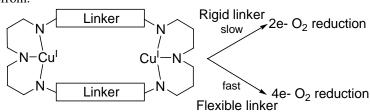
Cooperative Effects in O₂-Activation at Dinuclear Copper Complexes

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Modelling of dioxygen activation at dinuclear copper sites continues to be an interesting topic in biomimetic inorganic chemistry because of the implication of these reactions in a number of copper dependent metalloproteins that participate in O₂ metabolism. With the aim of better understanding cooperative effects played by dimetallic sites in the O₂ activation process, two new dinuclear copper complexes containing hexaaza type of ligands have been prepared and characterized in the solid state by X-ray analysis and in solution by variable temperature NMR. The two complexes exhibit nearly superimposable distorted planar trigonal metal coordination sites and long (> 7Å) Cu···Cu distances. In addition, the FT-IR spectra of the corresponding CO adducts exhibit coincident $\upsilon_{\text{Cu-CO}}$ stretching frequencies, suggesting that the electronic properties of the copper ions are comparable. The complexes differ though in the relative flexibility of the linker connecting the two copper binding sites in such a way that one of the complexes is rather rigid and does not allow the copper sites to approach each other, whereas in the other, the flexibility of the ligand may allow the metal ions to come into closer contact and give rise to cooperative effects. The reaction of the two dinuclear complexes with O₂ have been studied revealing dramatic differences in reaction rate, reaction mechanisms and nature of the species that derive therefrom.



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