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Reversible pressure-controlled depolymerization of a copper(II)-containing coordination polymer

Jack K. Clegg, Aidan J. Brock, Katrina A. Jolliffe, Leonard F. Lindoy, Simon Parsons, Peter A. Tasker and Fraser J. White

Abstract: A unique pressure-induced Cu-N bond breaking/bond forming reaction is reported: The variation of pressure on a single crystal of a one-dimensional copper(II)-containing coordination polymer (CuL₂(1-methylpiperazine))₆, where H₂L is 1,1’-(1,3-phenylene)-bis(4,4-dimethylpentane-1,3-dione), was monitored using single crystal X-ray diffraction with the aid of a diamond anvil cell. At a very low elevated pressure (~0.05 GPa) a remarkable reversible phase change was observed. The phase change results in the depolymerization of the material through the cleavage and formation of axial Cu-N bonds as well as “ring flips” of individual axially coordinated 1-methylpiperazine ligands. Overall, the pressure-induced phase change is associated with a surprising (and non-intuitive) shift in structure – from a 1-dimensional coordination polymer to a discrete dinuclear complex.

Biological systems are capable of responding to external stimuli leading to the adaptive behavior that is characteristic of life. Synthetic materials that respond to the application of light, magnetic, the presence of guest molecules or electric fields and/or temperature in unusual ways are required to underpin the design of the next generation of advanced devices and components. Coordination polymers and metal-organic frameworks (MOFs) in particular have been found to respond to such stimuli in interesting ways, including positive and negative thermal expansion, extreme compressibility, flexibility and breathing, allowing pore size control and selective guest uptake/release.

The effect of pressure, in particular, has received increasing interest, particularly when applied to both discrete and polymeric metal complexes, as highly anomalous structural changes can result. The application of significant hydrostatic pressure to a metal complex crystal usually results in structural perturbations that are reflected by compression of metal-ligand bond lengths, formation of new bonds, unit cell dimensional changes and/or crystallographic phase changes. Recrystallization of previously reported [CuL₂(THF)]₆ (CuL₂ = 1; R = t-Bu) [12] from N-methylmorpholine resulted in the discrete binuclear complex, [CuL₂(N,N-methylmorpholine)]₂ (CuL₂ = 1; R = t-Bu) [12]. We have investigated the effect of pressure on this product by X-ray diffraction with the aid of a diamond anvil cell (DAC). Increasing the pressure to 0.91 GPa resulted in the compression of the axial Cu-N and intermolecular Cu-O distances by 0.092(9) and 0.287(10) Å, respectively, with no new bonds being formed nor bonds broken.

![Diagram of copper(II) complexes](attachment://diagram.png)

We now present the results of an investigation of the effect of pressure on a related one-dimensional ribbon-like coordination polymer of stoichiometry [CuL₂(1-methylpiperazine)]₆ (R = t-Bu) formed from the reaction of 1 with the flexible saturated ditopic ligand, 1-methylpiperazine (2). Bright green crystals of this product (3) were grown by slow evaporation of a solution of 1 (R = t-Bu) dissolved in 1-methylpiperazine/THF (1:1) mixture (see SI). The 150 K X-ray structure (Figure 1) consists of alternating 5-coordinate and 6-coordinate dinuclear complexes. There are both bridging and non-bridging 1-methylpiperazine molecules present. The Jahn-Teller distorted 6-coordinate copper(II) centres are only bound to tertiary nitrogen atoms (Cu(2)-N(2), 2.747(3) Å; Cu(2)-N(3), 2.791(3) Å), while the 5-coordinate copper centres are bound only to secondary nitrogen atoms with a significantly shorter length (Cu(1)-N(1), 2.270(3) Å).

The secondary amine of each 1-methylpiperazine molecule points towards the centre of the ribbon and is hydrogen-bonded to the adjacent secondary nitrogen atom (N(1)-H···N(4) 2.10(4) Å, 168(3)°). The 1-methylpiperazine molecules adopt chair conformations with the nitrogen-bound methyl groups in equatorial positions which are aligned towards the aliphatic regions containing the t-butyl groups. The N(4)-H and the N(1)-H hydrogen atoms have axial and equatorial orientations. The copper atoms bridged by a piperazine unit are separated by 6.7477(6) Å. The structure of 3 differs markedly from that of [CuL₂(1-methylpiperazine)]₂(1-methylpiperazine) (R = t-Bu) (4) reported previously [12] which is a discrete dinuclear species with 5-coordinate copper(II) centres.

Supporting information for this article is given via a link at the end of the document.

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to which axial 1-methylpiperazine coligands are bound on opposite sides of the Cu2(L): coordination plane via their secondary N-donors (Figure S4); this product was synthesized employing different conditions from those used for 3.

![Figure 1. A fragment of the X-ray structure of the one-dimensional ribbon-like polymer ([Cu2(L)2(1-methylpiperazine)2]3) at 150 K. Hydrogen atoms and regions of disorder not shown for clarity.](image)

At 290 K, although the structure remains triclinic, the Cu(2)-N(3) separation increases to 2.973(3) Å from the value of 2.791(3) found at 150 K, resulting in the detachment of the non-bridging 1-methylpiperazine ligand from the Cu(2) copper(II) ion. This maintains the polymeric connectivity, but decreases the coordination number of Cu(2) from six to five. This is accompanied by a shortening of the Cu(2)-O distances which span 1.922(2) to 1.937(2) Å at 150 K and 1.914(2) – 1.9299(18) Å at 290 K. Although the now uncoordinated piperazine molecule became partly disordered, the N···HN H-bond distance involving the major disordered component decreases from 2.10 Å to 2.00 Å. The Cu(1)···Cu(2) distance across the bridging piperazine increases slightly from 6.7477(6) Å to 6.7928(7) Å.

Evidently the non-bridging piperazine bound solely via the N(3) tertiary amine group resides in an unusually flexible binding environment; we therefore investigated the effect of applying pressure, hypothesizing its application might lead to an increase in the coordination number of the copper(II) centres.

A single crystal of 3 was mounted in a diamond anvil cell, and prior to application of pressure, diffraction data were collected to confirm that the initial phase was the triclinic form described above. A series of data collections was then carried out up to 2.03 GPa (the limit of the system for paraffin as hydrostatic medium). Data suitable for full structure refinement were obtained up to 1.19 GPa. The pressure was measured using ruby fluorescence; the error of these readings is approximately 0.05 GPa. The unit cell parameters at each pressure are listed in Table 1 and other details of the structure determinations are summarized in Table S2.

A minor increase in pressure from ambient to ~0.05 GPa led to a single-crystal to single-crystal phase transition in which the symmetry increases from triclinic (PT) to monoclinic (P2_1/n). Analysis of the unit cell axial relationships before and after the transition (see SI) shows that the molecules reorient to become more nearly perpendicular to the b-axis. This generates higher translational symmetry along the b direction, halving both the number of copper(II) centres in the asymmetric unit and the b-axis length (14.6059(7) Å at ambient pressure to 6.8859(4) Å at 0.05 GPa). As can be seen from animations available in the SI, the transition involves substantial molecular reorientation, involving breaking and formation of bonds (see below).

As higher pressures were applied to the P2_1/n form after the phase transition the length of each axis and the cell volume decreased in nearly linear fashion (Figure S2) such that, by 2.03 GPa, the volume of the unit cell had further decreased by 14.6 % to 2117(2) Å³.

We expected that this decrease in unit cell volume would be accompanied by the formation of more 6-coordinate copper(II) centres. Instead, a de-polymerization process results from the breaking and formation of coordinate bonds producing a new discrete dinuclear complex, (5) (Figure 2), of formula [Cu2(L)2(1-methylpiperazine)2] (R = t-Bu) in which the Cu(II) centres are both 5-coordinate with axial 1-methylpiperazine ligands bound to a copper(II) by their tertiary amine groups (Cu(1)-N(1), 2.437(14) Å).
The transformation from the polymeric ambient-pressure structure, \([\text{Cu}_3(\text{L})_2(1\text{-methylpiperazine})_2\text{]}_\infty\) (3), to the discrete elevated pressure structure, \([\text{Cu}_3(\text{L})_2(1\text{-methylpiperazine})_2\text{]}_2\) (5), is associated with the breaking of two copper-tertiary amine bonds and two copper-secondary amine bonds, while two new two copper-tertiary amine bonds are formed (Figure S3). This requires all of the 1-methylpiperazine ligands which are coordinated via their secondary nitrogen atoms, to undergo “ring flips” (see Figure S4). The ring-flips are likely aided by the presence of hydrogen bonds between pairs of secondary amine groups in 3 which are maintained as intermolecular hydrogen bonds in the discrete (elevated pressure) structure (N(2)···N(2), 3.23 Å). The ring-flips result in closer alignment of the piperazine ring normal to the b-axis in the monoclinic phase (13.7°) than in the triclinic phase (32.5° in the case of the N1 containing ring). The projection of the ring down the b-axis is therefore smaller in the monoclinic phase, enabling the b-axis length to decrease below the value of b(triclinic)/2. The ring-flip is thus a mechanism for volume minimization.

The bulk modulus of 5 is calculated to be 8.6(5) GPa (see S1), which lies between that of a van der Waals solid such as Ru(II)CO$_3$ (6.6 GPa)[$^{16}$] and a hydrogen bonded solid such as L-alanine (13.4(7) GPa)[$^{17}$]. The largest component of the strain tensor lies along the crystallographic b-axis. This is reflected by successive decreases in distance between the nearest copper atoms in adjacent molecules as the pressure is increased. In the 0.05 GPa structure the (Cu(1)-Cu(1)) separation is 6.89 Å but by 1.19 GPa this is reduced to 6.55 Å. Over the pressure range investigated, each platform also becomes more distorted, with the intramolecular separation between its copper(II) centres decreasing slightly from 7.51 Å to 7.47 Å. A shearing motion between adjacent platforms also occurs as the pressure is increased (see Figure 3). The axial Cu(1)-N(1) distances also decrease, from 2.420(10) Å at 0.05 GPa to 2.332(9) Å at 1.19 GPa. The Cu-O bond distances do not change significantly over the same pressure range.

Table 1. Unit cell parameters for pressure studies of 3. \(\Delta V\) (%) is the difference between the unit cell volumes of the elevated and ambient pressure structures. \(\Delta\) (%) is taken as the change between the elevated and ~0.05 GPa structures.

<table>
<thead>
<tr>
<th>P (GPa)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å$^3$)</th>
<th>(\Delta V) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ambient</td>
<td>11.1354(5)</td>
<td>14.6059(7)</td>
<td>16.6644(9)</td>
<td>2581.2(2)</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>19.211(2)</td>
<td>6.8859(4)</td>
<td>20.676(2)</td>
<td>2477.6(4)</td>
<td>4.0</td>
</tr>
<tr>
<td>0.38</td>
<td>19.203(10)</td>
<td>6.789(14)</td>
<td>20.420(9)</td>
<td>2408.1(17)</td>
<td>6.7</td>
</tr>
<tr>
<td>1.19</td>
<td>18.843(2)</td>
<td>6.5460(4)</td>
<td>20.099(2)</td>
<td>2239.6(4)</td>
<td>13.2</td>
</tr>
<tr>
<td>1.31</td>
<td>18.747(13)</td>
<td>6.493(2)</td>
<td>20.022(11)</td>
<td>2202(2)</td>
<td>14.7</td>
</tr>
<tr>
<td>2.03</td>
<td>18.607(15)</td>
<td>6.360(2)</td>
<td>19.768(15)</td>
<td>2117(3)</td>
<td>18.0</td>
</tr>
<tr>
<td>(\Delta) (%)</td>
<td>3.1</td>
<td>7.6</td>
<td>4.4</td>
<td>14.6</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. The X-ray structure of 5 at elevated pressure. Hydrogen atoms and regions of disorder not shown for clarity.

Significantly, if the pressure is released after the phase transition has been induced, the phase transition and associated bond-breaking and bond-forming reactions are reversed. While this also resulted in the cracking of the crystal, each fragment retained crystallinity and the indexing of one such fragment confirmed the presence of the original PT form. In order to probe the prospect of an optical readout being coupled to the above switching behavior, the Raman spectrum was measured on either side of the phase change (see Figure S3). While, as expected, the major features of each spectrum were quite similar, differences were also evident. Most prominently, a sharp peak observed at ~990 cm$^{-1}$ in the elevated pressure spectrum is absent in the spectrum at ambient pressure. The presence or absence of this peak thus provides a clear optical marker for the crystal form present.

The reversible structural changes observed above represent a pressure-induced single-crystal to single-crystal transformation, involving both bond-breaking and bond-forming chemical reactions that are triggered at an uncommonly low applied pressure. The structural changes correspond to an unexpected (and non-intuitive) transformation – from a 1-dimensional metal coordination polymer to a discrete dinuclear entity. The modest pressure at which the above transformation occurs and the major structural changes associated with it, coupled with the reversibility of the process and the availability of an optical readout, all point towards possible application as a low pressure switch or sensor for use in optoelectronic or other suitable devices.

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Keywords: Stimuli Responsive · coordination polymer · high-pressure chemistry · X-ray structure · copper(II) complex


The application of elevated pressure to single crystals of a copper(II)-containing coordination polymer induces a reversible depolymerization reaction and single-crystal single-crystal transformation.


Page No. – Page No.
Reversible pressure-controlled depolymerization of a copper(II)-containing coordination polymer