Rational Design of Metal-Organic Frameworks Based on 5-(4-Pyridyl)tetrazolate: From 2D Grids to 3D Porous Networks

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The hydrothermal reactions of $Zn(ClO_4)_2·6H_2O$/$Cu(NO_3)_2·6H_2O$ with 5-(4-pyridyl)tetrazole in an ethanol/water or ethanol/water/pyridine medium yield one 2D and one 3D metal-organic coordination framework [$Zn_2(OH)$(4-ptz)$_3$] (**1**) and [Cu(4-ptz)·0.5(py)] (**3**) [4-ptz = 5-(4-pyridyl)-tetrazolate, py = pyridine], respectively. Complex **1** possesses two identical and independent rectangular grid sheets with twofold parallel interpenetration, in which the four-connected nodes of the net are provided by $Zn_2(OH)$ units connected to one another through 4-ptz and (4-ptz)$_2$ bridges. These composite sheets are stacked one on top of another by hydrogen-bonding interactions to afford a 3D structure. There are many structural similarities between complex **1** and the recently reported 2D layered network [Zn(OH)(4-ptz)(H_2O)] (**2**), in particular the components of the network, the coordination mode of the 4-ptz ligand and the in situ formation of hydroxy groups. Complex **2** can be synthesized by the hydrothermal reaction of $Zn(ClO_4)_2·6H_2O$ and 5-(4-pyridyl)tetrazole in an ethanol/water/pyridine medium. The structural characterization of complex **3** shows a porous structure that contains the guest pyridine molecules. Additionally, compounds **1** and **2** exhibit strong fluorescence at room temperature in the solid state.

Introduction

The study of coordination frameworks has received increasing attention over recent years with a growing range of structural motifs being discovered. As far as is known, the functions of materials come from their structural features.[1] Many functional materials can be prepared by supramolecular self-assembly because the required structural variety and thermal stability can be obtained. For instance, the combination of organic spacers and transition-metal centers in coordination frameworks can affect the assembly of supramolecules, giving new types of electroluminescent materials, which have potential applications as light-emitting diodes (LEDs).[2] Also, a variety of NLO materials have been obtained by noncentrosymmetric organization of molecular building blocks,[3] while magnetic compounds have been synthesized by supramolecular chemistry dealing with open-shell units.[4] Therefore, the discovery of methods to control the assembly and solid-state structures in three dimensions has become one of the main challenges in crystal engineering. Many of these studies have heightened the awareness of the influence of the metal ion and ligand,[5] as well as the anion[6] and the solvent[7] on self-assembly. Recently, many chemists have focused on the control exerted by organic ligands on the supramolecular structure. Among them, N-donor bridging ligands,[1] in particular those with pyridyl[8] and nitrile[9] donor groups, have been used to construct coordination frameworks showing novel structural features. Due to the aromaticity and multiple N-donor atoms, tetrazolate is also an excellent donor group with potential applications in the construction of coordination frameworks.[10] Recently, three coordination frameworks, [$Zn_2(OH)$(4-ptz)$_3$] (**1**), [Zn(OH)(4-ptz)(H_2O)] (**2**), and [Cu(4-ptz)0.5(py)] (**3**), were prepared in our laboratory with 5-(4-pyridyl)tetrazolate (4-ptz) ligands. The present report is concerned with the syntheses, crystal structures and luminescent properties of these compounds.

Results and Discussion

Complex **1** was prepared by treating $Zn(ClO_4)_2·6H_2O$ with 5-(4-pyridyl)tetrazole in ethanol and water under hydrothermal conditions (Scheme 1). Addition of pyridine to the reaction solutions gave complex **2** under the same conditions as for complex **1**. The proportion of hydroxy groups in complex **2** is higher than that in complex **1**; they are presumably formed from water in situ. Complex **3** was prepared by the same method as complex **2** (Scheme 1), except that $Cu(NO_3)_2·6H_2O$ was used instead of $Zn(ClO_4)_2·6H_2O$; the Cu^+ ions are likely formed by the re-

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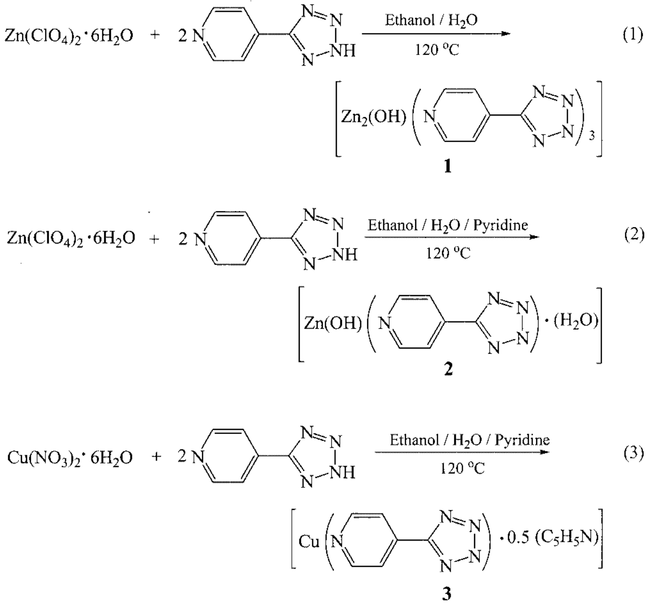
duction of Cu^{2+} by ethanol in situ.[11] The observed tetrazolate stretching frequencies (1624 and 1435 cm^{-1} in **1** and 1627 and 1439 cm^{-1} in **2** and 1616 and 1442 cm^{-1} in **3**) in the IR spectra of these compounds are consistent with those of other tetrazolate-based assemblies reported previously.[10]



Scheme 1

Structural Description

[Zn$_2$(OH)(4-ptz)$_3$] (1) and [Zn(OH)(4-ptz)(H$_2$O)] (2)

The asymmetric unit of complex **1** comprises two Zn atoms, three 4-ptz ligands and a hydroxy group (Figure 1). Two crystallographically distinct zinc centers, Zn1 and Zn2, are linked by one hydroxy group with a Zn–O–Zn angle of 120.4(2)° [123.18(14)° in complex **2**]. Each doubly bridging 4-ptz ligand coordinates through the two nitrogen atoms of the tetrazolate and the pyridine moiety. Each zinc center is in a tetrahedral environment surrounded by one hydroxy group and three different 4-ptz ligands (in complex **2**, the zinc center is surrounded by two hydroxy groups and two different 4-ptz ligands) with the difference being that the Zn1 center is coordinated to two tetrazolate nitrogen atoms and one pyridine nitrogen atom, while the Zn2 center is coordinated to two pyridine nitrogen atoms and one tetrazolate nitrogen atom. The N–Zn–N(O) angles vary from 101.9(2) to 109.2(2)° [104.09(12) to 110.46(12)° in complex **2**], while O1–Zn1–N7 [127.0(2)°] and O1–Zn2–N10 [120.7(2)°] are much larger [O–Zn–O of 120.47(13)° in complex **2**]. All donor atoms form reasonably strong bonds with the zinc atom: the Zn–N bond lengths range from 1.991(5) to 2.048(6) Å [2.021(3) and 2.079(4) Å in complex **2**], and the Zn–O bond lengths of Zn1 and Zn2 are 1.902(4) and 1.908(5) Å, respectively [1.922(3) and 1.936(3) Å in complex **2**].

The structure of complex **1** consists of two identical and independent rectangular grid sheets, interpenetrating parallelly in the manner shown in Figures 2 and 3. This mode of interpenetration is topologically equivalent to that in [Cu(tcm)(bipy)], as can be appreciated from its topological essence.[12] The four-connected nodes of the net are provided by Zn$_2$(OH) units, which are connected to one another through 4-ptz and (4-ptz)$_2$ bridges, with grid lengths of 13.1 and 11.5 Å, respectively, and a grid angle of 91°. Individual sheets are corrugated so as to allow this interweaving. There are π–π interactions between the pyridyl or tetrazolate groups from two independent interpenetrat-

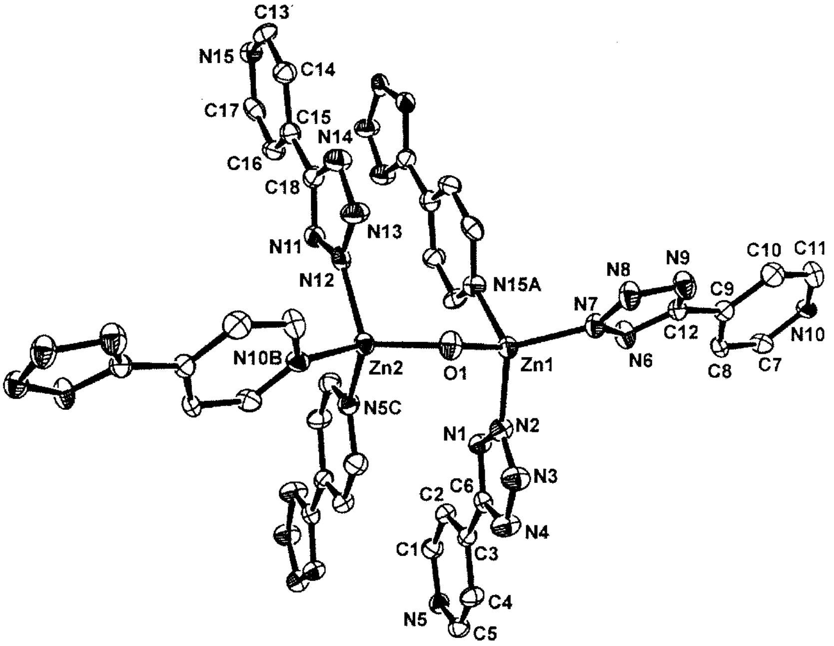


Figure 1. ORTEP drawing of **1** showing the local coordination environment of two crystallographically distinct Zn$^{\text{II}}$ centers (thermal ellipsoids at 50% probability)

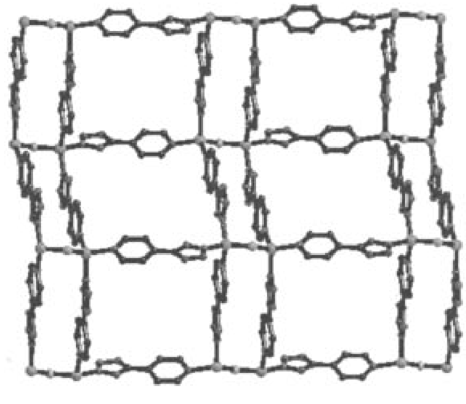


Figure 2. 2D rectangular grid net in **1**

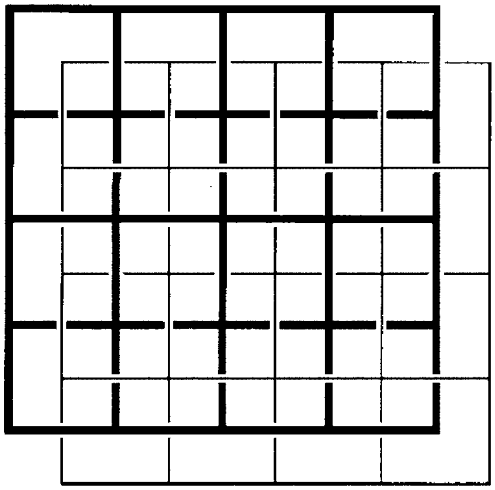


Figure 3. Schematic representation of the mode of interpenetration of two parallel rectangular grid nets; the four-connected nodes shown represent the centers of the $Zn_2(OH)$ aggregates

ing nets, which can be regarded as a stabilizing factor for the interpenetration. The composite structure resulting from this form of interpenetration is itself two-dimensional, and these composite sheets are stacked one on top of another by hydrogen-bonding interactions [O1···N3 (at $-x$, $-y$, $-z + 1$), 2.843 Å] forming a 3D structure (Figure 4).

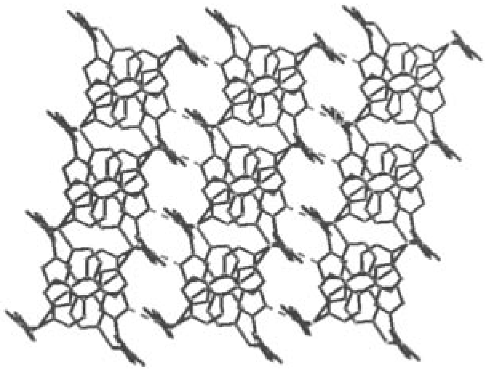


Figure 4. Three layers of the internally interwoven double sheets viewed approximately "edge-on"; the dashed lines represent the hydrogen bonding between layers in **1**

Comparing the structure of complex **1** with the recently reported 2D layered network [Zn(OH)(4-ptz)(H_2O)] (**2**),[10c] we can find many structural similarities involving the components of the network, the coordination mode of the 4-ptz ligand and in situ formation of the hydroxy groups. Complexes **1** and **2** differ mainly in their metal/ligand proportion, the presence of intercalated water molecules, and the topology and connectivity of their 2D coordination networks.[13] Comparing the 2D networks in complexes **1** and **2**, half of the hydroxy groups in complex **2** are replaced by 4-ptz ligands for complex **1**, which makes the grid sheets in complex **1** have bigger grid windows than in complex **2**. Thus, in complex **1** the grid sheets can undergo a twofold parallel interpenetration (see Supporting Information). The structural features exhibited by complexes **1** and **2** imply that the different pH values of the reaction solutions leads to different coordination environments of the metal ion and thus affects the self-assembly progress, resulting in a variety of coordination frameworks.

[Cu(4-ptz)·0.5(py)] (3)

The asymmetric unit of complex **3** comprises one Cu atom, one 4-ptz ligand and half a pyridine molecule (Figure 5). Each Cu atom coordinates to three tetrazolate nitrogen atoms and to one pyridyl nitrogen atom of four different 4-ptz ligands. Each Cu center adopts a highly distorted tetrahedral geometry. The bond angles vary from 90.41(14) to 123.57(14)°; this large range of bond angles is due to the large bulk of the tetrazolate and pyridyl groups compared with the radius of Cu^+. As such, each 4-ptz ligand is coordinated to four Cu atoms through the 1-, 2-, and 4-nitrogen atoms of tetrazolate, and the pyridyl nitrogen atom. The nitrogen donor atoms form strong bonds with the copper atom [from 1.985(3) to 2.130(3) Å]. The tetrazolate groups link the Cu atoms into a one-dimensional chain along the *a* axis (Figure 6). These chains are then interconnected by pyridyl groups from the 4-ptz ligands to give the resulting three-dimensional structure. Because of the bulkiness of the pyridyl groups of the 4-ptz ligands, channels form along the

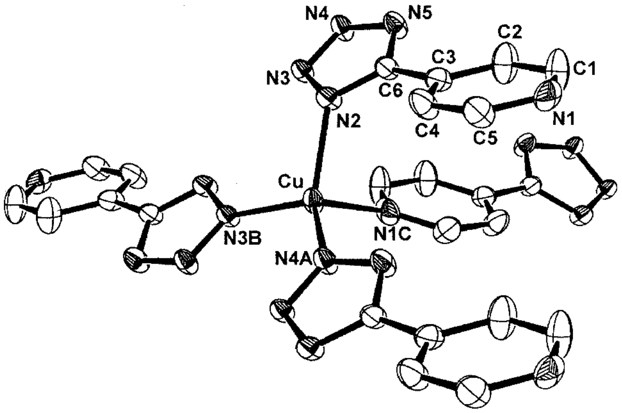


Figure 5. ORTEP drawing of **2** showing the local coordination environment of the Cu^I center (thermal ellipsoids at 50% probability)

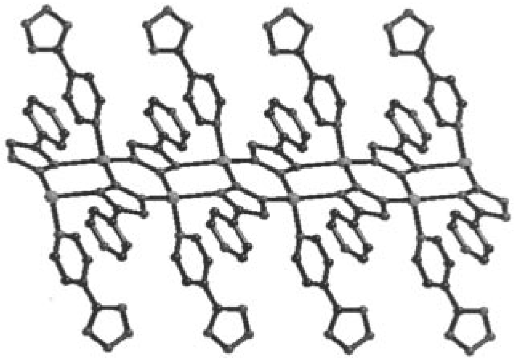


Figure 6. View of the one-dimensional copper chain linked by tetrazolate groups

a axis with an approximate cross-section of 4.4 × 4.4 Å (Figure 7). The solvent pyridine molecules reside in these channels (see Supporting Information). Thermogravimetric analysis showed that **3** loses 15.2% of its total weight in the 103−205 °C temperature range, which corresponds to the expected weight loss of half a pyridine molecule per formula unit (15.9%). Further details of the desolvation processes of complex **3** will form part of a future study.

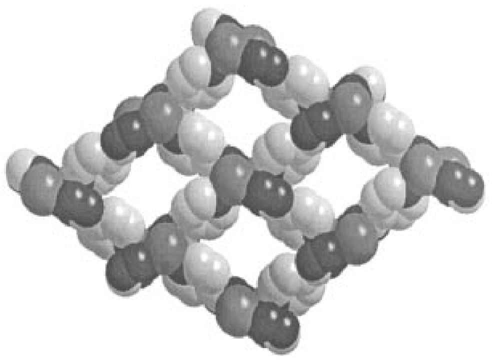


Figure 7. Space-filling view of the three-dimensional structure of **2** along the *a* axis

Structural Analysis

From the structures of complexes **1**, **2** and **3**, it can be seen that the metal ions in the three complexes all adopt a tetrahedral coordination environment, the difference being that Cu^+ in complex **3** possesses a more distorted coordination geometry than Zn^{2+} in complexes **1** and **2**. Complex **1** has a bridging μ_2-OH group between two zinc ions and complex **2** possesses a Zn−OH−Zn−OH chain. As far as we know, the radius of Zn^{2+} (0.74 Å) is smaller than that of Cu^+ (0.96 Å) so that there is a restriction of the coordination space around Zn^{2+} in comparison with Cu^+. As a result, Cu^+ can tolerate a more congested tetrahedral coordination environment while Zn^{2+} has to employ bridging μ_2-OH ligands to extend its coordination space and thereby relax the crowded coordination sphere. On the other hand, the Pauling electronegativity of Cu is 1.90 while that of Zn is 1.65. As a result of this difference, copper has a stronger coordination capability than zinc. Due to this strong coordination capability and the larger coordination space of copper, three nitrogen atoms from the tetrazolate group of 4-ptz take part in the coordination in complex **3**, resulting in the three-dimensional framework. These observations confirm that different metals can affect or control the self-assembly process of a supramolecular coordination framework even when the ligands in the supramolecule are the same and the reaction conditions are similar.

Fluorescent Properties

The luminescent properties of complexes **1**, **2** and **3** were investigated in the solid state (Figure 8). Upon excitation at 296 nm, complex **1** shows a strong emission peak at 356 nm. The emission of complex **1** is neither MLCT (metal-to-ligand charge transfer) nor LMCT (ligand-to-metal charge transfer) in nature, and can probably be assigned to intraligand fluorescent emission since a similar emission (λ_{max} = 352 nm) is also observed for free 5-(4-pyridyl)tetrazole.

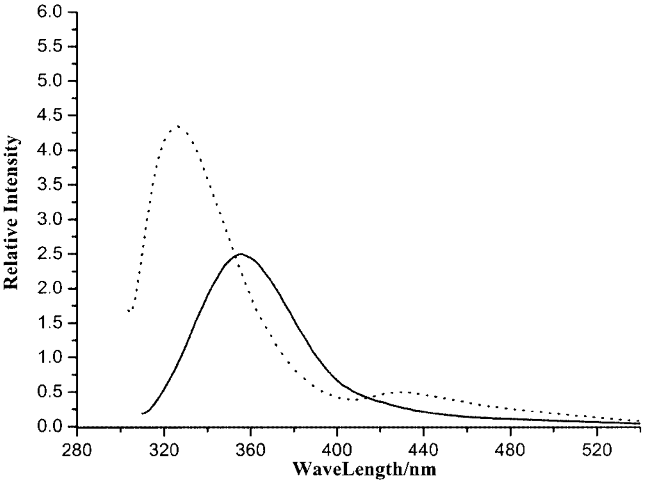


Figure 8. Excitation spectra and emission spectra of complex **1** (solid line) and complex **3** (dotted line) in the solid state at room temperature

Upon excitation at 294 nm, complex **2** displays a strong emission peak at 326 nm that can also be assigned to an intraligand fluorescent emission. Complex **2** shows an enhancement of the fluorescent intensity, which is almost twice that of free 5-(4-pyridyl)tetrazole. A relatively weak peak at 428 nm is also observed for **2**, and this peak may be tentatively assigned to phosphorescence.[10b] The Zn−OH−Zn−OH chain of complex **2** may be responsible for this phosphorescent emission since complex **1** only displays a strong emission peak at 352 nm. The exact phosphorescent-emission mechanism for complex **2** is unclear.

Complex **3** only displays a weak emission peak at 532 nm. The thermal stability of complexes **1** and **2** up to about 300 °C (TGA measurement) and their insolubility in common solvents make them good candidates for potential fluorescent materials.

Conclusions

In summary, we have prepared two new coordination frameworks containing the 5-(4-pyridyl)tetrazolate ligand. The structural features exhibited by complexes **1**, **2** and **3** show the coordination flexibility of the tetrazolate group. The radius of the coordination metal ion also has a great influence on the self-assembly in a crystal, which provides a crucial clue for possible modification and tuning of the supramolecular framework. The luminescent results indicate that metal coordination and formation of coordination framework can affect the emission wavelength and intensity of the organic material. A more detailed study in this area is in progress in our laboratory.

Experimental Section

General Remarks: The ligand 5-(4-pyridyl)tetrazole was prepared from NaN_3 and 4-cyanopyridine according to a reported procedure.[14] Zinc perchlorate hexahydrate was prepared by the reaction of zinc hydroxide with perchloric acid.[15] ***Caution:*** *$Zn(ClO_4)_2$·$6H_2O$ is potentially explosive and should be used with care!* All other chemicals were of AR grade. Elemental analyses (C, H, N) were performed using an Elementar Vario ELIII elemental analyser. IR spectra as KBr discs were recorded with a Bruker VECTOR-22 FT-IR spectrophotometer. Thermal gravimetric analysis was performed with a Shimadzu TGA-50H Thermal Gravimetric Analyzer at a heating rate of 5 °C·min^{-1}. Excitation and emission spectra were recorded with a Perkin−Elmer LS55 instruments luminescence spectrometer.

Preparation of 1: Hydrothermal treatment of $Zn(ClO_4)_2$·$6H_2O$ (0.1 mmol, 0.037 g), 5-(4-pyridyl)tetrazole (0.2 mmol, 0.015 g), ethanol (0.6 mL), and water (0.2 mL) at 120 °C for 12 h yielded colorless plate crystals (0.015 g, only one pure phase) in 51% yield based on $Zn(ClO_4)_2$·$6H_2O$. $C_{18}H_{13}N_{15}OZn_2$ (586.17): calcd. C 36.88, H 2.24, N 35.84; found C 37.02, H 2.19, N 35.97. IR (KBr): $\tilde{\nu}$ = 3444 (w), 1624 (s), 1556 (m), 1435 (s), 1374 (m), 1228 (m), 1176 (m), 1031 (s), 1011 (m), 976 (m), 850 (m), 756 (m), 719 (m), 556 (m), 532 (s), 496 (m) cm^{-1}.

Preparation of 2: Hydrothermal treatment of $Zn(ClO_4)_2$·$6H_2O$ (0.1 mmol, 0.037 g), 5-(4-pyridyl)tetrazole (0.2 mmol, 0.015 g), ethanol (0.6 mL), water (0.2 mL) and pyridine (0.2 mL) at 120 °C for 12 h yielded colorless plate crystals (0.014 g, only one pure phase) in 57% yield based on $Zn(ClO_4)_2$·$6H_2O$. $C_6H_7N_5O_2Zn$ (246.54): calcd. C 29.20, H 2.84, N 28.39; found C 29.33, H 2.94, N 28.54. IR (KBr): $\tilde{\nu}$ = 3250 (m), 3043 (w), 1626 (s), 1557 (w), 1453 (w), 1439 (s), 1382 (w), 1230 (m), 1172 (w), 1087 (w), 1049 (w), 1018 (m), 854 (m), 754 (w), 719 (m), 538 (w), 512 (m), 472 (w) cm^{-1}.

Preparation of 3: Hydrothermal treatment of $Cu(NO_3)_2$·$6H_2O$ (0.1 mmol, 0.030 g), 5-(4-pyridyl)tetrazole (0.2 mmol, 0.015 g), ethanol (0.6 mL), water (0.2 mL), and pyridine (0.2 mL) at 120 °C for 48 h yielded yellow block crystals (0.011 g, only one pure phase) in 43% yield based on $Cu(NO_3)_2$·$6H_2O$. $C_{17}H_{13}Cu_2N_{11}$ (498.46): calcd. C 40.96, H 2.63, N 30.91; found C 41.09, H 2.54, N 31.12. IR (KBr): $\tilde{\nu}$ = 3443 (w), 2919 (m), 1616 (s), 1442 (s), 1212 (m), 1059 (m), 1045 (m), 1007 (m), 840 (m), 754 (m), 708 (m), 530 (m), 470 (m) cm^{-1}.

X-ray Crystallographic Study: Crystal data and details of the structure refinements are presented in Table 1. Intensity data were collected with an R-AXIS-IV four-circle diffractometer using Mo-K_α radiation (λ = 0.71073 Å) at 291 K for compound **1**, and with a CCD area detector diffractometer at 293 K for compound **3**. The structure solutions and refinements were carried out using SHELXS-96[16] and SHELXL-97, respectively.[17] All hydrogen atoms were identified from difference maps and were included in the successive refinement cycles. All non-hydrogen atoms (including those of solvent water molecules) were refined anisotropically. CCDC-212430 (**1**) and -228746 (**3**) 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.) + 44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystallographic data and refinement details for **1** and **3**

	1	3
Empirical formula	$C_{18}H_{13}N_{15}OZn_2$	$C_{17}H_{13}Cu_2N_{11}$
M	586.17	498.46
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a [Å]	10.069(2)	5.726(7)
b [Å]	10.453(2)	16.474(2)
c [Å]	11.887(2)	9.941(2)
α [°]	71.16(3)	90
β [°]	67.16(3)	94.29(4)
γ [°]	79.14(3)	90
V [Å^3]	1088.4(4)	935.2(2)
Z	2	2
$D_{calcd.}$ [g cm^{-3}]	1.789	1.770
μ(Mo-K_α) [mm^{-1}]	2.253	2.305
F(000)	588	500
T [K]	291(2)	293(2)
Total data	3479	3847
Unique data	3479	1573
R_{int}	0.00	0.0320
Data [$I > 2\sigma(I)$[	2531	1324
$R1$[a] [$I > 2\sigma(I)$]	0.0497	0.0415
$wR2$[b] [$I > 2\sigma(I)$]	0.1205	0.1091
GOF[c]	1.124	0.979
Residuals [e·Å^{-3}]	0.633, −0.775	0.511, −0.680

GOF = $\{\Sigma[w(F_o^2 - F_c^2)2]/(n - p)\}^{1/2}$.

Acknowledgments

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