

Temperature-Controlled Solvothermal Syntheses, Structures and Characterizations of a Novel Class of Zn Complexes Constructed from 1,4-Bis[2-(5-phenyloxazolyl)]benzene

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Three novel complexes, $\text{ZnCl}_2(\text{H}_2\text{O})(\text{POPOP})\cdot\text{POPOP}$ (**1**), $[\text{ZnCl}_2(\text{POPOP})]_n$ (**2**), and $\{\text{Zn}_2(\text{CH}_3\text{COO})(\text{POPOP})_{1.5}\text{Cl}_3\}_n$ (**3**) [$\text{POPOP} = 1,4\text{-bis}[2\text{-(5-phenyloxazolyl)}]\text{benzene}$], of zinc–POPOP coordination polymers have been obtained from an identical starting mixture using temperature as the only independent variable. Complexes **1–3** all crystallize in the triclinic $P\bar{1}$ space group, but their Zn^{II} centers adopt different coordinations. Complex **1** consists of POPOP-coordinated

zinc units and discrete POPOP molecules, **2** features an interesting zigzag chain structure, and **3** consists of unique ladder-like double-chains bridged by POPOP units. Furthermore, **1–3** display some different fluorescent emissions based on their different coordination architectures.

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Introduction

Transition metal containing organic materials have attracted considerable recent interest because of their potential applications in optical and electrooptical devices such as organic light-emitting diodes (OLEDs), electrochromic, photovoltaic and photoconductive devices, and photorefractive optical elements.^[1–9] Polynuclear d^{10} metal (Cu^{I} , Ag^{I} , Au^{I} , Zn^{II} , or Cd^{II}) complexes have also attracted extensive interest owing to their appealing structures and photoluminescent properties. A series of d^{10} metal organic frameworks have been described.^[10,11] Some organic N-donors such as bipyridine or related species are often chosen to fabricate these various species.^[12,13] Interest in the chemistry of transition metal–diimine compounds with a conjugated π -system has grown rapidly because of their unique physical properties. Molecular structure-property relationships of organic π -conjugated materials have been explored.^[14–16] POPOP {POPOP = $1,4\text{-bis}[2\text{-(5-phenyloxazolyl)}]\text{benzene}$ } is a long π -conjugated ligand and often acts as a photoluminescent chromophore.^[17] However, to the best of our knowledge, no studies have been reported based on POPOP with transition metals. To understand the coordination chemistry of POPOP and to

prepare new materials with interesting structural topology and excellent physical properties, we have been particularly concerned with such polymers and attempted to prepare some materials with interesting physical properties.

In addition, the design and synthesis of novel coordination architectures controlled by varying the reaction conditions (including temperature,^[18,19] metal/ligand ratio,^[20] pH,^[21] solvents,^[22] and counter anions^[23,24]) are of great interest in coordination chemistry and reactions. Appropriate control of the reaction conditions makes it possible to construct new materials with useful properties. For example, Forster and co-workers have carried out systematic studies on the role of synthesis temperature as an isolated reaction variable.^[19] In this paper, we report the synthesis of three novel complexes of zinc–POPOP coordination polymers, $\text{ZnCl}_2(\text{H}_2\text{O})(\text{POPOP})\cdot\text{POPOP}$ (**1**), $[\text{ZnCl}_2(\text{POPOP})]_n$ (**2**), and $\{\text{Zn}_2(\text{CH}_3\text{COO})(\text{POPOP})_{1.5}\text{Cl}_3\}_n$ (**3**), from identical starting materials but at different temperatures.

Results and Discussion

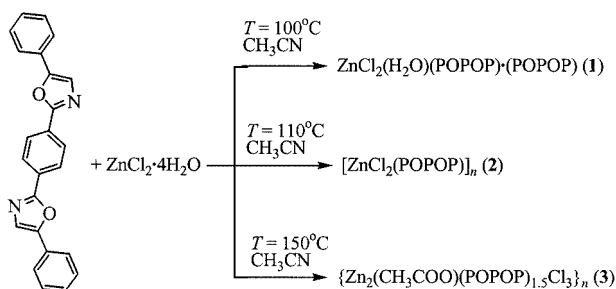
Synthesis and General Characterization

To design new organic–inorganic hybrid compounds with some multifunctional ligands, hydro(solvo)thermal synthesis is a powerful method. At such a relatively low temperature and under autogenous pressure, the problems of ligand solubility and reactivity are minimized, and appropriate O- and N-donor ligands can be selected by the metal centers for efficient molecular constructions during crystallization. Complexes **1–3** were synthesized simply un-

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der solvothermal reaction conditions. As mentioned above, POPOP is a long π -conjugated ligand that can offer two N atoms for coordination. The synthesis of zinc–POPOP described here demonstrates that a single starting mixture can be used to obtain different zinc–POPOP structures by varying only the reaction temperatures. The same precursors under different reaction temperatures lead to three novel complexes, **1**–**3**, exhibiting different architectures with different coordination fashions (Scheme 1). The coordination numbers of Zn^{II} ions in **1**–**3** are the same, but their differing topologies are a discrete arrangement, a 1D zigzag chain arrangement, and a 1D ladder-like double-chain arrangement, respectively.



Scheme 1. Role of temperature in the synthesis of zinc–POPOP complexes

Crystal Structures of Complexes

$\text{ZnCl}_2(\text{H}_2\text{O})(\text{POPOP}) \cdot (\text{POPOP})$ (**1**)

The structure determination reveals that complex **1** is discrete, consisting of POPOP-coordinated zinc units and POPOP molecules (Figure 1). The zinc(II) atom exhibits a tetrahedral configuration coordinated by two chlorine atoms [$\text{Zn}(1)–\text{Cl}(1) = 2.2238(4)$ Å, $\text{Zn}(1)–\text{Cl}(2) = 2.2124(4)$ Å], one nitrogen atom of the POPOP ligand with a $\text{Zn}(1)–\text{N}(1)$ bond length of $2.0629(11)$ Å, and one oxygen atom [$\text{Zn}(1)–\text{Ow}1 = 2.0193(10)$ Å] of a water group. There are three crystallographically independent POPOP ligands with different orientations in one unit: one monodentately coordinates to one Zn center, while the other two do not participate in coordination and orient vertically to each other. Interestingly, each POPOP ligand is almost coplanar. Figure 2 shows that there is a discrete POPOP unit

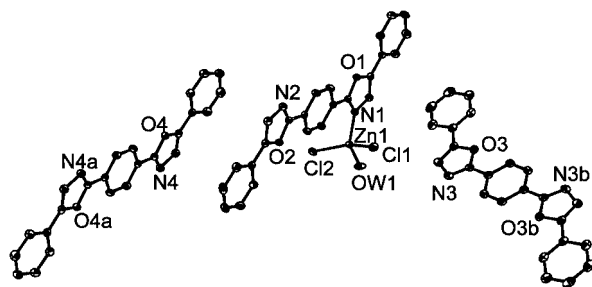


Figure 1. ORTEP drawing of $\text{ZnCl}_2(\text{H}_2\text{O})(\text{POPOP}) \cdot (\text{POPOP})$ (**1**), showing the local coordination of Zn^{II} and atomic numbering scheme (30% probability thermal ellipsoids)

between two adjacent POPOP-coordinated zinc units in which Zn^{II} atoms are located on opposite direction mutually. These three units are parallel and combine to form a basic group by obvious π – π interactions, with distances of $3.518(5)–3.929(6)$ Å. A further POPOP molecule, which is vertical relative to the parallel layers, fills in the large cavity formed by the staggered arrangement of four groups.

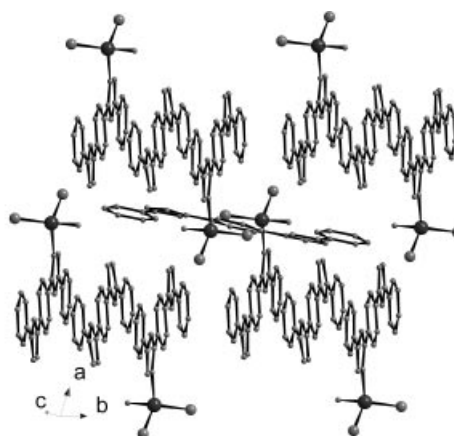


Figure 2. Ball-and-stick representation of the packing diagram of **1**

$[\text{ZnCl}_2(\text{POPOP})]_n$ (**2**)

A single-crystal X-ray structural analysis shows that complex **2** has an interesting one-dimensional zigzag chain framework, which is built up by one POPOP linked to two Zn atoms. The zinc(II) atom has a tetrahedral configuration coordinated by two chlorine atoms [$\text{Zn}(1)–\text{Cl}(1) = 2.2258(6)$ Å, $\text{Zn}(1)–\text{Cl}(2) = 2.2114(7)$ Å] and two nitrogen atoms [$\text{Zn}(1)–\text{N}(1) = 2.0596(12)$ Å, $\text{Zn}(1)–\text{N}(2) = 2.0587(12)$ Å] from two different POPOP ligands (Figure 3). $\text{Cl}–\text{Zn}–\text{Cl}$ and $\text{N}–\text{Zn}–\text{N}$ bond angles are $115.15(3)^\circ$ and $96.73(5)^\circ$ respectively. $\text{N}–\text{Zn}–\text{Cl}$ bond angles range from $105.96(3)$ to $109.56(3)^\circ$. The shortest $\text{Zn} \cdots \text{Zn}$ distance between POPOP ligands is 9.184 Å. Figure 4 shows that each Zn atom is coordinated by two POPOP ligands, i.e. each POPOP ligand is connected with two zinc atoms. Based on this coordination mode, the 1D infinite chain framework is formed. The most interesting feature of complex **2** is that such a coordination mode produces a unique zigzag chain structure. The two dihedral angles between the 5-phenyloxazolyl rings and the center benzene ring plane are 25.05° .

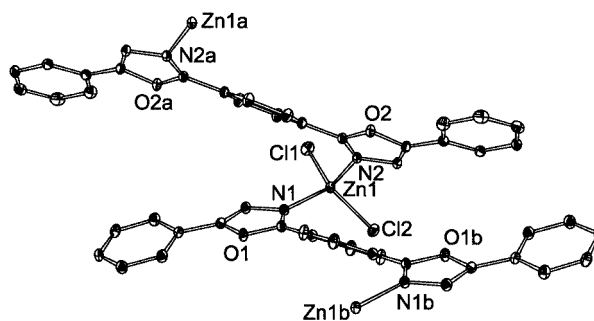


Figure 3. ORTEP drawing of $[\text{ZnCl}_2(\text{POPOP})]_n$ (**2**)

This is presumably a consequence of the bridging nature of the ligands, with effective coordination to the metals being of primary importance.

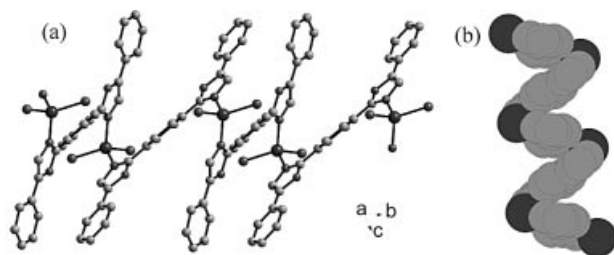


Figure 4. (a) Zig-zag chain structure in **2**; (b) space-filling plots of the zig-zag chain

$\{Zn_2(CH_3COO)(POPOP)_{1.5}Cl_3\}_n$ (**3**)

X-ray crystallographic analysis reveals that complex **3** consists of an infinite ladder-like double-chain bridged by POPOP ligands. The fundamental unit is shown in Figure 5. There are two crystallographically different Zn centers in the asymmetric unit, both displaying tetrahedral coordination geometry. The Zn(1) center is defined by two chlorine atoms [$Zn(1)-Cl(1) = 2.2160(9)$ Å, $Zn(1)-Cl(2) = 2.2166(10)$ Å], one nitrogen atom from a distorted POPOP ligand with a $Zn(1)-N(2)$ bond length of $2.100(2)$ Å, and one oxygen atom [$Zn(1)-O(4) = 2.007(2)$ Å] of a carboxylate group. $N-Zn(1)-Cl$ bond angles are $109.64(7)^\circ$ and $109.79(7)^\circ$, and $O-Zn-Cl$ bond angles are $106.08(7)^\circ$ and $113.99(7)^\circ$, respectively. $O-Zn-N$ and $Cl-Zn-Cl$ bond angles are $95.67(9)^\circ$ and $119.12(4)^\circ$ respectively. The Zn(2) center is coordinated by one chlorine atom [$Zn(2)-Cl(3) = 2.2099(9)$ Å], two nitrogen atoms [$Zn(2)-N(1) = 2.047(3)$ Å, $Zn(2)-N(3) = 2.044(2)$ Å] from one rather distorted POPOP ligand and one slightly distorted POPOP ligand, and one oxygen atom [$Zn(2)-O(5) = 1.964(2)$ Å] of a carboxylate group. Unlike in **1** and **2**, carboxyl groups, arising from the hydrolyzation of CH_3CN solvent, also coordinate with Zn atoms. There are also two crystallographically different POPOP ligands in the asymmetric unit: one is strongly distorted, with dihedral angles between the 5-phenyloxazolyl ring and the center benzene ring plane of 37.64° and 9.36° respectively,

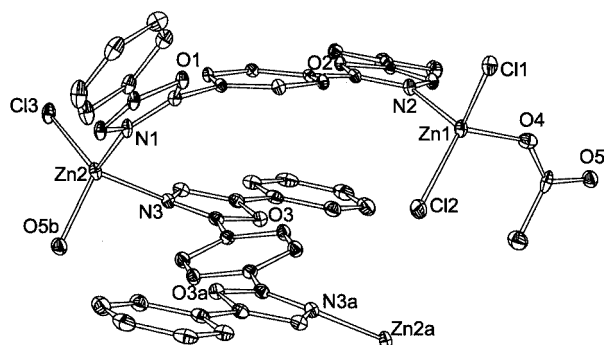


Figure 5. ORTEP drawing of $\{Zn_2(CH_3COO)(POPOP)_{1.5}Cl_3\}_n$ (**3**)

and coordinates to two different Zn centers. The second is slightly distorted, with dihedral angles of 25.91° , and coordinates to two symmetric relative Zn centers. In other words, each carboxyl group coordinates to two Zn atoms and each strongly distorted POPOP ligand provides two N atoms to coordinate with Zn atoms to form an interesting infinite chain. In addition, the slightly distorted POPOP ligands bridge two adjacent chains to produce the final ladder-like double-chain (Figure 6).

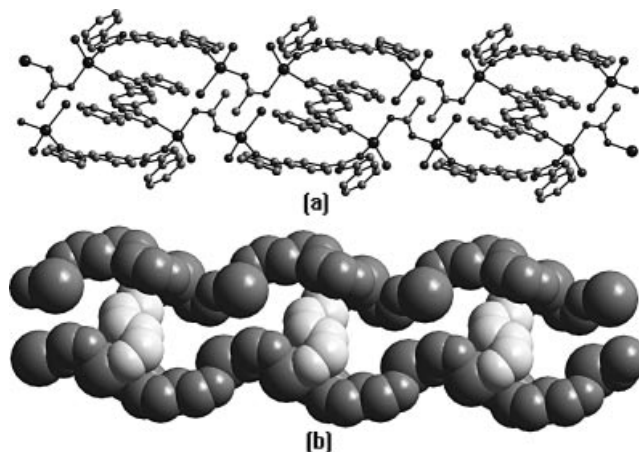


Figure 6. (a) 1D ladder-like double-chain structure in **3**; (b) space-filling plots of the 1D ladder-like double-chain (for clarity, only the backbone is shown)

The above structural descriptions show that temperature plays a crucial role in the formation of the complexes. A water molecule coordinates to Zn in complex **1**, but no water molecule exists in **2** or **3**. However, with increasing temperature some CH_3CN solvent was hydrolyzed to form CH_3COO^- ligands in **3**. At the same time, the co-planar POPOP ligand also becomes distorted on going from complex **1** to **3**. Complexes **1–3** show increasing condensation and density at higher synthesis temperatures. Increasing temperatures also lead to changes in topological structure and favor higher overall dimensionality. The overall dimensionality of structures **1–3** also increases – from discrete at $100^\circ C$, to a 1D chain at $110^\circ C$, and a 1D double-chain at $150^\circ C$, respectively. The successful preparation of **1–3** reveals a clear relationship between synthesis temperature and structure.

Thermogravimetric Analysis (TGA)

The stability of **2** and **3** was examined by thermogravimetric analysis (TGA), which revealed an onset temperature for decomposition above $330^\circ C$. Such stabilities make the compounds potential candidates for practical applications.

Photoluminescence Properties

Emission spectra of complexes **1–3** in the solid state at room temperature show intense emissions at 452 nm ($\lambda_{ex} = 396$ nm) for **1**, 452 nm ($\lambda_{ex} = 396$ nm) for **2** and 460 nm ($\lambda_{ex} = 397$ nm) for **3**. To understand the nature of these

emission bands, we analyzed the photoluminescence properties of the POPOP ligand and found that the strongest emission peak for POPOP is at 448 nm, which is near to the above values. Notably, the four values do differ slightly, which may be attributable to ligand center charge transfer. Similar enhancements of intraligand fluorescence occur in (polypyridyl)metal polymers.^[25–26] Especially, the emission intensity is strongest in complex **3**, and its emission peak is also slightly larger, which may be ascribed to the presence of (CH₃COO) coordinated to Zn atoms.

Conclusion

We have successfully combined Zn metal and POPOP {1,4-bis[2-(5-phenyloxazolyl)]benzene} to obtain three novel zinc–POPOP coordination polymers, ZnCl₂(H₂O)·(POPOP)·(POPOP) (**1**), [ZnCl₂(POPOP)]_n (**2**), and {Zn₂(CH₃COO)(POPOP)_{1.5}Cl₃}_n (**3**), with different coordination architectures under solvothermal reactions. We have also investigated the photoluminescence properties of POPOP with a d¹⁰ transition metal. Incorporation of Zn^{II} complexes into the π -electron system of a conjugated molecule revealed a clear relationship between synthesis temperature and structure.

Experimental Section

General Remarks: All syntheses were performed in poly(tetrafluoroethylene)-lined stainless steel autoclaves under autogenous pressure. Reagents were purchased commercially and were used without further purification. Elemental analyses of C and H were performed with an EA1110 CHNS-O CE elemental analyzer. IR (KBr pellets) spectra were recorded with a Nicolet Magna 750FT-IR spectrometer. Fluorescent data were collected with an Edinburgh

FLS920 TCSPC system. TGA analyses were carried under nitrogen with an STA449C integration thermal analyzer.

ZnCl₂(H₂O)(POPOP)·(POPOP) (1**):** A mixture of POPOP (0.036 g, 0.10 mmol), ZnCl₂·4H₂O (0.10 g, 0.48 mmol) and CH₃CN (10 mL) was heated in a stainless steel reactor with a Teflon liner at 100 °C for 72 h. After cooling, within 24 h yellow crystals of **1** were obtained in 68% yield (0.030 g based on POPOP). C₄₈H₃₄Cl₂N₄O₅Zn (883.06): calcd. C 65.45, H 3.89, N 6.36; found C 65.29, H 3.76, N 6.14. IR (KBr): $\tilde{\nu}$ = 3514 (m), 3124 (w), 1617 (m), 1594 (m), 1557 (w), 1483 (s), 1449 (w), 1416 (m), 1281 (m), 1151 (m), 1130 (w), 1025 (w), 948 (s), 849 (m), 827 (w), 762 (s), 722 (s), 688 (s), 564 (w), 492 (w) cm^{−1}.

[ZnCl₂(POPOP)]_n (2**):** A mixture of POPOP (0.036 g, 0.10 mmol), ZnCl₂·4H₂O (0.10 g, 0.48 mmol) and CH₃CN (10 mL) was heated in a stainless steel reactor with a Teflon liner at 110 °C for 72 h. After cooling, within 24 h yellow crystals of **2** were obtained in 65% yield (0.033 g based on POPOP). C₄₈H₃₂Cl₄N₄O₄Zn₂ (500.68): calcd. C 57.83, H 3.24, N 5.62; found C 57.58, H 3.15, N 5.64. IR (KBr): $\tilde{\nu}$ = 3454 (w), 3123 (w), 1649 (m), 1617 (m), 1595 (m), 1557 (m), 1483 (s), 1449 (w), 1416 (m), 1351 (w), 1271 (w), 1150 (s), 1130 (w), 1104 (w), 1027 (w), 981 (w), 947 (s), 868 (w), 849 (m), 829 (m), 762 (s), 722 (s), 687 (s), 659 (w), 564 (w), 492 (w) cm^{−1}.

{Zn₂(CH₃COO)(POPOP)_{1.5}Cl₃}_n (3**):** A mixture of POPOP (0.036 g, 0.10 mmol), ZnCl₂·4H₂O (0.10 g, 0.48 mmol) and CH₃CN (10 mL) was heated in a stainless steel reactor with a Teflon liner at 150 °C for 72 h. After cooling, within 24 h yellow crystals of **3** were obtained in 65% yield (0.037 g based on POPOP). C₃₈H₂₇Cl₃N₃O₅Zn₂ (842.72): calcd. C 54.42, H 3.25, N 5.01; found C 54.45, H 3.20, N 5.20. IR (KBr): $\tilde{\nu}$ = 3466 (w), 3123 (w), 3090 (w), 1615 (m), 1593 (m), 1559 (s), 1480 (s), 1415 (m), 1363 (w), 1239 (w), 1149 (m), 1124 (w), 1025 (w), 947 (s), 872 (w), 850 (m), 776 (m), 765 (s), 723 (s), 689 (s), 661 (w), 610 (w), 532 (w), 495 (w) cm^{−1}.

X-ray Crystallographic Study: X-ray intensities of complexes **1–3** were collected with a Bruker Smart CCD diffractometer equipped with graphite-monochromated Mo-K α radiation (λ = 0.71073 Å)

Table 1. Crystallographic data for complexes **1–3**

	1	2	3
Empirical formula	C ₄₈ H ₃₄ Cl ₂ N ₄ O ₅ Zn	C ₂₄ H ₁₆ Cl ₂ N ₂ O ₂ Zn	C ₃₈ H ₂₇ Cl ₃ N ₃ O ₅ Zn ₂
Formula mass	883.06	500.68	842.72
Crystal size [mm]	0.65 × 0.45 × 0.25	0.40 × 0.35 × 0.25	0.25 × 0.20 × 0.15
Crystal color	yellow	yellow	yellow
Crystal system	triclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	9.8858(10)	9.011(3)	12.264
<i>b</i> [Å]	12.8480(14)	10.790(3)	12.937
<i>c</i> [Å]	16.8502(13)	12.288(3)	13.399
α [°]	89.927(3)	64.604(6)	62.833(10)
β [°]	84.235(4)	89.571(9)	69.486(13)
γ [°]	69.942(5)	83.515(8)	75.666(14)
<i>V</i> [Å ³]	1999.0(3)	1071.3(5)	1761.6
<i>D</i> _{calcd.} [g·cm ^{−3}]	1.467	1.552	1.589
λ (Mo-K α) [Å]	0.71073	0.71073	0.71073
<i>Z</i>	2	2	2
<i>T</i> [K]	130.15	130.15	130.15
μ (Mo-K α) [mm ^{−1}]	0.803	1.420	1.638
<i>F</i> (000)	908	508	854
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0283, 0.0752	0.0234, 0.0625	0.0410, 0.1042
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0307, 0.0772	0.0250, 0.0641	0.0464, 0.1081

at 130.15 K. Empirical absorption corrections were applied to the data using the SADABS program. Structures were solved by the direct method and refined by full-matrix least squares on F^2 using the SHELXTL-97 program. All non-hydrogen atoms were refined anisotropically. A summary of crystallographic data and other pertinent information for **1–3** (Table 1) and selected bond lengths and angles (Table 2) are given here. CCDC-244407 to -244409 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].

Table 2. Selected bond lengths [Å] and angles [°] for **1–3**

Complex 1

Zn(1)–OW1	2.0193(10)	Zn(1)–Cl(2)	2.2124(4)
Zn(1)–N(1)	2.0629(11)	Zn(1)–Cl(1)	2.2238(4)
OW1–Zn(1)–N(1)	106.57(4)	OW1–Zn(1)–Cl(1)	108.72(4)
OW1–Zn(1)–Cl(2)	107.60(3)	N(1)–Zn(1)–Cl(1)	102.54(3)
N(1)–Zn(1)–Cl(2)	112.95(3)	Cl(2)–Zn(1)–Cl(1)	117.871(15)

Complex 2

Zn(1)–N(2)	2.0587(12)	Zn(1)–Cl(2)	2.2114(7)
Zn(1)–N(1)	2.0596(12)	Zn(1)–Cl(1)	2.2258(6)
N(2)–Zn(1)–N(1)	96.73(5)	N(2)–Zn(1)–Cl(1)	113.08(3)
N(2)–Zn(1)–Cl(2)	105.96(3)	N(1)–Zn(1)–Cl(1)	109.56(3)
N(1)–Zn(1)–Cl(2)	114.89(3)	Cl(2)–Zn(1)–Cl(1)	115.15(2)

Complex 3

Zn(1)–O(4)	2.014(3)	Zn(2)–O(5) ^[a]	1.965(2)
Zn(1)–N(2)	2.103(3)	Zn(2)–N(1)	2.045(3)
Zn(1)–Cl(1)	2.2154(10)	Zn(2)–N(3)	2.046(3)
Zn(1)–Cl(2)	2.2162(11)	Zn(2)–Cl(3)	2.2101(10)
O(4)–Zn(1)–N(2)	95.71(10)	O(5) ^[a] –Zn(2)–N(1)	117.71(11)
O(4)–Zn(1)–Cl(1)	106.04(7)	O(5) ^[a] –Zn(2)–N(3)	97.14(10)
N(2)–Zn(1)–Cl(1)	109.83(8)	N(1)–Zn(2)–N(3)	103.10(10)
O(4)–Zn(1)–Cl(2)	113.99(7)	O(5) ^[a] –Zn(2)–Cl(3)	114.91(8)
N(2)–Zn(1)–Cl(2)	109.59(8)	N(1)–Zn(2)–Cl(3)	112.06(8)
Cl(1)–Zn(1)–Cl(2)	119.14(4)	N(3)–Zn(2)–Cl(3)	109.79(8)

^[a] Symmetry transformations used to generate equivalent atoms: $x, y - 1, z$.

Supporting Information: The Supporting Information (see also the footnote on the first page of this article) contains TGA analyses for complexes **2** and **3**, IR and solid-state emission spectra of the three complexes, and the 3D packing structures of **2** and **3**.

Acknowledgments

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