

Characterization and Reactivity Studies of Tetrahedral Cupric-halide Complexes

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Copper plays essential roles both in nature and in industry owing to its readily accessible copper(I)/copper(II) redox pair. Among the several copper-containing enzymes, tetrahedral copper(II) center are found in the active sites of dopamine β -monooxygenase (D β M), peptidylglycine α -hydroxylating monooxygenase (PHM), and blue copper proteins.¹ However, artificial copper(II) complexes having a tetrahedral geometry are still very rare, since copper(II) ion favors five-coordinate square pyramidal and trigonal bipyramidal structures. In order to synthesize stable mononuclear tetrahedral copper(II) complexes having a labile coordination site, we have developed a tridentate N₃-ligand, TMG₃tach (2,2',2''-((1s,3s,5s)-cyclohexane-1,3,5-triyl)tris(1,1,3,3-tetramethyl guanidine) consisting with *cis,cis*-1,3,5-triamino-cyclohexane (tach) and three *N,N,N',N'*-tetramethylguanidine (TMG) substituents (Figure 1).²

In this study, we have synthesized and characterized a series of copper(II)-halide complexes, (TMG₃tach)Cu^{II}X (**1**^X; X = F⁻, Cl⁻, Br⁻, I⁻) to evaluate the geometric effects on the redox reactivity of mononuclear tetrahedral copper(II) complexes. We found that **1**^F, **1**^{Cl}, and **1**^{Br} were stable at room temperature, whereas **1**^I was gradually converted to the corresponding copper(I) complex and I• (obtained as I₃⁻) via homolytic Cu^{II}–I bond cleavage at room temperature. At a higher temperature, **1**^{Br} also underwent a similar Cu^{II}–Br bond cleavage. When the reaction of **1**^{Br} was conducted under aerobic conditions (under O₂), hydroxylation of one of the methyl groups of TMG substituent took place, indicating formation of a copper-active oxygen intermediate via the reaction of generated copper(I) complex and O₂. Reactivity of **1**^X toward external substrates has also been examined to evaluate the redox functions of copper(II)-halide complexes having a tetrahedral geometry.

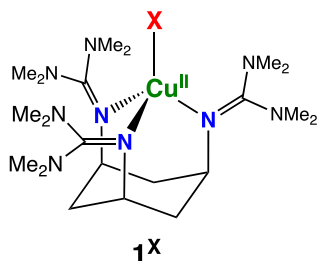


Figure 1. Copper(II)-halide complexes supported by TMG₃tach ligand

1) E. I. Solomon, *et al.*, Chem. Rev. **2014**, 114, 3659–3853.

2) S. Itoh, *et al.*, Inorg. Chem., **2017**, 56, 9634–9645.