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# An eight-coordinate zinc complex containing the highly pre-organized ligand 1,10-phenanthroline-2,9-dicarboxylic acid: Solvothermal synthesis, supramolecular structure and CSD studies

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## ABSTRACT

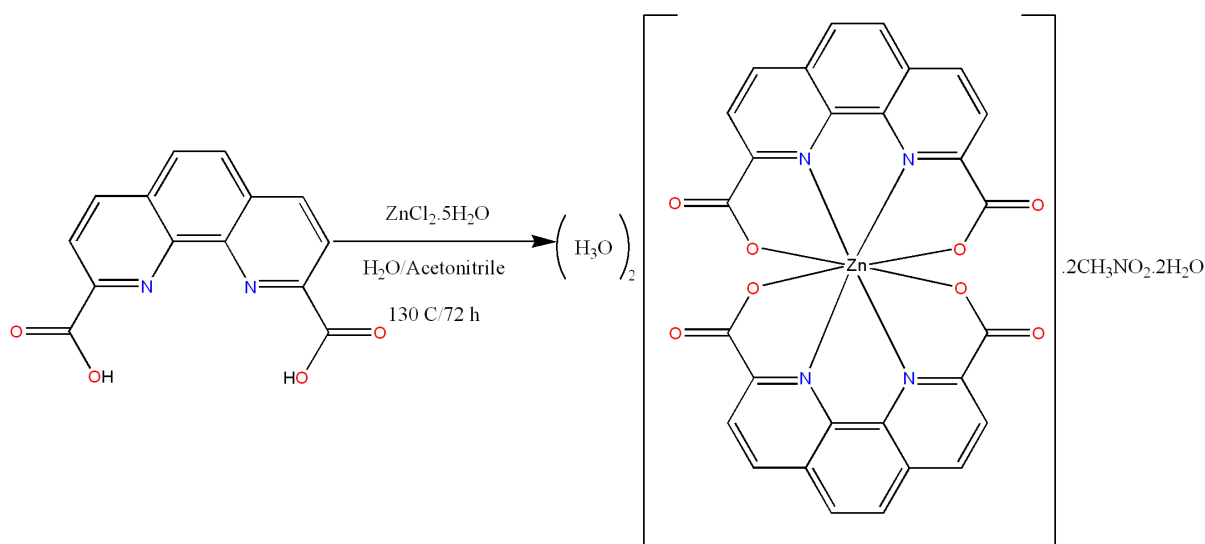
A new anionic coordination complex of Zn(II) containing the highly pre-organized ligand 1,10-phenanthroline-2,9-dicarboxylate (PDA),  $(\text{H}_3\text{O})_2[\text{Zn}(\text{PDA})_2] \cdot 2\text{CH}_3\text{NO}_2 \cdot 2\text{H}_2\text{O}$  (**1**), has been synthesized by solvothermal methods and characterised by elemental analysis, infrared spectroscopy and single-crystal X-ray diffraction. The last of these techniques revealed a coordination sphere around Zn(II) consisting of four N atoms and four O donors from two 1,10-phenanthroline-2,9-dicarboxylate ligands which features a distorted dodecahedral geometry. The ionic coordination motifs in **1** are held together by intermolecular O–H $\cdots$ O, N–H $\cdots$ O and C–H $\cdots$ O hydrogen bonding, C–H $\cdots$  $\pi$  and  $\pi$ – $\pi$  stacking interactions, to produce an extended 2D architecture.

**Keywords:** pre-organized ligand; 1,10-phenanthroline-2,9-dicarboxylic acid; zinc complex;  $\pi$ – $\pi$  stacking interaction; hydrogen bonding.

## 1. Introduction

Currently, a key goal for chemists lies in the design and synthesis of new materials with significantly improved properties and performance. In this arena, supramolecular chemistry offers powerful synthetic tools such as the ability to vary the metal centre [1–4], its counter ions [5–7], the steric, conformational and coordinative features of the ligand [8, 9] and the reaction conditions [10–13]. This flexibility allows us to exert control over the self-assembly process and construct desirable target architectures for potential real-world applications. Among these factors, the selection of suitable organic ligands plays a significant role [14]. Pre-organized ligands have proven to be important in inorganic, biomedical, environmental, and industrial chemistry [15]. Such ligands possess rigid backbones, resulting in minimal motion of the donor groups due to the conformation of the free ligand being closely similar to that in

the metal complex [16], allowing the pre-organized ligands to coordinate selectively to metal ions. The H<sub>2</sub>PDA ligand, with its planar, rigid phenanthroline skeleton and two carboxylate groups at the 2 and 9 positions, is thereby one of the most prominent such ligands and is used to prepare coordination compounds with selected metal ions [17] and luminescent [18] or magnetic properties [19]. A search of the Cambridge Structural Database [CSD version 5.38 (version of October 2017)/Conquest version 1.21]<<INSERT reference: Groom et al., 2016)>> revealed 49 coordination compounds of the PDA ligand which is mostly frequently found coordinated to metal ions with ionic radii of *ca.* 1 Å. With various functional groups, this symmetrically chelating ligand provides non-covalent interactions such as hydrogen bonding and aromatic stacking for controlling the intergrowth of supramolecular networks. In previous work, we focused on design and synthesis of lanthanoid coordination frameworks containing H<sub>2</sub>PDA [20]. As a continuation of our efforts to develop novel systems containing dicarboxylic acids [21–25] and in order to allow comparisons to be drawn with the previous work, we synthesized a zinc(II) coordination complex, (H<sub>3</sub>O)<sub>2</sub>[Zn(PDA)<sub>2</sub>]·2CH<sub>3</sub>NO<sub>2</sub>·2H<sub>2</sub>O, (**1**), using the H<sub>2</sub>PDA ligand. Complex **1** has been characterized by elemental analysis and infrared spectroscopy. Its solid-state structure was determined by single crystal X-ray diffraction analysis which showed that  $\pi$ - $\pi$  stacking and hydrogen bonding interactions are crucial to the formation and generation of higher-dimensional (D) network.



Scheme 1. The synthetic procedure of **1**.

## 2. Experimental

### 2.1. Materials and instrumentation

All commercially available chemicals were of reagent grade and were used without further purification, except for PDA which was synthesized according to literature methods [26]. Infrared spectra were recorded as KBr disks in the range (4000–600  $\text{cm}^{-1}$ ) on a Buck 500 Scientific spectrometer. Elemental analysis was carried out with a Thermo Finnigan Flash-1112EA microanalyzer and Perkin-Elmer 2004(II) apparatus. Melting points were determined on a Electrothermal Thermo Scientific IA 9000 apparatus.

### 2.2. Synthesis of $(\text{H}_3\text{O})_2[\text{Zn}(\text{PDA})_2]\cdot 2\text{CH}_3\text{NO}_2\cdot 2\text{H}_2\text{O}\cdot (1)$

A mixture of  $\text{H}_2\text{PDA}$  (54 mg, 0.2 mmol) and  $\text{ZnCl}_2\cdot 5\text{H}_2\text{O}$  (22 mg, 0.1 mmol) in deionized water/acetonitrile (15 ml; 1:1) was stirred for about 30 min. The mixture was then transferred into a 23 ml Teflon-lined autoclave and kept at 130  $^{\circ}\text{C}$  for 3 days. After slow cooling (5  $^{\circ}\text{C}\cdot\text{h}^{-1}$ ) to the room temperature, crystals of the complex **1** could be isolated as translucent light-yellow tablet crystals (see Scheme 1). Yield: 53 % (based on Zn). Anal. Calcd. For  $\text{C}_{30}\text{H}_{30}\text{ZnN}_6\text{O}_{16}$ : C, 45.27; H, 3.80; N, 10.56. Found: C, 46.85; H, 3.41; N, 11.25 %. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3377(s), 1637(s), 1570 (s), 1466(m), 1361(s), 1313(m), 1247(w), 867(m), 828(w), 780(m). m.p. > 400  $^{\circ}\text{C}$ .

### 2.3. X-ray crystallography

Single-crystal data collection for **1** was performed on a Bruker SMART APEX II CCD area detector diffractometer, equipped with an Oxford Cryosystems open-flow nitrogen cryostat operating at 120 K, using  $\omega$  scans and graphite-monochromated Cu  $K\alpha$  radiation ( $\lambda = 1.54184$  Å). The crystal was mounted on a thin glass fibre using paraffin oil. All data sets were corrected for Lorentz, polarization and absorption effects as specified in Table 1. The structure was solved by direct methods using *SHELXS97* [27], completed with difference Fourier synthesis, and refined on  $F^2$  by full-matrix least-squares using *SHELXL97* [28].

**Table 1** Selected crystal data and structure refinement details for **1**

Empirical formula	C <sub>28</sub> H <sub>12</sub> ZnN <sub>4</sub> O <sub>8</sub> ·2(CH <sub>3</sub> NO <sub>2</sub> )·2(H <sub>3</sub> O)·2(H <sub>2</sub> O)
Formula weight, g mol <sup>-1</sup>	795.97
Temperature, K	120(2)
Wavelength $\lambda$ , Å	1.54184
Crystal system	Tetragonal
Space group	<i>I</i> 4 <sub>1</sub> / <i>a</i>
<i>a</i> / Å	10.4342(2)
<i>b</i> / Å	10.4342(2)
<i>c</i> / Å	30.6744(6)
<i>V</i> / Å <sup>3</sup>	3339.60(14)
<i>Z</i>	4
<i>D<sub>c</sub></i> / Mgm <sup>-3</sup>	1.583
<i>F</i> <sub>000</sub>	1640
$\mu$ / mm <sup>-1</sup>	1.79
Crystal size/ mm <sup>3</sup>	0.26 × 0.17 × 0.03
Space range, °	4.5 to 67.9
Reflections collected	7862
Reflection independent	1520
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0678, 0.1967
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0697, 0.1987
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.05
Largest differences peak and hole, e Å <sup>-3</sup>	0.73 and -0.49

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

Zn1–N1	2.141(3)	Zn1–O2	2.579(3)
O2–Zn1–N1	67.16(9)	O2–Zn1–O2	149.10(9)
O2–Zn1–N1	143.72(9)	O2–Zn1–O2	94.07(9)
O2–Zn1–N1	76.55(9)	O2–Zn1–N1	79.31(9)
N1–Zn1–N1	76.64(8)	N1–Zn1–N1	127.99(8)

**Table 3** Selected hydrogen bonding interactions present in **1**

D–H...A	d(D–H)/Å	D(H–A)/Å	d(D–A)/Å	D–H–A/°
O2S–H2SA...O1	0.96	1.78	2.696(5)	158
O2S–H2SB...O1	0.93	1.83	2.719(5)	152
C3–H4...O2	0.95	2.44	3.325(11)	154

### 3. Results and discussion

#### 3.1. Vibrational spectrum

In addition to elemental analysis, complex **1** was initially characterized by its IR spectrum. The medium intense broad absorption in the 3377  $\text{cm}^{-1}$  region indicates the presence of water molecules. The observed bands at 1570 and 1361  $\text{cm}^{-1}$  are attributed to the antisymmetric  $\nu_{\text{as}}(\text{COO}^-)$  and symmetric  $\nu_{\text{s}}(\text{COO}^-)$  stretching vibrations of carboxylate groups. The resulting value of  $\Delta\nu$  ( $\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}} = 209 \text{ cm}^{-1}$ ) is characteristic of the monodentate bonding mode of the carboxylate group. The band at 867  $\text{cm}^{-1}$  is assigned as ring breathing mode of the phen ligand [29]. These assignments are supported by the results of the single-crystal X-ray diffraction analysis.

### 3.3. Description of crystal structure

Crystal data for compound **1** are shown in Table 1 while selected bond lengths and bond angles are given in Table 2 and hydrogen bond parameters are shown in Table 3. As shown in Fig. 1, molecular structure of **1** contains discrete 1,10-phenanthroline-2,9-dicarboxylate zinc(II) anions, hydronium cations, water and nitromethane molecules. In the anionic complex, each  $\text{Zn}^{\text{II}}$  ion is eight-coordinated and surrounded by four O and four N donors from two PDA ligands in a distorted dodecahedral geometry, with Zn–O and Zn–N distances of 2.579(3) and 2.141(3) Å, respectively. Each  $(\text{PDA})^{2-}$  acts as a tetradentate chelating ligand and the ligands are almost perpendicular to each other in a *cis* arrangement. As seen from Table 4, the bond distances in **1** are longer than the values reported in the literature. Connectivity within the coordination compound is supplemented by O–H $\cdots$ O [O $\cdots$ O distances are 2.696(5) and 2.719(5) Å] and C–H $\cdots$ O [C $\cdots$ O distance is 3.325(11) Å] hydrogen bonds between  $(\text{PDA})^{2-}$  carboxylate groups and hydronium cations. Hydronium cations connect discrete anionic complexes into 2D layers with the ring having the graph-set notation  $R_8^4(16)$  along the *ac* plane (Fig. 2). Additionally, C–H $\cdots$ O interactions involving the coordinated O of carboxylate and an H atoms from an aromatic ring create  $R_2^2(14)$  graph-sets along the crystallographic *c* axis (Fig. 3). It is worth mentioning that the three aromatic rings of the  $\text{PDA}^{2-}$  ligand play an important role in self-assembly *via*  $\pi$ – $\pi$  [centroid-centroid distances 3.993 Å (*Cg1* $\cdots$ *Cg2*) and dihedral angle 18.73°] stacking interactions along the crystallographic *a* axis. (Fig. 4). ~~These non-covalent interactions make the solid state structure of **1** more stable and assembled as a 3D supramolecular network.~~

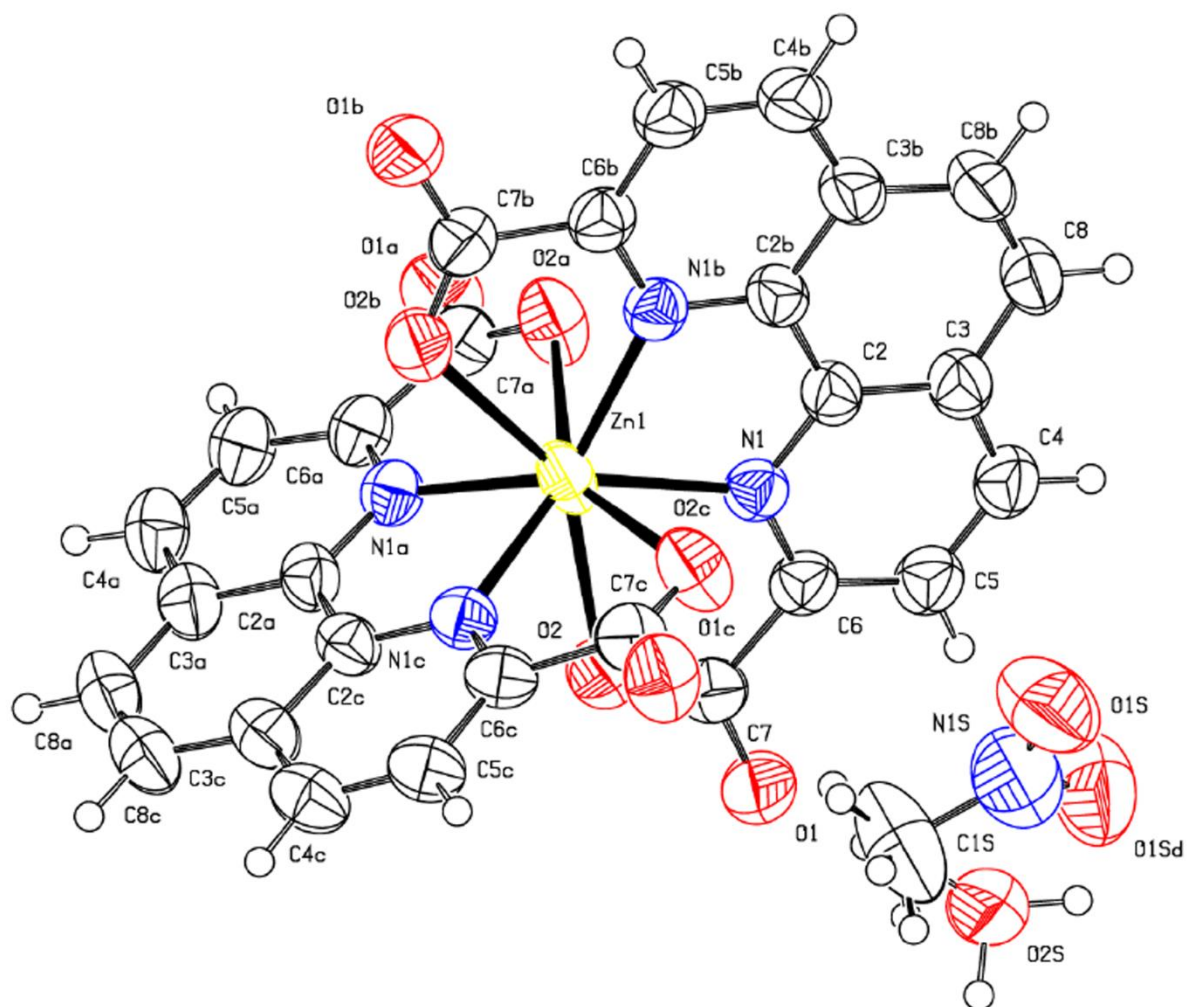


Fig 1. Ellipsoid plot of **1** showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

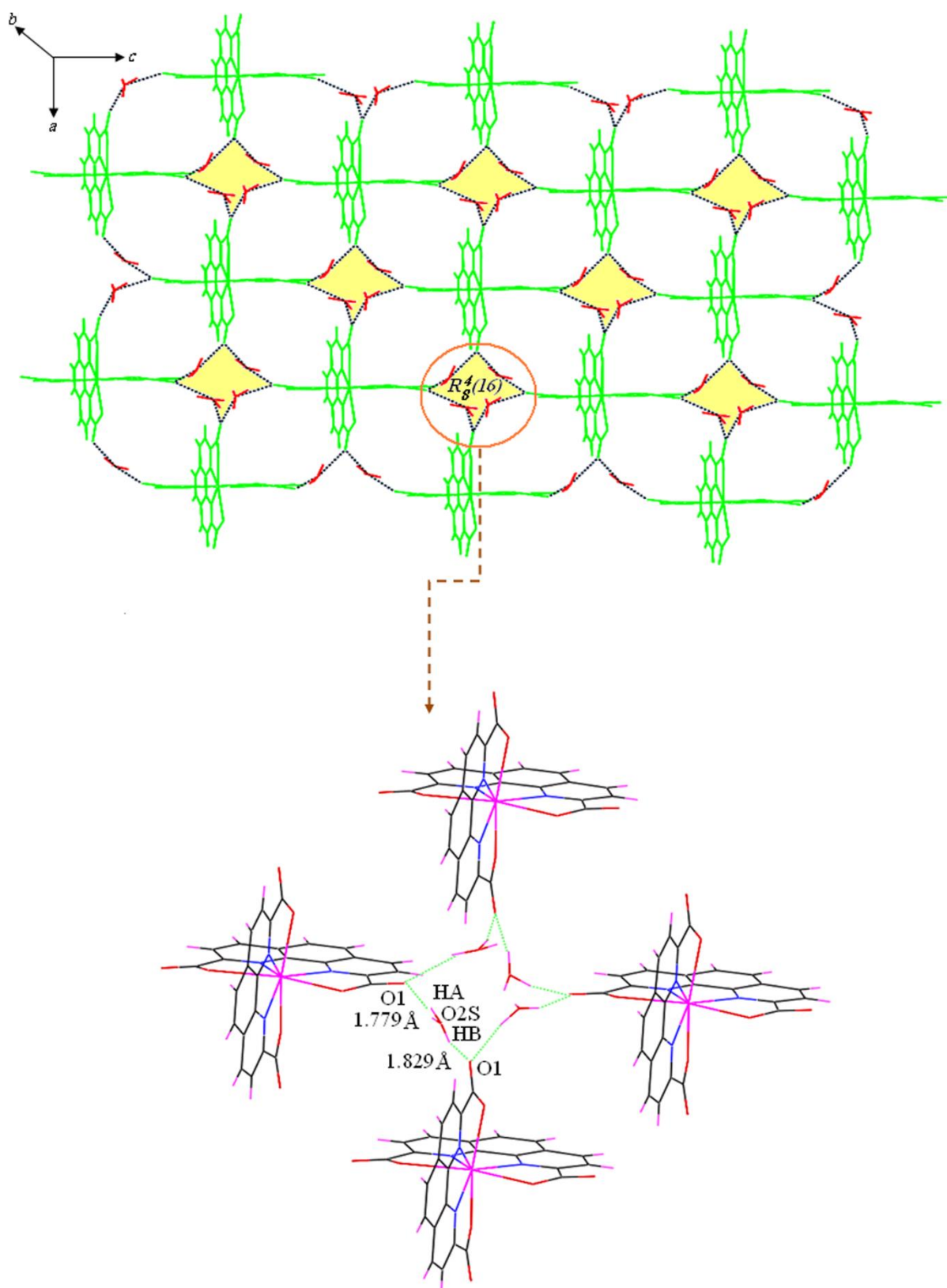


Fig 2. (Top) Hydrogen bonds present in **1** generate a 2D layer, here viewed along *ac* plane; (bottom) schematic representation of graph-sets.



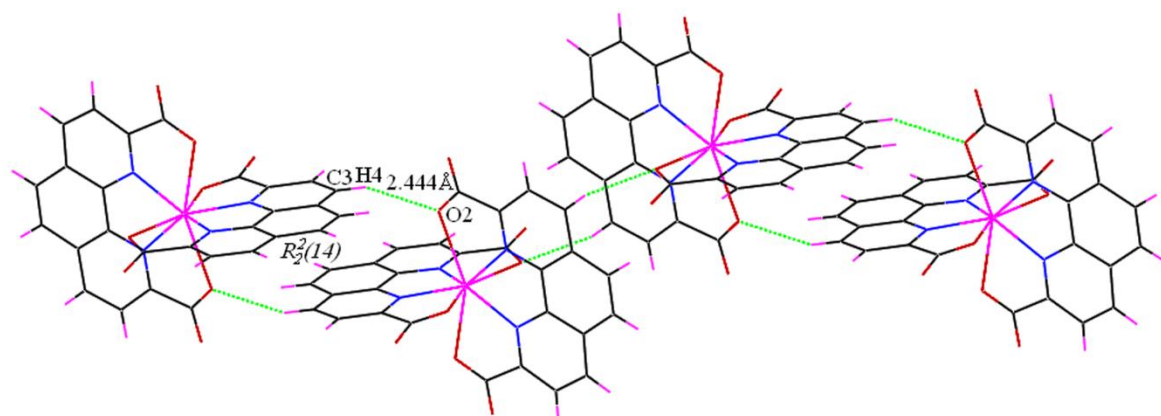


Fig 3. C–H $\cdots$ O hydrogen bonds generate  $R_2^2(14)$  graph-sets along the  $c$  axis.

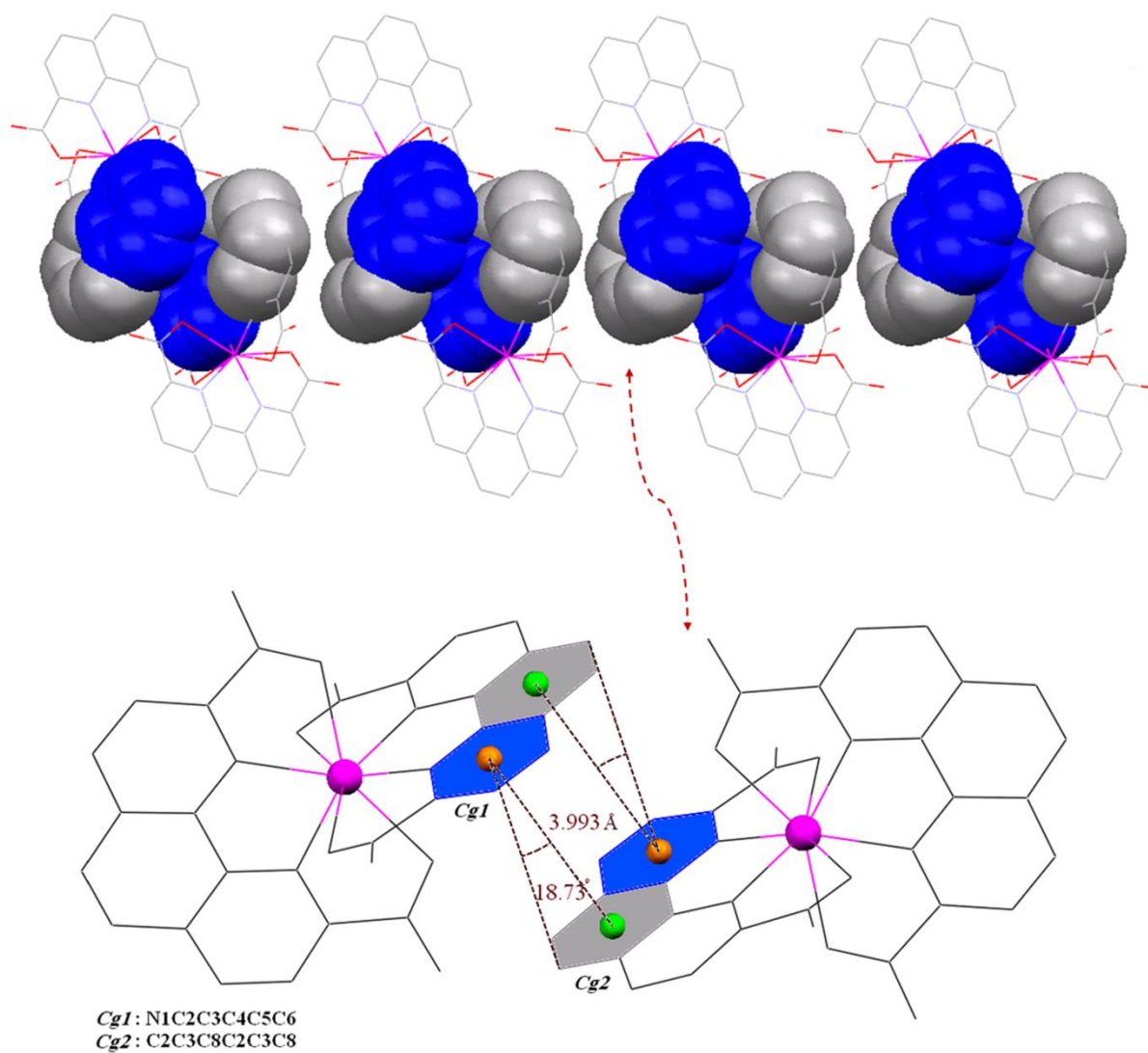


Fig 4. Partial view of the crystal packing of **1** with indication of the  $\pi$ - $\pi$  stacking interactions along the *a* axis.

**Table 4** Comparison of the bond distances (Å) within some PDA complexes

Chemical formula	M–O	Ref
(H <sub>3</sub> O) <sub>2</sub> [Zn(PDA) <sub>2</sub> ]·2CH <sub>3</sub> NO <sub>2</sub> ·2H <sub>2</sub> O ( <b>1</b> )	2.579	This work
Cu <sub>2</sub> (PDA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ·2H <sub>2</sub> O	1.904, 2.073	30
(Hpyda) <sub>2</sub> [Cu(PDA) <sub>2</sub> ]·10H <sub>2</sub> O	2.165, 2.232	31
[Ni(PDA)(H <sub>2</sub> O) <sub>3</sub> ]·H <sub>2</sub> O	2.116	32
[Co(PDA)(H <sub>2</sub> O) <sub>3</sub> ]·2H <sub>2</sub> O	2.336	33
[Fe(HPDA)(H <sub>2</sub> O) <sub>3</sub> ] (ClO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O·1/2H <sub>5</sub> O <sub>2</sub>	2.120	34
[Mn(PDA)(H <sub>2</sub> O) <sub>3</sub> ]	2.350	35
(Hpyda)[Cr(PDA) <sub>2</sub> ]·5H <sub>2</sub> O	1.976, 1.953	36

Abbreviation: pyda = pyridine-2,6-diamine

**Database studies.** << It would be valuable to specify the CSD search parameters that gave these 49 hits.>> Upon examination of the crystal structure of **1** and the crystal structures identified in the CSD search the following interesting issues arise. First, in the 49 complexes containing PDA as ligand, the highest and lowest abundances are related to lanthanoid and main group metals, respectively. The reason is that the highly pre-organised PDA ligand with its rigid backbone skeleton tends to form complex with metals whose ionic radii are close to 1 Å. As a result, PDA complexes with first-row transition metals and main group metals are less stable than those with lanthanoids. Also, as Fig. 5 clearly shows, no complexes have previously been reported between PDA and Zn, making complex **1** the first. Scheme 2 represents coordination modes of PDA in transition metal complexes. In most cases, the PDA ligand does not use its entire donor capacity for link to metal ion, but in **1** two (PDA)<sup>2-</sup> act as tetradentate chelating ligands and are almost perpendicular to each other in a *cis* arrangement. This observation can be related to the electron configuration of Zn<sup>2+</sup> (*d*<sup>10</sup>) which makes it similar to the main group metals.

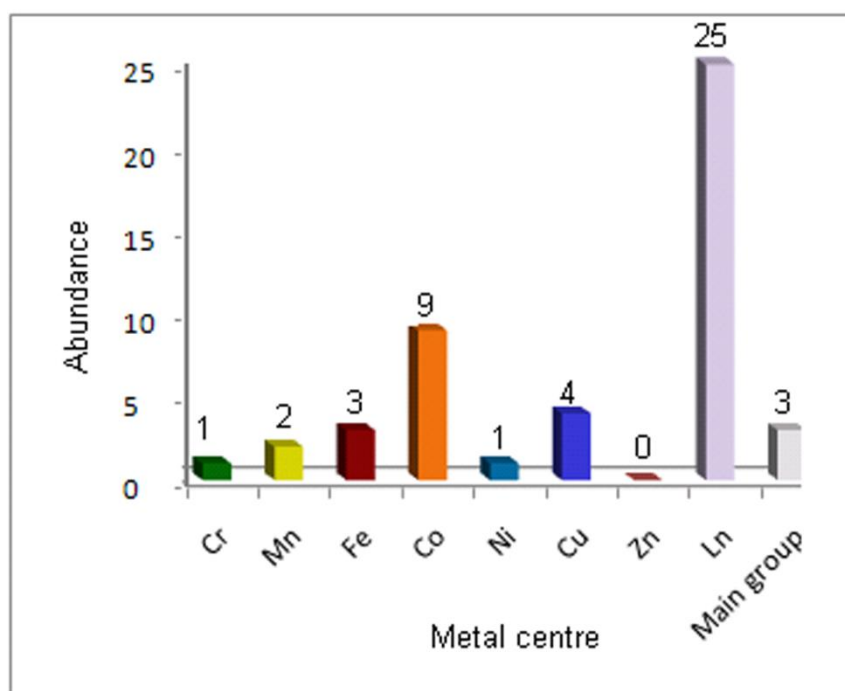
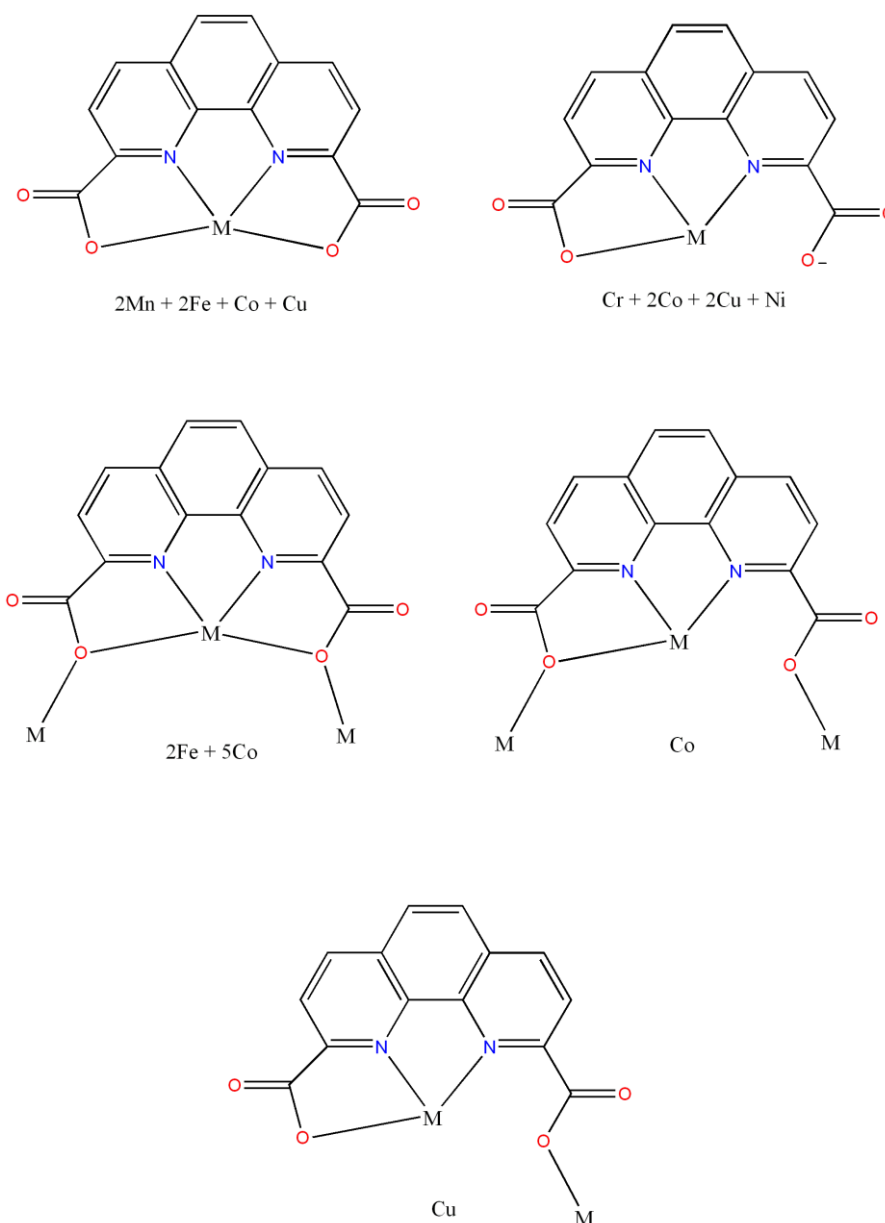


Fig 5. Abundance of coordination compounds containing PDA as a ligand as a function of metal centre.



Scheme 2. Coordination modes of PDA in the first-row transition metal complexes.

## 4. Conclusions

We report herein the synthesis and structural characterisation of the first zinc complex involving  $(\text{PDA})^{2-}$  ligand,  $(\text{H}_3\text{O})_2[\text{Zn}(\text{PDA})_2] \cdot 2\text{CH}_3\text{NO}_2 \cdot 2\text{H}_2\text{O}$  (**1**). The presence of an organic ligand with three aromatic rings in these systems provides an extended net of noncovalent interactions, namely hydrogen bonds and  $\pi$ - $\pi$  stacking interactions, which play a prominent role in the assembly of low-dimensional entities into a high-dimensional supramolecular

network. Additionally, in order to investigate the influence of the metal ion on the geometry of PDA complexes, we undertook a statistical study based on the results of database searching.. The results clearly show that the coordination mode of the pre-organized ligand is strongly dependent on ionic radius and electron configuration of metal centre.

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## Appendix A. Supplementary material

CCDC 1835767 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica.2014.10.032>.

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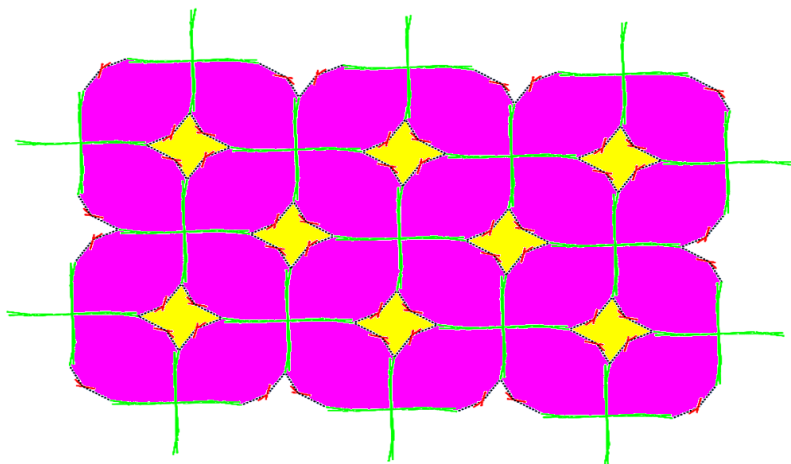
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### Graphical Abstract

#### Highlights

- The first zinc(II) complex containing PDA as a highly pre-organised ligand.
- Aromatic rings increase the stability of complex via  $\pi$ - $\pi$  stacking interactions.
- Coordination mode depends on ionic radius and electron configuration of the metal.