The structural and magnetic properties of polymeric complexes bridged by azido ligands have received considerable attention. The two main reasons for this interest are (i) the remarkable ability of the azido ligand to transmit magnetic interactions when adopting different bridging modes; (ii) its great versatility as a ligand which affords a great variety of structural types spanning from discrete molecules to three-dimensional networks. We report herein a unique three-dimensional Cu(II) compound bridged by azido ligands with \( \text{P} \) bridged mode. The title complex was prepared by slow diffusion in an H-shape tube of methanolic solution of NaN\(_3\) on one arm, and Cu(ClO\(_4\))\(_2\) and the ligand \( \text{P} \) to form this unique three-dimensional network with large cavities as depicted above (from b-direction). The shortest Cu-Cu separation in the chains along c-direction is 13.616 Å and the Ag distances separated by the cis-bpob bridge is 10.463(8) Å. There are close π-π interactions (3.33 Å) between two benzene rings of two chains in helices.

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