O_2-Activation by Copper(I) Complexes of N-Alkyl Derivatives of *cis,cis*-1,3,5-Triaminocyclohexane

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Reaction of O_2 with copper(I) plays a vital role in enzymes and synthetic oxidative catalysis. Especially, bis(μ-oxo)dicopper(III) complexes is quite interested as an isomer of μ-η^2:η^2-peroxodicopper(II) complex that is generated in biological system. We recently reported that addition of O_2 to [Cu(MeCN)(**RL**)]SbF_6 (**3**) (**L** = *cis,cis*-1,3,5-triaminocyclohexane; **R** = *i*-Bu) in THF at 183 K afforded a bis(μ-oxo)dicopper(III) complex (**6**)[1]. Herein, we report that the preparation and crystal structures of Cu(I) and Cu(II) complexes ($[Cu(MeCN)(\mathbf{RL})]^+$ (R = Et (**1**), Bn (**2**)), $[Cu_2(OH)_2(\mathbf{RL})_2]^{2+}$ (**R** = Et (**7**), Bn (**8**)) and the reactivity of Cu(I) complexes with O_2.

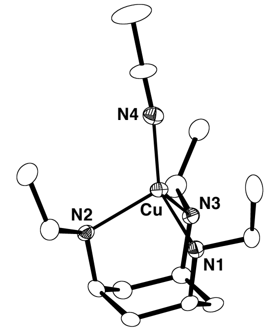

Figure 1. ORTEP view of the cationic portion in [Cu(MeCN)(EtL)]SbF_6.

Two Cu(I) complexes **1** and **2** were synthesized under anaerobic conditions (Figure 1), which reacted with O_2 in CH_2Cl_2 at 193 K to form bis(μ-oxo)dicopper(III) complexes $[Cu_2(\mu\text{-}O)_2(\mathbf{RL})_2]^{2+}$ [**R** = Et (**4**; λ_{max} = 309, 408 nm; $\nu_{Cu\text{-}O^{16}}$ = 553, 581 cm^{-1}) and Bn (**5**; λ_{max} = 306, 413 nm; $\nu_{Cu\text{-}O^{16}}$ = 570 cm^{-1})], respectively. The half-life periods of **4** and **6** were 530 and 69 sec. in CH_2Cl_2 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 $[Cu_2(OH)_2(\mathbf{RL})_2]^{2+}$ (**R**: Et, Bn, and *i*-Bu) (Figure 2).

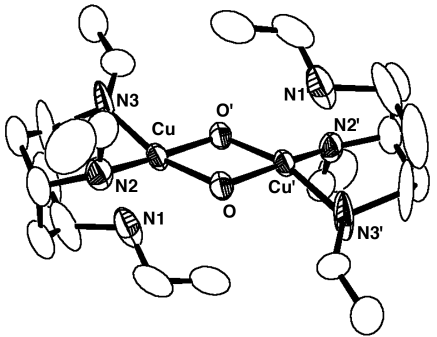

Figure 2. ORTEP view of the cationic portion in $[Cu_2(OH)_2(EtL)_2](OTf)_2$.

1) H. Arii et al. *Chem. Lett.,* **32**, 156 (2003).