

Synthesis, Structural Characterization and Properties of Copper(II) and Zinc(II) Coordination Polymers with a New Bridging Chelating Ligand

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Two new coordination polymers $[\text{Cu}_3(\text{cpida})_2(\text{H}_2\text{O})_4]_n \cdot 4n\text{H}_2\text{O}$ (**1**) and $[\text{Zn}(\text{Hcpida})]_n \cdot n\text{H}_2\text{O}$ (**2**) have been synthesized with a new bridging chelating ligand *N*-(4-carboxyphenyl)iminodiacetic acid (H_3cpida). X-ray diffraction analysis reveals that complex **1** consists of 1D parallelogram-shaped molecular-box chains constructed from unusual linear trinuclear Cu^{II} secondary building units (SBUs), which further extend into 2D layers by perfect parallel AA stacking. Complex **2** adopts a 2D framework comprised of tetrahedral Zn^{II} centres isolated from each other by the bridging bidentate carboxylate groups of the Hcpida^{2-} ligands. Compound **2** possesses alter-

nate open and closed channels along the *a* direction. The dehydration and rehydration experiments showed that compound **2** undergoes a reversible inclusion process to some extent. However, the removal of guest water molecules from **1** results in the collapse of the polymeric networks owing to the loss of the coordinated water molecules. Compound **2** also shows strong photoluminescence and may be a good candidate for a photoactive or porous material.

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Introduction

Metal-organic coordination polymers built up from metallic clusters and multi-carboxylate building blocks have been widely studied in recent years due to their interesting topologies^[1] and potential applications as functional materials.^[2] The most commonly used strategy to obtain coordination polymers is to employ appropriate bridging ligands that are capable of binding to several metal centres through direct bond formation. Multi-carboxylate building blocks with special configurations can yield desired networks in metal-organic coordination polymers^[3–5] because they can act as either bridging or chelating ligands. A chelating ligand provides stronger connectivity and enhances rigidity around the coordination centre, which results in higher stability of the resulting framework materials.^[6] Thus, one of the most necessary tasks of current research is the synthesis of new bridging, chelating multi-carboxylate ligands because they have a pre-programmed tendency to form supramolecular motifs of defined geometry.^[7–9] We are currently focusing our attentions on the design and synthesis of new bridging, chelating ligands and have recently obtained a new bridging, chelating multi-carboxylate ligand *N*-(4-carboxyphenyl)iminodiacetic acid (H_3cpida), which has two important features: (a) unlike rigid groups such as benzene-

tricarboxylate, the iminodiacetate group is more flexible and can adopt different coordination modes; (b) the introduced aromatic rings can offer additional $\pi-\pi$ interactions which may stabilize the frameworks.^[10]

We describe here the synthesis, structural characterization and properties of two new coordination polymers $[\text{Cu}_3(\text{cpida})_2(\text{H}_2\text{O})_4]_n \cdot 4n\text{H}_2\text{O}$ (**1**) and $[\text{Zn}(\text{Hcpida})]_n \cdot n\text{H}_2\text{O}$ (**2**) obtained from the H_3cpida building block. Compound **1** is a rare 1D molecular-box chain constructed from unusual linear trinuclear Cu^{II} SBUs. Compound **2** is a new 2D framework constituted by tetrahedrally coordinated Zn^{II} with strong fluorescent emission.

Results and Discussion

Compound **1** was prepared by heating a mixture of basic copper carbonate and H_3cpida in water under steam bath conditions, while compound **2** was synthesized by treating $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with H_3cpida in $\text{KOH}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ under hydrothermal conditions (Scheme 1). The presence of the characteristic band at 1703 cm^{-1} for compound **2** indicates that the deprotonation of H_3cpida ligand is incomplete, which is consistent with the crystal structure of **2**.

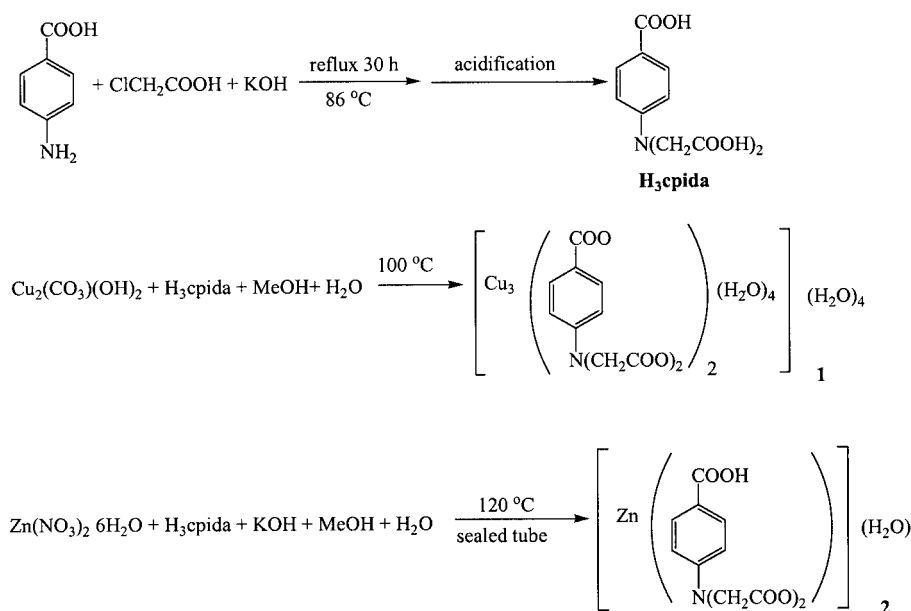
Description of Crystal Structures

$[\text{Cu}_3(\text{cpida})_2(\text{H}_2\text{O})_4]_n \cdot 4n\text{H}_2\text{O}$ (**1**)

The polymeric structure of **1** was confirmed by an X-ray single-crystal structure determination. The trinuclear entity of compound **1** with the atomic labelling scheme is shown

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Scheme 1. Preparation of H₃cpida and complexes **1** and **2**

in Figure 1a. The two terminal Cu^{II} atoms (Cu1 and Cu1a) adopt a Jahn–Teller-distorted octahedral coordination environment, resulting in a longer axial Cu1–O6 bond [2.344(2) Å] from the coordinated water molecule and Cu1–N1 bond [2.496(2) Å] from the cpida^{3–} ligand. The equatorial plane is defined by four oxygen atoms, which come from the bridging monodentate (O1), the monodentate (O3) and the bridging bidentate (O7a) carboxylate groups of two deprotonated cpida^{3–} ligands, and the coordinated water molecule (O5). The bond lengths Cu1–O are in the range 1.947(2)–1.978(2) Å (Table 1). The central Cu2 atom presents a Jahn–Teller octahedral environment, resulting in very long axial Cu2–O6 bonds [2.608(2) Å] to the coordinated water molecule. The equatorial plane geometry is formed from the O1, O1a, O8 and O8a atoms of the bridging monodentate and bidentate carboxylate groups of four cpida^{3–} ligands [Cu2–O = 1.916(2) and 1.958(2) Å].

The adjacent Cu^{II} centres are bridged by one oxygen atom of the monodentate carboxylate group and two oxygen atoms of the bidentate carboxylate groups of two cpida^{3–} ligands, leading to a linear trinuclear Cu^{II} SBU (Figure 1a). The three Cu^{II} atoms are arranged in a strictly linear fashion (Cu1–Cu2–Cu1a = 180°) with Cu2 at the inversion centre; the distance between Cu1 and Cu2 is 3.232 Å. Complex **1** is a rare example of a polynuclear metal cluster bridged by carboxylate groups from only one kind of ligand (cpida^{3–}). To the best of our knowledge, only a limited number of linear trinuclear Cu^{II} compounds have been reported,^[11–13] and few metal-organic coordination frameworks containing a linear trinuclear Cu^{II} unit have been documented.^[14] It is worth noting that **1** is the first linear trinuclear Cu^{II} compound in which the three Cu^{II} centres are linked by μ -carboxylato groups of only one type of ligand (cpida^{3–}); other reported examples^[11–14] are mixed-

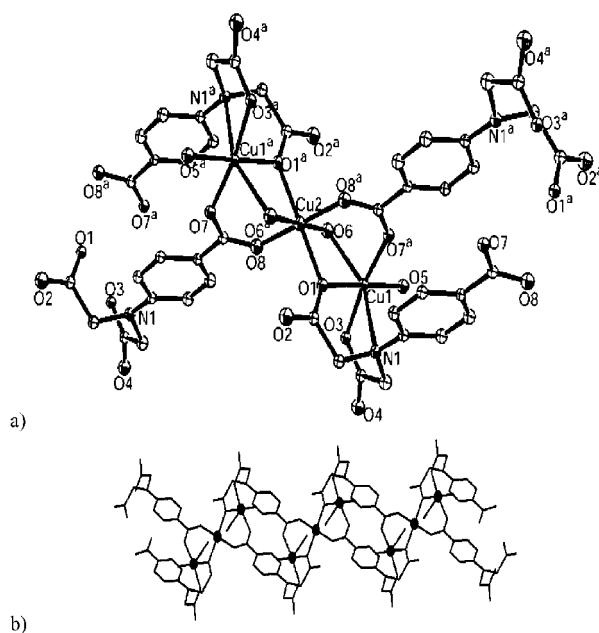


Figure 1. a) ORTEP diagram of the coordination environment around the linear trinuclear Cu^{II} unit in **1**; thermal ellipsoids are drawn at the 50% probability level; all hydrogen atoms are omitted for clarity; symmetry code: a: $-x, -y, -z$; b) 1D molecular-box chain of **1** along the c axis; the black spheres represent copper atoms

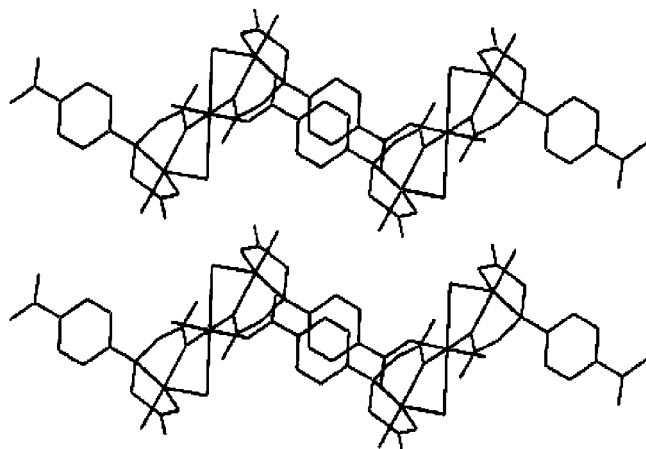
bridged compounds containing μ -hydroxo, μ -carboxylato, μ -acetato, etc.

Compound **1** possesses a 1D chain structure constructed from linear trinuclear Cu₃ SBUs. Interestingly, four Cu^{II} atoms of two Cu₃ SBUs are linked by two cpida^{3–} spacers in a head-to-tail mode leading to a parallelogram-shaped molecular box, as shown in Figure 1b. In each molecular box there are offset π – π stacking interactions between two cpida^{3–} aromatic rings (centroid $\cdots$ centroid = 4.32 Å). Each

Table 1. Selected bond lengths [Å] and angles [°] for complexes **1** and **2**

1		2	
Cu(1)–O(1)	1.978(2)	Zn(1)–O(1A)	1.958(5)
Cu(1)–O(3)	1.973(2)	Zn(1)–O(2)	1.983(5)
Cu(1)–O(5)	1.952(2)	Zn(1)–O(3)	1.996(6)
Cu(1)–O(6)	2.344(2)	Zn(1)–O(4B)	2.002(5)
Cu(1)–O(7a)	1.947(2)	Zn(1)–N(1)	2.399(6)
Cu(2)–O(1)	1.958(2)		
Cu(2)–O(1a)	1.958(2)		
Cu(2)–O(8)	1.916(2)		
Cu(2)–O(8a)	1.916(2)		
O(1)–Cu(1)–O(3)	93.14(8)	O(1A)–Zn(1)–O(2)	100.7(2)
O(1)–Cu(1)–O(5)	177.87(9)	O(1A)–Zn(1)–O(3)	143.5(2)
O(1)–Cu(1)–O(6)	81.37(9)	O(1A)–Zn(1)–O(4B)	104.0(2)
O(1)–Cu(1)–O(7a)	92.67(9)	O(2)–Zn(1)–O(3)	110.0(2)
O(3)–Cu(1)–O(5)	85.94(10)	O(2)–Zn(1)–O(4B)	98.5(2)
O(3)–Cu(1)–O(6)	99.20(9)	O(3)–Zn(1)–O(4B)	90.8(2)
O(3)–Cu(1)–O(7a)	171.45(9)	O(1A)–Zn(1)–N(1)	90.7(2)
O(5)–Cu(1)–O(6)	100.67(10)	O(2)–Zn(1)–N(1)	79.1(2)
O(5)–Cu(1)–O(7a)	88.03(10)	O(3)–Zn(1)–N(1)	76.6(2)
O(6)–Cu(1)–O(7a)	87.86(9)	O(4B)–Zn(1)–N(1)	165.3(2)
O(1)–Cu(2)–O(1a)	180.00(14)		
O(1)–Cu(2)–O(8)	91.32(9)		
O(1)–Cu(2)–O(8a)	88.68(9)		
O(8)–Cu(2)–O(1a)	88.68(9)		
O(8)–Cu(2)–O(8a)	180.0(2)		
O(8a)–Cu(2)–O(1a)	91.32(9)		

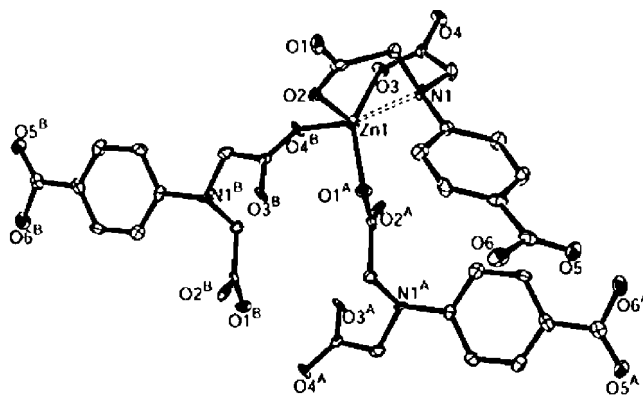
parallelogram-shaped molecular box is then linked together by the bridging bidentate carboxylate groups, which results in the formation of a 1D molecular box coordination polymer. It is notable that the 1D molecular box chains propagate into 2D layers by an AA stacking pattern^[15] in the *bc* plane, as shown in Figure 2.

Figure 2. A view of the 2D layer of **1** down the *a* axis, showing the AA stacking pattern of the 1D molecular box chains

One guest water molecule (O9) forms a hydrogen bond with a coordinated water molecule (O9...O5 = 2.695 Å), and another guest water molecule (O10) forms hydrogen bonds with the coordinated water molecule (O10...O5 = 2.576 Å) and the noncoordinated carboxylate oxygen atom (O10...O2 = 2.725 Å).

[Zn(Hcpida)]_n·*n*H₂O (**2**)

The asymmetric unit of **2** consists of one Zn^{II} atom, one Hcpida^{2−} ligand and one guest water molecule. Each Zn^{II} centre is coordinated by two oxygen atoms (O1A, O4B) from the bridging bidentate carboxylate groups of two Hcpida^{2−} ligands, and two oxygen atoms (O2, O3) from one chelating bidentate Hcpida^{2−} ligand, leading to a distorted tetrahedral coordination geometry (Figure 3). The Zn–O bond lengths vary from 1.958(5) Å to 2.002(5) Å. The bond angles around the Zn^{II} centre range from 90.8(2)° to 143.5(2)°. There is an unusual structural feature around the Zn^{II} centre: the Zn^{II} centre has four nearest-neighboring oxygen atoms [*d*(Zn–O) < 2.002 Å] in an approximately tetrahedral arrangement, although the O1A–Zn1–O3 bond angle [143.5(2)°] is particularly obtuse. There is one nitrogen atom associated with the Zn atom [*d*(Zn–N) = 2.399 Å], which does not constitute a “bond” in any real sense. This association may be considered as a weak interaction.^[16] The geometry at the Zn centre can be visualized as a mono-capped tetrahedron (Figure 3).^[17] Because the Zn1–N1 bond (2.399 Å) is much longer than the Zn1–O4 bond (2.002 Å), the ZnO₄N unit should not be described as distorted trigonal-bipyramidal but as mono-capped tetrahedral. On the other hand, the Zn atom is displaced off-center by 0.317 Å, when the associated nitrogen atom is considered. These results support the validity of regarding this geometry as mono-capped tetrahedral.

Figure 3. ORTEP diagram of the coordination environment around the Zn^{II} centre in **2**; thermal ellipsoids are drawn at the 50% probability level; all hydrogen atoms are omitted for clarity; symmetry code: A: *x*, *−y* − 1/2, *z* − 1/2; B: *−x*, *y* + 1/2, *−z* + 1/2

The coordinated H₃cpida ligand has an unchelated carboxylic group. The C–O bond [C11–O6 = 1.344(10) Å] is much longer than C–O [C11–O5 = 1.190(9) Å] in the carboxylic group, so C11–O5 can be assigned as the double bond and C11–O6 as the single bond. This shows that deprotonation of the H₃cpida ligand is incomplete.

The crystal structure of **2** consists of an infinite 2D network. The Zn1 centre is connected to four adjacent Zn centres through the bridging bidentate carboxylate groups of Hcpida^{2−} ligands leading to a Zn₄(Hcpida)₄ unit, which further extends into a 2D polymeric network with alternate large and small pseudo-square grid motifs in the *bc* plane

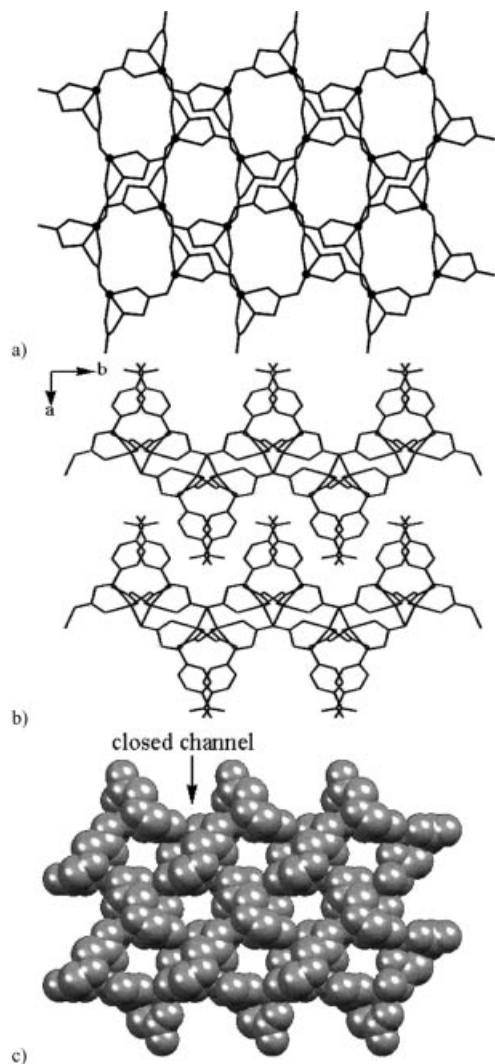


Figure 4. a) The 2D network of **2** as viewed down the *a* axis, showing alternate large and small pseudo-square grids (phenyl rings omitted for clarity); b) a view of the 2D wave-like layer of **2** down the *c* axis, showing the AA stacking pattern between the layers; c) a space-filling diagram showing alternate open and closed channels created perpendicularly to the *bc* plane; the alternate open channels are occupied by the guest water molecules, which have been omitted for clarity

(Figure 4a). In each large pseudo-square grid, the Zn–Zn separations are 4.90 and 5.20 Å, while the Zn–Zn–Zn angles are 80.73° and 99.27°. Each acetate group of the Hcpida^{2−} ligand adopts a bidentate bridging mode to connect two Zn centres. Four Zn centres are connected together by μ_2 -acetato groups to form a 2D grid network. However, according to the flexibility of the iminodiacetate groups of the Hcpida^{2−} ligand, compound **2** does not adopt one kind of grid but alternate large and small grid motifs, as shown in Figure 5. The wave-like nature of the 2D layers of **2** can be clearly shown with a view of **2** down the *c* axis (Figure 4b). Interestingly, the 2D layers in **2** adopt an AA stacking pattern in the *ab* plane, and the convex phenylcarboxylic groups of Hcpida^{2−} in one layer sit above or below the small grids of the adjacent layers along the *a* direction (Figure 4b). Thus, compound **2** possesses alternate open (large grids) and closed (small grids) channels that are perpen-

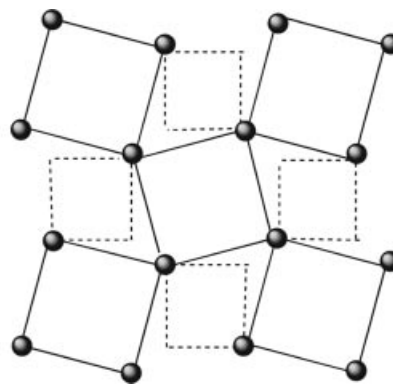


Figure 5. A topological illustration of the alternate large and small grids of compound **2**

dicular to the *bc* plane and parallel to the *a* axis (Figure 4c). Each alternate open channel is approximately 4.9×5.7 Å. The guest water molecules occupy the open channels resulting in the formation of the water columns along the *a* direction.^[18] It should be noted that in the crystal packing there are offset π – π stacking interactions between two Hcpida^{2−} aromatic rings (centroid...centroid = 4.10 Å), as shown in Figure 6. The guest water molecule (O7) forms hydrogen bonds with the coordinated carboxylate oxygen atoms (O7...O1 = 2.850 Å; O7...O4 = 2.961 Å) and the noncoordinated carboxylate oxygen atom (O7...O6 = 2.680 Å).

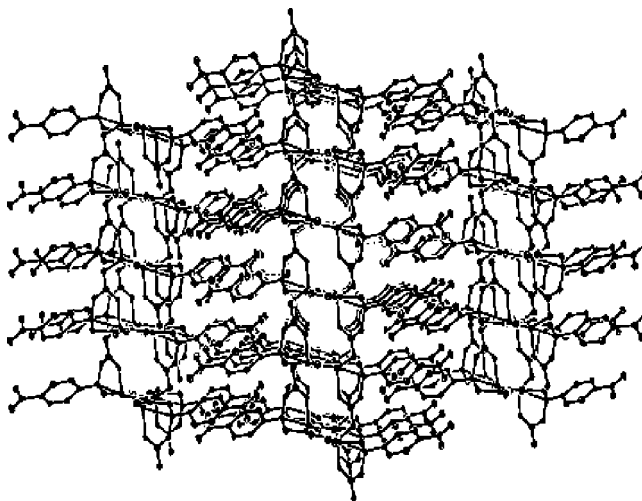


Figure 6. The 3D structure of **2** as viewed down the *b* axis, showing the offset π – π stacking interactions

Removal of the Guest Water Molecules: TGA and PXRD Studies

The X-ray single-crystal structures clearly indicate that compound **2** possesses alternate open channels along the *a* axis, and we became intrigued by the possibility of generating a cavity by removing the guest water molecules. The TGA curve of compound **1** exhibits a continuous weight

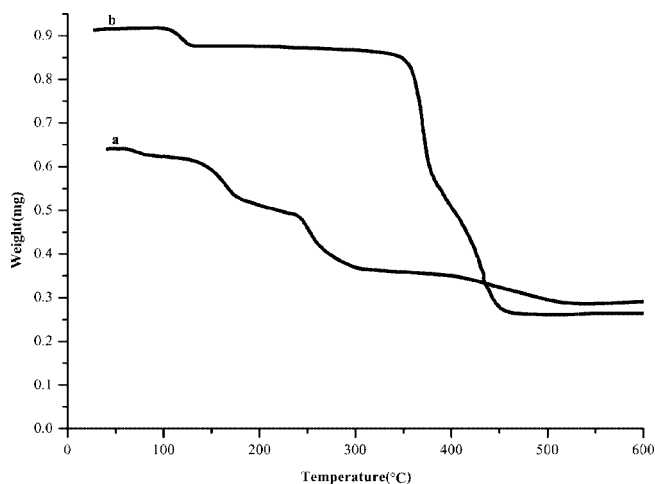


Figure 7. TGA curves for **1** (a) and **2** (b)

loss (curve a in Figure 7): the loss of the guest water molecules is accompanied by the loss of the coordinated water molecules, and the loss of the coordinated water molecules is accompanied by the loss of the ligands. As a result, it is difficult to give exact weight losses as a percentage for each weight-loss step in the TGA curve. The removal of the guest water molecules from **1** results in the collapse of the framework structure (see Supporting Information). The TGA curve of compound **2** exhibits an initial weight loss at an onset temperature of 120 °C (5.43%), corresponding to the removal of the guest water molecule (calcd. 5.38%). The second weight loss occurs between 340 and 480 °C (69.23%) and corresponds to the release of the Hcpida²⁻ ligand (curve b in Figure 7). The remaining weight of 25.34% corresponds to the percentage of ZnO (calcd. 24.32%). Although the hydrogen bonds increase the difficulty of removing the guest water molecule (O7) from **2**,^[19] the framework structure of the dehydrated sample is similar to that of compound **2** in terms of their powder X-ray diffraction (PXRD) patterns (see Supporting Information). The rehydrated sample also exhibits a similar PXRD pattern to compound **2** (Supporting Information). In particular, the existence of the strongest peak at a 2θ value of 6.56° in the three PXRD patterns shows that the layer framework of **2** does not change upon dehydration and rehydration. Therefore, compound **2** not only maintains its 2D layer framework after dehydration but the inclusion process is reversible to some extent. This can be attributed to the absence of coordinated water molecules in compound **2** and the higher decomposition temperature (340 °C) of the Hcpida²⁻ ligand.

Photoluminescence Properties of H₃cpida and **2**

The solid-state photoluminescence spectra of H₃cpida and compound **2** at room temperature are depicted in Figure 8; H₃cpida exhibits a broad strong blue-fluorescent emission around 422 nm upon excitation at 332 nm (curve a in Figure 8). Interestingly, in the case of the metal-organic polymer **2**, a blue-shifted photoluminescence with the main emission at 366 nm and with a shoulder at about 480 nm upon excitation at 313 nm is observed (curve b in Figure 8).

This emission arises from ligand-to-metal charge transfer (LMCT).^[20] TGA indicated that **2** is thermally stable up to 340 °C. Thus, compound **2** may be a good candidate for highly thermally stable and solvent-resistant photoactive material because it is almost insoluble in common polar and nonpolar solvents.^[4a] Compound **2** may also have potential as a porous material after removing the guest water molecules.

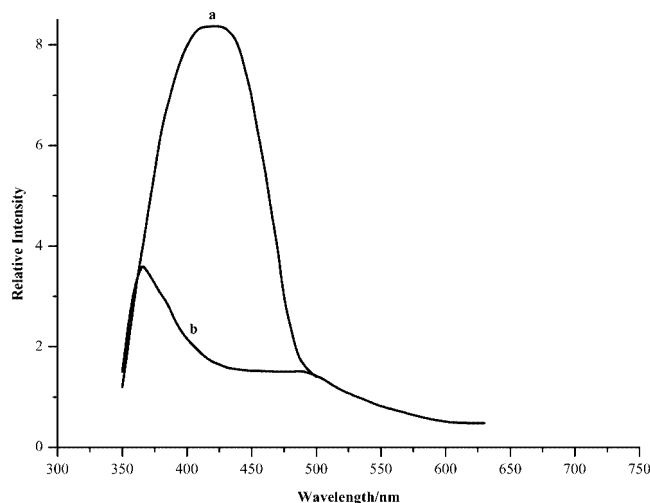


Figure 8. The emission spectra of the H₃cpida ligand (a) and compound **2** (b) in the solid state at room temperature

Conclusions

Two new metal-organic coordination polymers have been synthesised. Compound **1** is a linear trinuclear Cu^{II} compound in which the three Cu^{II} centres are linked only by μ -carboxylato groups of the same ligand (cpida³⁻). A 1D parallelogram-shaped molecular-box chain is constructed from these unusual linear trinuclear Cu^{II} SBUs. Compound **2** possesses alternate open and closed channels and shows strong photoluminescence, thus it may be a good candidate for a photoactive or porous material.

Experimental Section

General Remarks: All commercially available chemicals were of reagent grade and used as received without further purification. Infrared spectra were recorded with a Bruker VECTOR-22 FT-IR spectrophotometer as KBr pellets. ¹H NMR spectra were measured with an Avance AV400 NMR spectrometer at room temperature. Powder X-ray diffraction (PXRD) patterns were obtained with an MXP4HF rotating-anode X-ray diffractometer. The luminescence spectra for the solid samples were recorded at room temperature with a Hitachi 850 fluorescence spectrophotometer. Thermogravimetric analyses (TGA) were performed under air with a heating rate of 10 °C·min⁻¹ using a Shimadzu TGA-50H TG analyzer.

N-(4-Carboxyphenyl)iminodiacetic Acid (H₃cpida): A solution of KOH (33.6 g, 0.6 mol) in water (100 mL) was added dropwise to a solution of chloroacetic acid (28.4 g, 0.3 mol) in water (100 mL). *p*-Aminobenzoic acid (13.7 g, 0.1 mol) was slowly added to the re-

sulting alkaline solution, and the mixture was refluxed at 86 °C for 30 h. The reaction mixture was then cooled to room temperature and acidified with HCl (6 M) until the desired acid precipitated as a white solid (pH $\approx$ 2.5) (Scheme 1). This precipitate was collected by filtration, washed with water and recrystallised from water (yield: 32% based on *p*-aminobenzoic acid). IR (KBr): $\tilde{\nu}$ = 3458, 2919, 1714, 1612, 1530, 1462, 1388, 1239, 1192, 975, 771, 692 cm⁻¹. ¹H NMR (400 MHz, D₂O, 25 °C): δ = 7.84 (d, *J* = 8.9 Hz, AAB, 2 H), 6.58 (d, *J* = 8.9 Hz, AAB, 2 H), 4.23 (s, 4 H, CH₂-COO) ppm.

[Cu₃(cpida)₂(H₂O)₄] $\cdot$ 4nH₂O (1): This compound was prepared by a solvent evaporation method. A mixture of basic copper carbonate (0.111 g, 0.5 mmol) and H₃cpida (0.25 g, 1.0 mmol) in 15 mL of water was heated in a steam bath for 1 h, and then filtered. Methanol (5 mL) was then added to the filtrate (Scheme 1). Blue single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent from the filtrate at room temperature (yield: 72% based on Cu). IR (KBr): $\tilde{\nu}$ = 3418, 2919, 1645, 1605, 1538, 1412, 1260, 1217, 1170, 968, 925, 839, 778, 698, 643, 511 cm⁻¹.

[Zn(Hcpida)]_n $\cdot$ nH₂O (2): This compound was synthesized hydrothermally in a thick-walled Pyrex tube containing Zn(NO₃)₂ $\cdot$ 6H₂O, H₃cpida, KOH, methanol and H₂O in a molar ratio of 3:2:1:78:222 under autogenous pressure. The tube was cooled in liquid N₂, sealed under vacuum, and placed inside an oven at 120 °C for 2 d (Scheme 1). The resulting colourless crystals were collected and washed with ethanol (yield: 58% based on Zn). IR (KBr): $\tilde{\nu}$ = 3491, 2977, 1703, 1573, 1518, 1460, 1412, 1352, 1308, 1262, 1197, 1146, 1122, 1016, 923, 851, 781, 755, 731, 699, 648, 585, 508 cm⁻¹.

X-ray Single-Crystal Structure Determination: Crystallographic data for **1** and **2** were collected at 173 K for **1** and 293 K for **2** with a Siemens Smart CCD diffractometer with Mo-*K* α radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97^[21] and refined by full-matrix least-squares method against *F*² (SHELXL-97).^[22] All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in geometrically calculated positions; oxygen-bound hydrogen atoms were located in the difference Fourier map and kept fixed in that position. The crystallographic data for **1** and **2** are listed in Table 2; selected bond lengths and angles for **1** and **2** are presented in

Table 2. Crystal data and structure refinement for complexes **1** and **2**

	1	2
Empirical formula	C ₂₂ H ₃₂ Cu ₃ N ₂ O ₂₀	C ₁₁ H ₁₁ NO ₇ Zn
Formula mass	835.12	334.56
Temperature [K]	173(2)	293(2)
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	8.5094(17)	13.900(3)
<i>b</i> [Å]	9.3206(19)	9.513(2)
<i>c</i> [Å]	10.392(2)	9.375(2)
α [°]	92.274(4)	90
β [°]	93.803(4)	101.136(5)
γ [°]	112.850(4)	90
<i>V</i> [Å ³]	756.0(3)	1216.4(5)
<i>Z</i>	1	4
μ [mm ⁻¹]	2.183	2.041
Reflections collected	3991	5090
Independent reflections (<i>R</i> _{int})	3181 (0.0131)	1746 (0.0566)
Observed reflections	2614	1326
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> $\geq$ 2 σ (<i>I</i>)]	0.0374, 0.0882	0.0634, 0.1481

Table 1. CCDC-228511 (**1**) and -228512 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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