Copper(II) Complexes of a Series of New Polypyridine Ligands Possessing a 1,2-Bis(2-pyridyl)ethane Common Moiety. Incorporation and Hydrolysis of Phosphate Esters

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Two tetradentate ligands 1,2-bis[2-(*N*,*N*-dimethylaminomethyl)-6-pyridyl]ethane (L1) and 1,2-bis[2-(*N*-piperidinomethyl)-6-pyridyl]ethane (L2) and a hexadentate ligand 1,2-bis(2-((*N*-methyl-*N*-pyridylmethyl)aminomethyl-6-pyridyl)ethane (L3) were prepared as part of a series of new polypyridine ligands possessing a 1,2-bis(2-pyridyl)ethane common moiety. L1 and L2 form mononuclear Cu(II) complexes $[Cu(L)(Cl)](ClO_4)$ [L = L1 (**1**) and L2 (**2**)], respectively. L3 forms a dinuclear Cu(II) complex $[Cu_2(L3)((PhO)_2PO_2)_2](ClO_4)_2$ (**3**) or a hexanuclear Cu(II) complex $[Cu_6(L3)_3((PhO)PO_3)_4](ClO_4)_4$ (**4**) in the presence of $(PhO)_2PO_2^-$ monoanion or $(PhO)PO_3^{2-}$ dianion, respectively. The structures of **1**-**4** were determined by X-ray analysis. The structures in solution were investigated by means of FAB and CSI MS spectrometers. The structural flexibility of the common 1,2-bis(2-pyridyl)ethane moiety and of the pendant groups allows complexes **1**-**4** to adapt to the various structures. Each Cu ion in **1** and **2** adopts a square pyramidal geometry with one Cl ion and two pendant groups (L1 and L2) binding in a bis-bidentate chelate mode. There is no steric repulsion between the pendant groups, so that the ligands specifically stabilize the mononuclear structures. L3 binds two Cu(II) ions with two pendant groups in tridentate chelate modes and, with the incorporation of phosphate esters, various dinuclear units are formed in **3** and **4**. In **4**, a dinuclear unit of $[Cu_2(L3)]^{4+}$ links two dinuclear units of $[Cu_2(L3)(PhOPO_3)_2]$ with four μ_3-1,3-$PhOPO_3^{2-}$ bridges. The hydrolytic activity of **2** and a dicopper(II) complex of L3 was examined with tris(*p*-nitrophenyl)phosphate (TNP) as a substrate.