

Electronic Supplementary Information

Two Types of Nitrito Support for μ_4 -Oxido Bridged [Cu₄] Complexes: Synthesis, Crystal Structures, Magnetic Properties and DFT Analysis

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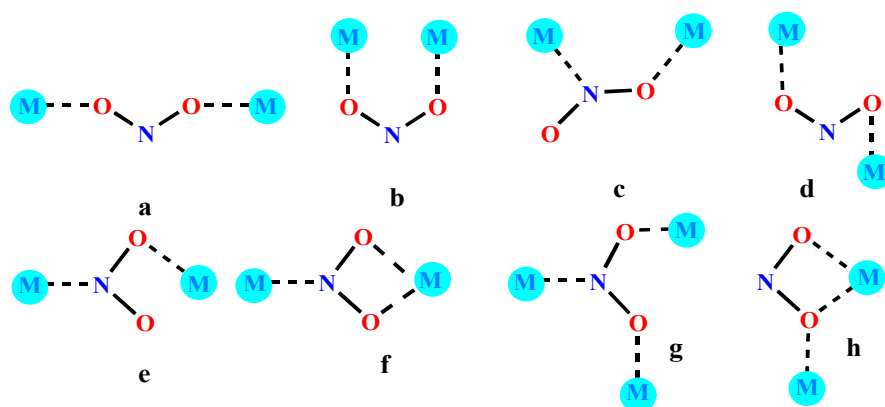
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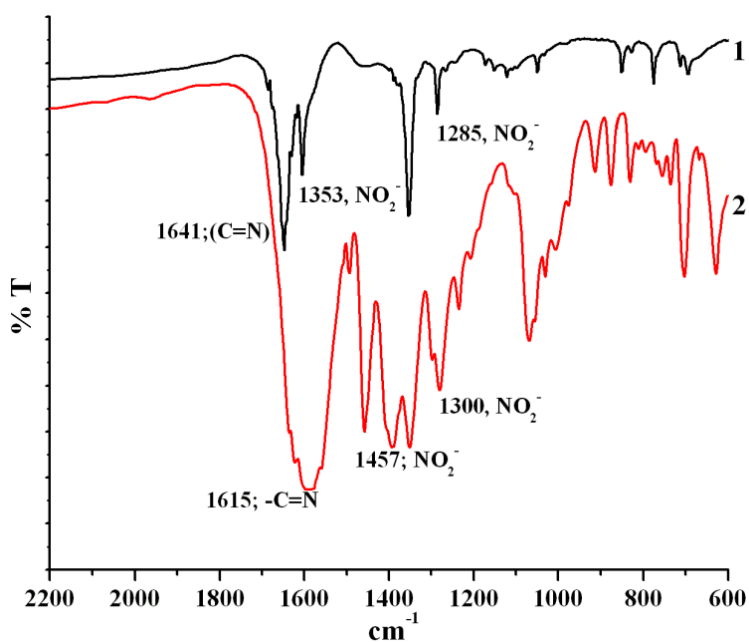
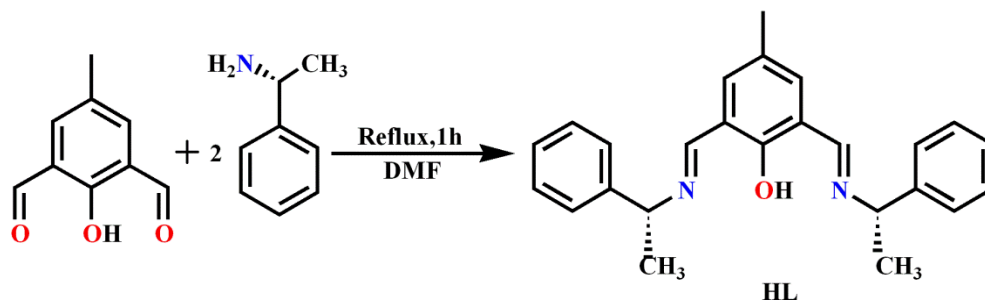
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Scheme S1 Coordination modes of nitrito ion

Synthesis of {4-methyl-2,6-bis-(1-phenyl-ethylimino)-methyl phenol} (HL) Ligand: A methanolic solution of 2,6-diformyl-5-methylphenol (1.640 g, 10 mmol) and R-(+)-1-phenyl ethylamine (2.42 g, 20 mmol) are refluxed for 1h in DMF (40 mL). An orange colored solution

was obtained which was concentrated on rotary evaporator to dryness. Orange gammy product was washed several times with toluene and dried. Infrared spectrum (cm^{-1} , KBr disk): 3045(br), 1621(vs), 1604(s), 1446(s), 1065(m), 791(s), 670(s). ^1H NMR (CDCl_3 , ppm): 8.15 (2H, imineH), 7.78-7.18 (12H, ArH), 4.94 (4H, methyleneH), 2.28 (3H, methylH), 1.53 (6H, methylH).



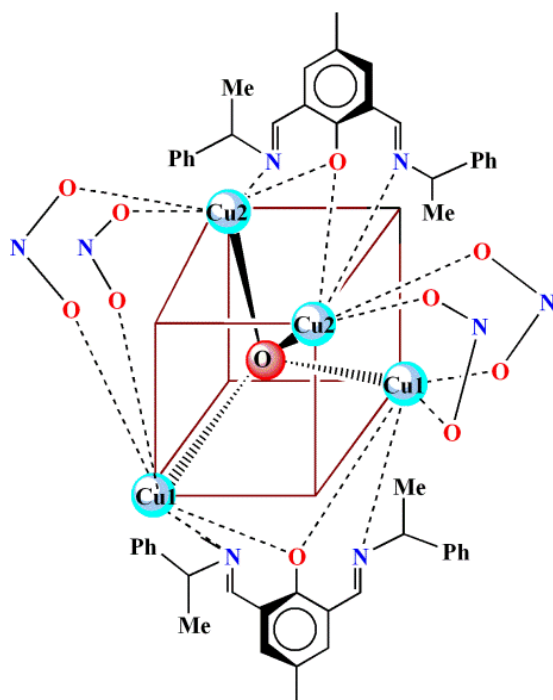


Fig. S2 Single μ_4 -O²⁻ atom nucleating self-assembly of **1**, showing that the binding of four nitrite ligands are in two opposite faces of the cube.

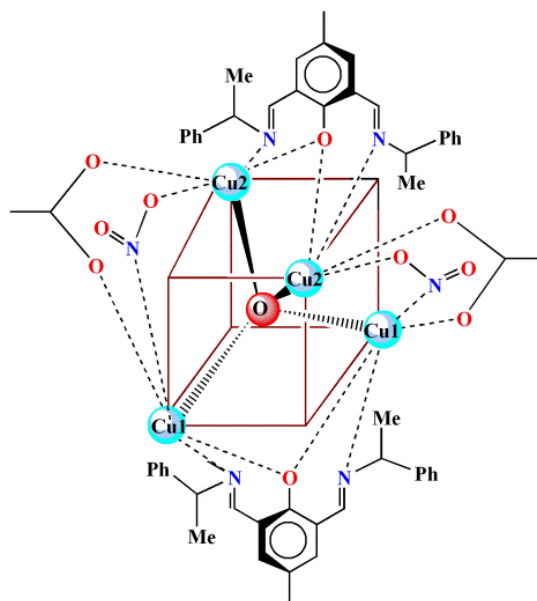


Fig. S3 Single μ_4 -O²⁻ atom nucleating self-assembly of **2**, showing that the binding of two nitrite and two carboxylate ligands are in two opposite faces of the cube

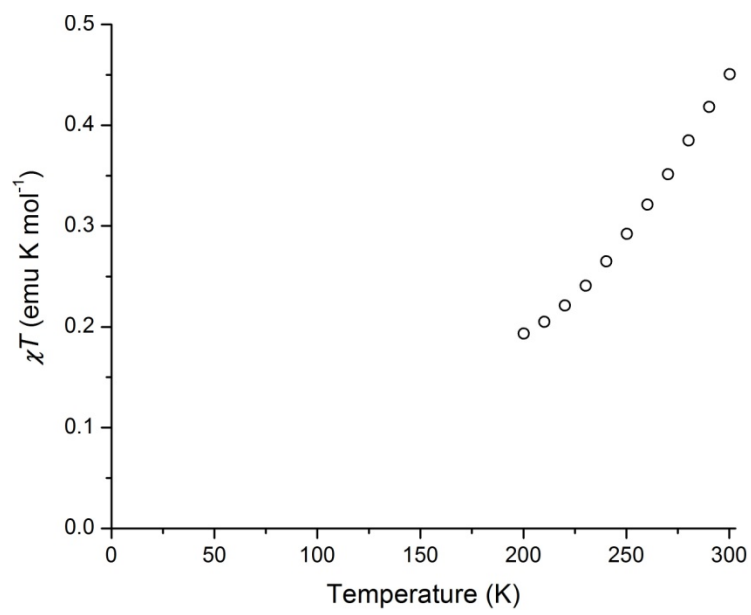


Fig. S4 χT vs. T dependence for complex 1 above 200 K