Tetranuclear Copper Complexes of Bisimidazole-Amino Acid Based Ligands and their Catecholase Activity

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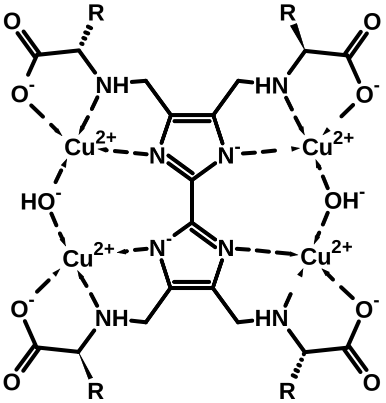
The chemistry of polynucleating ligands containing imidazole moieties has been of great interest in bioinorganic chemistry, because their polynuclear complexes can be used as suitable models of type III copper proteins, such as catechol oxidase. Their structure allows the approach of two copper ions promoting the introduction of bridging groups. These bridges can confer the complexes special features such as catalytic activity in oxidation reactions using molecular oxygen as the primary oxidant, and also allow an anti-ferromagnetic coupling giving EPR non-detectable species.

By means of the Mannich reaction we synthesized a new kind of polynucleating ligands derived from bisimidazole and amino acids, which have been fully characterized. Their tetranuclear copper complexes were also prepared and characterized. Evidences of structural differences in solution with pH variation, including diverse bridges between copper centers, such as imidazolato and hydroxo bridges, are presented and analyzed. We also present formation constants (K_f's) for these complexes.

Their catecholase activity and EPR studies in solution with pH variation are discussed, both are in accordance with each other and with K_f's.



Schematic representation of the tetranuclear complexes where both imidazolato and hydroxo bridges are shown. The R residue depends on the amino-acid used.