DALTON
FULL PAPER

Syntheses and crystal structures of the dimer [{Zn(SPh)$_2$(bpy)}$_2$(μ-bpy)] and two forms of the zigzag co-ordination polymer [{Zn(SPh)$_2$(μ-bpy)}$_n$], (bpy = 4,4′-bipyridyl)

Jeyagowry T. Sampanthar and Jagadese J. Vittal *

Department of Chemistry, National University of Singapore, Kent Ridge, 119 260, Singapore.
E-mail: chmjjv@nus.edu.sg

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The reaction between Zn(SPh)$_2$ and bpy proceeded through the polymer intermediate [{Zn(SPh)$_2$(μ-bpy)}$_n$] to form the dimer [{Zn(SPh)$_2$(bpy)}$_2$(μ-bpy)]. The isolation of the products depended on the crystallisation chemistry, *i.e.* the nature of the solvents, reaction time and method of preparation (diffusion or evaporation techniques). The dimer was isolated from DMF–THF or DMF–THF–DMSO by the evaporation method when the ratio of Zn(SPh)$_2$: bpy was 1 : (1.5–4.0). A one dimensional zigzag co-ordination polymer was isolated from the same reactants by the diffusion method, from a three layer system containing Zn(SPh)$_2$ in DMF and/or DMSO, bpy in CH_2Cl_2, $CHCl_3$, MeCN, MeOH, THF or acetone and Et_2O as the top layer. In the diffusion method two forms of co-ordination polymers, namely solvated and unsolvated [{Zn(SPh)$_2$(μ-bpy)}$_n$], were obtained depending on the concentration of CH_2Cl_2 in the reaction mixture. The crystalline products were structurally characterised by X-ray crystallography.

Introduction

Factors influencing the formation of co-ordination polymers are not well understood. For a simple bifunctional ligand 4,4′-bipyridyl (bpy) the metal to ligand ratio is important in the construction of novel architectures[1] such as linear, zigzag chains, square grids, diamondoid, honeycomb, T-shaped, ladder, brick wall, *etc*. Various other factors like the nature of the metal ions (co-ordination number and geometry)[2] and the counter anions (shape, size and charge)[3] may also influence the formation of one structure over the other. Experimental conditions such as the choice of the solvent,[4] concentration, temperature,[5] pH of the solution,[6] *etc*. can add to the complexity of the problem and variation of these may lead to polymorphism.[7] Very recently, two papers have reported the important role that solvents may play in the formation of molecular architectures.[8,9] In the present work we report the influence of crystallisation chemistry on the nature of products formed between Zn(SPh)$_2$ and bpy. Factors studied include the nature of the solvents used, concentration, reaction time and method used for synthesis (diffusion, evaporation techniques, *etc*.). We also present the crystal structures of the dimer [{Zn(SPh)$_2$(bpy)}$_2$(μ-bpy)] **1**, and two forms ('pseudo polymorphs') of co-ordination polymers [{Zn(SPh)$_2$(μ-bpy)}$_n$] **2** and [{Zn(SPh)$_2$(μ-bpy)}$_n$]·0.25CH_2Cl_2·H_2O **3**.

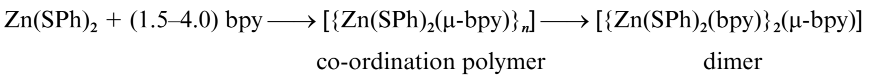
Results and discussion

The dimer **1** was prepared by the slow addition of bpy (in DMSO, THF, MeOH, acetone, MeCN, CH_2Cl_2 or $CHCl_3$) to Zn(SPh)$_2$ in DMF, in the ratio of (1.5–4.0) : 1 to get a clear solution which was left for slow evaporation to dryness. Yellow crystals in the shape of distorted hexagonal blocks were obtained in high yield and characterised by elemental analysis, NMR spectroscopy, and by single crystal X-ray diffraction techniques.

A slow diffusion method, using the same ratio of the above reactants, in the presence of CH_2Cl_2, yielded unsolvated, **2**, or solvated, **3**, co-ordination polymers depending on the ratio of the CH_2Cl_2 solvent in the reaction mixture. For instance, **2** was obtained when the ratio CH_2Cl_2 : DMF was 2 : 1 v/v while **3** formed when this ratio was 6 : 1 v/v. When the ratio was in between these two values both **2** and **3** were formed. The yellow crystals of **3** lose solvent and change slowly into opaque orange crystals on standing in air. The crystals of **2** are unchanged on standing. Initially it was thought that the products obtained were influenced by the presence or absence of CH_2Cl_2 solvent. In order to determine the exact role of the solvents, a series of experiments was conducted that include change of solvent, concentration of the reactants, ratios of the solvents, reaction time and method of synthesis (diffusion and evaporation method). The results are summarised below. The products in each experiment were characterised by one or more of elemental analysis, visual observation and/or determination of cell parameters of the single crystals, X-ray powder pattern, or integration of peaks in ^1H NMR spectra.

The compound Zn(SPh)$_2$ is soluble in DMF or DMSO only. When a DMF and/or DMSO solution of it was mixed slowly with bpy in CH_2Cl_2, $CHCl_3$, MeCN, Et_2O, MeOH, THF or acetone, in the ratio of 1 : (1.5–4.0) by the diffusion method, yellow elongated block-like crystals started depositing in 5 min to 1 h. These crystals analysed as the 1 : 1 polymer, **2**. When the reaction mixture was left alone the crystals redissolved and distorted hexagonal shaped crystals started appearing in 2–3 d. These were found to be the dimer, **1**. The formation and/or the disappearance of **2** depend on the concentration of solutes and solvents, the ratios and the nature of the solvents used. When the solution was diluted with liquids such as CH_2Cl_2, $CHCl_3$, MeCN, Et_2O, MeOH, THF or acetone, **2** crystallised from the solution quantitatively. If the same reaction mixture was left aside it was found that **2** redissolved slowly. When the solution was concentrated by evaporation over two days at room temperature, the dimer **1** started crystallising from the solution. In the absence of the CH_2Cl_2, $CHCl_3$, MeCN, Et_2O, MeOH, THF or acetone only **1** was isolated as the final product.

It appears that the first product to form in the reaction between Zn(SPh)$_2$ and bpy is the 1 : 1 compound, **2**, as given in Scheme 1. However, this product was isolable only when the solution was diluted with CH_2Cl_2, $CHCl_3$, MeCN, MeOH, acetone, Et_2O or THF in which it is poorly soluble. During the course of the reaction at room temperature **2** redissolved due to



$$\mathrm{Zn(SPh)_2 + (1.5\text{–}4.0)\ bpy \longrightarrow \underset{\text{co-ordination polymer}}{[\{Zn(SPh)_2(\mu\text{-}bpy)\}_n]} \longrightarrow \underset{\text{dimer}}{[\{Zn(SPh)_2(bpy)\}_2(\mu\text{-}bpy)]}}$$

Scheme 1

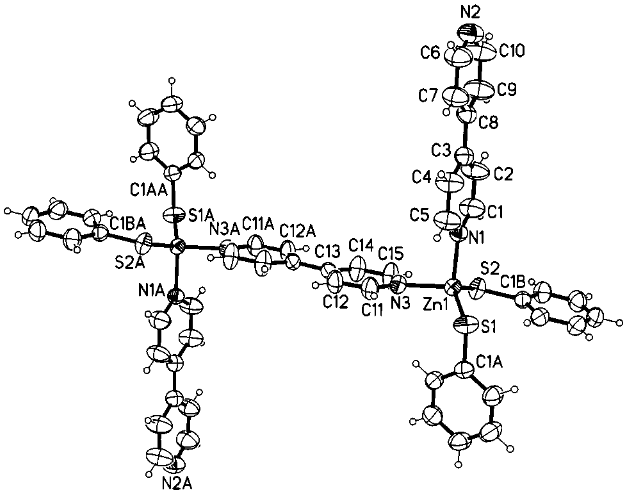


Fig. 1 A perspective view of the dimer **1**. The non-hydrogen atoms are drawn as 50% probability thermal ellipsoids.

Table 1 Selected bond lengths (Å) and angles (°) in compound **1**

Zn(1)–N(1)	2.113(2)	N(1)–C(1)	1.316(3)
Zn(1)–N(3)	2.094(2)	N(1)–C(5)	1.329(3)
Zn(1)–S(1)	2.2672(7)	N(2)–C(6)	1.319(4)
Zn(1)–S(2)	2.2882(7)	N(2)–C(6)	1.375(4)
S(1)–C(1A)	1.776(2)	N(3)–C(15)	1.326(3)
S(2)–C(1B)	1.766(2)	N(3)–C(11)	1.330(3)
N(3)–Zn(1)–N(1)	98.17(7)	C(1)–N(1)–C(5)	116.2(2)
N(3)–Zn(1)–S(1)	114.88(6)	C(1)–N(1)–Zn(1)	117.9(2)
N(1)–Zn(1)–S(1)	103.06(5)	C(5)–N(1)–Zn(1)	125.8(2)
N(3)–Zn(1)–S(2)	99.73(6)	C(10)–N(2)–C(6)	114.9(3)
N(1)–Zn(1)–S(2)	109.04(6)	C(15)–N(3)–C(11)	115.9(2)
S(1)–Zn(1)–S(2)	128.17(3)	C(15)–N(3)–Zn(1)	119.1(2)
C(1A)–S(1)–Zn(1)	102.56(8)	C(11)–N(3)–Zn(1)	124.7(2)
C(1B)–S(2)–Zn(1)	109.84(8)		

the evaporation of these volatile components over 2 d, and the crystallisation of **1** occurred upon the evaporation of DMF and/or DMSO over several days.

Bridging behaviour by thiolates has been well established.[10] Thiolates are, therefore, expected to compete as well as, if not better than, bpy for bridging sites between zinc(II) centres. In order to test the bridging ability of the PhS$^-$ in the presence of bpy a synthesis of the $[(bpy)_2Zn(\mu\text{-}SPh)_2Zn(bpy)_2]^{2+}$ cation was attempted. However, the product obtained analysed as dimer **1**. Many attempts to prepare the monomer $[Zn(SPh)_2(bpy)_2]$ also resulted in the formation of **1**. Benzenethiolate, therefore, appears to be a poor bridging ligand for Zn^{II} in the presence of bpy. We were unable to isolate any other compounds under the experimental conditions used.

Crystal and molecular structures

A perspective view of compound **1** is shown in Fig. 1 and selected bond distances and the bond angles are given in Table 1. The compound is a discrete neutral dimer in which two zinc atoms are bridged by a bpy, and tetrahedral co-ordination of zinc atoms is completed by two terminal benzenethiolates and a monodentate, non-bridging bpy. Each terminal bpy ligand has an unco-ordinated N atom. There is a crystallographically imposed centre of symmetry in the molecule. The Zn–S distances, 2.2672(7) and 2.2882(7) Å, are not equal. The C–S–Zn angles, 102.56(8) and 109.84(8)°, are also different. The Zn(1)–N(1) distance is slightly longer than Zn(1)–N(3). It is interesting that the two rings of the bpy ligand are almost on the same plane. The dihedral angle between the two pyridine rings of the bridging bpy is 0.0(2)° and the same for the terminal bpy is 2.9(2)°.

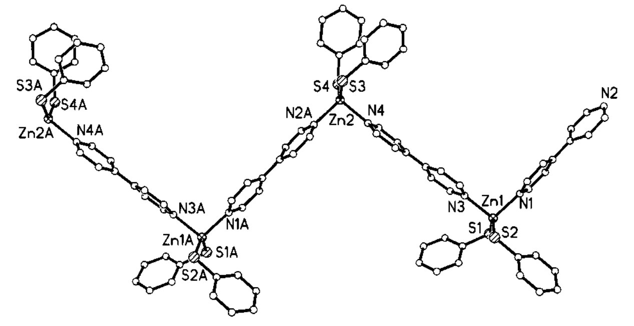


Fig. 2 A segment of the zigzag co-ordination polymer **2**. The hydrogen atoms and minor disordered phenyl rings are omitted for clarity.

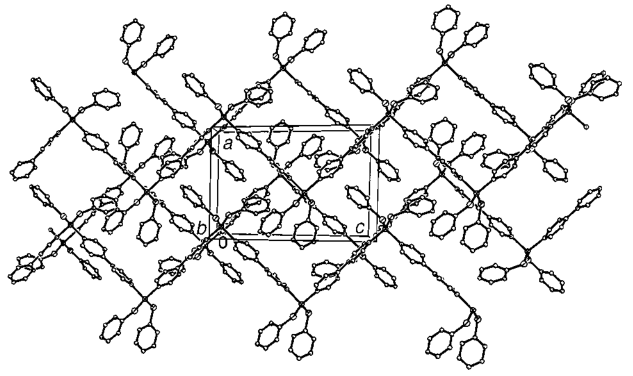


Fig. 3 Packing diagram of compound **2** viewed down the *b* axis. The hydrogen atoms and the minor disordered phenyl rings are omitted for clarity.

X-Ray crystallography confirmed the structures of compounds **2** and **3**. Selected bond lengths and bond angles are given in Table 2 for **2** and Table 3 for **3**. A segment of the zigzag co-ordination polymer, **2**, is shown in Fig. 2. There are two independent $[Zn(SPh)_2(bpy)]$ units ("dimers") in **2** and four such units in **3**. Each zinc metal is bound to two nitrogen atoms, one from each of two bpy ligands, and two S atoms of the terminal benzenethiolate ligands, to give a tetrahedral co-ordination geometry. The dihedral planes between the pyridine rings of the bpy have increased [24.0(6) and 34.6(5)° in **2** and 21.0(3) to 43.5(3)° in **3**] as compared to those in **1**. Although the structures of the co-ordination polymers in **2** and **3** are quite similar, the way these strands are arranged in three-dimensional space is different. The polymer strand runs along the *c* axis in **2** as shown in Fig. 3, In contrast, these one dimensional 'zigzag' co-ordination polymers in **3** are packed in the *bc* plane as depicted in Fig. 4. The solvent molecules occupy the space between the phenyl rings.

An inspection of Table 4 indicates that the volume per $[Zn(SPh)_2(bpy)]$ unit is smaller (increase in density) for the solvated lattice in compound **3** as compared to that in **2**. In other words the packing efficiency of the solvated crystal **3** is better than that of **2**. The empty voids available are better used for the guest solvents in **3**. The presence of disordered CH_2Cl_2 and water in the crystal structure of **3** indicates that the space available can accommodate bigger guest solvents. This may also be attributed to the shape misfit of the small molecules in the lattice. Unfortunately, disorder present in the solvent region

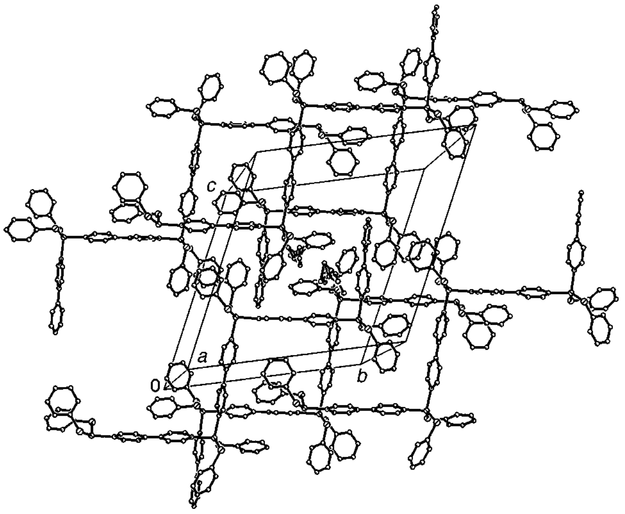


Fig. 4 Packing diagram of compound **3** viewed down the *a* axis. The hydrogen atoms and the minor disordered phenyl rings are omitted for clarity. Only one layer of the polymer network is shown.

Table 2 Selected bond lengths (Å) and angles (°) in compound **2**

Zn(1)–N(1)	2.123(10)	S(3)–C(1C)	1.719(11)
Zn(1)–N(3)	2.121(11)	S(3)–C(1C′)	1.721(11)
Zn(1)–S(1)	2.277(4)	S(4)–C(1D)	1.760(10)
Zn(1)–S(2)	2.285(4)	N(1)–C(1)	1.288(14)
Zn(2)–N(4)	2.105(11)	N(1)–C(5)	1.301(15)
Zn(2)–N(2^1)	2.112(10)	N(2)–C(6)	1.325(14)
Zn(2)–S(3)	2.264(3)	N(2)–C(10)	1.361(14)
Zn(2)–S(4)	2.288(4)	N(3)–C(11)	1.334(15)
S(1)–C(1A)	1.766(11)	N(3)–C(15)	1.357(15)
S(1)–C(1A′)	1.782(16)	N(4)–C(16)	1.364(17)
S(2)–C(1B)	1.723(9)	N(4)–C(20)	1.320(15)
N(3)–Zn(1)–N(1)	99.1(4)	C(1C)–S(3)–C(1C′)	93.9(9)
N(3)–Zn(1)–S(1)	107.7(3)	C(1C)–S(3)–Zn(2)	111.6(6)
N(1)–Zn(1)–S(1)	105.9(3)	C(1C′)–S(3)–Zn(2)	114.4(6)
N(3)–Zn(1)–S(2)	101.1(3)	C(1D)–S(4)–Zn(2)	100.9(5)
N(1)–Zn(1)–S(2)	111.3(3)	C(1)–N(1)–C(5)	116.8(11)
S(1)–Zn(1)–S(2)	127.84(16)	C(1)–N(1)–Zn(1)	122.4(8)
N(4)–Zn(2)–N(2^1)	97.5(4)	C(5)–N(1)–Zn(1)	120.8(8)
N(4)–Zn(2)–S(3)	105.7(3)	C(6)–N(2)–C(10)	116.6(10)
N(2^1)–Zn(2)–S(3)	106.8(3)	C(6)–N(2)–Zn(2^2)	120.7(8)
N(4)–Zn(2)–S(4)	107.5(3)	C(10)–N(2)–Zn(2^2)	122.6(7)
N(2^1)–Zn(2)–S(4)	108.1(3)	C(11)–N(3)–C(15)	116.6(12)
S(3)–Zn(2)–S(4)	127.33(15)	C(11)–N(3)–Zn(1)	121.9(9)
C(1A)–S(1)–C(1A′)	76.4(19)	C(15)–N(3)–Zn(1)	121.6(10)
C(1A)–S(1)–Zn(1)	98.8(6)	C(20)–N(4)–C(16)	116.1(12)
C(1A′)–S(1)–Zn(1)	108.8(19)	C(20)–N(4)–Zn(2)	122.4(10)
C(1B)–S(2)–Zn(1)	110.3(6)	C(16)–N(4)–Zn(2)	121.4(10)

Symmetry transformations used to generate equivalent atoms: 1 *x*, *y*, *z* + 1; 2 *x*, *y*, *z* − 1.

Table 3 Selected bond lengths (Å) and angles (°) in compound **3**

Zn(1)–N(1)	2.099(7)	S(5)–C(1E)	1.801(6)
Zn(1)–N(3)	2.113(8)	S(6)–C(1F)	1.780(6)
Zn(1)–S(1)	2.265(3)	S(7)–C(1G)	1.782(6)
Zn(1)–S(2)	2.271(3)	S(8)–C(1H)	1.770(9)
Zn(2)–N(5)	2.095(7)	N(1)–C(5)	1.328(12)
Zn(2)–N(4)	2.119(7)	N(1)–C(1)	1.341(11)
Zn(2)–S(4)	2.261(3)	N(2)–C(10)	1.318(11)
Zn(2)–S(3)	2.270(3)	N(2)–C(6)	1.344(11)
Zn(3)–N(6)	2.082(7)	N(3)–C(11)	1.342(12)
Zn(3)–N(7)	2.093(6)	N(3)–C(15)	1.343(12)
Zn(3)–S(5)	2.270(2)	N(4)–C(20)	1.338(11)
Zn(3)–S(6)	2.275(2)	N(4)–C(16)	1.341(11)
Zn(4)–N(2^1)	2.101(7)	N(5)–C(25)	1.337(11)
Zn(4)–N(8)	2.104(7)	N(5)–C(21)	1.341(11)
Zn(4)–S(7)	2.265(3)	N(6)–C(30)	1.323(10)
Zn(4)–S(8)	2.268(3)	N(6)–C(26)	1.344(10)
S(1)–C(1A)	1.751(12)	N(7)–C(35)	1.331(10)
S(1)–C(1A′)	1.824(16)	N(7)–C(31)	1.335(10)
S(2)–C(1B)	1.771(8)	N(8)–C(36)	1.336(10)
S(3)–C(1C)	1.782(7)	N(8)–C(40)	1.347(11)
S(4)–C(1D)	1.775(6)		
N(1)–Zn(1)–N(3)	97.1(3)	N(6)–Zn(3)–N(7)	98.6(3)
N(1)–Zn(1)–S(1)	105.7(2)	N(6)–Zn(3)–S(5)	106.4(2)
N(3)–Zn(1)–S(1)	109.5(2)	N(7)–Zn(3)–S(5)	107.9(2)
N(1)–Zn(1)–S(2)	110.0(2)	N(6)–Zn(3)–S(6)	111.7(2)
N(3)–Zn(1)–S(2)	100.6(2)	N(7)–Zn(3)–S(6)	101.4(2)
S(1)–Zn(1)–S(2)	129.28(12)	S(5)–Zn(3)–S(6)	127.0(1)
N(5)–Zn(2)–N(4)	97.5(3)	N(2^1)–Zn(4)–N(8)	96.9(3)
N(5)–Zn(2)–S(4)	103.8(2)	N(2^1)–Zn(4)–S(7)	111.5(2)
N(4)–Zn(2)–S(4)	110.2(2)	N(8)–Zn(4)–S(7)	99.9(2)
N(5)–Zn(2)–S(3)	108.9(2)	N(2^1)–Zn(4)–S(8)	105.9(2)
N(4)–Zn(2)–S(3)	106.6(2)	N(8)–Zn(4)–S(8)	108.3(2)
S(4)–Zn(2)–S(3)	126.15(11)	S(7)–Zn(4)–S(8)	129.3(1)
C(1A)–S(1)–C(1A′)	8.0(9)	C(11)–N(3)–Zn(1)	120.7(6)
C(1A)–S(1)–Zn(1)	104.1(6)	C(15)–N(3)–Zn(1)	122.5(6)
C(1A′)–S(1)–Zn(1)	106.9(7)	C(20)–N(4)–C(16)	116.6(8)
C(1B)–S(2)–Zn(1)	107.2(4)	C(20)–N(4)–Zn(2)	122.3(6)
C(1C)–S(3)–Zn(2)	100.6(3)	C(16)–N(4)–Zn(2)	121.1(6)
C(1D)–S(4)–Zn(2)	106.5(2)	C(25)–N(5)–C(21)	117.4(7)
C(1E)–S(5)–Zn(3)	98.1(2)	C(25)–N(5)–Zn(2)	121.0(6)
C(1F)–S(6)–Zn(3)	107.9(2)	C(21)–N(5)–Zn(2)	121.6(6)
C(1G)–S(7)–Zn(4)	108.3(2)	C(30)–N(6)–C(26)	116.0(7)
C(1H)–S(8)–Zn(4)	102.9(4)	C(30)–N(6)–Zn(3)	121.7(6)
C(5)–N(1)–C(1)	116.4(8)	C(26)–N(6)–Zn(3)	122.1(6)
C(5)–N(1)–Zn(1)	120.7(6)	C(35)–N(7)–C(31)	117.4(7)
C(1)–N(1)–Zn(1)	122.9(6)	C(35)–N(7)–Zn(3)	120.3(5)
C(10)–N(2)–C(6)	117.5(8)	C(31)–N(7)–Zn(3)	122.3(5)
C(10)–N(2)–Zn(4^2)	121.3(6)	C(36)–N(8)–C(40)	117.1(7)
C(6)–N(2)–Zn(4^2)	121.0(5)	C(36)–N(8)–Zn(4)	123.1(6)
C(11)–N(3)–C(15)	116.8(8)	C(40)–N(8)–Zn(4)	119.8(6)

Symmetry transformations used to generate equivalent atoms: 1 *x*, *y* − 1, *z* − 1; 2 *x*, *y* + 1, *z* + 1.

precludes any further analysis. The presence of phenyl ring disorder and high thermal motions (see Experimental section) appears to indicate, again, that there is more free space available in the crystal lattices of **2** and **3**. There appears to be no phenyl ring stacking. Investigations are underway to study the influence of the bulky solvents on the packing of these polymers.

Thermogravimetric analysis

The TG traces of compounds **1** and **2** are given in Fig. 5. The dimer **1** started decomposing around 190 °C under N_2. The weight of the residue corresponds to the formation of ZnS (observed, 19.7%; expected, 18.8%). The TG curve of polymer **2** is also very similar to that of **1**. The final product of decomposition appears to be ZnS based on the residual weight (observed, 22.0%; calculated, 22.1%). It appears that both compounds **1** and **2** are potential 'single-source' precursors for the ZnS materials. Further investigations are in progress in this direction.

Conclusion

We consider the following features of this study to be particularly salient. The reaction between $Zn(SPh)_2$ and bpy proceeds to the formation of dimer $[\{Zn(SPh)_2(bpy)\}_2(\mu\text{-bpy})]$ **1** through the intermediate, 1:1 polymer $[\{Zn(SPh)_2(bpy)\}_n]$, **2**. Crystallisation chemistry plays an important role in the nature of the products isolated. With slow mixing of reactants (the diffusion method) when the ratio of bpy to Zn is low the insoluble polymer crystallises, but when the proportion of bpy increases (on mixing through diffusion) the dimer crystallises. Dilution with various solvents facilitates the isolation of the polymer in quantitative yield. By changing the concentration of CH_2Cl_2, either the solvated or unsolvated crystalline form of $[\{Zn(SPh)_2(bpy)\}_n]$ has been isolated. Our present investigation indicates that benzenethiolate is a poor bridging ligand between Zn atoms in the presence of bpy. The formation of

Table 4 Crystal data and structure refinement for compounds **1**, **2** and **3**

	1	**2**	**3**
Formula	$C_{54}H_{44}N_6S_4Zn_2$	$C_{44}H_{36}N_4S_4Zn_2$	$C_{44.25}H_{38.5}Cl_{0.5}N_4OS_4Zn_2$
M	1035.93	879.75	919.0
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	14.4276(3)	10.8329(4)	13.6823(3)
b/Å	17.5358(1)	13.7844(5)	19.7171(3)
c/Å	9.9439(2)	17.0215(4)	20.2532(4)
α/°		69.593(1)	65.093(1)
β/°	104.85(1)	88.253(2)	71.897(1)
γ/°		87.946(1)	73.909(1)
U/Å^3	2431.78(7)	2380.25(14)	4642.0(2)
Z	4	2	4
D_c/Mg m^{-3}	1.415	1.227	1.315
μ/mm^{-1}	1.202	1.215	1.278
F(000)	1068	904	1890
T_{max}, T_{min}	0.7353, 0.5562	0.8016, 0.6050	0.7872, 0.6005
Data [$I > 2\sigma(I)$]/parameters	4312/299	3440/324	11427/686
Goodness of fit on F^2	1.039	1.058	1.132
Final $R1$ and $wR2$ [$I > 2\sigma(I)$]	0.0426, 0.0754	0.1183, 0.3297	0.1023, 0.2337
(all data)	0.0697, 0.0839	0.1871, 0.3663	0.1345, 0.2549
Extinction coefficient	0.0006(3)	0.009(2)	0.00042(17)

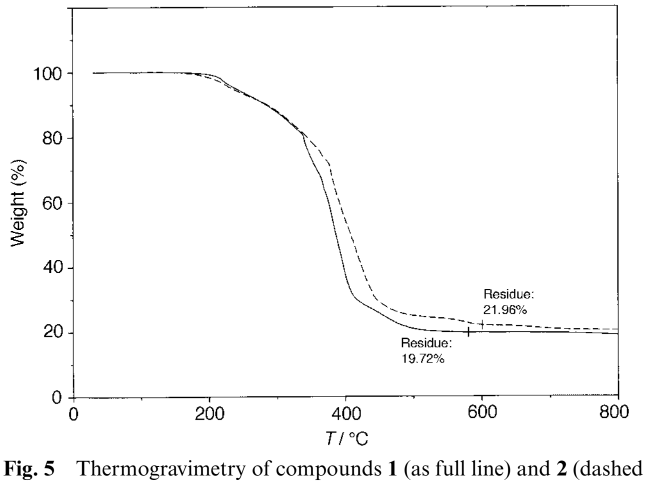


Fig. 5 Thermogravimetry of compounds **1** (as full line) and **2** (dashed line).

the co-ordination polymer **2** or **3** does not depend on the metal : ligand ratio only. We were not able to isolate any other network by varying this ratio under the experimental conditions employed. Compounds **1** and **2** appear to be potential candidates as 'single-source' precursors for ZnS materials as they thermally decompose to ZnS in the temperature range 190–500 °C.

Experimental

The chemicals and solvents were obtained commercially and used as received. The solvents were dried over 3 Å molecular sieves. The Microanalytical laboratory at National University of Singapore performed the elemental analyses. The ^{1}H and ^{13}C-{^{1}H} NMR spectra were recorded on a Bruker ACF spectrometer at 300 MHz using TMS as an internal reference at 25 °C in d$_6$-DMSO solvent. X-Ray powder patterns were obtained using a D5005 Siemens diffractrometer. Thermogravimetric analyses were carried out using a SDT 2980 TGA thermal analyser with a heating rate of 10 °C min^{-1} in a nitrogen atmosphere using a sample size of about 5–10 mg per run.

Syntheses

All the three compounds once isolated in the solid state were found to be insoluble in most of the solvents tried (MeCN, acetone, CH_2Cl_2, $CHCl_3$, alcohols and water), but sparingly soluble in DMF and DMSO. The solubilities of **1** and **2** in DMF at 25 °C are 8.5 and 13.6 mg ml^{-1} respectively.

[{Zn(SPh)$_2$(bpy)}$_2$(μ-bpy)] 1. A solution of bpy (0.165 g, 1.06 mmol) in 10 ml of THF was added dropwise with stirring to a solution of Zn(SPh)$_2$ (0.200 g, 0.70 mmol) in 2 ml of DMF to obtain a clear yellow solution. On leaving the solution for slow evaporation, hexagonal shaped crystals were obtained. These were separated by decantation, washed with MeOH and Et_2O and dried in air (78% yield). Compound **1** was also obtained when the synthesis was done in DMF– and DMSO–THF mixtures (Calc. for $C_{27}H_{22}N_3S_2Zn$: C, 62.60; H, 4.28; N, 8.11; S, 12.38%. Found: C, 62.45; H, 4.39; N, 8.16; S, 12.25%), mp 211–213 °C. ^{1}H NMR: δ 8.72 (d, $J = 6$, 12 H, $H_{\alpha(bpy)}$); 7.85 (d, $J = 6$, 12 H, $H_{\beta(bpy)}$); 7.34 (d, $J = 9$, 8 H, $H^2_{(SPh)}$); 6.98 (t, $J = 7$, 8 H, $H^3_{(SPh)}$ and 6.85 (t, $J = 7$ Hz, 4 H, $H^4_{(SPh)}$). ^{13}C NMR: δ 150.23 ($C_{\alpha(bpy)}$); 144.59 ($C_{\gamma(bpy)}$); 142.67 ($C^1_{(SPh)}$); 132.30 ($C^2_{(SPh)}$); 127.67 ($C^3_{(SPh)}$); 121.95 ($C^4_{(SPh)}$) and 121.56 ($C_{\beta(bpy)}$).

[{Zn(SPh)$_2$(μ-bpy)}$_n$] 2. A solution of bpy (55 mg, 0.35 mmol) in 6.0 ml of CH_2Cl_2 was added to a solution of Zn(SPh)$_2$ (100 mg, 0.35 mmol) in 3 ml DMF. The clear yellow solution formed was layered with Et_2O to obtain yellow crystals within a few minutes. The crystals were washed with MeOH and diethyl ether. Yield: 83% (Calc. for $C_{22}H_{18}N_2S_2Zn$: C, 60.07; H, 4.12; N, 6.37; S, 14.58; Zn, 14.86. Found: C, 59.49; H, 3.97; N, 6.66; S, 14.59, Zn, 14.88%), mp 222–225 °C. ^{1}H NMR: δ 8.72 (d, $J = 6$, 12 H, $H_{\alpha(bpy)}$); 7.85 (d, $J = 6$, 12 H, $H_{\beta(bpy)}$); 7.32 (d, $J = 9$, 8 H, $H^2_{(SPh)}$); 6.98 (t, $J = 7$, 8 H, $H^3_{(SPh)}$) and 6.85 (t, $J = 7$ Hz, 4 H, $H^4_{(SPh)}$). ^{13}C NMR: δ 150.28 ($C_{\alpha(bpy)}$); 144.52 ($C_{\gamma(bpy)}$); 142.72 ($C^1_{(SPh)}$); 132.30 ($C^2_{(SPh)}$); 127.67 ($C^3_{(SPh)}$); 121.93 ($C^4_{(SPh)}$) and 121.47 ($C_{\beta(bpy)}$).

[{Zn(SPh)$_2$(μ-bpy)}$_n$]·0.25CH$_2$Cl$_2$·H$_2$O 3. A solution of bpy (56 mg, 0.36 mmol) in 6 ml of CH_2Cl_2 was added to a solution of Zn(SPh)$_2$ (100 mg, 0.35 mmol) in 1 ml DMF. A clear yellow solution formed immediately, which was left to form yellow crystals. These were washed with MeOH and diethyl ether. Yield: 74% (Calc. for $C_{44.25}H_{36.5}Cl_{0.5}N_4S_4Zn_2$: C, 58.98; H, 4.08; N, 6.22; S, 14.22. Found: C, 58.46; H, 3.93; N, 6.65; S, 14.95%).

Attempted synthesis of [(bpy)$_2$Zn(μ-SPh)$_2$Zn(bpy)$_2$][ClO$_4$]$_2$. The compounds Zn(SPh)$_2$ (100 mg, 0.35 mmol) and Zn(ClO$_4$)$_2$ (137 mg, 0.37 mmol) were dissolved in 2 ml DMF then diluted by 3 ml of THF. A solution containing bpy (220 mg, 1.41 mmol) in 6 ml of THF was added slowly dropwise. Yellow crystals were obtained when the clear yellow solution was left for slow evaporation. They analysed as **1**.

Attempted synthesis of [Zn(SPh)$_2$(bpy)$_2$]. The compounds Zn(ClO$_4$)$_2$ (500 mg, 1.34 mmol) and bpy (524 mg, 3.35 mmol) were dissolved in 20 ml of MeOH to obtain a clear solution. A methanolic solution of NaSPh [prepared from PhSH (0.3 ml, 2.69 mmol) and Na (65 mg, 2.69 mmol) in 8 ml of MeOH] was added as a layer on top of this and the whole was left for slow evaporation to obtain yellow crystals which were analysed as dimer **1**.

In another experiment Zn(SPh)$_2$ (103 mg, 0.36 mmol) in 2 ml DMF and bpy (116 mg, 0.73 mmol) in 10 ml of CH_2Cl_2 or THF gave a yellow solution. Yellow block-like crystals of compound **2** were obtained in 10 min and when the mixture was left aside and the solvents evaporated completely hexagonal-shaped crystals of **1** were obtained.

X-Ray crystallography

The diffraction experiments were carried out on a Bruker AXS SMART CCD 3-circle diffractometer with a Mo-Kα sealed tube at 23 °C. The softwares used were: SMART[11] for collecting frames of data, indexing reflections and determination of lattice parameters; SAINT[11] for integration of intensity of reflections and scaling; SADABS[12] for empirical absorption correction; and SHELXTL[13] for space group determination, structure solution and least-squares refinements on F^2. The crystals of compounds **2** and **3** were sealed in glass capillary tubes. Full details are given in Table 4.

Compound 1. Total of 15177 reflections collected in the 2θ range 1.87–29.28° ($-18 \le h \le 19$, $-24 \le k \le 116$, $-13 \le l \le 13$) of which 5936 ($R_{\text{int}} = 0.0270$) were independent. Anisotropic thermal parameters were refined for all the non-hydrogen atoms. An extinction coefficient was refined to 0.0006(3). The electron densities fluctuated between 0.268 and −0.213 e Å^{-3} in the Fourier difference map.

Compound 2. The number of reflections collected in the 2θ range 2.25–25.0° ($-12 \le h \le 12$, $-7 \le k \le 16$, $-20 \le l \le 20$) was 9260, of which 7208 ($R_{\text{int}} = 0.0452$) were independent. A few of the phenyl rings show large thermal motions indicating the possibility of disorder. However, the disordered phenyl rings were resolved only for those attached to S1 and S3. Common isotropic thermal parameters were refined (with occupancies of 0.75 and 0.25 for the S1 phenyl ring and 0.55 and 0.45 for the S3 phenyl ring). Common isotropic thermal parameters were refined for the phenyl rings attached to S2 and S4. Isotropic thermal parameters were refined for the rest of the thiolate phenyl rings.

Compound 3. In total 29776 reflections were collected in the 2θ range 1.66–25.00° ($-16 \le h \le 16$, $-23 \le k \le 23$, $-23 \le l \le 24$) of which 15334 ($R_{\text{int}} = 0.0605$) were independent. Anisotropic thermal parameters were refined for all Zn, S, N and bpy carbon atoms. The isotropic thermal parameters of the carbon atoms of the thiolate phenyl rings were relatively high indicating the possibility of disorder. However, disorder models were successfully resolved only for the phenyl ring attached to S1. The Fourier-difference routine showed severely disordered solvent regions. These were assigned to 0.25CH_2Cl_2 (the Cl atoms were disordered) and one H_2O disordered in 10 difference places in the crystal lattice. The assignment of oxygen atoms of water was quite arbitrary and may have come from the solvents used for synthesis.

To improve the quality of the structures **2** and **3**, data were collected using crystals from different batches at room temperature. The problem of disorder and higher thermal activity of the phenyl rings persisted. In spite of high agreement factors, the connectivity in the polymeric network is well established beyond any doubt.

CCDC reference number 186/1437.

See http://www.rsc.org/suppdata/dt/1999/1993/ for crystallographic files in .cif format.

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