MS19-1-2 Correlating Chemical Bonds with Glass Formation in Coordination Polymers: A Combined X-ray Electron Density and High-pressure Single-Crystal X-ray Diffraction Study
#MS19-1-2

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Abstract
Amorphous metal-organic frameworks (MOF)/coordination polymer (CP) represents a new class of hybrid functional materials with novel short-range structures and potential applications such as gas mixture separations (H_2/CH_4, CO_2/N_2), optical luminescence materials, anode material in lithium ion batteries.[1] Pioneering work on amorphous MOFs is carried out on melt-quenched glasses formed especially by the zeolitic imidazolate frameworks (ZIFs).[2] In our recent work[3], we have demonstrated the key roles of the metal–ligand bonds and the internal imidazole bonds in controlling the subtle balance between melting and decomposition process in prototypical glass forming ZIF-zni MOF. In addition to melt-quenched MOFs, mechanically induced amorphization which directly converts crystals into a glassy state was first demonstrated in CdTz CP.[4] To understand the root of mechanically induced amorphization in CP, the role of chemical bonds and structural changes under pressure should be investigated.
In this work, we compare the electron density distribution of two isostructural CP molecules-MnTz and ZnTz ([M(II)(1,2,4-triazole)2(H_2PO_4)$_2$], using high-resolution single-crystal X-ray diffraction data measured at 100 K. MnTz undergoes a direct crystal-to-glass phase transition through mechanical milling whereas ZnTz retains its crystalline form under similar mechanical treatment.[5] Quantitative chemical bonding analysis using several topological parameters based on Bader's QTAIM theory[6] shows that Mn–ligand bonds are primarily closed shell ionic in nature with a spherical $3d^5$ electron density of Mn atom (Figure 1). On the other hand, aspherical electron density features are seen on Zn atom (Figure 1). The respective Zn–ligand bonds in ZnTz have partial polar covalent features.
High-pressure single crystal diffraction study was carried out at several pressure points upto 3.5 GPa and 7.5 GPa for MnTz and ZnTz respectively. The metal–ligand bonds shows higher linear compressibility in MnTz (~9.5 TPa^{-1}) as compared to ZnTz (~8 TPa^{-1}) (Figure 2). Interestingly, both molecules exhibit pressure induced phase transition from orthorhombic (*Pbcn*) to monoclinic ($P2_1/c$) phase at elevated pressures (3.1-3.6 GPa for MnTz, 4.6-5.9 GPa for ZnTz). These high-pressure monoclinic phases are similar to the ambient crystal structure of CdTz CP which also form glass under mechanical milling.[4]

References
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2D deformation maps plotted at ± 0.1eÅ-3 level.

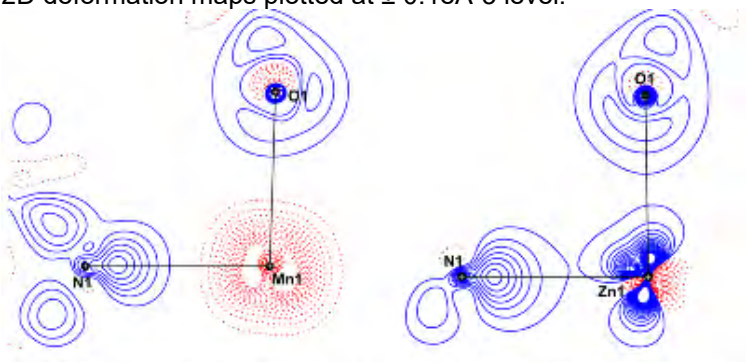

Figure 1. 2D deformation maps along N_1–M_1–O_1 plane plotted at a contour level of ± 0.1 eÅ^{-3}. Blue represents charge concentration, and red represents charge depletion regions.

Variation in metal-ligand bond lengths with pressure

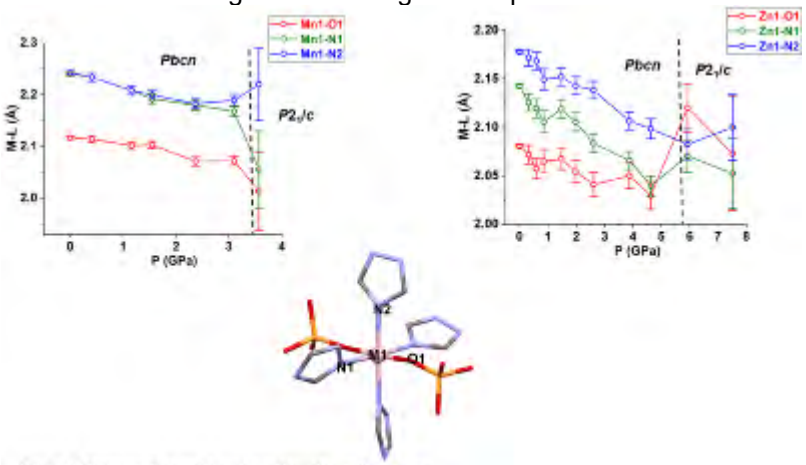

Figure 2. Variation in metal–ligand bond lengths with pressure