Anion-directed assembly of supramolecular zinc(II) halides with N,N'-bis-4-methyl-pyridyl oxalamide

Biing-Chiau Tzeng,*[a] Bo-So Chen,[a] Shih-Yang Lee,[a] Wei-Hsin Liu,[a] Gene-Hsiang Lee[b] and Shie-Ming Peng[b]

[a] Department of Chemistry and Biochemistry, National Chung Cheng University, 168, University Rd., Min-Hsiung, Chia-Yi, Taiwan 621
[b] Department of Chemistry, National Taiwan University, 1, Sec. 4, Roosevelt Road, Taipei, Taiwan 106

We report here the supramolecular structures and solid state luminescence of zinc(II) halides with N,N'-bis-4-methyl-pyridyl oxalamide (**L**), where the supramolecular assembly formed is dependent on the halide, and led to the formation of one-dimensional coordination polymers for Cl ($[ZnCl_2(L)]_n$) and Br ($[ZnBr_2(L)]_n$) or a discrete macrocycle for I ($[ZnI_2(L)]_2$), respectively. The rectangular structure of iodo compounds with pyridyl amide **L** shows an interesting nanotube framework built from $\pi \cdots \pi$ interactions in combination with hydrogen bonding. To our knowledge, these are rare examples of the anion-directed assembly of supramolecular structures. The low energy emission at *ca.* 500 nm for $[ZnI_2(L)]_2$ is assigned to a ligand-to-metal charge-transfer (LMCT) transition.

Introduction

The widespread use of the coordinative bond approach in the construction of supramolecular coordination compounds with one-, two- and three-dimensional frameworks by self-assembly is well established.[1] Their functionalities[2] have also been reported recently. Moreover, it is possible, in parallel, to use highly directional hydrogen bonds as a means of controlling self-assembly in supramolecular systems. A variety of discrete and a wide range of infinite coordination architectures with hydrogen-bonded frameworks have been achieved in the last decade.[3,4] In this regard, the combination of the coordinative bond approach, hydrogen bonding and/or other weak interactions has recently been recognized as a very powerful and versatile strategy in supramolecular design and materials synthesis.[5]

Organic amides have proved to be very useful in self-assembly through hydrogen bonding, and the assembled products have relevance to biological systems. Most remarkably, cyclic oligoamides can give interesting nanotube frameworks through inter-ring NH···O=C hydrogen bonding, as reported by Ghadiri *et al.*[6] In this context, it prompted us to initiate a study on metal-containing cyclic amide systems which feature cyclic peptides that may be expected to self-assemble to give interesting supramolecular or nanotube structures. Puddephatt *et al.*[7] first reported an interesting molecular triangle containing Pt(II) ions as corners and 4-NC₅H₄C(=O)NH-4-C₅H₄N units as edges, leading to a dimer of triangles formed through NH···O=C hydrogen bonding as well as Pt···O=C interactions. Although this Pt(II) complex cannot form nanotubes in the solid state, it opened up a possible opportunity for the formation of metal-containing cyclic peptides that have nanotube frameworks with functional properties.[6]

Dipyridyl amide ligands have been designed and synthesized for purposes in crystal engineering, and amide–amide hydrogen bonding has been successfully demonstrated to increase supramolecular complexity.[8] So far, only one example regarding the Pt(IV) hydrogen-bonded polymer with N,N'-bis-4-methylpyridyl oxalamide (**L**) has been reported,[9] and thus it was chosen as a building block for the construction of supramolecular coordination compounds in this work. Because it has a flexible backbone containing bifunctional binding sites (both pyridyl groups), as well as a strong capacity for hydrogen bonding of the amide groups, it is anticipated to play a vital role in the assembly of supramolecular coordination compounds. We report here the supramolecular structures and solid state luminescence of zinc(II) halides with N,N'-bis-4-methyl-pyridyl oxalamide, where the supramolecular assembly is dependent on the halide, leading to the formation of either a one-dimensional coordination polymer or a discrete macrocycle. To our knowledge, these are rare examples regarding anion-directed assembly of supramolecular zinc(II) halides with N,N'-bis-4-methyl-pyridyl oxalamide.

Experimental

General information

All solvents for syntheses (analytical grade) were used without further purification, and the metal salts (ZnCl₂, ZnBr₂, and ZnI₂) were commercially available. N,N'-bis-4-methylpyridyl oxalamide was prepared by the literature method.[9] NMR: Bruker DPX 400 MHz; deuterated solvents were used with the usual standards. MS: Positive ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Steady state emission spectra were recorded on a SPEX Fluorolog-2 spectrophotometer.

Synthesis of $[ZnCl_2(L)]_n$ (1), $[ZnBr_2(L)]_n$ (2) and $[ZnI_2(L)]_2$ (3)

1·2CH₃OH: ZnCl₂ (14 mg, 0.1 mmol) dissolved in CH₃OH (7 cm⁻³) was carefully layered onto an aqueous solution of **L** (27 mg, 0.1 mmol, dissolved in 7 cm⁻³ DMF). Colorless crystals

L
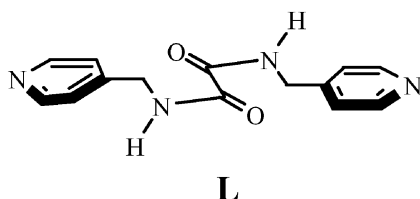
Table 1 Crystallographic data for $\mathbf{1} \cdot 2CH_3OH$, $\mathbf{2} \cdot 2CH_3OH$ and $\mathbf{3} \cdot CH_3OH$

	$\mathbf{1} \cdot 2CH_3OH$	$\mathbf{2} \cdot 2CH_3OH$	$\mathbf{3} \cdot CH_3OH$
Empirical formula	$C_{16}H_{22}Cl_2N_4O_4Zn$	$C_{16}H_{22}Br_2N_4O_4Zn$	$C_{29}H_{32}I_4N_8O_5Zn_2$
Formula weight	470.65	559.57	1211.01
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	$Pnna$	$Pnna$	$P\text{-}1$
$a/\text{Å}$	7.4152(2)	7.5852(11)	8.2323(1)
$b/\text{Å}$	11.8222(3)	12.1545(17)	10.9481(1)
$c/\text{Å}$	22.7057(7)	22.8290(30)	12.0332(2)
$\alpha/°$	90	90	105.9078(10)
$\beta/°$	90	90	96.5427(9)
$\gamma/°$	90	90	102.9071(8)
$V/\text{Å}^3$, Z	1990.47(10), 4	2104.7(5), 4	998.73(2), 1
$F(000)$/e	824	968	588
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	1.513	4.974	4.341
T/K	150(1)	295(2)	150(1)
Reflections collected	11990	12020	14409
Independent reflections	2294 ($R_{int} = 0.055$)	2547 ($R_{int} = 0.024$)	4568 ($R_{int} = 0.038$)
Observed reflections			
$Fo \geq 2\sigma(Fo)$	2294	2547	4568
Refined parameters	122	125	229
Goodness-of-fit on F^2	1.103	1.033	1.044
R^a, $R_w{}^b$ ($I \geq 2\sigma(I)$)	0.050, 0.115	0.033, 0.080	0.029, 0.072
R^a, $R_w{}^b$ (all data)	0.089, 0.129	0.048, 0.088	0.034, 0.074
ρ_{fin} (max/min)/e Å^{-3}	0.435/−0.391	0.713/−0.370	0.821/−1.168

^{a} $R = \Sigma F_o - F_c/\Sigma F_o$. ^{b} $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{\frac{1}{2}}$.

were obtained within 1 week in *ca.* 71% yield. δ_H (400 MHz, DMSO-d$_6$, 25 °C): 4.36 (4 H, d, C*H*$_2$), 7.27–8.48 (8 H, d, py) and 9.44 (2 H, t, N*H*). FT-IR (KBr): $\nu_{NH} = 3197$ and $\nu_{C=O} = 1691$ cm^{-1}. Found: C, 40.98; H, 3.88; N, 14.09. $C_{14}H_{14}Cl_2N_4O_2Zn$ requires C, 41.36; H, 3.47; N, 13.78%.
$\mathbf{2} \cdot 2CH_3OH$: This compound was prepared by a similar method to $\mathbf{1}$, except using ZnBr$_2$ instead of ZnCl$_2$, and the colorless crystals were obtained in a *ca.* 61% yield. δ_H (400 MHz, DMSO-d$_6$, 25 °C): 4.36 (4 H, d, C*H*$_2$), 7.26–8.48 (8 H, d, py) and 9.44 (2 H, t, N*H*). FT-IR (KBr): $\nu_{NH} = 3331$ and $\nu_{C=O} = 1694$ cm^{-1}. Found: C, 34.25; H, 2.98; N, 11.69. $C_{14}H_{14}Br_2N_4O_2Zn$ requires: C, 33.94; H, 2.85; N, 11.31%.
$\mathbf{3} \cdot CH_3OH$: This compound was also prepared by a similar method to $\mathbf{1}$, except using ZnI$_2$ instead of ZnCl$_2$, and the colorless crystals were obtained in a *ca.* 54% yield. MS (FAB): $m/z = 460$ ((M − (2 × I))/2, 100%). δ_H (400 MHz, DMSO-d$_6$, 25 °C): 4.36 (4 H, d, C*H*$_2$), 7.26–8.46 (8 H, d, py) and 9.43 (2 H, t, N*H*). FT-IR (KBr): $\nu_{NH} = 3321$ and $\nu_{C=O} = 1668$ cm^{-1}. Found: C, 28.13; H, 2.58; N, 10.09. $C_{28}H_{28}I_4N_8O_4Zn_2$ requires: C, 28.52; H, 2.39; N, 9.50%.

X-Ray crystallography†

Suitable single crystals were mounted on a glass capillary. Data collection was carried out on a Bruker SMART CCD diffractometer with Mo-Kα radiation at 150(1) K for $\mathbf{1} \cdot 2CH_3OH$ and $\mathbf{3} \cdot CH_3OH$, and at room temperature for $\mathbf{2} \cdot 2CH_3OH$, respectively. A preliminary orientation matrix and the unit cell parameters were determined from 3 runs of 15 frames each, each frame corresponding to a 0.3° scan in 15 s, followed by spot integration and least-squares refinement. Data were measured using an ω scan of 0.3° per frame for 20 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART[10] software and refined with SAINT[11] on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the

† CCDC reference numbers CCDC 269329, 269330 and 272141. See http://dx.doi.org/10.1039/b508293e for crystallographic data in CIF or other electronic format.

program SADABS.[12] The structure was solved by direct methods with the SHELX-93[13] program and refined by full-matrix least-squares methods on F^2 with SHEXLTL-PC v 5.03.[13] All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically-generated positions. Detailed data collection and refinement parameters of the complexes are summarized in Table 1.

Results and discussion

The dipyridyl-amide ligand N,N'-bis-4-methylpyridyl oxalamide has been chosen and synthesized here for the purposes of a crystal engineering study. The amide–amide hydrogen bonding has been successfully demonstrated to increase the supramolecular complexity of the Pt(IV) hydrogen-bonded polymer with N,N'-bis-4-methylpyridyl oxalamide,[9] where two N,N'-bis-4-methylpyridyl oxalamide ligands are *trans* to each other in an octahedral geometry. The Zn(II) ion favors a tetrahedral geometry, and this geometric preference is quite different from that of the octahedral Pt(IV) ion. This may result in a dramatically different structural motif due to the different contributions from the hydrogen bonding present in both Pt(IV) and Zn(II) complexes.

A methanolic solution of ZnX$_2$ (X = Cl, Br, I) was carefully layered onto a DMF solution of **L**, from where the colorless crystals of $\mathbf{1} \cdot 2CH_3OH$, $\mathbf{2} \cdot 2CH_3OH$ and $\mathbf{3} \cdot CH_3OH$ were obtained in medium yields (50–70%) within one week, respectively.

Description of crystal structures

$\mathbf{1}$, $\mathbf{2}$ and $\mathbf{3}$ have been isolated and their crystal structures determined by X-ray diffraction studies.† The chloro and bromo complexes are isomorphous and form one-dimensional coordination polymers, with tetrahedral Zn(II) centers coordinating to two halides (Cl or Br) and two bridging ligands, **L**, as shown in Fig. 1(a). Interestingly, the cavity of *ca.* 8.5 × 8.5 Å^2 is formed by the two interwoven chains and further stacked to give a one-dimensional channel in Fig. 1(b) (void percentage: 41.6% for $\mathbf{1}$ and 43.4% for $\mathbf{2}$, calculated using Platon
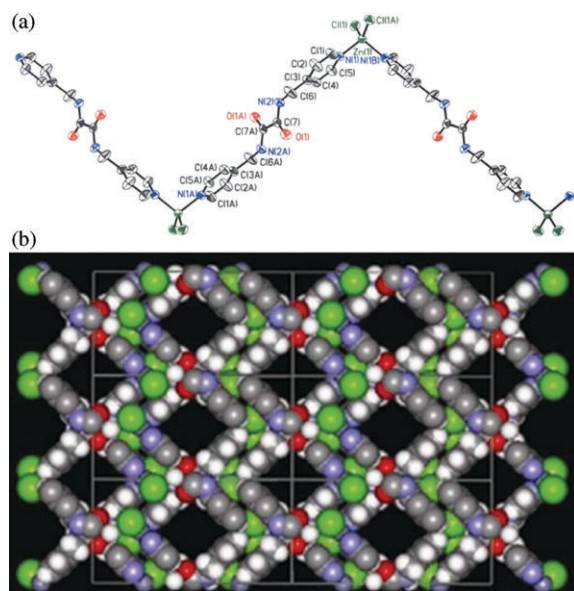
Fig. 1 (a) Molecular structure of complex **1**. ORTEP diagram showing 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Zn(1)–N(1) 2.039(3), Zn(1)–Cl(1) 2.232(1); N(1)–Zn(1)–Cl(1) 111.39(8). (b) The extended framework showing a one-dimensional channel structure with a dimension of *ca.* 8.5 × 8.5 Å^2 in the solid state.
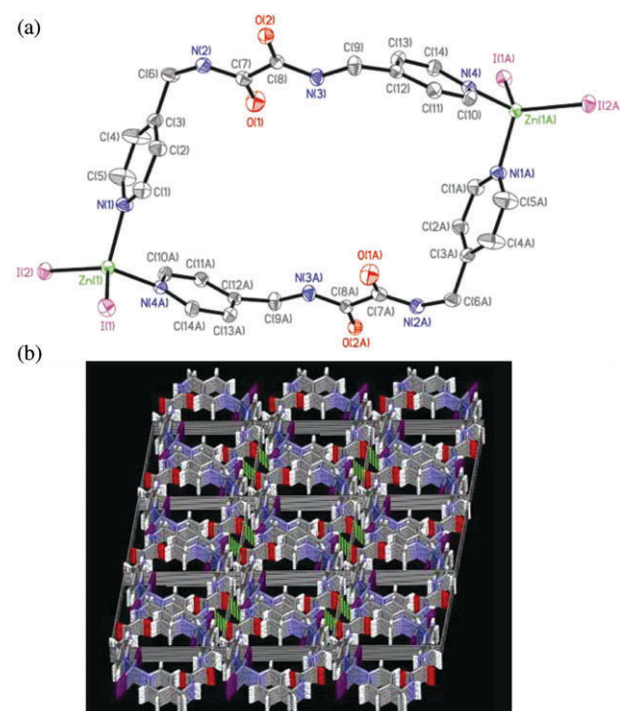

Fig. 2 (a) Molecular structure of complex **3**. ORTEP diagram showing 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Zn(1)–N(1) 2.059(3), Zn(1)–I(1) 2.5540(4), Zn(1)–I(2) 2.5506(4); N(1)–Zn(1)–I(1) 108.8(1), N(1)–Zn(1)–I(2) 109.5(1), I(1)–Zn(1)–I(2) 120.4(2). (b) The hydrogen-bonded extended framework showing a one-dimensional channel structure with a dimension of *ca.* 6.4 × 11.0 Å^2 in the solid state.

Graphics[14] upon removal of the solvated methanol). Four methanol molecules sit inside each cavity for **1** and **2**, and those in **1** are highly disordered. Two slightly slipped pyridyl rings of pyridyl amide groups show the shortest distances of 3.54 Å for **1** and 3.72 Å for **2** between the C(N) and C(N) atoms (the distances between the two centroids of the pyridyl rings and the dihedral angles between them are 3.989 Å/168.4° and 4.225 Å/164.2°, respectively), indicative of the presence of weak π···π interactions.[15] In addition, there are also some non-classical hydrogen bonds present in the solid state.[16] Thus, these interesting one-dimensional channel structures for **1** and **2** may be constructed by π···π interactions in combination with some weak hydrogen bonding.

Unlike those of **1** and **2**, the iodo analogue **3** surprisingly forms a distinct structural motif as a molecular rectangle, shown in Fig. 2(a). Furthermore, the rectangular cavity of *ca.* 6.4 × 11.0 Å^2 is stacked to give one-dimensional rectangular channels in the solid state, as shown in Fig. 2(b) (void percentage: 38.7% for **3** calculated using Platon Graphics[14] upon removal of the solvated methanol). Double hydrogen bonding interactions (N(3)–H(3A)···O(1): N(3)–H(3A) 0.860 Å, H(3A)···O(1) 2.224 Å, N(3)···O(1) 2.893(10) Å; N(3)–H(3A)···O(1) 134.5°) are observed in the solid state, and these are anticipated to be responsible for the one-dimensional rectangular channels. This is reminiscent of the novel nanotube frameworks for cyclic peptides reported by Ghadiri *et al.*,[6] where the amide–amide hydrogen bonding contributes to the formation of supramolecular nanotubes. Each rectangle encapsulates a disordered CH$_3$OH molecule inside the cavity. TGA analysis has been conducted to examine thermostability, with the framework being thermally stable up to 250 °C and the lattice remaining intact upon solvent removal. The weight loss of 2.17% is comparable to the calculated value of 2.61% for a CH$_3$OH molecule, and the X-ray powder diffraction pattern upon solvent removal at 200 °C is almost the same as the one before solvent removal. The shortest distance of 3.570 Å between the C(N) atoms of the parallel pyridyl rings of **3** (the distance between the centroids of two pyridyl rings is 3.837 Å) is suggestive of the presence of π···π interactions. Thus, the interesting nanotube framework for **3** is built from π···π interactions in combination with hydrogen bonding. Additionally, the dramatic structural motif of **3** may be due to the bigger

iodo atom, compared with chloro and bromo atoms, inducing a delicate stacking effect on the formation of different supramolecular structures. It is noted that supramolecular synthesis of different structural frameworks, *i.e.*, coordination polymers or macrocycles, from the same ligands is not uncommon,[7b,8a,17] but to our knowledge, the anion-directed assembly of supramolecular zinc(II) halides is rare yet represented by the examples reported here.

Solid state emission spectra

Fig. 3 shows the solid state emission spectra of **L** and **1**–**3** measured at room temperature. Upon photoexcitation at 350 nm, both **1** and **2** show high energy emissions with a maximum at *ca.* 395 nm, and **3** shows interesting dual emissions, with emission maxima at *ca.* 440 and 500 nm. Since **L** displays only a high energy maximum at *ca.* 440 nm, which is almost the same as the high energy one of **3**, ascribed to an intraligand transition. However, the high energy emissions at *ca.* 395 nm for **1** and **2** and the low energy one at *ca.* 500 nm for **3** are unlikely to be related to intraligand transitions. The significant red shift from **1** and **2** to **3** is tentatively assigned to a ligand-to-metal charge-transfer transition, since lower transition energies for an iodo-to-zinc(II) charge-transfer transition are known, compared to those of chloro- or bromo-to-zinc(II) transitions.[18] Nevertheless, it is still possible that these ligand-to-metal transitions mix with an intraligand transition.

Conclusion

The supramolecular coordination compounds of zinc(II) halides with *N,N'*-bis-4-methyl-pyridyl oxalamide have been isolated and their crystal structures determined by X-ray diffraction studies. The supramolecular assembly is dependent on the halide, leading to the formation of either one-dimensional coordination polymers for Cl and Br or a discrete macrocycle for I, respectively. These compounds all form channel struc-
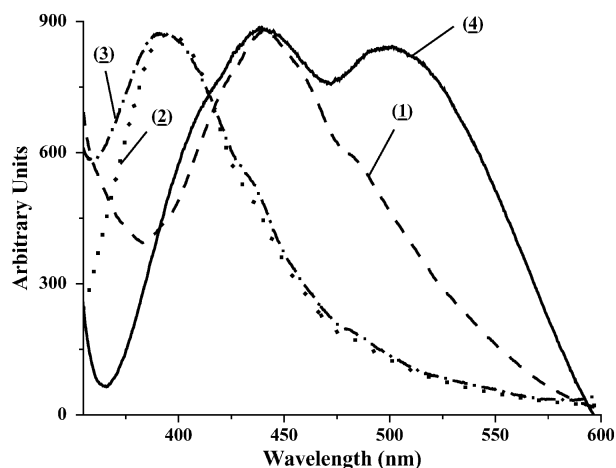
Fig. 3 The solid state emission spectra of **L** (<u>1</u>), **1** (<u>2</u>), **2** (<u>3</u>) and **3** (<u>4</u>) measured at room temperature with an excitation wavelength of 350 nm.

tures in the solid state with solvated methanol inside their cavities. Notably, **3** forms an interesting molecular rectangle which is reminiscent of the novel nanotube frameworks for cyclic peptides reported by Ghadiri *et al.*[6] To our knowledge, these are rare examples of the anion-directed assembly of supramolecular structures. Additionally, the solid state luminescence has also been studied for **1–3**, where **3** shows dual emissions with emission maxima at *ca.* 440 and 500 nm. The *ca.* 440 nm emission is ascribed to an intraligand transition, and the one at *ca.* 500 nm due to an iodo-to-zinc(II) charge-transfer transition. The channel structure and hydrogen bonding functions for the rectangular structure of **3** in the solid state, as well as its low energy excited state, are anticipated to hold potential as properties of new luminescent sensory materials.

Acknowledgements

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