O₂-Activation by Copper(I) Complexes of N-Alkyl Derivatives of cis,cis-1,3,5-Triaminocyclohexane

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Reaction of O₂ with copper(I) plays a vital role in enzymes and synthetic oxidative catalysis. Especially, bis(☐-oxo)dicopper(III) complexes is quite interested as an isomer of ☐²-☐²-peroxodicopper(II) complex that is generated in biological system. We recently reported that addition of O₂ to [Cu(MeCN)(RL)]SbF₆ (3) (L = cis,cis-1,3,5-triaminocyclohexane; R = i-Bu) in THF at 183 K afforded a bis(☐-oxo)dicopper(III) complex (6)³. Herein, we report that the preparation and crystal structures of Cu(I) and Cu(II) complexes ([Cu(MeCN)(RL)]⁺ (R = Et (1), Bn (2)), [Cu₂(OH)₂(RL)₂]⁻² (R = Et (7), Bn (8)) and the reactivity of Cu(I) complexes with O₂.

Two Cu(I) complexes 1 and 2 were synthesized under anaerobic conditions (Figure 1), which reacted with O₂ in CH₂Cl₂ at 193 K to form bis(☐-oxo)dicopper(III) complexes [Cu₂(☐-O)₂(RL)₂]⁻² (R = Et (4; ☐max = 309, 408 nm; ☐Cu-O = 553, 581 cm⁻¹) and Bn (5; ☐max = 306, 413 nm; ☐Cu-O = 570 cm⁻¹), respectively. The half-life periods of 4 and 6 were 530 and 69 sec. in CH₂Cl₂ at 193 K, respectively, and that of 5 was too fast to follow. Those of 4-6 were 160, 8, and 280 sec. in THF at 193 K, respectively. We will discuss the relationship between the thermal stabilities and the reactivities of 4-6 on the basis of three crystal structures of [Cu₂(OH)₂(rl)₂]⁻² (R: Et, Bn, and i-Bu) (Figure 2).