One- and two-dimensional coordination polymers of zinc(II) with pyrazine. Solid state reactions and decomposition kinetics of the interconversion reactions

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The reaction of zinc(II) bromide with pyrazine yielded the two coordination polymers $[ZnBr_2(pyz)]$ **1** and $[ZnBr_2(pyz)_2]$ **2**. Crystal structures of these two compounds show that **1** is a 1-D zigzag chain polymer while **2** forms a regular square-grid (4,4) network. Adjacent grids in **2** are slipped in one direction so that the axial bromide ions on one layer project into the cavities of the grids in adjacent layers. The solid-state reaction of **1** with pyrazine yields **2**, and **2** in its turn is readily converted into **1** by heating. The activation energy of the latter process has been determined as 99.8 kJ mol^{-1}.

Introduction

The crystal engineering of solid-state materials is of ever-increasing interest to chemists and materials scientists alike.[1,2] Such is the importance of this field that a recent issue of *Dalton Transactions* was devoted to inorganic crystal engineering.[3] In recent years various workers have attempted to prepare new materials based on an understanding of the factors that determine crystal packing such as π–π stacking, hydrogen bonding or coordination bonding.[4–6] It has become apparent that coordination polymers of specific network topology may be prepared by the appropriate selection of metal nodes and multifunctional ligands. This approach has led to the preparation of a wide range of 1-D,[7] 2-D[8,9] and 3-D[10–12] networks. Linear bifunctional ligands predominate, and Zaworotko and coworkers have recently reviewed the formation of 2-D square grid structures formed with 4,4′-bipyridine[13] and described the puckered rectangular grids that are formed when 1,2-bis(4-pyridyl)ethane is used as ligand.[14] The network architecture obtained has been shown to depend on the choice of metal ion,[15] ligand functionality[11a,16] and even reaction solvent.[17] Phase transitions between polymorphs of organometallic compounds have recently been reviewed.[18] Other solid-state transitions which have been reported include interconversion reactions by exchange of ligands[19] or anions[20] and the formation of a hydrated complex by grinding the anhydrous material in ambient humidity.[21]

Of particular interest to us are the forces driving the formation of coordination polymers and the kinetic factors favouring the formation of one type of framework over another. In this article we report the formation and characterization of two coordination polymers, $[ZnBr_2(pyz)]$ **1** and $[ZnBr_2(pyz)_2]$ **2** (pyz = pyrazine). Both consist of the same metal node and ligand building units and we show here that each can be formed from the other by reversible solid-state reactions (Scheme 1). The kinetics of the reverse reaction, **2** ⟶ **1**, has been studied by isothermal thermogravimetry.

Results and discussion

Molecular structures of $[ZnBr_2(pyz)]$ and $[ZnBr_2(pyz)_2]$

The reaction of zinc(II) bromide with pyrazine results in the formation of two coordination polymers: $[ZnBr_2(pyz)]$ **1** and $[ZnBr_2(pyz)_2]$ **2**.

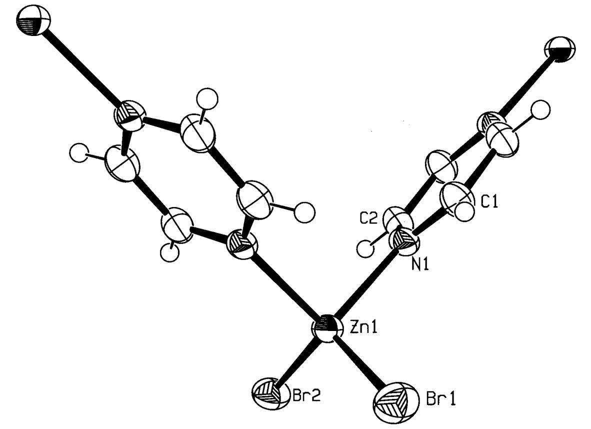
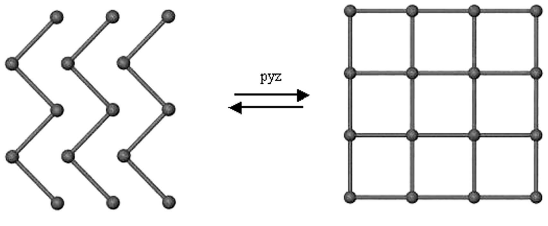
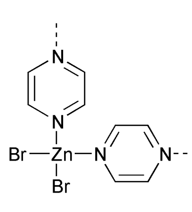


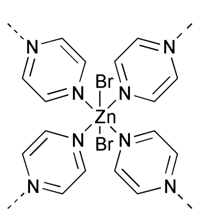
Fig. 1 The coordination geometry about the zinc(II) ion in the coordination polymer **1**. The atomic labelling used is shown with non-hydrogen atoms drawn with 50% probability displacement.



Scheme 1 A representation of the reversible solid-state reactions converting compound **1** into **2** and *vice versa*.



1



2

In **1** the Zn^{2+} ion (Fig. 1) is coordinated by two bromide anions and two pyrazine ligands in a tetrahedral arrangement. Bond lengths and angles around the zinc are listed in Table 1.

Each pyrazine ligand is coordinated to two zinc ions leading to the formation of infinite 1-D zigzag chains along [0 1 0] (Fig. 2). Zigzag 1-D chains are frequently observed when tetrahedral metal ions are involved.[7c–f]

The Zn^{2+} ion in compound **2** is coordinated by two bromide anions and four pyrazine ligands, giving rise to octahedral geometry (Fig. 3 and Table 1). The pyrazine ligands are disordered over two positions, with shared nitrogen atoms, with the mean planes of the two aromatic rings perpendicular. The carbon and hydrogen atoms of the two rings were refined with site occupancy factors of 52 and 48%. Each pyrazine ligand is coordinated to two zinc centres through the ring nitrogen atoms, leading to the formation of a square-grid (4,4) network[15a] (Fig. 4(a)). The metal coordination network is neutral and contains inner cavities with effective dimensions *ca.* 6 × 6 Å. The interplanar spacing is 6.6 Å; adjacent grids are slipped in one direction by approximately 10 Å so that the axial bromide ions on one layer project into the cavities of the grids in adjacent layers (Fig. 4(b)), leaving a pore size of *ca.* 2 × 2 Å. This packing arrangement precludes the inclusion of guest molecules. A related structure has been reported for $[CoCl_2(pyz)_2]$.[22]

Table 1 Selected bond lengths (Å) and angles (°) for compounds **1** and **2**

	1	**2**
Zn–Br	2.323(1); 2.330(1)	2.582(1)
Zn–N	2.084(4)	2.210(2)
Br–Zn–Br	122.1(1)	180
N–Zn–Br	108.2(1); 109.7(1)	90.3(2); 89.7(2)
N–Zn–N	95.59(1)	179.2(1); 89.9(1)

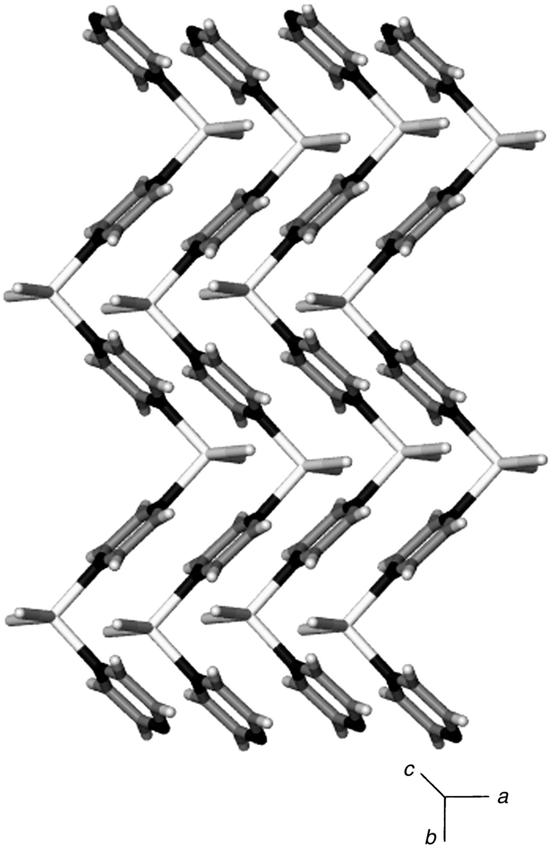


Fig. 2 View of the structure of $[ZnBr_2(pyz)]$ showing the 1-D zigzag chains.

Solid state reaction, 1 ⟶ 2

Stirring a mixture of $ZnBr_2$ and pyrazine (1 : 4) overnight in ethanol produced a crystalline powder, which microanalysis indicated was compound **1**. X-Ray powder diffraction confirmed that **1** had been formed (Fig. 5(a) shows the measured XRPD pattern *vs.* that calculated for the crystal structure of **1**). A 1 : 1 mixture of this powder and solid pyrazine was ground together for approximately 30 minutes. The resulting powdered product was analysed by XRPD and thermal analysis (microanalysis results could be misleading; a physical mixture of **1** and pyrazine would give the same results as a new compound). Both indicated that the product was **2** (see Fig. 5(b) for XRPD patterns). This reaction requires the additional coordination of two bridging pyrazine ligands to each zinc ion. The change in coordination geometry to octahedral causes the chains to

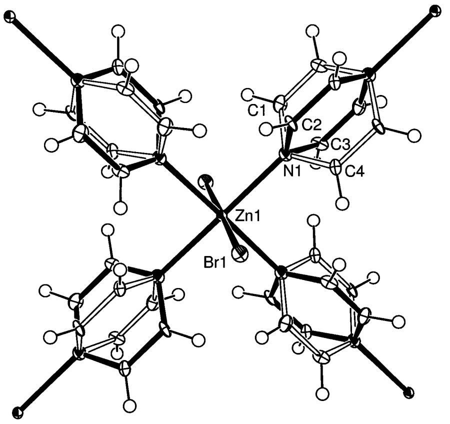


Fig. 3 The geometry about the zinc ion in the coordination polymer **2**. Details as in Fig. 1.

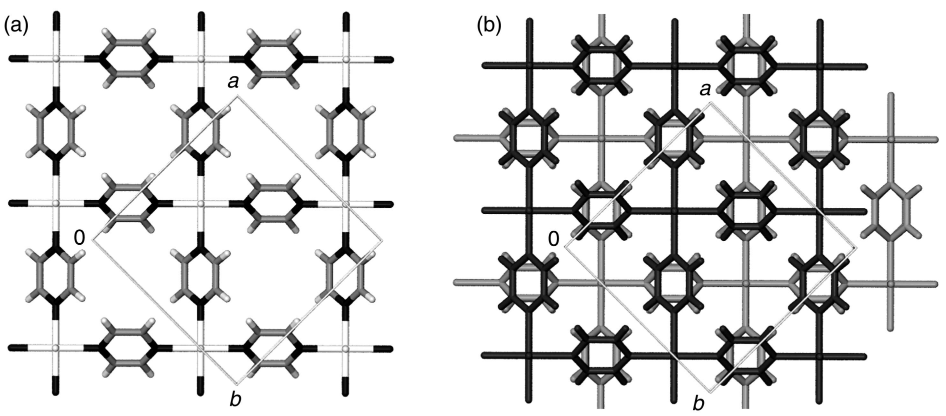


Fig. 4 (a) 2-Dimensional grids formed in compound **2**. For clarity, only one orientation of the pyrazine rings is shown. (b) Packing of grids along [0 0 1], showing the penetration of bromide ions into the 2-D cavities.

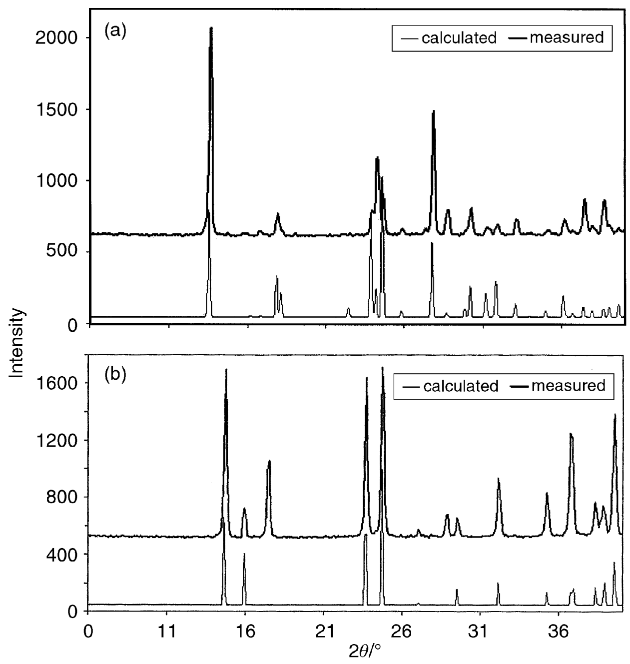


Fig. 5 (a) XRPD (experimental and calculated) for compound **1**. (b) XRPD of the solid state reaction product (measured) *vs.* calculated from the crystal structure of compound **2**. Three extraneous peaks appear in the measured pattern, which correspond to unchanged pyrazine.

straighten and link each other into the square-grid network described above.

Decomposition kinetics, $\mathbf{2} \longrightarrow \mathbf{1}$

The reverse reaction of that described above is the loss of a pyrazine ligand from compound **2** to form **1**. This reaction was followed by isothermal thermogravimetry at a number of temperatures in the range 85–110 °C and the activation energy of the reaction was determined. For the release of one pyrazine ligand from **2** the best kinetic model was found to be the contracting area deceleratory model (R2) with $f(\alpha) = 1 - (1 - \alpha)^{\frac{1}{2}}$. The data were isokinetic, so that the Arrhenius equation could be applied.[23] This gave an activation energy, E_a, of 99.8 kJ mol^{-1} for $\mathbf{2} \longrightarrow \mathbf{1}$. This value compares well with activation energies calculated for decomposition reactions of metal–ligand complexes.[24]

Conclusion

Two coordination polymers can be formed by the combination of zinc(II) and pyrazine: a 1-D zigzag chain, **1**, or the 2-D square-grid (4,4) network, **2**. **1** is readily converted into **2** by means of a simple solid state mixing of **1** with pyrazine. Heating of **2** results in its conversion into **1**. Either of these processes requires the change of coordination geometry about the zinc(II) ion, from tetrahedral to octahedral and *vice versa*. The results we have obtained here should readily be expandable to larger coordination architectures, and we are actively investigating several such systems.

Experimental

Preparation of complexes

$ZnBr_2$ and pyrazine were of reagent grade and used as received, without further purification.

[ZnBr$_2$(pyz)] 1. In a typical reaction, 0.016 g $ZnBr_2$ (0.072 mmol) was added to pyrazine (0.025 g, 0.031 mmol) and dissolved in 6 cm^3 ethanol. The solution was allowed to evaporate at 10 °C until crystallization occurred (Found: C, 16.39; H, 1.13; N, 9.18%. $C_4H_4Br_2N_2Zn$ requires C, 15.74; H, 1.32; N, 9.18%).

Table 2 Crystal data and refinement parameters for compounds **1** and **2**

	1	2
Molecular formula	$C_4H_4Br_2N_2Zn$	$C_8H_8Br_2N_4Zn$
M	305.28	385.37
T/K	298	173
λ/Å	0.7107	0.7107
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/m$	$Ccca$
a/Å	6.0068(4)	10.1904(4)
b/Å	9.9518(8)	10.1981(6)
c/Å	6.9936(6)	11.1516(7)
β/°	110.472(5)	
V/Å^3	391.66	1158.90
Z	2	4
Reflections collected	2012	3623
Independent reflections	987 (R_{int} = 0.074)	675 (R_{int} = 0.062)
Final $R1$, $wR2$ indices		
($I > 2\sigma I$)	0.0677, 0.1739	0.0301, 0.0737
(all data)	0.0758, 0.1864	0.0451, 0.0841

A microcrystalline sample of compound **1** was prepared by dissolving a sample of $ZnBr_2$ (0.28 g, 1.25 mmol) and pyrazine (0.40 g, 5.0 mmol) in 30 cm^3 of ethanol. The solution was stirred overnight at a slightly elevated temperature. The resulting creamy white powder was filtered off and allowed to dry in air at room temperature (Found: C, 15.84; H, 1.21; N, 9.02%).

[ZnBr$_2$(pyz)$_2$] 2. A sample of $ZnBr_2$ (0.023 g, 0.10 mmol) and pyrazine (0.032 g, 0.40 mmol) was dissolved in ethanol (5 cm^3) and allowed to evaporate at room temperature. A single large, pale yellow crystal of compound **2** was isolated (Found: C, 25.21; H, 1.73; N, 13.83%. $C_8H_8Br_2N_4Zn$ requires C, 24.93; H, 2.09; N, 14.54%).

2 was also prepared from compound **1** by a solid state reaction: 0.039 g (0.49 mmol) pyrazine was added to 0.150 g (0.49 mmol) of powdered **1** (prepared as described above). The mixture was shaken in a WIG-L-BUG for 30 min at room temperature. The resulting compound was analysed using XRPD.

Crystallography

Crystal data and data collection parameters are summarized in Table 2. Crystals were mounted on a glass fibre using paratone oil. **2** was cooled on the diffractometer using an Oxford Cryostream low temperature attachment. Crystallographic measurements were carried out on a Nonius KappaCCD diffractometer equipped with graphite monochromated Mo-Kα radiation using φ rotations with 1° frames and a detector to crystal distance of 35 mm. Integration was carried out by the program DENZO-SMN.[25a] Data sets were corrected for Lorentz and polarization effects and for absorption by the program Scalepack.[25b] Both structures were solved using the direct methods option in SHELXS 97 and developed using least-squares refinement and Fourier difference synthesis in SHELXL 97.[26] All non-hydrogen atoms were refined anisotropically; hydrogens on the pyrazine groups were fixed in idealized positions and allowed to ride with thermal parameters 1.2 times those of their parent carbons. The pyrazine rings in compound **2** were disordered and modelled using two sets of positions with site occupancies which refined to 52 and 48%. **2** crystallizes in the orthorhombic space group $Ccca$, with $a \approx b$. Analysis of the reflections of the $hk2$ and $hk3$ layers exhibited mm symmetry, which confirmed the orthorhombic (rather than tetragonal) symmetry of this structure. The X-SEED interface[27] was used on an IBM-PC compatible personal computer to carry out these computations and to generate packing diagrams using

POV-Ray.[25c] Diagrams were generated using ORTEP-III for Windows.[28] The calculated XRPD patterns were generated using Lazy-Pulverix.[29]

CCDC reference numbers 154178 and 154179.

See http://www.rsc.org/suppdata/dt/b0/b009771n/ for crystallographic data in CIF or other electronic format.

Instrumental techniques

Microanalyses were performed in duplicate on a Fisons Elemental Analyser 1108. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed using Perkin-Elmer Series 7 instruments in a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Sample masses were between 2 and 5 mg; an open platinum pan was used for TG; DSC was performed using a vented aluminium pan. On heating, **2** loses mass between 100 and 160 °C (observed mass loss 19.7%, calculated for one pyrazine 20.8%) to form **1**. This mass loss in the TG corresponds to a broad endotherm in the DSC with onset temperature of 95.4 °C. Above 160 °C **1** is stable until it begins to decompose at approximately 260 °C.

X-Ray powder diffraction (XRPD) was carried out on a Philips PW1752/00 diffractometer using Cu-Kα radiation ($\lambda = 1.5418$ Å). The powdered sample was ground to obtain a uniform particle size and loaded into an aluminium tray; the surface was cut to avoid preferred orientation of particles.

Decomposition kinetics

Isothermal TG was performed on compound **2** at various temperatures in the range 85–110 °C. Each TG curve was converted into an extent of reaction (α) *vs.* time curve where $\alpha = (m_i - m_t)/(m_i - m_f)$, m_i = initial mass, m_f = final mass and m_t = mass at time t. Various kinetic models, of the form $f(\alpha) = kt$, were fitted to the α *vs.* time data and the model for which $f(\alpha)$ was linear over the largest range of α was chosen as the best-fit model.

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