

mu 3-vs. mu-Hydroxido Bridges - Peripheral Function Controls the Nuclearity of Hydroxido-Bridged Copper(II) Complexes

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Abstract/Résumé : The synthesis and characterization of three monohydroxido-bridged dinuclear CuII complexes, $[\{Cu_2(L1)_2(\mu-OH)\}(ClO_4)\{Cu_2(L1)_2(\mu-OH)\}](ClO_4) \cdot 5.5H_2O$ (1), $Cu_2(L2)_2(OH)(ClO_4)(H_2O)_2$ (2), $[\{Cu_2(L3)_2(\mu-OH)(ClO_4)\}_2] \cdot 5H_2O$ (3) and three monohydroxido-bridged trinuclear CuII complexes, $[Cu_3(L4)_3(\mu^3-OMe)(ClO_4)_2]$ (4), $[Cu_3(L5)_3(\mu^3-OH)(ClO_4)_2] \cdot 0.5\{(CH_3)_2CO\} \cdot 0.5(H_2O)$ (5), $[Cu_3(L6)_3(\mu^3-OH)(ClO_4)_2]$ (6), is reported (HL1HL6 = tridentate N2O ligands resulting from the Schiff base condensation of salicylaldehyde or 3-methoxysalicylaldehyde with ethylenediamine, 1,2-diaminopropane, 2-methylpropane-1,2-diamine or 1,2-diaminocyclohexane). The six new complexes are obtained through aggregation of the corresponding mononuclear precursor $Cu(Li)(py)(ClO_4)$ in the presence of HO (MeO) anions in methanol. The nuclearity of the resulting complex depends on the steric requirement of Li: in the presence of an OMe substituent α to the Ophenoxido atom (L1L3), μ -HO single-bridged dinuclear compounds are obtained (13); in the absence of an α -substituent (L4L6), the aggregation proceeds to the μ^3 -OH (μ^3 -OMe) bridged trinuclear compounds 46. The molecular structures of 1, 3 and 46 have been established through single-crystal X-ray studies. Antiferromagnetic interactions operate in 1 ($J = 57 \text{ cm}^{-1}$, 2J1S2 formalism), 2 is paramagnetic, and 3 is the first example of a ferromagnetic monohydroxido-bridged dinuclear CuII complex ($J = 16 \text{ cm}^{-1}$). The structural and magnetic parameters for the 22 μ -HO single-bridged dinuclear CuII compounds reported to date are compared. Antiferromagnetic interactions operate in all three monohydroxido-bridged trinuclear CuII complexes 4, 5, and 6 ($J = 16.9, 6.3, \text{ and } 6.7 \text{ cm}^{-1}$, respectively). The structural and magnetic parameters for the seven μ^3 -hydroxido (methoxido) bridged trinuclear CuII compounds presently known in the series based on tridentate Schiff bases that result from condensation of diamines with salicylaldehydes are compared.

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