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Universiteit Leiden



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Title: Biomimetic redox reactions of the Cu(II) μ -thiolate complex

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Propositions (Stellingen)

accompanying the thesis

Biomimetic Redox Reactions of the Cu^{II} μ -Thiolate Complex

1. In a reaction of a disulfide ligand with a Cu^I salt, the Cu^{II} μ -thiolate complex is generally the kinetic product while the Cu^I disulfide species is the thermodynamic product.
This thesis, Chapter 2
2. In contrast to a report describing the conversion of a Cu^{II} μ -thiolate complex to a Cu^I disulfide species upon protonation, ligand dissociation takes place after addition of only one H⁺ per copper center.
A. M. Thomas et.al., *J. Am. Chem. Soc.* **2013**, *135*, 18912-18919; *This thesis, Chapter 3*
3. Crystal structures of accidentally formed crystals within a mixture – even when they are non-reproducible – can provide interesting clues concerning formation of intermediates or degradation pathways.
This thesis, Chapter 4 and 6
4. A purple copper complex with a Raman band and UV-vis absorptions matching those reported for Cu^{II}₂ μ - η^2 : η^2 -peroxide species is not necessarily a Cu₂O₂ compound.
This thesis, Chapter 6
5. Biomimetic models should not be used to draw conclusions about the biological system, but to support theories and data concerning enzymatic structures and reactions.
This thesis, Chapter 8
6. A publication focusing on differences in coordination geometries of Cu^{II} compounds as determined from crystal structures should be supported by the crystallographic information files.
S. Itoh et.al., *J. Am. Chem. Soc.* **2001**, *123*, 4087-4088

7. The use of the term 'Cu_A site' should be restricted to the dinuclear thiolate-bridged copper active site in enzymes.
A. Kunishita et.al., *Inorg. Chem.* **2012**, 51, 9465-9480
8. One cannot conclude that CO₂ is reduced to oxalate by Cu^{II} α-ketocarboxylate complexes when oxalate is also produced in the absence of CO₂.
H. Takisawa et.al., *Inorg. Chem.* **2014**, 53, 8191-8193
9. In an aprotic system, the full conversion of a purple Cu^{II} species to a Cu^I complex cannot be explained by reduction followed by protonation.
S. Kundu et.al., *J. Am. Chem. Soc.* **2012**, 134, 14710-14713
10. Fundamental science is becoming an endangered species that needs preservation.
11. Getting your manuscript published is facilitated substantially by having the right friends in the right places.
12. There is no such thing as too many crystal structures.

Erica Ording-Wenker
Leiden, March 2015