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Review

# Charge and spin coupling in copper compounds with hemilabile noninnocent ligands – Ambivalence in three dimensions

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ABSTRACT

Both the copper(I) and copper(II) states exhibit coordinative ambiguity as well as a typically increased coordination number after oxidation. This tendency can be used in dynamic redox systems, employing hemilabile innocent ligands. With *noninnocent* hemilabile ligands such as thioether- or selenoether-substituted *o*-semiquinone imines there is a complementary reactivity on the ligand side, viz., stepwise electron transfer and coordinative ambivalence. Some resulting combinations have been analyzed for two systems, involving one copper center and one camphorquinone imine or two *o*-benzoquinone imine components ($Q^n$). Combining redox ($Cu^{I/II}$, $Q^{0/\cdot-/2-}$) *and* coordinatively ambivalent metal and ligand components (hemilability) creates variable electronic situations which require experimental and theoretical analysis.

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## Contents

## 1. Introduction and background examples for variable coordination by copper

The concept of hemilability [1] of chelate ligands with significantly different donor atom characteristics has been enormously fruitful for several aspects of coordination chemistry, including catalytic processes [2] (→ reversible opening of substrate coordination sites, Scheme 1) and information processing such as redox switching [3,4].

In addition to the specified requirement for the multidentate ligand there are also metal configurations which favor hemilabile activity as sketched in Scheme 1. It will be shown in this review that both the +II and +I oxidation states of copper are highly suitable for undergoing pertinent coordination changes because of their distinct difference and their common tendency to adopt fractional coordination numbers.

In the case of the $3d^9$ configuration of copper(II) this usually involves a Jahn–Teller-type distortion [5], leading to square or square-pyramidal structures (4+1 coordination). The very strong preference for such a distortion is illustrated by the breaking of the threefold symmetry of the tacn ligand (tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane, Fig. 1) in a catecholate complex (Fig. 2) [6].

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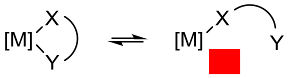


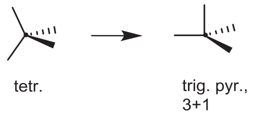
**Scheme 1.** Reversible opening of a coordination site in a chelate complex with a hemilabile ligand.

For complexes of the 3d$^{10}$ species Cu$^I$ there are no ligand-field effects to be considered, however, many structural studies [7,8] have pointed to a tendency toward a 3+1 coordination geometry (Scheme 2).

Starting from a regular tetrahedron, a corresponding distortion would lead toward a trigonal-pyramidal structure, with symmetry lowering, alteration of angles and the typical lengthening of one bond. Diamagnetic and paramagnetic (i.e. radical containing) copper(I) complexes have exhibited such type of distortion [7,8]. If the chelate dimensions change, the individual coordinative interactions may become rather weak, with increasing Cu-donor distances up to the range of the sum of the van der Waals radii [9] and beyond. Complexes of copper(I) with guanines and similar purine ligands (Figs. 3 and 4) represent such examples (Figs. 5 and 6) [10,11]. In those cases the strong bond to N7 is complemented by a more or less weakly coordination of O6 [10].

The tendency of copper(I) and copper(II) centers for fractional coordination patterns toward chelate ligands can be exploited in systems involving the Cu$^I$/Cu$^{II}$ electron transfer. One obvious such example is shown in Scheme 3, where two NNS donor ligands leave the weakly basic thioether function uncoordinated in the copper(I) complex but exhibit the binding of *one* S donor at 2.43 Å after metal-based oxidation [12], resulting in the preferred 4+1 coordination.

Adding a dynamic dimension, the use of chelate-containing macrocycles in interlocked copper catenate complexes of Livoreil and Sauvage [13] has shown how the copper(I) conversion to the EPR active Cu$^{II}$ forms results in a large-amplitude motion, a rotation of a ring within another ring [14], on the time scale of minutes as observed through conventional EPR spectroscopy (Scheme 4) [15].



**Scheme 2.** Distortion from tetrahedral to trigonal-pyramidal configuration in a four-coordinate complex.

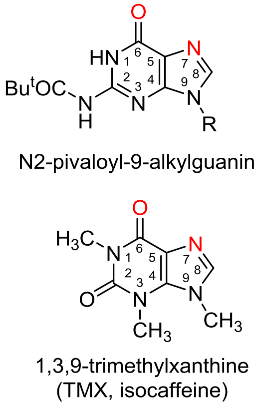


**Fig. 3.** Purine-based hemilabile N,O chelate ligands [10].

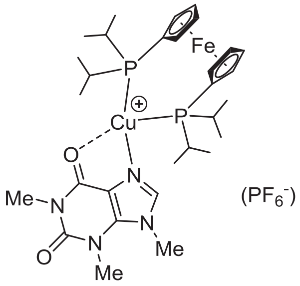


**Fig. 4.** Asymmetric chelation (Cu–N 2.006(2) Å, Cu–O 2.772(2) Å) [10].

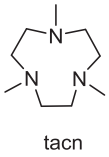


**Fig. 1.** The tacn ligand.

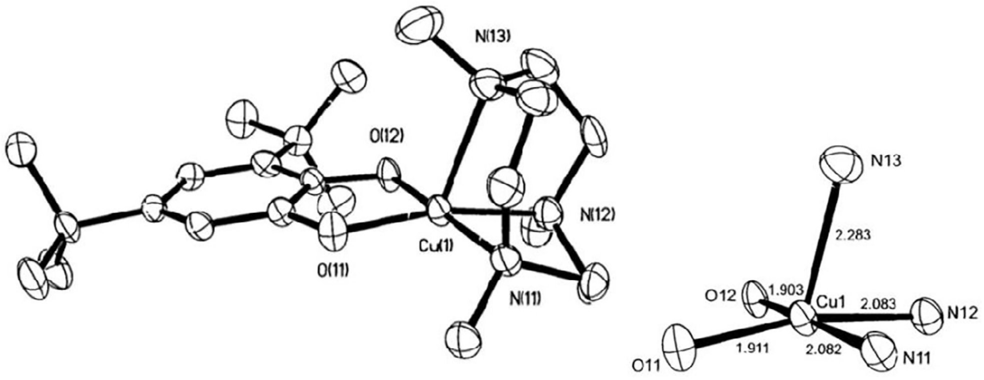


**Fig. 2.** Molecular structure of [Cu$^{II}$(tacn)(Q$^{2-}$)], Q = 3,5-di-*tert*-butyl-*o*-quinone [6].

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