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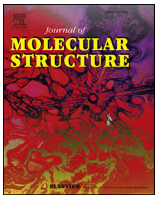

An eight-coordinate zinc complex containing the highly pre-organized ligand 1,10-phenanthroline-2,9-dicarboxylic acid: Solvothermal synthesis, supramolecular structure and CSD studies

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A new anionic coordination complex of Zn(II) containing the highly pre-organized ligand 1,10-phenanthroline-2,9-dicarboxylate (PDA), $(H_3O)_2[Zn(PDA)_2]\cdot 2CH_3NO_2\cdot 2H_2O\cdot$(**1**), has been synthesized by solvothermal methods and characterized 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⋯O, N–H⋯O and C–H⋯O hydrogen bonding, C–H⋯π and $\pi-\pi$ stacking interactions, to produce an extended 2D architecture.

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_2PDA 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] [20] 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_2PDA [21]. As a continuation of our efforts to develop novel systems containing dicarboxylic acids [22–25] and in order to allow comparisons to be drawn with the previous work, we synthesized a zinc(II) coordination complex, $(H_3O)_2[Zn(PDA)_2]\cdot 2CH_3NO_2\cdot 2H_2O$, (**1**), using the H_2PDA 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 π-π stacking and hydrogen bonding interactions are crucial to the formation and generation of higher-dimensional (D) network.

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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 cm^{-1}) on a Buck 500 Scientific spectrometer. Elemental analysis was carried out with a Thermo Finnigan Flash-1112 EA microanalyzer and Perkin-Elmer 2004(II) apparatus. Melting points were determined on a Electrothermal Thermo Scientific IA 9000 apparatus.

2.2. Synthesis of $(H_3O)_2[Zn(PDA)_2]\cdot 2CH_3NO_2\cdot 2H_2O\cdot(1)$

A mixture of H_2PDA (54 mg, 0.2 mmol) and $ZnCl_2\cdot 5H_2O$ (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 °C for 3 days. After slow cooling (5 °C·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 $C_{30}H_{30}ZnN_6O_{16}$: C, 45.27; H, 3.80; N, 10.56. Found: C, 46.85; H, 3.41; N, 11.25%. IR (KBr pellet, 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 °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 ω scans and graphite-monochromated Cu *Kα* 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].

3. Results and discussion

3.1. Vibrational spectrum

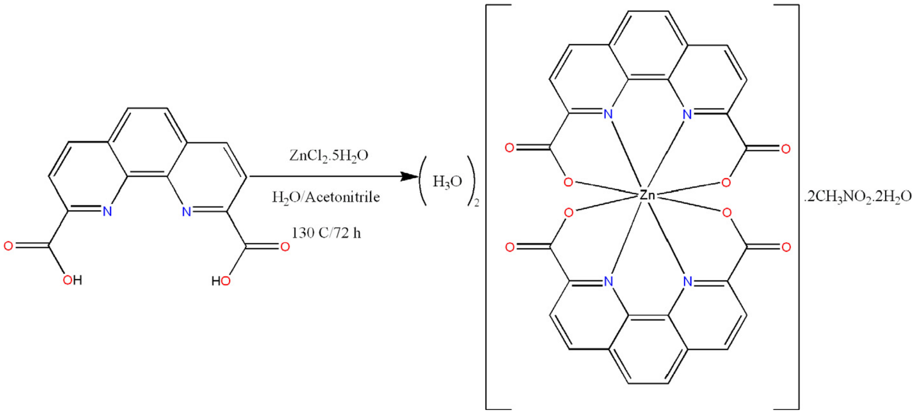
In addition to elemental analysis, complex **1** was initially characterized by its IR spectrum. The medium intense broad absorption in the 3377 cm^{-1} region indicates the presence of water molecules. The observed bands at 1570 and 1361 cm^{-1} are attributed to the antisymmetric $\nu_{as}(COO^-)$ and symmetric $\nu_s(COO^-)$ stretching vibrations of carboxylate groups. The resulting value of Δν ($\Delta\nu = \nu_{as}$-$\nu_s = 209$ cm^{-1}) is characteristic of the monodentate bonding mode of the carboxylate group. The band at 867 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.

3.2. 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 Zn^{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 $(PDA)^{2-}$ acts as a tetradentate chelating ligand and the ligands are almost perpendicular to each other in a *cis* arrangement. As seen

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

Empirical formula	$C_{28}H_{12}ZnN_4O_8\cdot 2(CH_3NO_2)\cdot 2(H_3O)\cdot 2(H_2O)$
Formula weight, g mol^{-1}	795.97
Temperature, K	120(2)
Wavelength λ, Å	1.54184
Crystal system	Tetragonal
Space group	$I4_1/a$
a/Å	10.4342(2)
b/Å	10.4342(2)
c/Å	30.6744(6)
V/Å^3	3339.60(14)
Z	4
D_c/Mgm^{-3}	1.583
F_{000}	1640
μ/mm^{-1}	1.79
Crystal size/mm^3	0.26 × 0.17 × 0.03
Space range,°	4.5 to 67.9
Reflections collected	7862
Reflection independent	1520
R_1,wR_2[$I > 2\sigma(I)$]	0.0678, 0.1967
R_1, wR_2 (all data)	0.0697, 0.1987
Goodness-of-fit on F^2	1.05
Largest differences peak and hole, e Å^{-3}	0.73 and −0.49



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