Coordination Polymers Containing a Glycine-Derived Trimellitic Acid Imide

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Abstract. A trimellitic imide ligand (GlyTMI$_2$), derived from glycine, has been used in the formation of three coordination polymers as a means towards understanding the role of the aromatic core of the ligand in determining structure. The polymeric structures poly-{(N(CH$_3$)$_2$H$_2$)(OAc)(DMF)$_{6.5}$(CH$_3$OH)$_{0.5}$(CH$_3$OH)} (1), poly-{[Cd$_2$(GlyTMI)$_2$(DMF)$_3$]} (2), and poly-{{[Cd$_2$(GlyTMI)$_2$(4,4'-bipy)$_2$]}·2H$_2$O·DMF} (3) have different dimensionalities, attributed to the change in size of the metal ion (Zn vs. Cd).

1. Introduction
Coordination polymers, infinite arrays of metal ion/clusters and organic ligands, have been explored since the concept of their deliberate geometric design was demonstrated by Robson in the late 1980s [1]. The predictions made in this seminal paper have largely proven accurate with coordination polymers, and their porous sub-set metal organic frameworks (MOFs), being exploited for numerous applications including guest storage, separations and conductive properties [2].

Whilst there is much research directed at the applications of coordination polymers, there is also a significant body of work dedicated to understanding the self-assembling construction of these materials, known as crystal engineering [3]. Control of the final topology can be somewhat designed by the synthetic choices that are made such as the metal ions used (with preferential coordination geometries) and the connectivity and directionality of the organic ligand.

In recent years, our group has explored the use of diimide-based ligands for the construction of both coordination polymers and discrete supramolecular species [4,5]. Typically with rigid cores, these ligands have shown a great diversity in the structures that form yet with repeatable motifs evident in most cases. The use of amino acids to form the imide groups gives a synthetic versatility to the approach and, specifically with chiral amino acids, demonstrates a steric influence that impacts the substructures that are formed [6]. Work using naphthalenediimides has shown a propensity for the overall structures to be dominated by π-interactions, and our intention in this current work was to examine whether smaller aromatic ligands would be subject to this same driving force.

Herein we report the synthesis and application of a small, low symmetry monoimide ligand, GlyTMI$_2^-$, derived from benzene-1,2,4-tricarboxylic acid (trimellitic acid) anhydride and contrast its structural behavior to that of the larger diimide analogues. H$_2$GlyTMI has previously been reported in the synthesis of discrete Mn$^{II}$, Ni$^{II}$ and Zn$^{II}$ coordination complexes [M(HGlyTMI)(OH)$_2$]$_3$ and a series of hydrogen-bonded salts [7,8]. Other related derivatives of this ligand have also been reported in coordination complexes/polymer such as the N-benzoate [9], N-pyridyl [10], N-aminobenzene [11], and N-picoyl derivatives [12].
2. Experimental Details

2.1. Synthesis
All reagents and solvents were purchased from standard commercial suppliers and used without purification. Basic zinc acetate was synthesized according to a literature procedure. NMR spectra were collected using a Bruker Avance 400 operating at 400 MHz. Mass spectrometry was performed using a Micromass Platform Electrospray system using DMSO as the mobile phase. IR spectra were collected using an Agilent Cary 630 diamond ATR spectrometer.

2.1.1. \( \text{H}_2\text{GlyTMI} \). Trimesic anhydride (1.50 g, 7.81 mmol) and glycine (0.59 g, 7.81 mmol) were mixed in 10 mL of DMF and stirred at 120 °C overnight. The resulting yellow mixture was then placed in 100 mL of 5% HCl solution, with a white precipitate forming over the course of an hour. All precipitates were collected by filtration and dried under vacuum. Yield 0.83 g, 43%. m.p. 263-265 °C. Found C, 52.92; H, 2.77; N, 5.71 %, C\(_{17}\)H\(_{30}\)N\(_5\)O\(_6\) requires C, 53.02; H, 2.83; N, 5.62 %. δH (400 MHz, \( d_\text{6}-\text{DMSO} \)): 4.35 (s, 2H), 8.06 (d, J=7.8 Hz, 1H), 8.28 (s, 1H), 8.40 (d, J=7.8 Hz, 1H). FT-IR, \( \nu_{\text{max}}/\text{cm}^{-1} \): 2860w, 1693s, 1566m, 1378s, 963m, 756s, 721s. Bulk purity confirmed by PXRD (Figure 1).

2.1.2. Poly-\{(N(CH\(_2\)_3)H\(_2\)}[Zn\(_2\)(GlyTMI)\(_2\)](OAc)(DMF)\(_{0.5}\)(CH\(_3\)OH)\(_{0.5}\)}[CH\(_3\)OH] \( (I) \). \( \text{H}_2\text{GlyTMI} \) (10 mg, 40.1 µmol) and \([\text{Zn}_{\text{d}}(\text{OAc})\text{O}] \) (9 mg, 13.4 µmol) were added to a 2:1 mixture of DMF:methanol (3 mL) and sonicated to dissolve. The solution was heated at 70 °C for 48 hours in a heat block to yield a colourless crystalline material. Isolated yield 11.1 mg, 59%. FT-IR, \( \nu_{\text{max}}/\text{cm}^{-1} \): 3094w, 1713m, 1624s, 1576s, 1374s, 1107m, 973m, 751m, 721s. Bulk purity confirmed by PXRD (Figure 1).

2.1.3. Poly-\{Cd\(_2\)(GlyTMI)\(_2\)](DMF)\(_2\)} \( (2) \): \( \text{H}_2\text{GlyTMI} \) (10 mg, 40.1 µmol) and \( \text{Cd(NO}_3\text{)}_2\)-4H\(_2\)O (19 mg, 80.2 µmol) were added to a 2:1 mixture of DMF:methanol (3 mL) and sonicated to dissolve. The solution was heated at 85 °C for 2 weeks in a heat block to yield a colourless crystalline material. Isolated yield 2.9 mg, 29%. FTIR, \( \nu_{\text{max}}/\text{cm}^{-1} \): 3400w, 1694s, 1566m, 1378s, 963m, 756s, 721s. Bulk purity confirmed by PXRD (Figure 1).

2.1.4. Poly-\{Cd\(_2\)(GlyTMI)\(_2\)](4,4’-bipy)\}_2\text{H}_2\text{O·DMF} \). \( \text{H}_2\text{GlyTMI} \) (10 mg, 40.1 µmol), \( \text{Cd(NO}_3\text{)}_2\)-4H\(_2\)O (19 mg, 80.2 µmol) and 4,4’-bipyridine (6 mg, 40.1 µmol) were added to a 2:1:1 mixture of DMF:methanol:water (3 mL) and sonicated to dissolve. The solution was heated at 85 °C for 48 hours in a heat block to yield a colourless crystalline material. Isolated yield 15.7 mg, 54%. FTIR, \( \nu_{\text{max}}/\text{cm}^{-1} \): 3469w, 1703s, 1599s, 1580s, 1560s, 1377s, 1317m, 973m, 805s, 757m, 816s. Bulk purity confirmed by PXRD (Figure 1).

2.2. X-Ray Crystallography
Crystallographic data for compounds 1 and 3 was collected using the MX1 beamline at the Australian Synchrotron operating at 17.4 KeV (\( \lambda = 0.7108 \) Å).[13] Data collection was controlled using the Blucce software [14], and initial data processing and reduction was conducted using the XDS software suite [15]. Data for compound 2 was collected using an Oxford Gemini diffractometer using graphite-monochromated Cu-Kα radiation (\( \lambda = 1.54084 \) Å), with data processing conducted using CryAliPro [16]. All structures were solved by Direct methods using SHELXS-2014 and refined against F\(^2\) using SHELXL-2018 [17]. X-Seed was used as a graphical interface [18]. All non-hydrogen atoms were refined using an anisotropic model. All hydrogen atoms were refined using a riding model. Data are deposited with the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk). Crystallographic details and refinement parameters are given in Table 1.

Compound 1 contains a mixed MeOH/DMF ligand position (modelled with fixed 50:50 occupancies and no OH hydrogen atom included on MeOH) and a disordered acetate ligand (modelled with refined occupancies 65:35).
Compound 3 contains a disordered, non-coordinated DMF molecule (modelled with refined occupancies 63:37) and an apparent disordered water molecule (modelled with fixed 50:50 occupancies and no hydrogen atoms included in its model).

### Table 1. Crystallographic details and refinement parameters for all compounds.

| Compound | Formula | 1 | 2 | 3 |
|----------|---------|---|---|---|
|          | C₂₉H₃₀.₃N₃.₂O₁₆Zn₂ | C₃₅H₃₆Cd₉N₉O₁₅ | C₄₅H₃₇Cd₂N₇O₁₅ |
| FW       | 814.81  | 938.41 | 1140.61 |
| Crystal system | Monoclinic | Triclinic | Triclinic |
| Space group | P₂₁/c | P-1 | P-1 |
| a / Å     | 7.8620(16) | 9.3117(14) | 8.3660(17) |
| b / Å     | 17.021(3) | 11.3770(15) | 11.644(2) |
| c / Å     | 24.724(5) | 17.587(2) | 24.395(5) |
| α / °     | 90 | 74.549(11) | 99.73(3) |
| β / °     | 95.62(3) | 83.317(11) | 92.73(3) |
| γ / °     | 90 | 82.085(11) | 110.76(3) |
| V / Å³    | 3292.7(12) | 1772.5(4) | 2175.2(9) |
| Z         | 4 | 2 | 2 |
| µ / mm⁻¹  | 1.538 | 10.294 | 1.060 |
| F(000)    | 1668 | 936 | 1144 |
| 2θ range collected | 2.91 to 55.888 | 5.23 to 133.628 | 3.48 to 55.898 |
| Index ranges | -10 ≤ h ≤ 10 | -8 ≤ h ≤ 11 | -11 ≤ h ≤ 11 |
|           | -22 ≤ k ≤ 22 | -13 ≤ k ≤ 13 | -15 ≤ k ≤ 15 |
|           | -32 ≤ l ≤ 32 | -20 ≤ l ≤ 20 | -32 ≤ l ≤ 32 |
| Refs. collected | 53158 | 15005 | 72971 |
| Independent refs. | 7794 | 6229 | 10360 |
| R_int     | 0.0525 | 0.1012 | 0.0305 |
| GooF      | 1.068 | 1.062 | 1.048 |
| Final R indexes [I>=2σ (I)] | R₁ = 0.0497 | R₁ = 0.0545 | R₁ = 0.0462 |
|           | wR₂ = 0.1376 | wR₂ = 0.1361 | wR₂ = 0.1067 |
| Final R indexes [all data] | R₁ = 0.0582 | R₁ = 0.0747 | R₁ = 0.0572 |
|           | wR₂ = 0.1432 | wR₂ = 0.1507 | wR₂ = 0.1133 |

### 3. Results and Discussion

#### 3.1. Synthesis

The diacid H₂GlyTMI was synthesized by reaction of glycine with trimellitic anhydride in DMF (Scheme 1). Precipitation from the reaction mixture using HCl afforded the product in modest yield. Three coordination polymers were synthesised using H₂GlyTMI, namely poly-{{(N(CH₃)₂H₂)Zn₂(GlyTMI)₂(OAc)(DMF)₀.₅(CH₃OH)₀.₅}·CH₃OH} (1), poly-{{Cd₂(GlyTMI)₂(DMF)₃} (2), and poly-{{Cd₂(GlyTMI)₂(4,4'-bipy)₂}·2H₂O·DMF} (3). All compounds were synthesized in DMF:MeOH or DMF:MeOH:H₂O at elevated temperatures and produced crystalline materials suitable for single crystal X-ray diffraction. The synthesis of 3, which incorporates 4,4’-bipyridine, was deliberately conducted after observing the 2D structure of 2 and the potential to bridge the sheets with a charge-neutral co-ligand.

#### 3.2. Structural Descriptions

##### 3.2.1. Poly-{{(N(CH₃)₂H₂)Zn₂(GlyTMI)₂(OAc)(DMF)₀.₅(CH₃OH)₀.₅}·CH₃OH} (1)

The structure of 1 was solved and refined in the monoclinic space group P₂₁/c, with the asymmetric unit containing one formula unit. The compound contains a one-dimensional anionic coordination, with the charged
balanced by dimethylammonium cations (a product of the hydrolysis of DMF). The coordination polymer contains a dinuclear zinc node with the metal ions bridged by one acetate ligand and two carboxylates from the imide ends of two GlyTMI ligands (Figure 2). The benzoate ends of the two unique GlyTMI ligands coordinate in a monodentate manner to the metal centres (one to each metal). One of the metal ions adopts a distorted tetrahedral geometry, with four carboxylates coordinated to it, whilst the other has a trigonal bipyramidal geometry and has an additional coordinated solvent molecule. There is disorder associated with the solvent position, which is modelled as 50:50 DMF:MeOH with no restraints applied. Pairs of GlyTMI ligands bridge the bimetallic nodes, in a cyclic motif reminiscent of our earlier work using NDI ligands.[4,6] The two ligands are not parallel, although a closest C···C distance of 3.57 Å indicates that there is π-stacking between the two phthalimide ring systems. There are also π-π interactions between adjacent 1D chains with a shortest C···C distance of 3.44 Å. The dimethylammonium counter cation and methanol molecule are involved in a hydrogen bonding chain that bridges across a bimetallic node between a carboxylate and an imide oxygen (Figure 2). It is interesting to note that the GlyTMI ligand, whilst much shorter and with a smaller aromatic profile than the related NDI ligands, still forms a macrocyclic motif between nodes, and that π-interactions appear to remain a dominant influence on the crystal structure.

Figure 1. PXRD comparisons of experimental data at room temperature vs. calculated patterns from low temperature single crystal data; top left, compound 1; top right, compound 2; bottom, compound 3.

Scheme 1. Synthesis of the dicarboxylic acid H₂GlyTMI.
Figure 2. The anionic 1D coordination polymer in the structure of poly-\{(N(CH_3)_2)H_2)[Zn_2(GlyTMI)_2(OAc)(DMF)_{0.5}CH_3OH]_{0.5}]·CH_3OH\} 1 (top) and the hydrogen bonding motif involving the dimethylammonium cation and methanol molecule (bottom) and the disorder acetate and solvent positions. Hydrogen atoms are omitted for clarity.

3.2.2. Poly-[Cd_2(GlyTMI)_2(DMF)_3] (2). The structure of 2 was solved and refined in the triclinic space group P-1, with the asymmetric unit containing one formula unit. The two crystallographically unique metals both adopt a distorted octahedral coordination geometry and form a bimetallic node (Figure 3). The metal ions in the node are bridged by one benzoate group and one glycine-derived carboxylate (in a chelating-bridging coordination mode). The nodes are bridged in one direction by a carboxylate to give a 1D metal-carboxylate chain propagating parallel to the crystallographic a axis. The chains are connected by the GlyTMI ligands, and overall the coordination polymer is a 2D sheet. The GlyTMI ligands are arranged such that they are parallel and aligned with the imides oriented in the same direction within a given sheet (inversion between adjacent sheets means that the orientation of ligands between sheets is antiparallel). The adjacent GlyTMI ligands have closest C···C contacts of ca. 3.4 Å and 3.6 Å between the crystallographically unique pairs, indicating that the formation of the sheet is likely driven by π-π interactions. The ligated DMF molecules point above and below the plane of the sheet.

3.2.3. Poly-\{[Cd_2(GlyTMI)_2(4,4'-bipy)_2]·2H_2O·DMF\} (3). The structure of 3 was solved and refined in the triclinic space group P-1, with the asymmetric unit containing one formula unit. The 3D coordination polymer contains two types of bimetallic nodes, both of which contain coordination from only one end of the GlyTMI ligands in addition to coordination by the 4,4'-bipyridine ligands (Figure 4). These nodes have near identical coordination environments and connect to six other bimetallic nodes (two of their ‘own kind’ through the bipyridyline ligands and four others through the GlyTMI ligands). The metal-bipyridine chains run in diagonally opposing directions, with π-π interactions within these ‘double-pillars’ and the GlyTMI ligands bridge between these chains, arranged in pairs with π-π interactions, rather than in an infinite stacking arrangement as found in the structure of 2. There is only one crystallographically unique pair of GlyTMI ligands; these are non-parallel and have a closest C···C contact of ca. 3.6 Å. There is one well-ordered water molecule that forms hydrogen bonding interactions
between a carboxylate and an imide oxygen atom. There is also a disorder DMF position that occupies the space between adjacent GlyTMI pairs, potentially with some interaction to the nearly parallel ligands, and a disordered water position was located. It can be seen from packing diagrams that there are no accessible solvent voids/channels within the 3D network (Figure 4).

Figure 3. Top-down and side-one views of the 2D coordination polymer in the structure of poly-[Cd₂(GlyTMI)₂(DMF)₃] 2. Hydrogen atoms are omitted for clarity.

3.3. Discussion
The three coordination polymers that have been isolated containing the GlyTMI²⁻ ligand differ in their dimensionality; compound 1 is 1D, compound 2 is 2D, and compound 3 is 3D. This difference can in some way be attributed to their constituent parts. Compound 1 contains zinc(II) which has a smaller ionic radius than cadmium(II) and is satisfied by 4- and 5-coordinate geometries, thereby limiting the dimensionality when carboxylate ligands are employed. Additionally, the serendipitous incorporation of acetate prevents propagation in some directions as it is not able to bridge in the same manner as GlyTMI. Compound 2 contains the larger cadmium(II) ion and is able to be 4-connecting through the GlyTMI ligands and form a 2D sheet. The coordination polymer appears to be ‘templated’ to some extent by the infinite arrays of face-to-face π-interactions between these ligands. It is clear that our attempts to lessen the influence of such interactions by using a smaller ligand are ineffective. Given the solvent ligands protruding from the top and bottom of the 2D sheets in compound 2, we decided to
employ 4,4'-bipyridine as a co-ligand, to hopefully displace these DMF ligands and bridge the 2D networks to form a porous material. This strategy met with only partial success in compound 3, with no coordinated solvent and the 4,4'-bipyridine ligands bridging between bimetallic nodes; however, the 2D sheet of 2 did not persist and a close-packed 3D coordination polymer resulted.

Figure 4. The two unique bimetallic nodes in the structure of poly-\{[Cd₂(GlyTMI)₂(4,4'-bipy)₂]·2H₂O·DMF\} 3 (top) and two views of the 3D coordination polymer along the crystallographic \(b\) and \(a\) axes (bottom left and right, respectively). Hydrogen atoms and solvent molecules are omitted for clarity.

4. Conclusion
Coordination polymers formed using the GlyTMI\(^2\) ligand show the promise of this class of ligands in the formation of metal-organic materials. It is evident that \(\pi\)-interactions are a dominant force in controlling the structures that are obtained, although the influence of metal ion and co-ligands appears to have a significant influence on the dimensionality of the networks that form.

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