranges	$-14 \leq h \leq 22$ $-12 \leq k \leq 12$ $-21 \leq l \leq 22$	$-21 \leq h \leq 19$ $-11 \leq k \leq 8$ $-18 \leq l \leq 21$	$-17 \leq h \leq 16$ $-7 \leq k \leq 4$ $-27 \leq l \leq 12$	$-33 \leq h \leq 27$, $-12 \leq k \leq 17$ $-7 \leq l \leq 4$
Reflections collected	13,135	12,308	4666	2980
Independent reflections, R(int)	6552, 0.0367	5452, 0.0163	1927, 0.0284	1599, 0.0206
Data/restraints/parameters	6552/3/437	5452/0/421	1927/0/181	1599/1/181
Goodness of fit on F^2	1.022	1.091	1.173	1.081
Final R indices [I > 2sigma(I)]^{a,b}	$R_1 = 0.0485$, $wR_2 = 0.1251$	$R_1 = 0.0431$, $wR_2 = 0.1338$	$R_1 = 0.0571$, $wR_2 = 0.1406$	$R_1 = 0.0255$, $wR_2 = 0.0679$
R indices (all data)^{a,b}	$R_1 = 0.0649$, $wR_2 = 0.1375$	$R_1 = 0.0451$, $wR_2 = 0.1353$	$R_1 = 0.0643$, $wR_2 = 0.1438$	$R_1 = 0.0259$, $wR_2 = 0.0682$
Largest diff. peak and hole (e.Å^{-3})	0.90/−0.54	1.65/−0.88	0.81/−0.82	0.37/−0.41

^{a} $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_c|$, ^{b} $wR_2 = (\Sigma[w(F_0{}^2 - F_c{}^2)^2]/\Sigma[w(F_0{}^2)^2)^{1/2}$.

3. Results and Discussion

3.1. Synthesis of the Complexes

The coordination compounds were prepared by directly mixing aqueous solutions of the corresponding copper salts and H_3cpida, setting the pH value in the 4.0–5.2 range, and using a 1.5 copper-to-ligand ratio (Scheme 1).



Scheme 1. Synthesis of the complexes **1**–**4**.

The crystals were characterized via infrared spectroscopy and elemental analysis. IR spectra of compounds **1**, **2,** and **4** exhibit a broad band in the 3200–3600 cm^{-1} region. The presence of this band is indicative of the existence of water molecules in the crystal structures. The small absorption peaks that appeared in the 3000–2850 cm^{-1} region for the four complexes correspond to the $\nu_{C–H}$ vibration modes of the $–CH_2–$ groups in the alkyl chains on the $cpida^{3-}$ anion (Figures S1–S4 Supplementary Material). The absence of the distinctive band of $\nu_{as}(COOH)$ at *ca.* 1700 cm^{-1} indicates that the carboxylate groups of the ligand are fully deprotonated in these compounds. For complexes **1** and **2**, the $\nu_{as}(COO^-)$ vibrations appeared at ca. 1600 cm^{-1}, whereas those of $\nu_s(COO^-)$ occurred at ca. 1410 cm^{-1}. In the case of compounds **3** and **4**, the bands around 1635 cm^{-1} can be assigned to the asymmetric stretching of the COO^- of the complexes while those that appeared in the proximity of 1400 cm^{-1} correspond to $\nu_s(COO^-)$. In all cases, the elemental analysis is consistent with the proposed empirical formula.

The TGA curve for compound **1** (Figure S5, Supplementary Material) shows, below 140 °C, a dehydration process that occurs in two steps, with a weight loss of 16.2%. The dehydration process is consistent with the loss of seven water molecules, comprising both lattice water molecules and coordinated ones. This is followed by a 46% weight loss step that involves the decomposition of the organic ligand. This is similar to what has previously been observed in the TG analysis of complexes containing the cpida ligand [43,44,50,51,53]. In the case of compound **4**, the TGA curve (Figure S6, Supplementary Material) shows a weight loss of 8% below 120 °C, consistent with a two-molecule dehydration process, and a two-step decomposition process with a weight loss of circa 56%, corresponding to the decomposition of the organic ligand. Single crystals for the complexes were obtained through slow evaporation of the solvent (**1**), and slow diffusion of ethanol (**2**), acetone (**3**), and methanol (**4**), at room temperature. Crystallographic data of compounds **1** to **4** are summarized in Table 1.

3.2. Crystal Structure of $[Cu_2(cpida)(H_2O)_4][Cu(cpida)]\cdot 3H_2O$ (**1**) and of $[[Cu_2(cpida)(H_2O)_4][Cu(cpida)]\cdot H_2O\cdot 1/2EtOH]$ (**2**)

Compound **1** crystallizes in the monoclinic $P\ 2_1/n$ space group (Table 1). Selected bond lengths and angles for **1** are presented in Table 2 and in Table S1 (Supporting Information). The asymmetric unit of $[Cu_2(cpida)(H_2O)_4][Cu(cpida)]$ is shown in Figure 2a. Compound **1** is a salt formed by the $[Cu(cpida)]^-$ anion and the $[Cu_2(cpida)(H_2O)_4]^+$ cation, both of them being polymeric, in a type of structure that is quite common with this kind of iminocarboxylic ligand [39,50]. The structure also presents three lattice water molecules. The anion is formed by [Cu(cpida)] units, connected by carboxylate oxygen atoms. Each unit contains a Cu(II) ion coordinated to a $cpida^{3-}$ anion, which acts as a tetradentate ligand. In order to assess the coordination geometry of Cu2, which shows five ligated atoms, the τ factor was determined. This is a geometrical parameter proposed by Addison and coworkers [59] to classify five coordinated structures in square pyramidal (τ factor = 0) or trigonal bipyramids (τ factor = 1). According to this parameter, the coordination polyhedron of the Cu2 atom can be depicted as a slightly distorted square pyramid (τ factor = 0.33), the donor atoms being the nitrogen atom N2, and three oxygen atoms of each carboxylate of the $cpida^{3-}$ anion (O8, O9, and O12, Figure 2b). The coordination sphere is completed by the O-carboxylate of a neighboring [Cu(cpida)] unit. Therefore, two of the carboxylate groups are coordinating in a monodentate mode, while the third is acting as bridging bidentate, in a *syn-anti* conformation and with a Cu–Cu separation of 5.25(7) Å. Cu(II) ida or substituted ida complexes have shown this kind of connection [44,60–62] as opposed to the one previously reported [50] where the bridging carboxylate group was the one attached to the phenyl ring.

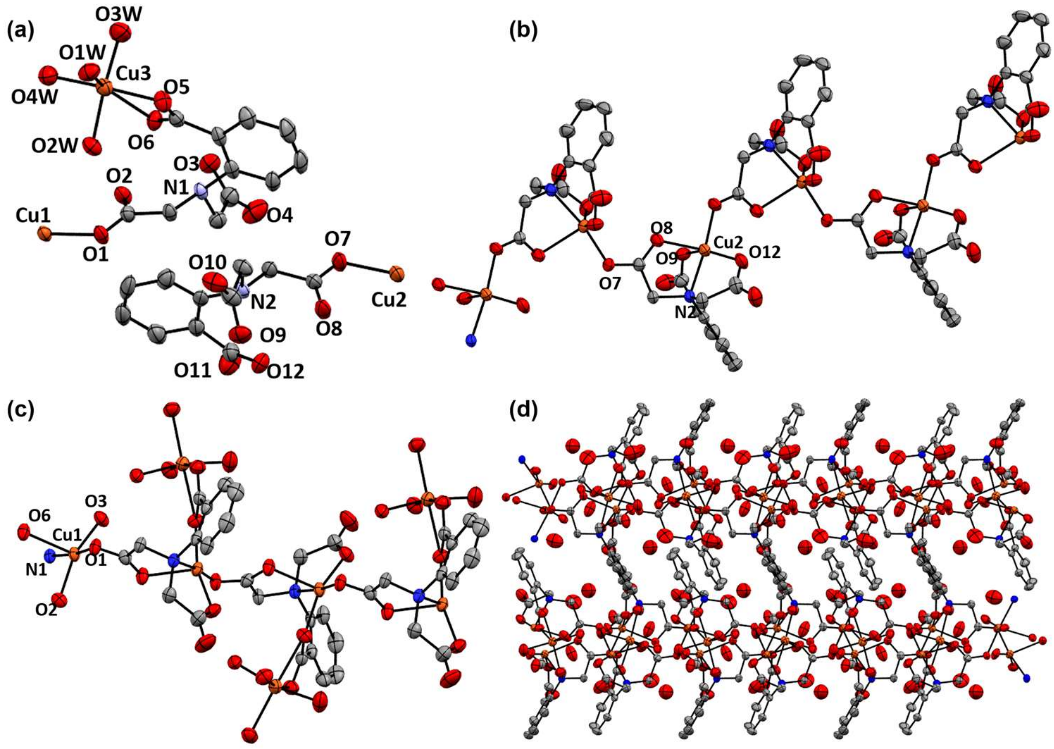


Figure 2. (**a**) Asymmetric unit of the structure of compound **1** with labeling; (**b**) chain-like structure of the $[Cu(cpida)]^-$ anion; (**c**) chain-like structure of the $[Cu_2(cpida)(H_2O)_4]^+$ cation; (**d**) 1D polymeric structure of compound 1 showing the arrangement of the adjacent chains. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity. Color code: O (red), N (blue), carbon (grey), Cu (orange).

The $[Cu_2(cpida)(H_2O)_4]^+$ cation is dinuclear and it is formed by [Cu(cpida)] units connected by carboxylate oxygen atoms. The coordination around Cu1 is also a distorted square pyramid (τ factor = 0.278) [59], with the donor atoms being three oxygen atoms, one of each carboxylate of the $cpida^{3-}$ ligand (O2, O3, and O6), and the nitrogen atom N1 (Figure 2c). The fifth coordination position is occupied by the O1 atom of a neighboring acetic group that is acting as a bridging bidentate group, in a *syn-anti* conformation and with a Cu1–Cu1 separation of 5.17(7) Å. In this way, a 1D chain of [Cu(cpida)] is formed, which is similar to the anionic chain in the structure. The cation presents a second Cu atom (Cu3), which is pentacoordinated, again with a very slightly distorted square pyramid (τ factor = 0.002) [59]. The donor atoms are the oxygen atoms of four water molecules (O1W, O2W, O3W, and O4W) and the O5 atom of a carboxylate group. This carboxylate group, which is directly attached to the phenyl ring, is bridging Cu1 and Cu3 in a *syn-anti* conformation. The equatorial positions of the square pyramid are occupied by the O5 atom and three of the coordinated water molecules (O2W, O3W, and O4W), while the fourth water molecule (O1W) is placed at the axial position. The crystal packing is reinforced by hydrogen bonds between the lattice water molecules and the carboxylate oxygen atoms with an average donor acceptor distance of $d(D\cdots A) = 2.74(8)$ Å and an average D-H· ·A angle of 161.8° (Table S3, Supporting Information).

Compound **2** was obtained under similar conditions as those used for compound **1,** save for the copper source and diffusion vapors. Selected bond lengths and angles for compound **2** are showed in Table 2 and in Table S1 (Supporting Information). The compound crystallizes in the monoclinic $P\,2_1/n$ space group (Table 1) and its structure is similar to that of compound **1**, with the difference that just one lattice water molecule and half a molecule of ethanol are present per asymmetric unit (Figure 3a). Compound **2** is also composed of the $[Cu_2(cpida)(H_2O)_4]^+$ cation and the $[Cu(cpida)]^-$ anion, both presenting a chain-like structure. In the $[Cu_2(cpida)(H_2O)_4]^+$ cation, the coordination polyhedron around Cu1 is also a distorted square pyramid (τ factor = 0.281) [59], with the donor atoms being three oxygen atoms of each carboxylate group of the cpida^{3-} anion (O2, O3, and O6, Figure 3a) and the nitrogen atom N1. The fifth coordination position is occupied by the O1 atom of a neighboring acetic group, which is acting as a bridging bidentate group in a *syn-anti* conformation, and with a Cu1–Cu1 separation of 5.17(7) Å. The Cu atom (Cu3) is pentacoordinated, and again with a slightly distorted square pyramid geometry (τ factor = 0.01) [59]. The donor atoms are the oxygen atoms of four water molecules (O1W, O2W, O3W, and O4W) and O5 of the carboxylate group attached to the phenyl ring. This carboxylate group is bridging Cu1 and Cu3 in a *syn-anti* conformation. Three water molecules (O1W, O2W, and O4W) and the O5 atom are occupying the equatorial positions of the square pyramid, while the fourth coordinated water molecule (O3W) is placed at the axial position.

In the [Cu(cpida)]$^-$ anion, the coordination geometry around the Cu2 atom can be described as a slightly distorted square pyramid (τ factor = 0.36) [59], with the donor atoms being the nitrogen atom N2 and three oxygen atoms, one of each carboxylate group of the cpida^{3-} anion (O8, O9, and O12, Figure 3a). The coordination polyhedron is completed by the O-carboxylate of a neighboring [Cu(cpida)] unit. One of the acetic carboxylate groups is acting as a bridging bidentate, in a *syn-anti* conformation and with a Cu–Cu separation of 5.25(7) Å.

The crystal packing is reinforced by hydrogen bonds between the lattice water molecules, the ethanol molecules, and the carboxylate oxygen atoms, with an average donor acceptor distance of d(D· ·A) = 2.73(5) Å and an average D-H· ·A angle of 162.2° (Table S4, Supporting Information). An unusual C(4)-H(4B)· ·O(13)$^{\#1}$ hydrogen bond between the ethanol O(13) atom and the CH_2 group of the cationic chain is also present (Table S4).

Given that the unit cells of **1** and **2** showed practically the same geometrical parameters and the same symmetry, we performed an analysis to further characterize these similarities. Using the COMPSTRU feature available on the Bilbao Crystallographic Server (https://www.cryst.ehu.es/ accessed on 14 April 2023), we checked the relationship between both structures, after removing the corresponding solvent molecules. It was found that there is no pair of atoms transformable with a one-angstrom tolerance. Mercury's structure overlay tool (Mercury version 2022.3.0) [63] was also employed, with us observing that when increasing the number of pairs of atoms to overlap, the RMSD between the chosen molecules increased more and more.

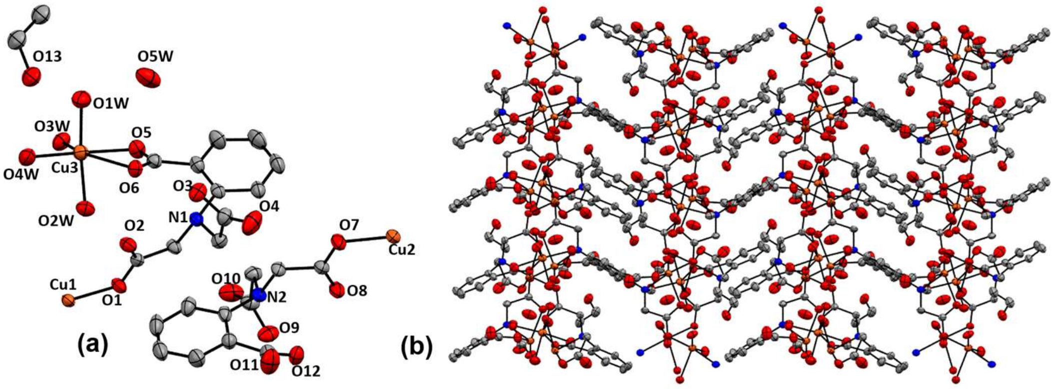


Figure 3. (**a**) Asymmetric unit of the structure of compound **2** with labeling. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity. (**b**) Packing of compound **2**, with view along the *c* axis; hydrogen atoms and solvent crystallization molecules are omitted for clarity.

Table 2. Selected bond distances (Å) for the coordination center in compounds **1** and **2** †.

Compound 1		**2**	
Distances			
Cu(1)–O(1)	1.918(3)	Cu(1)–O(1)	1.917(2)
Cu(1)–O(6)$^{\#1}$	1.936(3)	Cu(1)–O(6)$^{\#3}$	1.933(2)
Cu(1)–O(2)$^{\#1}$	2.239(3)	Cu(1)–O(2)$^{\#3}$	2.247(2)
Cu(1)–O(3)$^{\#1}$	1.943(3)	Cu(1)–O(3)$^{\#3}$	1.935(3)
Cu(1)–N(1)$^{\#1}$	2.043(3)	Cu(1)–N(1)$^{\#3}$	2.043(3)
Cu(2)–O(7)	1.911(3)	Cu(2)–O(8)$^{\#4}$	2.238(2)
Cu(2)–O(8)$^{\#2}$	2.251(3)	Cu(2)–O(7)	1.905(2)
Cu(2)–O(9)$^{\#2}$	1.975(3)	Cu(2)–O(12)$^{\#4}$	1.976(3)
Cu(2)–O(12)$^{\#2}$	1.959(3)	Cu(2)–O(9)$^{\#4}$	1.983(3)
Cu(2)–N(2)$^{\#2}$	2.028(3)	Cu(2)–N(2)$^{\#4}$	2.036(3)
Cu(3)–O(2W)	1.975(3)	Cu(3)–O(2W)	1.970(3)
Cu(3)–O(5)	1.976(3)	Cu(3)–O(5)	1.990(3)
Cu(3)–O(1W)	2.179(3)	Cu(3)–O(4W)	1.994(3)
Cu(3)–O(4W)	1.984(3)	Cu(3)–O(3W)	2.179(3)
Cu(3)–O(3W)	1.951(3)	Cu(3)–O(1W)	1.946(3)

† Symmetry codes: $^{\#1}$ −x + 1/2, y + 1/2, −z + 3/2; $^{\#2}$ −x + 1/2, y − 1/2, −z + 5/2; $^{\#3}$ −x + 3/2, y + 1/2, −z + 3/2; $^{\#4}$ −x + 1/2, y − 1/2, −z + 3/2.

3.3. *Crystal structure of Na[Cu(cpida)] (**3**)*

Compound **3** crystallizes in an orthorhombic *Pbca* space group (Table 1). Selected bond lengths and angles for **3** can be found in Table 3 and Table S2 (Supporting Information). The asymmetric unit (Figure 4a) is composed of the [Cu(cpida)]$^{-}$ anion with the cpida^{3-} ligand coordinated to the Cu cation in a tridentate manner. The coordination sphere of the copper center is square planar, with the donor atoms being N1, O5, O3, and the O1$^{\#5}$ atom of a neighboring [Cu(cpida)] unit, with an average Cu-O distance of 1.92(4) Å and a Cu-N distance of 2.046(5) Å. The O1 atom is located in an axial position, at a longer Cu1-O1 distance. Therefore, the [Cu(cpida)] fragments form a chain-like structure, in a zig-zag motif (Figure 4b). In the structure, there are also sodium cations, which are connected to the carboxylate oxygen atoms O5 and O1 and to the O(3)$^{\#6}$, O(3)$^{\#7}$, O(6)$^{\#8}$, O(4)$^{\#6}$, and O(2)$^{\#5}$ atoms, connecting the [Cu(cpida)] chains (Figure 4c). The packing of **3** viewed along the b axis is depicted in Figure 4d.

Table 3. Selected bond distances (Å) for the coordination center in compounds **3** and **4** †.

Compound 3		**4**	
Distances			
Cu(1)–O(1)$^{\#5}$	1.935(4)	Cu(1)–O(5)	1.903(2)
Cu(1)–O(5)	1.892(4)	Cu(1)–O(3)	1.947(2)
Cu(1)–O(3)	1.940(4)	Cu(1)–O(1)$^{\#9}$	1.952(2)
Cu(1)–N(1)	2.046(5)	Cu(1)–O(1)	2.390(3)
Na(1)–O(1)	2.706(5)	Cu(1)–N(1)	2.054(3)
Na(1)–O(5)	2.365(4)	Na(1)–O(5)	2.327(3)
Na(1)–O(3)$^{\#6}$	2.903(4)	Na(1)–O(3)$^{\#10}$	2.919(3)
Na(1)–O(3)$^{\#7}$	2.408(4)	Na(1)–O(3)$^{\#11}$	2.371(3)
Na(1)–O(6)$^{\#8}$	2.361(5)	Na(1)–O(2)$^{\#9}$	2.809(3)
Na(1)–O(4)$^{\#6}$	2.397(5)	Na(1)–O(6)$^{\#12}$	2.362(3)
Na(1)–O(2)$^{\#5}$	2.690(5)	Na(1)–O(4)$^{\#10}$	2.401(3)
		Na(1)–O(1)	2.701(3)

† Symmetry codes: $^{\#5}$ −x + 1, y + 1/2, −z + 1/2; $^{\#6}$ x + 1/2, y, −z + 1/2; $^{\#7}$ −x + 1, y − 1/2, −z + 1/2; $^{\#8}$ −x + 3/2, y − 1/2, z; $^{\#9}$ −x + 1/2,−y + 1/2, z − 1/2; $^{\#10}$ −x + 1/2, y + 1/2, z; $^{\#11}$ −x + 1/2, −y + 1/2,z + 1/2; $^{\#12}$ x, −y + 1, z + 1/2.

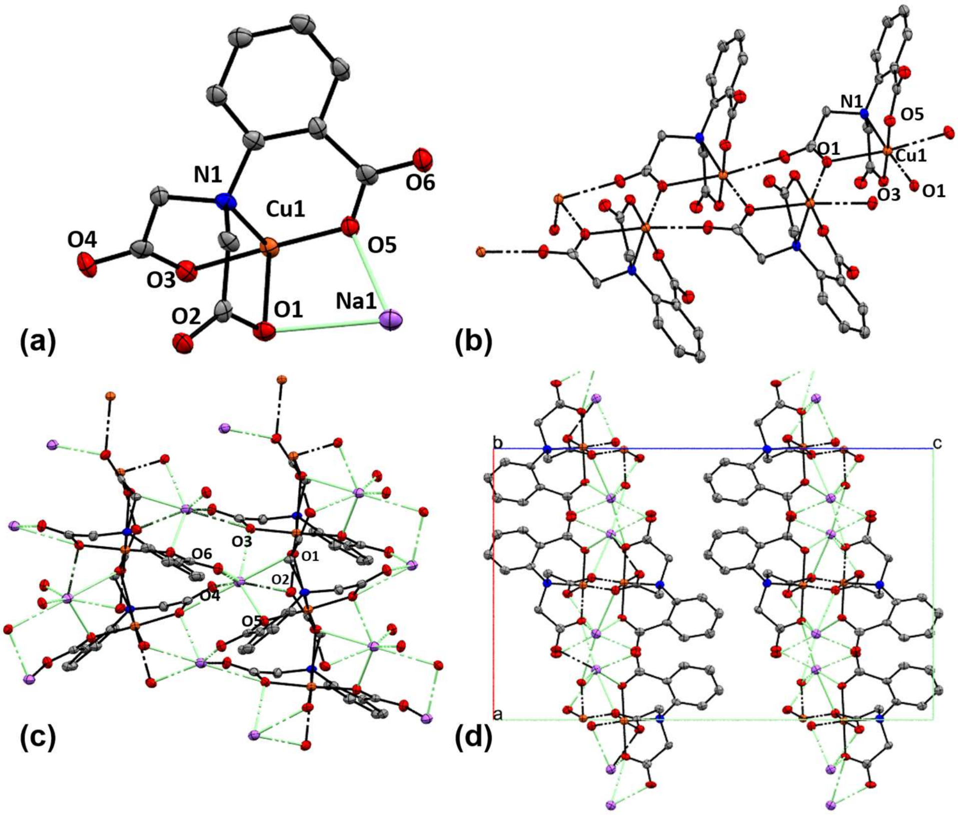


Figure 4. (**a**) Asymmetric unit of compound **3** with labeling. Thermal ellipsoids are shown at 50% probability; (**b**) Zig-zag motif of [Cu(cpida)]$^-$ fragments in **3.** Hydrogen atoms and sodium ions are omitted for clarity; (**c**) coordination environment of sodium ions; (**d**) packing of **3** viewed along the *b* axis. Hydrogen atoms are omitted for clarity.

*3.4. Crystal Structure of Na[Cu(cpida)]·2H$_2$O (**4**)*

Compound **4** crystallizes in the orthorhombic Iba2 space group (Table 1). Selected bond lengths and angles for **4** are displayed in Table 3 and Table S2 (Supporting Information). The composition of the asymmetric unit (Figure 5a) is like that of **3**. It contains the [Cu(cpida)]$^-$ anion with the cpida^{3-} ligand coordinated to the Cu cation in a tridentate fashion. The coordination sphere of the copper center is square planar, with the donor atoms being N1, O5, O3, and the O1$^{\#9}$ atom of a neighboring [Cu(cpida)] unit, with a Cu-N distance of 2.054(3) Å and an average Cu-O distance of 1.93(2) Å. The O1 atom is located in an axial position, at a longer Cu1-O1 distance. Again, the [Cu(cpida)] fragments form a chain-like structure, in a zig-zag motif (Figure 5b). In the structure, there are also sodium cations that are connected to the carboxylate oxygen atoms O5, O1, O(3)$^{\#10}$, O(3)$^{\#11}$, O(6)$^{\#12}$, O(4)$^{\#10}$, and O(2)$^{\#9}$, resulting in the overall stabilization of the [Cu(cpida)] chains (Figure 5c). Water crystallization molecules are present in the unit cell but, unfortunately, it was impossible to model it correctly and, therefore, a squeeze method was applied in this case. The analysis of the solvent mask we calculated gave 136 e$^-$ in a volume of 446 Å^3 in a void per unit cell. This is consistent with the presence of two water molecules per asymmetric unit. The total amount of solvent calculated through this procedure (solvent mask, squeeze) also reasonably matches the elemental analysis and the 8.0% mass loss observed in TGA up to 120 °C (Figure S6), with a calculated mass of 9.6% (two H$_2$O molecules per Na[Cu(cpida)]·2H$_2$O). The packing of **4** is depicted in Figure 5d.

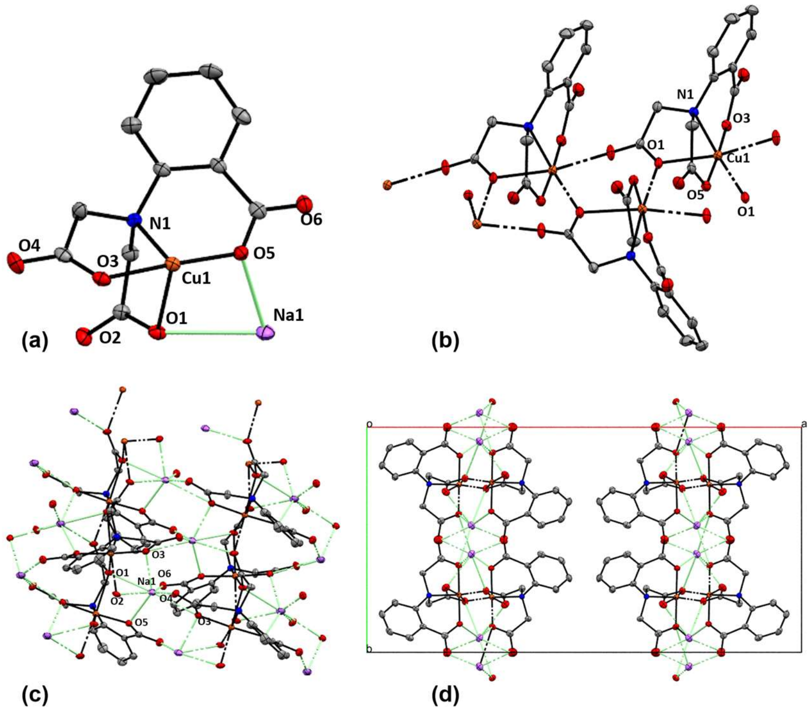


Figure 5. (**a**) Asymmetric unit of the structure of compound **4** with labeling. Thermal ellipsoids are shown at 50% probability. (**b**) Zig-zag motif of $[Cu(cpida)]^-$ fragments in **4.** Hydrogen atoms and sodium ions are omitted for clarity. (**c**) Coordination environment of sodium ions. (**d**) Packing of compound **4**, with view along the *c* axis. Hydrogen atoms are omitted for clarity.

4. Conclusions

In this work, we have reported the structure of four new Cu(II) polymeric complexes derived from the 2-(carboxyphenyl)iminodiacetic acid, H_3cpida, obtained under different crystal growing conditions.

Compounds $[Cu_2(cpida)(H_2O)_4][Cu(cpida)]\cdot 3H_2O$ (**1**) and $[Cu_2(cpida)(H_2O)_4][Cu(cpida)]\cdot H_2O\cdot 1/2EtOH$ (**2**), obtained through the evaporation of the solvent and ethanol vapor diffusion, respectively, are ionic, formed by the $[Cu(cpida)]^-$ anion and the $[Cu_2(cpida)(H_2O)_4]^+$ cation, both of them 1D coordination polymers. The structure of the anion is based on [Cu(cpida)] units connected by an acetic oxygen atom that is bridging the Cu centers in a chain-like structure. The $[Cu_2(cpida)(H_2O)_4]^+$ cation is dinuclear and it is formed by [Cu(cpida)] units connected by one of the acetic carboxylate groups, while the phenyl carboxylate group is bridging a second copper (II) ion whose coordination sphere is completed with water molecules. Solvent molecules are present in the unit cells of both compounds.

Through diffusion of acetone or methanol vapors, compounds **3**, Na[Cu(cpida)], and **4**, $Na[Cu(cpida)]\cdot 2H_2O$, are crystallized. They are also polymeric, with one of the acetic carboxylate groups of the ligand bridging the Cu(II) ions, forming an anionic chain-like structure. The sodium cations are balancing the negative charge, interacting with the oxygen atoms of different carboxylate groups, and connecting the $[Cu(cpida)]_n$ chains.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst13121669/s1, Figure S1: FT-IR spectrum of compound **1**; Figure S2: FT-IR spectrum of compound **2**; Figure S3: FT-IR spectrum of compound **3**; Figure S4: FT-IR spectrum of compound **4**; Figure S5: TGA diagram of compound **1**; Figure S6: TGA diagram of compound **4**; Table S1. Selected bond angles (°) for the coordination center in compounds **1** and **2**; Table S2. Selected bond angles (°) for the coordination center in compounds **3** and **4.** Table S3: Hydrogen bonds of **1**; Table S4: Hydrogen bonds for **2**.

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Data Availability Statement: Data are contained within the article and supplementary materials.

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