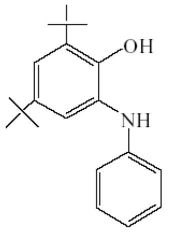
Switch of Spin Combinations through Weak Cu(II)-S Interaction Related to Type 1 Copper Proteins

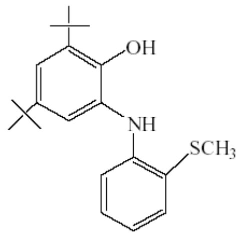
Shengfa Ye,[†] Biprajit Sarkar,[†] Falk Lissner,[†] Thomas Schleid,[†] Joris van Slageren,[‡] Jan Fiedler,[§] Wolfgang Kaim[†]*

[†]*Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart, Germany,* [‡] *1. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, D-70550 Stuttgart, Germany,* [§]*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-18223 Prague, Czech Republic*

The weak copper-thioether interaction due to typically long Cu-S(Met) distances at about 2.9 Å in type 1 copper proteins have received much interest in bioinorganic chemistry (Solomon et al., *Chem. Rev.* **2004**, *104, 419*). Using a new, potentially tridentate radical ligand ($Q_y^{\bullet-}$) obtained by addition of a thioether S donor function to the well-established non-innocent semiquinoimine ligand ($Q_x^{\bullet-}$) we have been able to produce a three-spin system (radical/metal/radical, $[(Q_y^{\bullet-})Cu^{II}(Q_y^{\bullet-})]$) with sterically unenforced non-planar copper(II) at the center. This unusual situation is caused by a weak Cu-S interaction (d_{Cu-S} = 3.198(1), 3.475(1) Å), an effect reminiscent of type 1 copper sites in proteins. In comparison to planar analogues $[(Q_x^{\bullet-})Cu^{II}(Q_x^{\bullet-})]$ (Chaudhuri, Wieghardt et al., *J. Am. Chem. Soc.* **2001**, *123* 2213), the distortion of the metal is responsible for a changed spin ground state as detected by EPR. While anion radical ligands yield already unusual complexes with transition metals in "normal" configurations, the possible distortion adds another dimension, as shown below, allowing for a striking switch of spin combinations.



H_2Q_x



H_2Q_y