

# Substituted pyridylmethanamide ligands and their zinc complexes

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## Abstract

Mononuclear zinc complexes of a family of pyridylmethanamide ligands abbreviated as HL, HL<sup>Ph</sup>, HL<sup>Me3</sup>, HL<sup>Ph3</sup>, and MeL<sup>SMe</sup> [HL = *N*-(2-pyridylmethyl)acetamide; HL<sup>Ph</sup> = 2-phenyl-*N*-(2-pyridylmethyl)acetamide; HL<sup>Me3</sup> = 2,2-dimethyl-*N*-(2-pyridylmethyl)propionamide; HL<sup>Ph3</sup> = 2,2,2-triphenyl-*N*-(2-pyridylmethyl)acetamide; MeL<sup>SMe</sup> = *N*-methyl-2-methylsulfanyl-*N*-pyridin-2-ylmethylacetamide] were synthesized and characterized spectroscopically and by single crystal X-ray structural analysis. The reaction of zinc(II) salts with the HL ligands yielded complexes [Zn(HL)<sub>2</sub>(OTf)<sub>2</sub>] (1), [Zn(HL)<sub>2</sub>(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> (2), [Zn(HL<sup>Ph3</sup>)<sub>2</sub>(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> (3), [Zn(HL<sup>Ph</sup>)Cl<sub>2</sub>] (4), [Zn(HL<sup>Me3</sup>)Cl<sub>2</sub>] (5), and [Zn(MeL<sup>SMe</sup>)Cl<sub>2</sub>] (6). The complexes are either four-, five- or six-coordinate, encompassing a variety of geometries including tetrahedral, square-pyramidal, trigonal-bipyramidal, and octahedral.

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**Keywords:** Zinc; Amide ligands; N,O ligands; Coordination modes; Ligand effects

## 1. Introduction

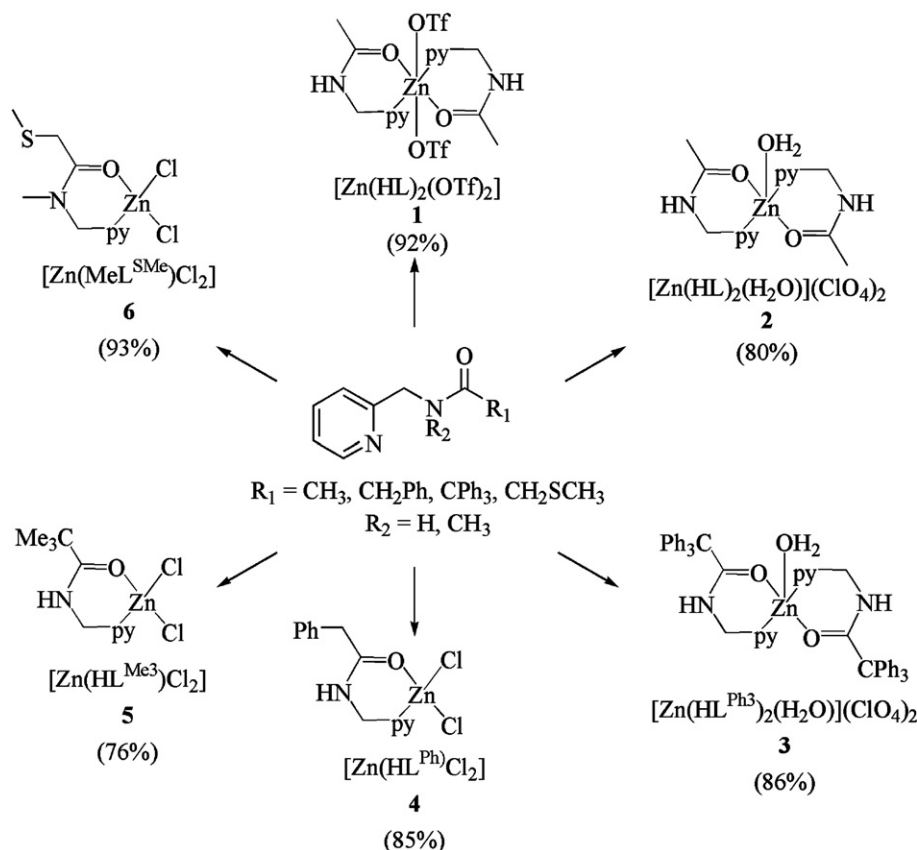
Zinc, the second most abundant transition metal and present in over 300 enzymes [1–3], is an essential element for normal function of most biological systems, including eukaryotes and prokaryotes. The human body contains about 3 g of zinc, and a zinc deficiency causes abnormalities in growth, decreases the resistance of the immune system, and increases susceptibility to disease. Zinc containing enzymes include zinc finger proteins, nucleases, peptidases and many more [4–11]. A majority of these enzyme sites contain a tetrahedral zinc center coordinated by three amino acid residues and a fourth site that is typically an aqua or hydroxo ligand. For a better understanding of the active-site structure and function of zinc metalloenzymes, small molecule model complexes have been synthesized and characterized [12–23]. Comparisons of the

structural and reactivity properties of synthetic analogues with those of the active-site can provide insight into structure/function relationships. Structural studies of zinc complexes can also provide an avenue to explore the coordinating properties of different ligand systems.

Zinc complexes of a common nitrogen containing ligand, tris(2-pyridylmethyl)amine (TPA), has been widely explored in the literature [24–26]. Zinc complexes of amide containing ligands have been extensively investigated as well [27–29]. Those with the 6-(pivaloylamido-2-pyridylmethyl)amine unit have been synthesized to serve as models for peptidases [30–33]. Zinc complexes of polyaza-macrocyclic ligands are also of relevance, and have received much attention in biomimetic research [34]. In our recent work, we synthesized a family of pyridylmethanamide ligands that have tremendous utility in forming multinuclear copper complexes owing to their ability to form mono-, di- and tetranuclear complexes with different coordination modes [35–37]. Inspired by our findings on the chemistry of copper, we chose to study the coordination chemistry of zinc with these ligands. Herein, we report the synthesis, characterization, and structures of the first

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Scheme 1. Complexes 1–6.

zinc complexes of the family of ligands depicted in [Scheme 1](#), specifically  $[\text{Zn}(\text{HL})_2(\text{OTf})_2]$  (**1**),  $[\text{Zn}(\text{HL})_2(\text{H}_2\text{O})](\text{ClO}_4)_2$  (**2**),  $[\text{Zn}(\text{HL}^{\text{Ph}_3})_2(\text{H}_2\text{O})](\text{ClO}_4)_2$  (**3**),  $[\text{Zn}(\text{HL}^{\text{Ph}})\text{Cl}_2]$  (**4**),  $[\text{Zn}(\text{HL}^{\text{Me}_3})\text{Cl}_2]$  (**5**), and  $[\text{Zn}(\text{MeL}^{\text{SMc}})\text{Cl}_2]$  (**6**).

## 2. Results and discussion

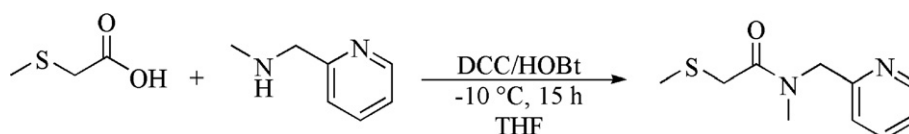
### 2.1. Synthesis and characterization

Our ligand design and synthesis originates from earlier reports wherein we synthesized a family of pyridylamide ligands, abbreviated HL,  $\text{HL}^{\text{Ph}}$ ,  $\text{HL}^{\text{Me}_3}$ , and  $\text{HL}^{\text{Ph}_3}$  [HL = *N*-(2-pyridylmethyl)acetamide;  $\text{HL}^{\text{Ph}}$  = 2-phenyl-*N*-(2-pyridylmethyl)acetamide;  $\text{HL}^{\text{Me}_3}$  = 2,2-dimethyl-*N*-(2-pyridylmethyl)propionamide;  $\text{HL}^{\text{Ph}_3}$  = 2,2,2-triphenyl-*N*-(2-pyridylmethyl)acetamide], and explored their coordination chemistry with copper [35]. In addition to these previously reported ligands, we report the synthesis of a new ligand,  $\text{MeL}^{\text{SMc}}$  (*N*-methyl-2-methylsulfanyl-*N*-pyridin-2-ylmethylacetamide), a new member of our family of pyridylamide

ligands. The synthesis of  $\text{MeL}^{\text{SMc}}$  was accomplished by DCC-mediated coupling of (methylthio)acetic acid with *N*-methyl(2-pyridyl)methanamine ([Scheme 2](#)). With the exception of the tertiary amide nitrogen, this ligand is identical to  $\text{HL}^{\text{SMc}}$  whose coordination chemistry has been thoroughly investigated [37].

The interesting coordination properties of the pyridylamide family of ligands with copper prompted us to investigate the coordination behavior with zinc. The zinc complexes **1–6** ([Scheme 1](#)) were synthesized by straightforward methods via the reaction of zinc(II) salts with solutions of the ligand. The zinc(II) salts utilized for the synthesis were zinc(II) triflate, zinc(II) perchlorate, and zinc(II) chloride. All the zinc complexes were fully characterized including X-ray crystal structure determination.

Complexes **1–6** were characterized by elemental analysis, solid state FTIR,  $^1\text{H}$  NMR, and mass spectrometry. The IR spectra of **2** and **3**, both of which contain aqua ligands, have characteristic  $\nu_{\text{OH}}$  stretches for the water molecule around  $3400\text{ cm}^{-1}$ . The  $\nu_{\text{ClO}_4^-}$  stretches for **2** and **3**

Scheme 2. Synthesis of  $\text{MeL}^{\text{SMc}}$ .

are at 1088 and 1118  $\text{cm}^{-1}$ , respectively, consistent with their structures. Complexes **1**, **2**, and **3** feature amide carbonyl stretching bands ( $\nu_{\text{CO}}$ ) between 1650 and 1667  $\text{cm}^{-1}$ . These data represent trivial shifts with respect to the free ligand (Table 1). In contrast, **4**, **5**, and **6** display  $\nu_{\text{CO}}$  bands shifted to lower frequencies relative to their free ligand by 24, 43, and 35  $\text{cm}^{-1}$ , respectively (Table 1). These differences between **1–3** and **4–6** are likely the result of the shorter and stronger Zn–O bonds in **4–6** (vide infra). The  $^1\text{H}$  NMR spectra of the complexes are very similar to the free ligands, with very slight shifts indicative of coordination to zinc.

The electrospray mass spectrometry (ESI-MS) of **1–6** confirm the presence of the molecular species in solution. Compound **1** has a molecular ion peak at  $m/z = 663.0$ , corresponding to  $[\text{Zn}(\text{HL})_2(\text{OTf})_2 + \text{H}]^+$ . Compounds **2** and **3** exhibit similar fragmentation patterns with peaks at  $m/z = 463.0$  and  $m/z = 920.4$ , corresponding to  $[\text{Zn}(\text{HL})_2\text{ClO}_4]^+$  and  $[\text{Zn}(\text{HL}^{\text{Ph}_3})_2\text{ClO}_4]^+$ , consistent with the loss of one perchlorate and a molecule of water. Complexes **4**, **5**, and **6** have a common trend in their fragmentation patterns. Peaks at  $m/z = 325.0$ ,  $m/z = 291.0$ , and  $m/z = 309.0$  in **4**, **5**, and **6** correspond to  $[\text{Zn}(\text{HL}^{\text{Ph}})\text{Cl}]^+$ ,  $[\text{Zn}(\text{HL}^{\text{Me}_3})\text{Cl}]^+$ , and  $[\text{Zn}(\text{MeL}^{\text{SMe}})\text{Cl}]^+$ , that arise from the loss of a chloride ion in each of them. Complexes **4** and **5** also have peaks at  $m/z = 689.0$  and  $m/z = 621.0$  sug-

gesting the possibility of the formation of dinuclear species in solution. Finally, **4–6** contain peaks at  $m/z = 551.1$ ,  $m/z = 485.2$ , and  $m/z = 519.0$  that correspond to fragments wherein zinc is coordinated to two ligands and a chloride ion. These data indicate the possibility of structural rearrangement in solution.

## 2.2. X-ray crystal structures

The structure of **1**, determined by X-ray diffraction (Fig. 1), consists of zinc ions in a distorted octahedral geometry coordinated by two HL ligands and two triflate anions. The zinc atom, which is on a crystallographic inversion center, is coordinated by the pyridyl nitrogens  $[\text{Zn}–\text{N} = 2.1036(8) \text{ \AA}]$  and carbonyl oxygens  $[\text{Zn}–\text{O} = 2.1243(7) \text{ \AA}]$  of two HL ligands forming the equatorial plane. The apical positions are occupied by oxygen atoms of two triflate ions at a slightly longer distance of 2.1870(10)  $\text{\AA}$ . The bond angles involving the equivalent trans ligands are  $180^\circ$  by symmetry, and the other angles range from  $86.50(4)^\circ$  to  $93.50(4)^\circ$ . The pyridyl rings are almost co-planar and the Zn atom lies in the square plane formed by atoms N1A, O1A, O1, and N1. The Zn–N<sub>pyridyl</sub> distances are similar to those observed for complexes with pyridyl containing ligands [24], and the Zn–O<sub>carbonyl</sub> distances seem to follow the trend as seen in the literature [33]. The amide NH of one molecule forms a hydrogen bond to the triflate oxygen of another molecule (intermolecular) with an N2–O3 distance of 2.8812(12)  $\text{\AA}$  (Fig. 1).

The crystal structures of **2** and **3** are illustrated in Figs. 2 and 3, respectively. Bond distances and angles relevant to the zinc coordination sphere for both compounds are listed in Table 2. Compounds **2** and **3** are both five-coordinate and structurally similar with respect to the ligand atom donor sets. Although **2** and **3** are both coordinated by two ligands (HL for **2** and HL<sup>Ph<sub>3</sub></sup> for **3**) and one water molecule, there are significant geometric differences

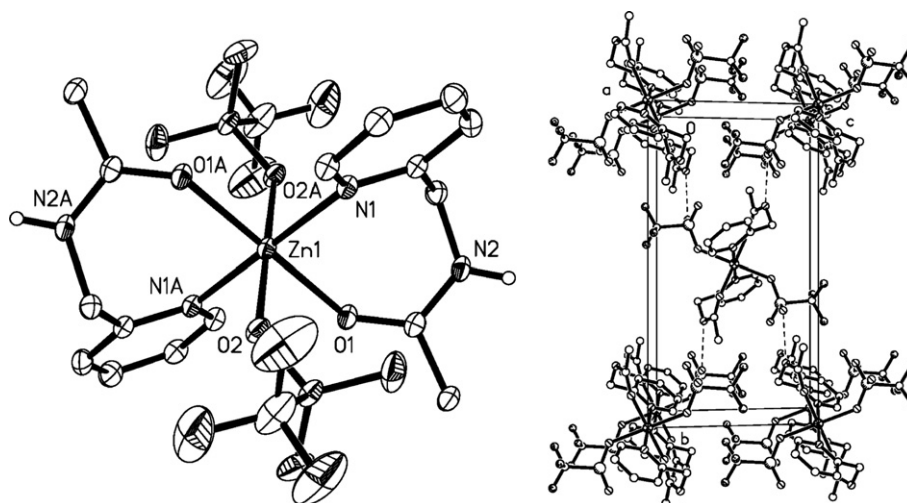


Fig. 1. Thermal ellipsoid representation of the X-ray crystal structure of  $[\text{Zn}(\text{HL})_2(\text{OTf})_2]$  (**1**, left). Thermal ellipsoids are drawn at the 50% level. All H atoms except for the amide H atoms are omitted for clarity. Packing diagram of **1** (right) showing hydrogen bonding interactions.

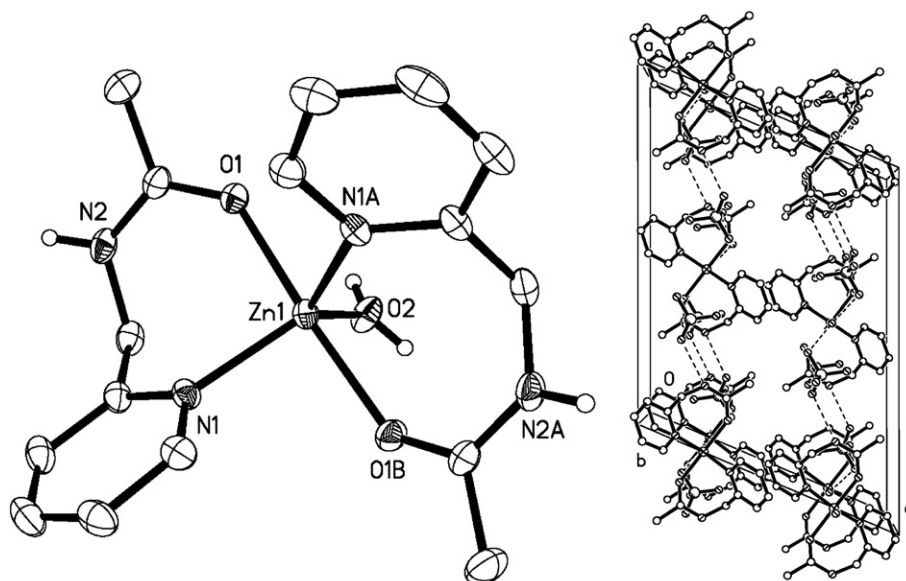


Fig. 2. Thermal ellipsoid representation of the X-ray crystal structure of  $[\text{Zn}(\text{HL})_2(\text{H}_2\text{O})](\text{ClO}_4)_2$  (**2**, left). Thermal ellipsoids are drawn at the 50% level. All H atoms except for the amide H atoms and water H atoms are omitted for clarity. Packing diagram of **2** (right) showing hydrogen bonding interactions.

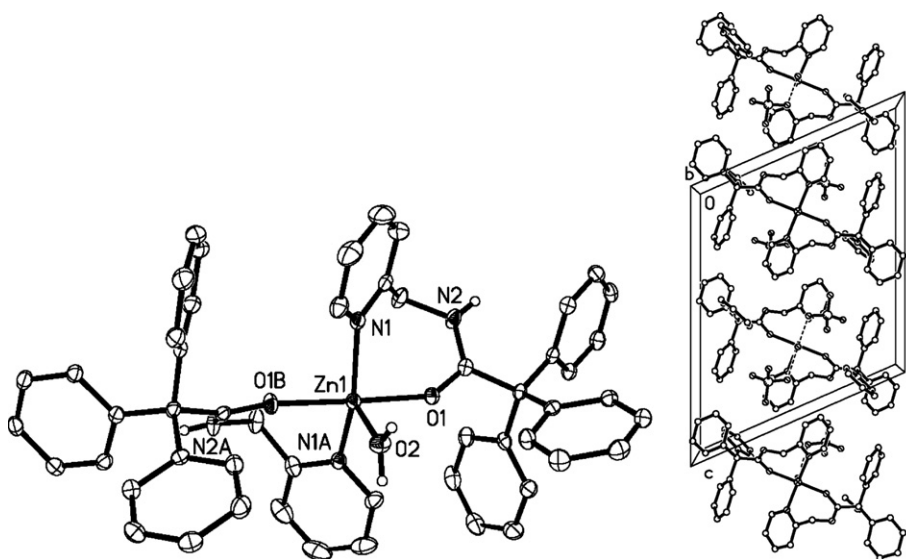


Fig. 3. Thermal ellipsoid representations of the X-ray crystal structure  $[\text{Zn}(\text{HL}^{\text{Ph}_3})_2(\text{H}_2\text{O})](\text{ClO}_4)_2$  (**3**, left). Thermal ellipsoids are drawn at the 50% level. All H atoms except for the amide H atoms and water H atoms are omitted for clarity. Packing diagram of **3** (right) showing hydrogen bonding interactions.

between **2** and **3**. Compounds **2** and **3** are both symmetrical with a twofold axis passing through the metal centers that divides the molecules into two equal halves. In complex **2**, which is best described as trigonal-bipyramidal, Zn1 is coordinated to two pyridyl nitrogens (N1 and N1A) at 2.037(2) Å and a water molecule (O2) at 1.976(3) Å, forming the equatorial plane. The Zn atom lies in the trigonal plane of N1, N1A, and O2, which is nearly planar. The carbonyl oxygens (O1 and O1B) at 2.112(2) Å are located axially, completing the distorted trigonal-bipyramid. An estimate of the degree of distortion from

ideal trigonal-bipyramidal geometry has been calculated according to the method of Addison et al. [38], indicating a geometry closest to trigonal-bipyramidal ( $\tau_5 = 0.82$  for **2**). The pyridyl rings of the two molecules are inclined at an angle of 99.8(2)° to each other. The crystal structure of **2** is held together by hydrogen bonding interactions. The coordinated water molecule (O2) hydrogen bonds intramolecularly to the carbonyl oxygens of the same molecule (O1 and O1B), with O2–O1/O1B distances of 2.710(4) and 2.810(12) Å. The amide nitrogen hydrogen bonds intermolecularly to the water oxygen O2A and the



Table 2  
Selected bond distances (Å) and angles (°) for **1**, **2**, and **3**

	<b>1</b>	<b>2</b>	<b>3</b>
Zn1–N1	2.1042(12)	2.037(2)	2.0353(12)
Zn1–O1	2.1243(10)	2.112(2)	2.0971(11)
Zn1–O2	2.1870(10)	1.976(3)	2.0148(16)
N1–Zn1–N1A	179.999(1)	116.33(12)	155.48(7)
O1–Zn1–O1A/O1B	180	171.16(12)	176.42(6)
N1–Zn1–O1A/O1B	86.90(4)	89.11(9)	89.10(5)
N1–Zn1–O1	93.10(4)	95.56(8)	90.14(5)
N1–Zn1–O2	86.50(4)	121.84(6)	102.26(4)
N1A–Zn1–O2	93.50(4)	121.84(6)	102.26(4)
O1A–Zn1–O2	91.21(4)	85.58(6)	91.79(3)
O1–Zn1–O2	88.79(4)	85.58(6)	91.79(3)

perchlorate oxygens O4 and O4A of an adjacent molecule. The N2–O2A distance is 3.050(14) Å and the N2–O4/O4A distances are ~3.016 Å (Fig. 2).

In contrast to **2**, **3** possesses a coordination geometry closer to square-pyramidal. The basal plane of the square pyramid is made up of two pyridyl nitrogens (N1 and N1A) and two carbonyl oxygens (O1 and O1B) at 2.0353(12) and 2.0971(11) Å, respectively. The fifth coordination site is occupied by a water molecule located axially at 2.0148(16) Å. The zinc atom lies 0.248 Å out of the least squares plane. The pyridyl rings of the two molecules are twisted by 83.3(2)° with respect to each other. The geometry around Zn1 is closer to distorted square-pyramidal, with a geometric index  $\tau_5$  of 0.35. Intramolecular hydrogen bonding interactions exist between the water oxygens and the perchlorate oxygens. The O2–O4A distance is 2.7259(15) Å (Fig. 3).

The Zn1–O<sub>carbonyl</sub> distances of ~2.11 Å in **2** and **3** lie in the same range as other five-coordinate zinc complexes of pyridyl ligands containing amino acids like L-phenylalanine [33]. However, these distances are longer than those observed in five-coordinate complexes containing the ligand unit (6-pivaloylamido-2-pyridylmethyl)amine, where the Zn–O<sub>carbonyl</sub> distances are in the range of 2.00–2.03 Å

[32]. This structural feature suggests that the amide oxygen binds somewhat more strongly to the zinc center in zinc complexes of (6-pivaloylamido-2-pyridylmethyl)amine compared to **2** and **3**. The Zn–N<sub>pyridyl</sub> distances in **2** and **3** are comparable to those reported in the literature [24–26].

Zinc complexes **4**, **5**, and **6** are isostructural, with slight variations in their bond lengths and angles. Their crystal structures are shown in Figs. 4–6, and their bond lengths and angles are listed in Table 3. The zinc atoms in **4**, **5**, and **6** are coordinated by two chlorides, and the pyridyl nitrogen and carbonyl oxygen of HL<sup>Ph</sup>, HL<sup>Me3</sup>, and MeL<sup>SMe</sup>, respectively. The Zn–N distances in **4–6** range from 2.039 to 2.055 Å and are quite similar to each other. The Zn–O distances are similarly quite close, ranging from 1.987 to 2.013 Å. The remaining coordination sites are occupied by two chloride anions with Zn–Cl distances ranging from 2.2093(3) to 2.2302(4) Å. The Zn–O, Zn–N, and Zn–Cl distances are very similar to the zinc complex of *N*-(2-pyridylmethyl)urea where Zn is coordinated to the pyridyl nitrogen, carbonyl oxygen, and the third and fourth coordination sites are occupied by chloride ions, forming a distorted tetrahedral structure [29]. The Zn–Cl distances are very similar to other tetrahedral zinc complexes of other pyridine based amine ligands [30], and complexes of benzimidazole ligands [39].

An estimate of the degree of distortion from idealized tetrahedral or square planar geometry for four-coordinate complexes has been calculated according to the method of Yang and Houser [40] with  $\tau_4$  values 0.94, 0.93, 0.90 for complexes **4**, **5**, and **6**, indicating geometries closest to distorted tetrahedral. The N–Zn–O and Cl–Zn–Cl angles range from 99.99(4)° to 119.27(14)°, and distortion is most pronounced in complex **6**. The dihedral angles between the N–Zn–O and the Cl1–Zn–Cl2 planes in **4**, **5**, and **6** are 86.6(2)°, 89.6(2)°, and 93.1(2)°, respectively. These values deviate only slightly from 90° of the idealized value for a tetrahedral structure.

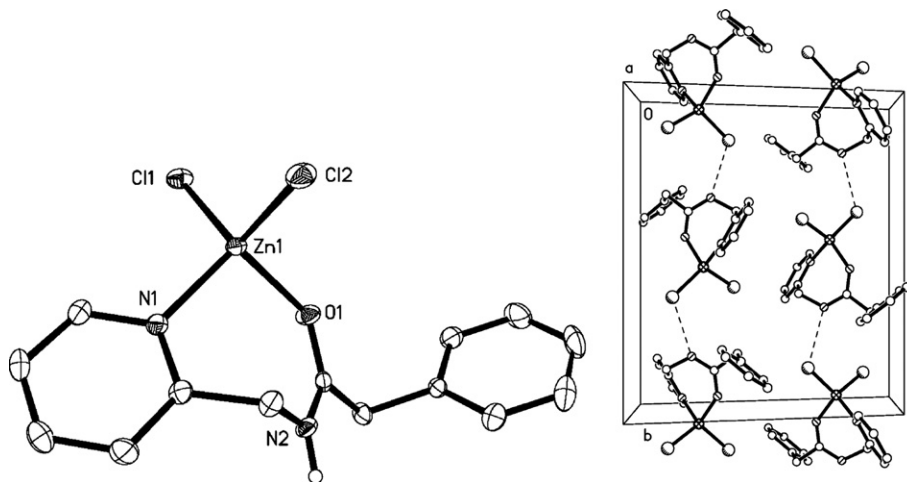


Fig. 4. Thermal ellipsoid representations of the X-ray crystal structures of [Zn(HL<sup>Ph</sup>)Cl<sub>2</sub>] (**4**, left). Thermal ellipsoids are drawn at the 50% level. All H atoms except for the amide H atoms are omitted for clarity. Packing diagram of **4** (right) showing hydrogen bonding interactions.

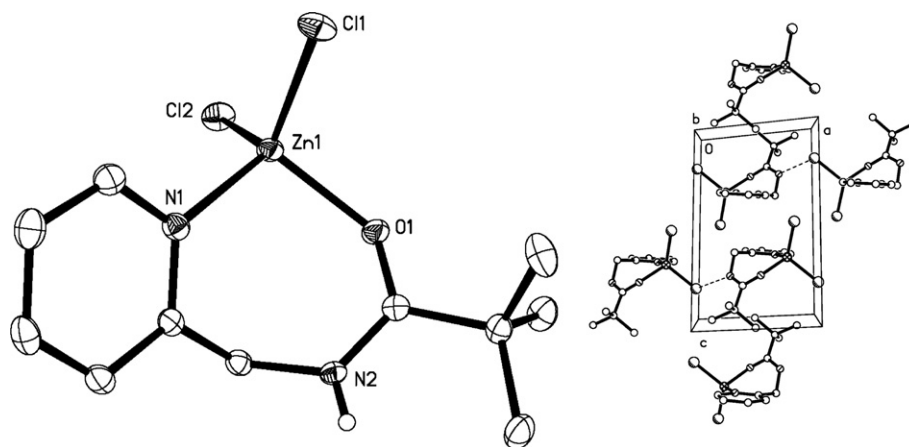


Fig. 5. Thermal ellipsoid representations of the X-ray crystal structures of  $[\text{Zn}(\text{HL}^{\text{Me}3})\text{Cl}_2]$  (**5**, left). Thermal ellipsoids are drawn at the 50% level. All H atoms except for the amide H atoms are omitted for clarity. Packing diagram of **5** (right) showing hydrogen bonding interactions.

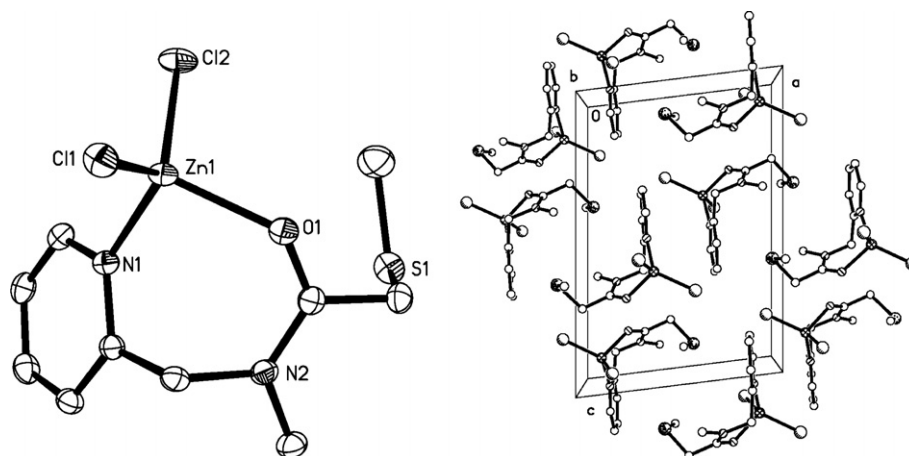


Fig. 6. Thermal ellipsoid representations of the X-ray crystal structures of  $[\text{Zn}(\text{MeL}^{\text{SMc}})\text{Cl}_2]$  (**6**, left). Thermal ellipsoids are drawn at the 50% level. All H atoms are omitted for clarity. Packing diagram of **6** (right) showing no hydrogen bonding interactions.

Table 3  
Selected bond distances (Å) and angles (°) for **4**, **5**, and **6**

	<b>4</b>	<b>5</b>	<b>6</b>
Zn1–N1	2.0403(15)	2.0550(11)	2.0393(11)
Zn1–O1	1.9881(13)	1.9931(10)	2.0138(10)
Zn1–Cl1	2.2227(5)	2.2302(4)	2.2122(4)
Zn1–Cl2	2.2184(5)	2.2151(4)	2.2092(4)
N1–Zn1–O1	100.12(6)	102.81(4)	100.00(4)
O1–Zn1–Cl1	112.01(4)	106.09(3)	106.37(3)
O1–Zn1–Cl2	108.12(4)	112.40(3)	108.14(3)
N1–Zn1–Cl1	108.19(5)	105.56(3)	114.28(3)
N1–Zn1–Cl2	113.52(5)	112.84(3)	106.92(3)
Cl2–Zn1–Cl1	114.06(2)	116.027(17)	119.271(15)

Intermolecular hydrogen bonding interactions exist in **4** and **5** between the amide hydrogen of one molecule and the chloride ions of an adjacent molecule forming linear chains. The N2–Cl distances in **4** and **5** are 3.2786(14) and 3.2040(12) Å, respectively (Figs. 4 and 5). Owing to

the fact that  $\text{MeL}^{\text{SMc}}$  does not contain an amide hydrogen, there are no such interactions in **6** as illustrated in Fig. 6. The fact that the thioether S atom in the structure of **6** does not coordinate to zinc is noteworthy, perhaps due to steric and/or geometric constraints. A five-coordinate structure with a S–Cu bond would lead to unfavourable geometric constraints, while a four-coordinate structure with a S–Cu bond in place of the O–Cu bond would lead to the formation of an eight-membered ring.

### 3. Conclusions

The synthesis, characterization, and structures of six new zinc complexes of the pyridylmethylamide family of ligands have been described. The complexes are four-, five-, and six-coordinate, possessing distorted tetrahedral, square-pyramidal, trigonal bipyramidal, and octahedral geometries. The counter anion plays a significant role in the coordination environment and geometry of each of

the complexes formed. When zinc triflate is used in the synthesis, the six-coordinate complex **1** forms with two HL ligands in the equatorial plane and the triflate ions occupying the axial coordination sites. With zinc perchlorate, the complexes formed are five-coordinate with either two HL ligands as in the case for **2**, or two HL<sup>Ph3</sup> ligands, as in the case for **3**, and a water molecule occupying the fifth site, either in the equatorial position for trigonal-bipyramidal **2**, or in the axial position for square-pyramidal **3**. Finally, when zinc chloride is used in the synthesis, complexes **4–6** with strongly coordinating chlorides were isolated. They are four-coordinate with only one ligand, and the third and fourth sites occupied by chloride ions. Hence the counter ion, rather than the ligand, has the greatest influence on the coordination behavior of the zinc complexes formed with the pyridylamide ligands. This stands in contrast to the copper(II) complexes of these ligands, which, due to their reduced flexibility with regard to coordination geometry as a result of the d<sup>9</sup> Jahn–Teller effect, were shown to have structures that were more strongly influenced by the ligands [35,36]. Furthermore, the copper(I) complexes of these ligands, which like zinc(II) are d<sup>10</sup>, are likewise quite different structurally, likely due predominantly to the differences in charge [40,41].

## 4. Experimental

### 4.1. General

All reagents were purchased from commercial sources and used without further purification. Solvents were dried and purified under nitrogen using standard methods and distilled immediately before use. <sup>1</sup>H NMR spectra were measured on a Varian 300 MHz spectrometer using solvent as an internal standard [<sup>1</sup>H δ (CHCl<sub>3</sub>) = 7.27 ppm; <sup>1</sup>H δ (CH<sub>3</sub>OH) = 4.87 ppm; <sup>13</sup>C δ (CHCl<sub>3</sub>) = 77.23 ppm]. Elemental analyses were carried out by Atlantic Microlabs (Norcross, GA). Mass spectra were recorded on a Q-TOF quadrupole time-of-flight mass spectrometer equipped with a Z-spray electrospray ionization (ESI) source (Micromass, Manchester, UK). IR spectra were recorded on a Nexus 470 FTIR spectrometer. The ligands *N*-(2-pyridylmethyl)acetamide (HL), 2-phenyl-*N*-(2-pyridylmethyl)acetamide (HL<sup>Ph</sup>), 2,2-dimethyl-*N*-(2-pyridylmethyl)propionamide (HL<sup>Me3</sup>), and 2,2,2-triphenyl-*N*-(2-pyridylmethyl)acetamide (HL<sup>Ph3</sup>) were synthesized according to published procedures [35,36]. *Caution:* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Although no problems were encountered in this work, only small amounts of material should be prepared and handled with caution.

### 4.2. *N*-Methyl-2-methylsulfanyl-*N*-pyridin-2-ylmethylacetamide (MeL<sup>SMe</sup>)

A solution of (methylthio)acetic acid (0.43 g, 4.09 mmol), HOBt (0.75 g, 4.91 mmol), and *N*-methyl(2-pyridyl)-

methaneamine (0.50 g, 4.09 mmol) in THF (10 mL) was cooled to −10 °C in an ice/salt bath. *N,N*-Dicyclohexylcarbodiimide monohydrate (DCC · H<sub>2</sub>O) (1.01 g, 4.91 mmol) was dissolved in a minimal volume of THF, cooled to −10 °C, and added in one portion to the (methylthio)acetic acid solution. The mixture was stirred at −10 °C for 1 h and allowed to warm to room temperature. Stirring was continued at room temperature for 30 h. The reaction mixture was then cooled to −40 °C and the DCU suspension was filtered off. The filtrate was concentrated *in vacuo* and dissolved in 6 mL of chloroform. This solution was loaded onto a RediSep (35 g) flash column. Impurities were eluted from the column with chloroform and the desired product was obtained in high purity as an orange oil following subsequent elution with methanol and removal of the solvent *in vacuo*. Yield: 0.86 g (95%). *Anal.* Calc. for C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>OS · 0.5H<sub>2</sub>O: C, 54.77; H, 6.89; N, 12.77. Found: C, 54.66; H, 6.94; N, 12.76%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 2.14 (s, 3H), 2.91 (s, 3H), 3.28 (s, 2H), 4.70 (s, 2H), 7.08–7.22 (m, 2H), 7.60 (m, 1H), 8.47 (m, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR: δ 16.16, 35.51, 53.43, 55.93, 121.90, 122.43, 137.30, 149.28, 157.22, 169.25 ppm. FTIR (KBr): 3062, 2920, 2855, 1717, 1644 (ν<sub>CO</sub>), 1590, 1571, 1476, 1435, 1397, 1300, 1257, 1151, 1099, 1049, 993, 939, 783, 753, 607 cm<sup>−1</sup>.

### 4.3. [Zn(HL)<sub>2</sub>(OTf)<sub>2</sub>] (**1**)

An acetonitrile solution of HL (0.096 g, 0.64 mmol) was added dropwise to an acetonitrile solution of Zn(OTf)<sub>2</sub> (0.117 g, 0.32 mmol) forming a white precipitate which was stirred for 4 h. The precipitate was collected by filtration and dissolved in methanol. Vapor diffusion of diethyl ether into this solution gave rise to the formation of X-ray quality crystals of **1**. Yield: 0.195 g (92%). *Anal.* Calc. for C<sub>18</sub>H<sub>20</sub>F<sub>6</sub>N<sub>4</sub>O<sub>8</sub>S<sub>2</sub>Zn: C, 32.56; H, 3.04; N, 8.44. Found: C, 32.68; H, 2.99; N, 8.42%. <sup>1</sup>H NMR (300 MHz, CH<sub>3</sub>OH-*d*<sub>4</sub>): δ 2.04 (s, 3H), 4.49 (d, 2H), 7.32–7.41 (m, 2H), 7.81–7.84 (t, 1H), 8.47–9.49 (d, 1H) ppm. ESI-MS (CH<sub>3</sub>OH): *m/z* = 663.0, [Zn(HL)<sub>2</sub>(OTf)<sub>2</sub>+H]<sup>+</sup>; 513.0, [Zn(HL)<sub>2</sub>(OTf)]<sup>+</sup>. FTIR (KBr): 3300 (ν<sub>NH</sub>), 3053, 1667 (ν<sub>CO</sub>), 1612, 1558, 1443, 1378, 1356, 1266, 1175, 1142, 1046, 1038, 776, 643, 520 cm<sup>−1</sup>.

### 4.4. [Zn(HL)<sub>2</sub>(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> (**2**)

A methanol solution of HL (0.075 g, 0.5 mmol) was added dropwise to a methanol solution of Zn(ClO<sub>4</sub>)<sub>2</sub> (0.093 g, 0.25 mmol). The reaction mixture was stirred for 1 h after which the solvent was removed to give a reddish white solid. The product was dissolved in methanol and vapor diffusion of diethyl ether gave rise to the formation of X-ray quality crystals of **2**. Yield: 0.120 g (80%). *Anal.* Calc. for C<sub>16</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>11</sub>Zn: C, 32.96; H, 3.77; N, 9.61. Found: C, 32.77; H, 3.82; N, 9.61%. <sup>1</sup>H NMR (300 MHz, CH<sub>3</sub>CN-*d*<sub>3</sub>): δ 2.02 (s, 3H), 2.62 (bs, 2H), 4.57 (d, 2H), 7.65 (m, 2H), 8.20 (m, 2H), 8.55 (d, 1H) ppm. ESI-MS (CH<sub>3</sub>CN): *m/z* = 463.0, [Zn(HL)<sub>2</sub>ClO<sub>4</sub>]<sup>+</sup>. FTIR (KBr):

3400 ( $\nu_{\text{OH}}$ ), 3299 ( $\nu_{\text{NH}}$ ), 2361, 1650 ( $\nu_{\text{CO}}$ ), 1613, 1558, 1490, 1444, 1421, 1373, 1355, 1312, 1145, 1088 ( $\nu_{\text{ClO}_4^-}$ ), 776, 636, 627  $\text{cm}^{-1}$ .

#### 4.5. $[\text{Zn}(\text{HL}^{\text{Ph}_3})_2(\text{H}_2\text{O})](\text{ClO}_4)_2$ (**3**)

A dichloromethane solution of  $\text{HL}^{\text{Ph}_3}$  (0.10 g, 0.13 mmol) was added dropwise to a methanol solution of  $\text{Zn}(\text{ClO}_4)_2$  (0.05 g, 0.13 mmol), resulting in a clear and colorless solution. Slow evaporation resulted in the formation of X-ray quality crystals of **3**. Yield: 0.12 g (86%).  $^1\text{H}$  NMR (300 MHz,  $\text{CH}_3\text{OH}-d_4$ ):  $\delta$  4.54 (d, 2H), 6.93–6.95 (m, 1H), 7.24–7.32 (m, 17H), 7.64 (t, 1H), 8.38–8.40 (d, 1H) ppm. ESI-MS ( $\text{CH}_3\text{OH}$ ):  $m/z = 920.4$ ,  $[\text{Zn}(\text{HL}^{\text{Ph}_3})_2\text{ClO}_4]^+$ ; 410.6,  $[\text{Zn}(\text{HL}^{\text{Ph}_3})_2]^{2+}$ . FTIR (KBr): 3415 ( $\nu_{\text{OH}}$ ), 3220 ( $\nu_{\text{NH}}$ ), 3056, 1666 ( $\nu_{\text{CO}}$ ), 1620, 1596, 1572, 1518, 1491, 1443, 1256, 1118 ( $\nu_{\text{ClO}_4^-}$ ), 1034, 1001, 765, 699, 639, 616, 516  $\text{cm}^{-1}$ .

#### 4.6. $[\text{Zn}(\text{HL}^{\text{Ph}})\text{Cl}_2]$ (**4**)

A methanol solution of  $\text{HL}^{\text{Ph}}$  (0.1013 g, 0.45 mmol) was added dropwise to a methanol solution of  $\text{ZnCl}_2$  (0.06 g, 0.45 mmol). Within minutes there was a formation of a white precipitate. The solution was allowed to stir overnight after which it was warmed and the solution was completely clear. Slow evaporation resulted in the formation of X-ray quality crystals of **4**. Yield: 0.14 g (85%). *Anal. Calc.* for  $\text{C}_{14}\text{H}_{14}\text{Cl}_2\text{N}_2\text{OZn}$ : C, 46.38; H, 3.89; N, 7.73. Found: C, 46.09; H, 3.83; N, 7.71%.  $^1\text{H}$  NMR (300 MHz,  $\text{CH}_3\text{OH}-d_4$ ):  $\delta$  3.59 (d, 2H), 4.50 (d, 2H), 7.27–7.31 (m, 7H), 7.77–7.78 (m, 1H), 8.47–8.49 (d, 1H) ppm. ESI-MS ( $\text{CH}_3\text{OH}$ ):  $m/z = 689.0$ ,  $[\text{Zn}_2(\text{HL}^{\text{Ph}})_2\text{Cl}_3]^+$ ; 551.1,  $[\text{Zn}(\text{HL}^{\text{Ph}})_2\text{Cl}]^+$ ; 325.0,  $[\text{Zn}(\text{HL}^{\text{Ph}})\text{Cl}]^+$ . FTIR (KBr): 3312 ( $\nu_{\text{NH}}$ ), 3083, 3033, 2931, 2361, 1617 ( $\nu_{\text{CO}}$ ), 1583, 1557, 1496, 1485, 1444, 1363, 1348, 1324, 1198, 1180, 1112, 1063, 1028, 1010, 919, 844, 764, 775, 732, 698, 667, 652, 616, 534, 510, 445, 416  $\text{cm}^{-1}$ .

#### 4.7. $[\text{Zn}(\text{HL}^{\text{Me}_3})\text{Cl}_2]$ (**5**)

A methanol solution of  $\text{HL}^{\text{Me}_3}$  (0.100 g, 0.51 mmol) was added dropwise to a methanol solution of  $\text{ZnCl}_2$  (0.070 g, 0.51 mmol). Within minutes there was a formation of a white precipitate. The solution was allowed to stir overnight after which it was warmed and the solution was completely clear. Slow evaporation resulted in the formation of X-ray quality crystals of **5**. Yield: 0.13 g (76%). *Anal. Calc.* for  $\text{C}_{11}\text{H}_{16}\text{Cl}_2\text{N}_2\text{OZn}$ : C, 40.21; H, 4.91; N, 8.53. Found: C, 40.18; H, 4.87; N, 8.54%. ESI-MS ( $\text{CH}_3\text{OH}$ ):  $m/z = 621.0$ ,  $[\text{Zn}_2(\text{HL}^{\text{Me}_3})_2\text{Cl}_3]^+$ ; 485.2,  $[\text{Zn}(\text{HL}^{\text{Me}_3})_2\text{Cl}]^+$ ; 291.0  $[\text{Zn}(\text{HL}^{\text{Me}_3})\text{Cl}]^+$ .  $^1\text{H}$  NMR ( $\text{CH}_3\text{OH}-d_4$ ):  $\delta$  1.20–1.22 (m, 9H), 4.53 (s, 2H), 7.36–7.39 (m, 2H), 7.87 (t, 1H), 8.52–8.54 (d, 1H) ppm. FTIR (KBr): 3302 ( $\nu_{\text{NH}}$ ), 3066, 2974, 2361, 1602 ( $\nu_{\text{CO}}$ ), 1584, 1547, 1484, 1443, 1396, 1363, 1307, 1253, 1161, 1105, 1061, 1027, 1057,

989, 967, 898, 863, 792, 779, 703, 649, 623, 591, 542, 425, 411  $\text{cm}^{-1}$ .

#### 4.8. $[\text{Zn}(\text{MeL}^{\text{SMe}})\text{Cl}_2]$ (**6**)

A methanol solution of  $\text{MeL}^{\text{SMe}}$  (0.250 g, 1.19 mmol) was added dropwise to a methanol solution of  $\text{ZnCl}_2$  (0.162 g, 1.07 mmol). The reaction mixture was stirred for 1 h after which the solvent was removed to give a tan powder. The tan powder was dissolved in chloroform and slow evaporation of a concentrated solution of the tan powder gave rise to the formation of X-ray quality crystals of **6**. Yield: (0.347 g, 93%). *Anal. Calc.* for  $\text{C}_{10}\text{H}_{14}\text{Cl}_2\text{N}_2\text{OSZn}$ : C, 34.65; H, 4.07; N, 8.08. Found: C, 34.72; H, 4.07; N, 8.09%.  $^1\text{H}$  NMR ( $\text{CH}_3\text{OH}-d_4$ ):  $\delta$  2.14 (s, 3H), 3.14 (s, 3H), 3.44 (s, 2H), 4.71–4.77 (m, 2H), 7.33–7.35 (m, 2H), 7.81–7.83 (t, 1H), 8.49–8.52 (m, 1H) ppm. ESI-MS ( $\text{CH}_3\text{OH}$ ):  $m/z = 519.0$ ,  $[\text{Zn}(\text{MeL}^{\text{SMe}})_2\text{Cl}]^+$ ; 309.0,  $[\text{Zn}(\text{MeL}^{\text{SMe}})\text{Cl}]^+$ . FTIR (KBr): 3435, 3106, 3054, 3031, 2991, 2959, 2916, 2829, 1609 ( $\nu_{\text{CO}}$ ), 1587, 1486, 1459, 1442, 1406, 1352, 1323, 1280, 1225, 1150, 1123, 1095, 1059, 1029, 1001, 986, 874, 836, 797, 775, 707, 660, 652, 618, 571, 534, 480, 464, 422  $\text{cm}^{-1}$ .

#### 4.9. X-ray crystal structure determination

Single crystals of **1–6** were obtained by either slow evaporation of methanol or acetonitrile solutions of the complex or by vapor diffusion of diethyl ether into solutions of the complex. Intensity data for **1–6** were collected on a Bruker Apex CCD area detector diffractometer with graphite-monochromated  $\text{Mo K}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. Cell parameters were determined from a non-linear least squares fit of the data. The data were corrected for absorption by the semi-empirical method. The structures were solved by direct methods by use of the SHELXTL program,

Table 4  
Crystallographic data for **1–3**

	1	2	3
Formula	$\text{C}_{18}\text{H}_{20}\text{F}_6\text{N}_4\text{O}_8\text{S}_2\text{Zn}$	$\text{C}_{16}\text{H}_{22}\text{Cl}_2\text{N}_4\text{O}_{11}\text{Zn}$	$\text{C}_{52}\text{H}_{46}\text{Cl}_2\text{N}_4\text{O}_{11}\text{Zn}$
<i>M</i>	663.87	582.65	1039.20
<i>T</i> (K)	110(2)	120(2)	120(2)
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2/ <i>c</i>
<i>a</i> (Å)	8.6860(6)	19.724(8)	15.468(2)
<i>b</i> (Å)	16.8188(12)	8.578(3)	8.7668(14)
<i>c</i> (Å)	9.0827(7)	15.147(5)	18.578(2)
$\alpha$ (°)	90	90	90
$\beta$ (°)	103.0670(10)	113.23(2)	113.786(5)
$\gamma$ (°)	90	90	90
<i>Z</i>	2	4	2
<i>V</i> (Å <sup>3</sup> )	1292.52(16)	2355.0(15)	2305.3(5)
$\rho_{\text{calc}}$ (g cm <sup>−3</sup> )	1.706	1.643	1.497
$\mu$ (mm <sup>−1</sup> )	1.206	1.333	0.718
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0230	0.0320	0.0291
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0607	0.0912	0.0812
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.093	1.004	1.002



Table 5  
Crystallographic data for 4–6

	4	5	6
Formula	C <sub>14</sub> H <sub>14</sub> Cl <sub>2</sub> N <sub>2</sub> OZn	C <sub>11</sub> H <sub>16</sub> Cl <sub>2</sub> N <sub>2</sub> OZn	C <sub>10</sub> H <sub>14</sub> Cl <sub>2</sub> N <sub>2</sub> OSZn
<i>M</i>	362.54	328.53	346.56
<i>T</i> (K)	120(2)	100(2)	120(2)
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> -1	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> (Å)	8.0075(7)	7.5486(10)	10.5046(5)
<i>b</i> (Å)	15.1720(13)	8.7671(12)	8.6334(4)
<i>c</i> (Å)	13.3883(11)	11.9684(16)	15.4007(8)
$\alpha$ (°)	90	70.469(5)	90
$\beta$ (°)	105.4550(10)	86.480(5)	97.0570(10)
$\gamma$ (°)	90	67.720(5)	90
<i>Z</i>	4	2	4
<i>V</i> (Å <sup>3</sup> )	1567.7(2)	688.81(16)	1386.11(12)
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.536	1.584	1.661
$\mu$ (mm <sup>-1</sup> )	1.903	2.156	2.292
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0269	0.0176	0.0178
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0714	0.0463	0.0476
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.059	1.003	1.083

and refined by full-matrix least squares on *F*<sup>2</sup> by use of all reflections [42,43]. Hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal data for 1–6 are summarized in Tables 4 and 5, and selected bond lengths and angles are listed in Tables 2 and 3.

## 5. Supplementary material

CCDC 625121, 625122, 625123, 625124, 625125, and 625126 contain the supplementary crystallographic data for 1, 2, 3, 4, 5, and 6. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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