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Structure and mechanical features of onedimensional coordination polymer *catena*-{(μ_2 adipato-O,O')-bis(pyridine-4-aldoxime)copper(II)}⁺

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The mechanical features of *catena*-{(μ_2 -adipato-*O*,*O'*)-bis(pyridine-4-aldoxime)-copper(III)} (1) were studied by the nanoindentation technique under different loads. The newly synthesised metal-organic material 1, with a one-dimensional coordination backbone, revealed plastic deformation evidenced by the sliding steps and nanoindentation load-displacement curves and the lack of cracks inside the indentations and in its neighborhood at all load tests. The pattern of the material movement in the crystal volume and its transfer to the surface associated with the shear-induced breakage of weak interlayer forces and the breakage of hydrogen bonds within the H-bonded layer is suggested.

The pioneering studies by Cheetham et al.¹⁻⁴ demonstrated undisputable advantages of the nanoindentation technique for estimation of the stability limits, anisotropy of hardness in different directions, and contribution of different types of interatomic and intermolecular forces to the overall crystal stability of hybrid metal-organic materials (MOMs).5 The recent findings by the same⁶⁻⁸ and other groups⁹⁻¹³ show the tuning of mechanical properties of metal-organic framework (MOF)¹⁴ materials via hydrogen bonding interactions and guest inclusion. The effects of negative linear compressibility of coordination networks and evaluation of mechanical characteristics of electrochemically grown MOF coatings were also reported.¹⁵ Our own recent findings in this area revealed the anisotropy of hardness and plasticity of the layer surface for the laminar structure $\{[Co(Ac)_2(bpe)(H_2O)] \cdot 0.5(dmf)\}_n$ where Ac = acetate, bpe = 4,4'-bipyridine ethane, dmf = N,N'dimethylformamide.16

For organic crystals on the other hand, the recent reports revealed the different mechanical properties for the polymorphs of sulfathiazole and curcumin,¹⁷ the impact of weak interactions on mechanical properties of caffeine cocrystals,¹⁸ and the deteriorated plasticity of piroxicam-saccharin cocrystals as a function of crystal packing.¹⁹ The mechanically induced molecular migrations reported for the layered homomolecular (thiohydantoin)²⁰ and heteromolecular (TCNB:pyrene) solids were explained in terms of mobility of the weakly bound arrays, and the nanoindentation technique was suggested as an effective tool to study layered crystal packing.²¹

In continuation of our efforts aimed at fabrication of soft hybrid materials^{22,23} with cooperative properties, we have prepared the title metal-organic compound, $[Cu(adi)(4-pyao)_2]_n$ 1, [where adi = bis-deprotonated residue of adipic acid, 4-pyao = pyridine-4-aldoxime ligand], and studied the structure-mechanical property relationship for this particular crystalline solid.²⁴ The choice of the ligands used in this study is justified by our recent results that revealed that the combination of flexible aliphatic dicarboxylic acids capable to act as multidentate linkers, with pyridine-4-aldoxime that acts as a bulky terminal ligand, provided an access to the spongy structures with luminescence properties in the case of d¹⁰ metals such as $Zn(\pi)$ and $Cd(\pi)$.²⁵ The survey of CSD (version 5.35, update February 2014) disclosed no structures that comprise Cu(II), adipic acid and pyridine-4-aldoxime molecules as co-ligands. On the other hand, the combination of Cu(II) with adipic acid and other N-type ligands (2,2'-bipyridine, 1,10phenanthroline, N,N-diethylethylenediamine 2-amino-1,3benzothiazole, melamine) resulted in different coordination networks.26-36

Blue block crystals of title compound $[Cu(adi)(4-pyao)_2]_n 1$ were obtained by solvent co-crystallization of $CuF_2 \cdot 2H_2O$ with 4-pyao and adipic acid from the water-methanol-dmf solvent mixture. The details are given in ref. 24. After mixing the components, the resulting solution was heated for 10 min,



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