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A zinc(II) coordination polymer containing flumequine: Synthesis, crystal structure and luminescence properties

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Abstract

The compound $[\text{Zn}_2(\text{flmq})_2(\text{bdc})(\text{H}_2\text{O})_2]$, **1**, based on flumequine (Hflmq) and 1,4-benzenedicarboxylate (bdc), has been synthesised and shown by single crystal X-ray analysis to contain one-dimensional chains linked into sheets by hydrogen bonding. Photoluminescent measurements on the complex in the solid state show that it displays strong photoluminescence at 467 nm.

Keywords: Flumequine, coordination polymer, zinc, crystal structure, luminescent

Inorganic–organic hybrid frameworks have attracted a great deal of attention over the last decade due to the fascinating range of structures and properties these materials exhibit.^[1–4] Much of this work has been focused on the nanoporous metal–organic frameworks (MOFs), which exhibit interesting gas storage^[5] and separation^[6] properties. Recently, however, denser frameworks with more flexible ligands have also drawn significant attention.^[7] These materials have been found to exhibit an intriguing array of structures from simple 1D coordination polymers to 2D and 3D networks, with both purely organic linkers, and combination of organic and inorganic linkers observed. With regard to the organic linkers, the most commonly employed are polycarboxylates.^[8]

A current area of interest in MOF chemistry is the inclusion of biologically active molecules, either as guests within the pores or as part of the framework, with a view to using the materials to overcome drug delivery issues.^[9] Flumequine (Hflmq),^[10, 11] a chiral synthetic quinolone,^[12] is used for treatment of urinary tract infections and, in

veterinary medicine, for the treatment of bacterial infections. In recent years, metal complexes of flmq with nickel,^[13] copper^[14] and zinc^[15, 16] have been reported, though there is no precedence for including flmq within a coordination polymer. We have recently reported inclusion of the iron chelator deferiprone as a terminal ligand within metal-organic frameworks, and investigated its release under acidic conditions.^[17] Inspired by these considerations, we elected to study the reaction between zinc(II) and flumequine (Hflmq) in the presence of 1,4-benzenedicarboxylic acid (H₂bdc).

*** insert Hflmq structure here ***

Zinc acetate reacted with flumequine and H₂bdc in the presence of base under hydrothermal conditions to give the coordination polymer [Zn₂(flmq)₂(bdc)(H₂O)₂], **1**, in reasonable yield.^[18] Compound **1** was characterised by IR spectroscopy, elemental analysis, and single crystal X-ray diffraction.

The X-ray analysis^[19] revealed that the asymmetric unit of **1** consists of two zinc centres, two independent 1,4-bdc halves, proximate to crystallographic inversion centres, two flmq ligands and two water ligands. Selected bond lengths and angles are given in Table 1, and these are similar to those in structurally related compounds.^[20] The two independent zinc(II) centres are bridged by two bidentate flmq ligands to give Zn₂(flmq)₂ dimers, with each zinc(II) centre additionally coordinated to a water ligand and a carboxylate group (Figure 1). This contrasts with the previously reported zinc-flmq compounds which are monomeric.^[15, 16] Each dimeric unit in **1** is supported by two intramolecular hydrogen bonds involving the aqua ligands and the uncoordinated oxygen atoms of the flmq carboxylate groups [O(11)⋯O(6) 2.1670 Å, H(11D)⋯O(6) 1.87 Å, O(11)–H(11D)⋯O(6) 137°; O(12)⋯O(2) 2.641 Å, H(12C)⋯O(2) 1.90 Å, O(12)–H(12C)⋯O(2) 130°].

*** insert Figure 1 here ***

Both zinc centres are five-coordinate, and τ values of 0.207 and 0.367, for Zn(1) and Zn(2) respectively, reveal they are best regarded as being distorted square-pyramidal.^[21] Each zinc centre is coordinated to five oxygen atoms, two from a bidentate flmq ligand, one from a bridging flmq ligand, one from an aqua ligand and one from the bdc ligand. Each flmq ligand adopts a bidentate bridging coordination mode, coordinating through the carboxylate and keto oxygen atoms and forming a 6-membered chelate ring, with bite angles of 84.3° and 88.2°.

The coordination of each of the two zinc centres to a carboxylate group ensures that the bdc ligands link the $Zn_2(\text{flmq})_2$ units into one-dimensional chains (Figure 2), with the capping flmq ligands preventing higher dimensionality in the network.

*** insert Figure 2 here ***

These chains are in turn linked into two-dimensional sheets by pairs of hydrogen bonds (Figure 3) in which the coordinated water molecules act as hydrogen bond donors and carboxylate oxygen atoms act as acceptors. Interestingly, the water molecule based on O(12), coordinated to Zn(1), forms a hydrogen bond with the non-coordinated carboxylate oxygen atom [O(12)···O(7) 2.651 Å, H(12D)···O(7) 1.69 Å, O(12)–H(12D)···O(7) 167°] generating 12-membered rings [graph set $R_2^2(12)$], whereas the water molecule based on O(11), coordinated to Zn(2), interacts with the coordinated carboxylate oxygen atom [O(11)···O(9) 2.662 Å, H(11C)···O(9) 1.73 Å, O(11)–H(11C)···O(9) 160°] generating 16-membered rings [graph set $R_2^2(16)$].

*** insert Figure 3 here ***

Complexes containing d^{10} ions such as Zn^{2+} , including coordination polymers, often possess photoluminescence properties.^[22] For example, $[Zn_4O(\text{bdc})_3]$, MOF-5, has been reported to be a blue luminescent material ($\lambda = 523\text{nm}$).^[23] Since **1** contains both Zn(II) centres and conjugated organic ligands, it was postulated that the complex may exhibit interesting luminescent behaviour. To verify this, the photoluminescence properties of **1** were investigated in the solid state at room temperature. It was observed that **1** exhibits an emission maximum at 467 nm when excited at 338 nm as shown in Figure 4. To understand the nature of the emission band, the photoluminescence properties of Hflmq were also analysed. It was found that one weak band could be observed at 325 nm when Hflmq was excited at 264 nm which is consistent with previously reported studies.^[24] In addition, recent studies have shown that solid $H_2\text{bdc}$ exhibits emission at 430 nm on excitation at 320 nm.^[25] Therefore the emission of **1** may be assigned to intra-ligand fluorescent emission. The enhancement of luminescence can be attributed to ligand chelation to the metal centre, which effectively increases the rigidity and asymmetry of the ligand and reduces the loss of energy by radiationless decay. These observations suggest that compound **1** may be an excellent candidate for potential photoactive materials.

*** insert Figure 4 here ***

To explore the thermal stability of **1**, thermogravimetric analysis (TGA) was performed under nitrogen atmosphere. The first mass loss of 5.45 %, between 140 and 160 °C,

corresponded to the loss of the two coordinated water molecules per formula unit (calcd. 5.75 %), and after this the sample was relatively stable up to 330 °C, at which decomposition of the framework commences.

In summary, we have prepared and characterised the first example of a coordination polymer based on flumequine. The complex $[\text{Zn}_2(\text{flmq})_2(\text{bdc})(\text{H}_2\text{O})_2]$ **1** was prepared and demonstrated to consist of one-dimensional coordination polymers, with hydrogen bonds between the aqua ligands and carboxylate oxygen atoms linking the chains into sheets. **1** displays a strong photoluminescence at 467 nm, suggesting potential as a photoactive material, and is thermally stable up until 330 °C.

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Appendix A. Supplementary material

CCDC 982791 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge 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. Supplementary data associated with this article can be found, in the online version, at doi:*****

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- [18] Synthesis of **1**. A mixture of Zn(OAc)₂•H₂O (87mg, 0.4 mmol), Hflmq (52 mg, 0.2 mmol), H₂bdc (33 mg, 0.2 mmol) and distilled water (8 ml) was adjusted to pH with KOH (22 mg, 0.4mmol) solution and then sealed in an 18 ml Teflon-lined autoclave which was heated in an oven at 150 °C for 72 h. After slow cooling to room temperature, brown block crystals of **1** were separated by filtration, washed with distilled water and dried at ambient temperature (Yield 48% based on Zn). Elemental analysis: Calcd. for C₃₆H₃₀F₂N₂O₁₂Zn₂: C, 50.74; H, 3.52; N, 3.29. Found: C, 51.20; H, 4.05; N, 3.52%. IR (KBr, cm⁻¹): 1385s, 1390vs, 1587vs, 1589s, 1625s, 1630vs.
- [19] Crystallographic data and structure refinement details for compound **1**:
 C₃₆H₃₀F₂N₂O₁₂Zn₂, *M_r* = 851.36, monoclinic, space group *P*2₁/*n*, *a* = 11.9930(2) Å, *b* = 22.5640(5) Å, *c* = 12.1050(2) Å, α = 90°, β = 99.673(1)°, γ = 90°, *V* = 3229.16(10) Å³, *Z* = 4, *D_c* = 1.751 g cm⁻³, μ(Mo-Kα) = 1.571 mm⁻¹, *T* = 150(2) K, crystal size 0.25 x 0.17 x 0.15 mm, 49269 reflections measured, 5702 independent reflections (*R_{int}* = 0.0925), Final *R*1 [*I* > 2σ(*I*)] = 0.0421, *wR*(*F*²) = 0.0964, goodness of fit = 1.028.
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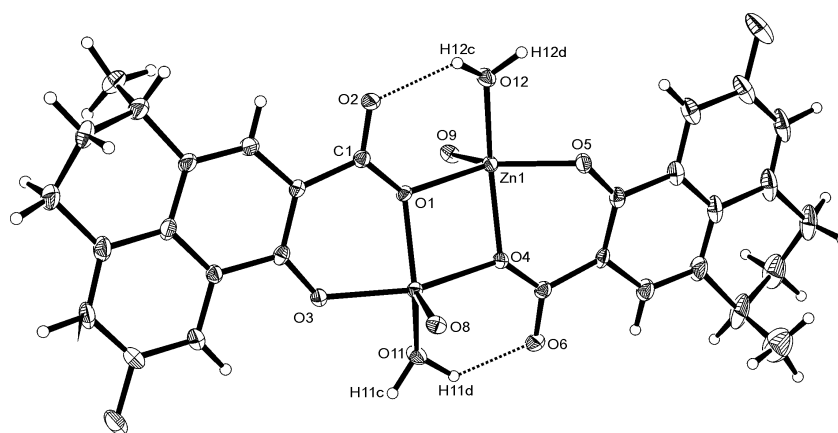
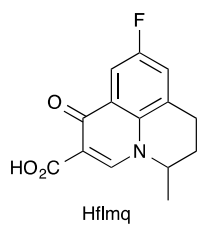


Figure 1 – The $[Zn_2(flmq)_2(H_2O)_2]^{2+}$ dimer units present in the structure of **1**.

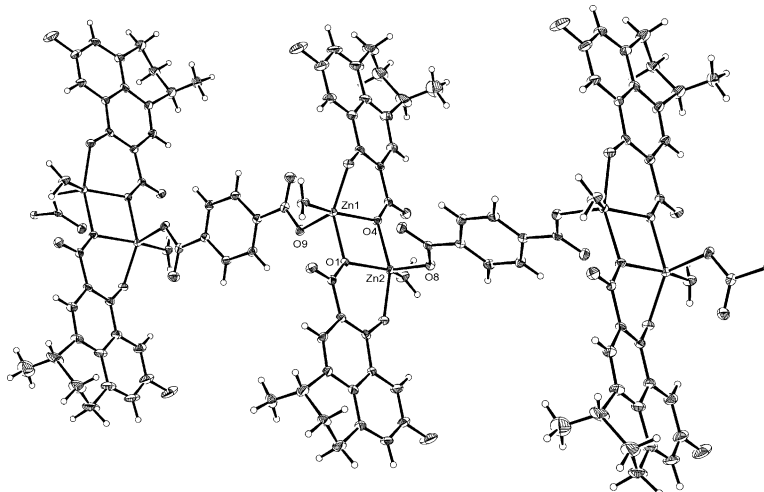


Figure 2 – The one-dimensional coordination polymers present in the structure of **1**.

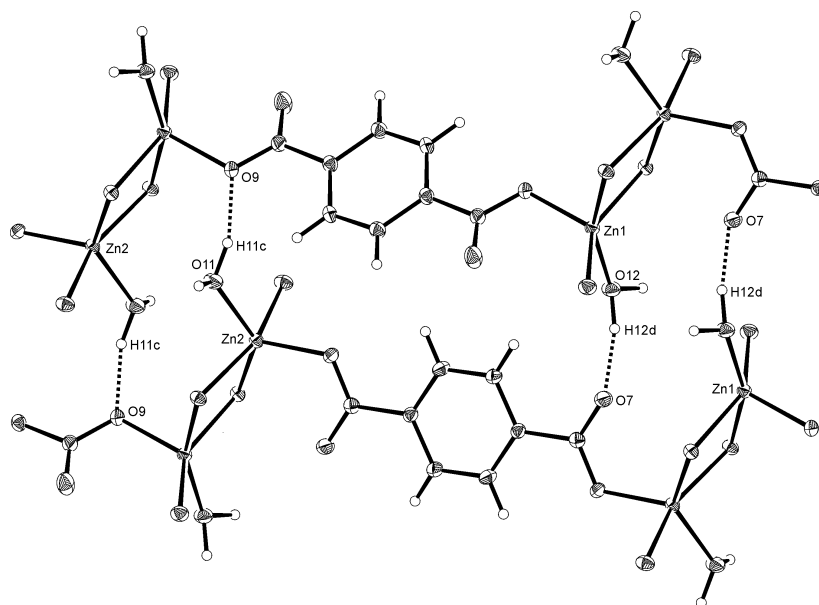


Figure 3 – Hydrogen bonds linking the coordination polymers present in the structure of **1** into sheets.

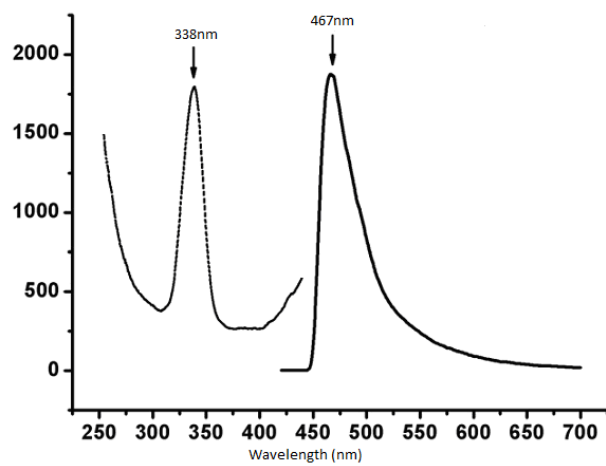


Figure 4 – Photoluminescence spectrum of **1** in the solid state at room temperature.

Table 1 – Selected bond lengths [\AA] and angles [$^\circ$] for **1**.

Zn(1)–O(9)	1.983(3)	Zn(1)–O(12)	1.994(3)
Zn(1)–O(5)	2.009(3)	Zn(1)–O(4)	2.081(3)
Zn(1)–O(1)	2.093(3)	Zn(2)–O(8)	1.962(3)
Zn(2)–O(11)	1.988(3)	Zn(2)–O(3)	2.030(3)
Zn(2)–O(1)	2.043(2)	Zn(2)–O(4)	2.130(3)
O(9)–Zn(1)–O(12)	103.08(12)	O(9)–Zn(1)–O(5)	124.09(11)
O(12)–Zn(1)–O(5)	89.02(11)	O(9)–Zn(1)–O(4)	99.26(11)
O(12)–Zn(1)–O(4)	156.53(11)	O(5)–Zn(1)–O(4)	84.36(11)
O(9)–Zn(1)–O(1)	89.87(10)	O(12)–Zn(1)–O(1)	94.48(11)
O(5)–Zn(1)–O(1)	144.12(10)	O(4)–Zn(1)–O(1)	78.36(10)
O(8)–Zn(2)–O(11)	112.00(12)	O(8)–Zn(2)–O(3)	96.41(11)
O(11)–Zn(2)–O(3)	91.48(11)	O(8)–Zn(2)–O(1)	113.16(10)
O(11)–Zn(2)–O(1)	134.57(11)	O(3)–Zn(2)–O(1)	88.23(10)
O(8)–Zn(2)–O(4)	106.47(11)	O(11)–Zn(2)–O(4)	84.66(11)
O(3)–Zn(2)–O(4)	156.58(11)	O(1)–Zn(2)–O(4)	78.37(10)

Highlights

- A new flumequine-containing zinc coordination polymer is reported.
- Flumequine coordinates in a bridging bidentate mode to give zinc dimers that are interconnected by dicarboxylate linkers.
- The new compound displays strong photoluminescence.

For graphical contents:

