

The supramolecular chemistry of bis- β -diketones: a remarkable single crystal-single crystal phase transition under pressure.

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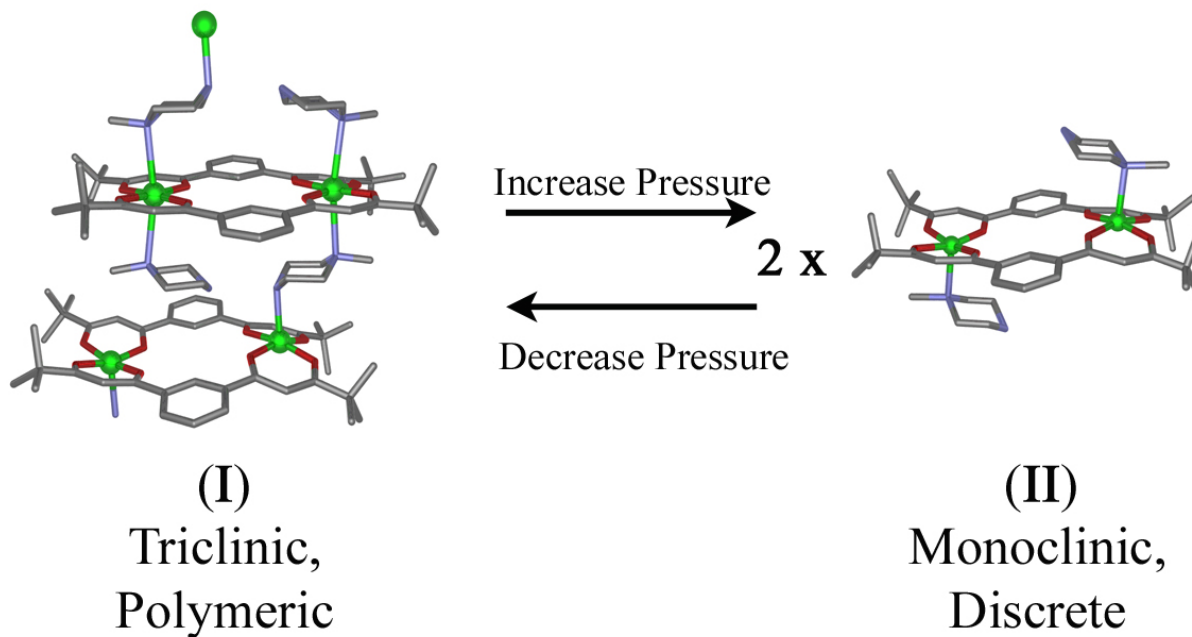
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The interaction of a variety of aryl-linked bis- β -diketones with cobalt(II), nickel(II), copper(II), zinc(II), gallium(III), iron(III) and zirconium(IV) has been investigated with the aim of obtaining new metallo-supramolecular assemblies. New binuclear, trinuclear and tetranuclear assemblies have been shown to form in a variety of geometries including helical, co-bifacial, triangular and tetrahedral arrangements that reflect the directional properties of the ligand and the metal ion. (1-2)

In particular, the use of copper(II) leads to the formation of neutral dinuclear and trinuclear species containing coordinatively unsaturated metal centres. These can then be reacted with nitrogen containing ligands to form extended 'linked' structures including discrete 'dimers of dimers' and a variety of 1D, 2D and 3D network solids.(3-4)

When N-methylpiperazine is employed as a 'linking' ligand a one dimensional chain polymer (I) results which crystallises in P-1. When a single crystal of this complex is loaded into a diamond anvil cell and the pressure increased a fully reversible phase change to Monoclinic P2₁/n results. Associated with the phase change is a significant chemical alteration with the structure transforming from a polymer to a discrete dimeric species (II), which is opposite of expectations from Le Chatelier's principle. The volume of the unit cell then continues to decrease as the pressure is increased to the limit of the system at 20 kbar.



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