Structural Changes in Coordination Polymers in Response to Small Changes in Steric Bulk (H *vs.* Me): An Experimental and Theoretical Study

Nicholas L. Kyratzis, Winnie Cao, Ekaterina I. Izgorodina and David R. Turner^{*} School of Chemistry, Monash University, Clayton, VIC 3800, Australia * david.turner@monash.edu

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1. X-Ray Crystallographic Refinement Details

$poly-[Co_4(GlyNDI)_4(DMF)_6(H_2O)_{1.5}]$ (1)

The data is of low quality (evidenced by high R_{int} and consequently high wR2 values); this is the best data obtainable even employing synchrotron radiation. One coordinated DMF ligand was disordered over two positions (FVAR = 0.55). Some RIGU and DIFX restraints were applied to these disordered sites. Hydrogen atoms of the aqua ligands could not be located from the Fourier difference map; these are therefore not included in the model but are counted in the formula moiety.

poly-{(H₂N(CH₃)₂)₂[Co(GlyNDI)₂)]} (2Co)

The NH hydrogen atoms of the dimethylammonium cation were located from the Fourier difference map and refined using DFIX restraints (with SHELX suggested value NH = 0.84 Å).

poly-{(H₂N(CH₃)₂)₂[Zn(GlyNDI)₂)]} (2Zn)

Poor data quality (the best obtainable using synchrotron radiation) gives a high R_{int} value (and consequently high wR2 values) and some refinement issues (large residual peaks). The structure is isostructural to **2Co** and therefore confidence in the overall model is high. Hydrogen atoms of the dimethylammonium cation could not be located from the Fourier difference map and are included in idealized positions.

poly-[Zn(GlyNDI)(OH₂)₂]·0.25H₂O (3)

A partial occupancy lattice water molecule appears to reside on a special position within the pore space; hydrogen atoms for this water molecule were not modelled but are included in the empirical formula. Hydrogen atoms for the aqua ligands are refined in idealized positions using HFIX.

poly-[Co(GlyNDI)(2,2'-bipy)] (4)

The sample diffracted poorly, but was the best available. Subsequently the R_{int} for the data is high (and consequently high wR2 values) and there is a large negative residual. The structure remains unambiguous and otherwise refines well.

poly-[Cu(GlyNDI)(dpe)] (5)

The structure has solvent accessible void space in which no solvents could be modelled. The data was processed using the SQUEEZE routine of PLATON which calculated one void per unit cell of 372 Å^3 containing 94 e⁻. As this material could not be isolated independently of other crystalline contaminants (6) the nature of this solvent could not be determined analytically.

$poly-\{(HN(CH_3)_2)_2[Cu(GlyNDI)_2]\cdot 2DMF\}$ (6)

DFIX restraints were required to sensibly model the lattice DMF molecule. NH hydrogen atoms of the dimethylammonium cation were located from the Fourier difference map and refined using DFIX restraints (N-H = 0.91 Å).

Poly-[Zn(GlyNDI)(dpe)] (7)

Poor diffraction quality results in a large Rint (0.18, and consequently high wR2 values) and some small, nonsensical residual peaks close to the positions of the metal ions. The data was processed using SQUEEZE which displayed a solvent void volume of 458 Å³ which corresponds to 167 electrons per unit cell.

Poly-[Cu₂(ibaNDI)₂(H₂ibaNDI)(2,2'-bipy)₂] (10)

Poor diffraction quality results in a large R_{int} (0.15, and consequently high wR2 values) and some small, nonsensical residual peaks close to the positions of the metal ions. The data was processed using SQUEEZE displaying a total solvent void volume of 860 Å³, containing 260 electrons, per unit cell (215 Å³ and 65 e⁻ per formula unit), in reasonable agreement with experimental analysis (see main manuscript).

2. X-Ray Powder Diffraction



re S1. Comparison between the experimental (294K, blue) and the calculated powder pattern (100K) for *poly*- $\{(H_2N(CH_3)_2)_2[Co(GlyNDI)_2)]\}$, **2Co** (orange) and *poly*- $[Co_4(GlyNDI)_4(DMF)_6(H_2O)_{1.5}]$, **1** (grey).



Figure S2. Comparison between the experimental (294K, orange) and the calculated powder pattern (100K) for *poly*-[Co(GlyNDI)(DMF)(H₂O)], **1** (blue).



Angle 2θ(°)

Figure S3. Comparison between the experimental (294K, orange) and the calculated powder pattern (100K) for *poly*-[Zn(GlyNDI)(OH₂)₂] \cdot 0.5H₂O **3**, (blue) and *poly*-{(H₂N(CH₃)₂)₂[Zn(GlyNDI)₂)]}, **2Zn** (grey).





Figure S4. Comparison between the experimental (294K, orange) and the calculated powder pattern (100K) for *poly*-[Co(GlyNDI)(2,2-bipy)] **4** (blue).



Figure S5. Comparison between the experimental (294K, orange) and the calculated powder pattern (100K) for *poly*-[Cu(GlyNDI)(dpe)] **5** (blue) and *poly*- $\{(H_2N(CH_3)_2)[Cu(GlyNDI)_2] \cdot 2DMF\}$ **6** (grey).



Figure S6. Comparison between the experimental (294K, orange) and the calculated powder pattern (100K) for *poly*-[Zn(GlyNDI)(dpe)] **7**, (blue) and *poly*-{(H₂N(CH₃)₂)₂[Zn(GlyNDI)₂)]} **2Zn** (grey).



Angle 2θ(°)

Figure S7. Comparison between the experimental (294K, orange) and the calculated powder pattern (100K) for *poly*-[Cu(ibaNDI)(DMF)₂] **8**, (blue).



Figure S8. Comparison between the experimental (294K, orange) and the calculated powder pattern (100K) for *poly*-[Co₂(ibaNDI)₂(4,4'-bipy)(DMF)₂] **9** (blue).



Figure S9. Comparison between the experimental (294K, orange) and the calculated powder pattern (100K) for *poly*- $\{[Cu_2(ibaNDI)_2(H_2ibaNDI)(2,2'-bipy)_2]$ **10** (blue).

3. Structural Overlays



Figure S10. Comparison of the lest-squares overlayed plots of the coordinating groups from structures containing (from left) AlaNDI, LeuNDI and PheNDI, highlighting the similarity between the preferred conformation regardless of the R group of the amino acid.



Figure S11. Energy profile for a relaxed rotational scan around the imide N- α C bond for glycinenaphthalenemonoimide, highlighting the structures of the minima/maxima.



Figure S12. Energy profile for a relaxed rotational scan around the imide N- α C bond for alaninenaphthalenemonoimide, highlighting the structures of the minima/maxima.



Dihedral angle/ °

Figure S13. Energy profile for a relaxed rotational scan around the imide N- α C bond for isobutyrate-naphthalenemonoimide, highlighting the structures of the minima/maxima.