NOVEL μ-1,2-PEROXO DICOPPER COMPLEXES FEATURING SQUARE PLANAR Cu(II) SITES: SYNTHESIS, STRUCTURE, AND REACTIVITY

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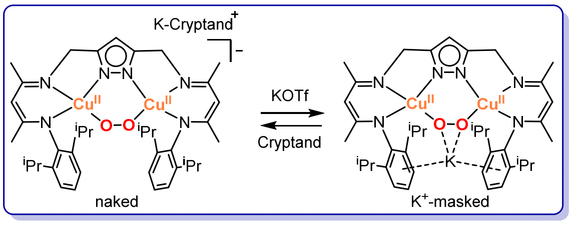
Copper enzymes play important roles in the binding and activation of dioxygen in biological systems, including the type III dicopper proteins. [1] Key dicopper/dioxygen intermediates have been identified and studied in synthetic analogues of the metalloprotein active sites, including end-on *cis/trans*-μ-η^1:η^1-peroxodicopper(II) ($^{C/T}$**P**) and side-on μ-η^2:η^2-peroxodicopper(II) (^{S}**P**) species, as well as bis-μ-oxo dicopper(III) (**O**) species. [2,3] These studies conclude that ligand effects constitute one of the most critical factors in determining the geometric structures and properties of the dicopper/dioxygen adducts, especially the denticity of the ligand. [4,5]

SCXRD√
rRaman√
UV-vis√
SQUID√
THz-EPR√
DFT√



- **First example of tridentate-chelating μ-1,2-peroxodicopper intermediates;**
- **Perpendicular binding geometry of Cu_2/O_2 core;**
- **Ferromagnetic coupling (S = 1);**
- **Amphiphilic reactivities: OAT and aldehyde oxidation**

Herein, we report the synthesis and characterization of a bioinspired dinuclear (bis)tridentate copper chelate system that forms an unprecedented end-on μ-η^1:η^1-peroxo complex with square planar Cu^{II} sites. This peroxo compound shows strong affinity for K$^+$, resulting in a K$^+$-masked μ-1,2-peroxodicopper(II) complex with markedly enhanced thermal stability. These two peroxo compounds are well characterized by X-ray crystallography, rRaman and UV-vis spectroscopies. The Cu-O-O-Cu torsions are close to 90°, thus they could be best described as a $^{\perp}$**P** system right in between ^{T}**P** and ^{C}**P**,[5,6] which results in ferromagnetic coupling between the copper(II) ions based on magnetic measurements and THz-EPR. Theoretical studies elucidate the orbital interaction between the peroxide and Cu^{II} sites, and reveal the key role of the K$^+$ ion in stabilizing the Cu_2/O_2 core. The peroxo compounds display both electrophilic oxygen-atom-transfer (OAT) reactivity with PMe_3 as well as nucleophilic aldehyde oxidation reactivity with PhCHO, which indicates the amphiphilic reactivity of the μ-1,2-peroxodicopper(II) complex. These findings provide a structural basis for bis{N_3} ligated μ-1,2-peroxodicopper(II) intermediates, which represent a snapshot of the initial stages of O_2 binding at type III dicopper sites.

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