

# Formation of a dicopper(I) helicate by oxidative dehydrogenation of a monomeric copper(II) polyamine complex

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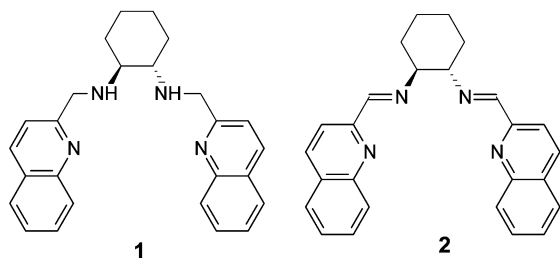
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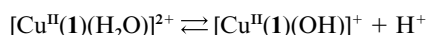
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Reaction of the monomeric polyamine complex  $[\text{Cu}^{\text{II}}(\mathbf{1})]^{2+}$  with  $\text{OH}^-$  and  $\text{O}_2$  gives the dimeric double-helix complex  $[\text{Cu}_2^{\text{I}}(\mathbf{2})_2]^{2+}$ , in which the  $-\text{CH}_2-\text{NH}-$  amine groups have been dehydrogenated to  $-\text{CH}=\text{N}-$  functions.

We describe here the unusual case of the oxidation with dioxygen in basic solution of the  $\text{Cu}^{\text{II}}$  complex with the tetra-aza chelating agent *N,N'*-bis-quinolin-2-ylmethyl-cyclohexane-*trans*-1,2-diamine, **1**, which leads to the formation of the solution stable dimeric double-helix  $\text{Cu}^{\text{I}}$  complex of the parent unsaturated ligand *N,N'*-bis-quinolin-2-ylmethylene-cyclohexane-*trans*-1,2-diamine, **2**. The process involves the deprotonation of the amine groups of **1** coordinated to  $\text{Cu}^{\text{II}}$ , their oxidative dehydrogenation to imine, and, following intramolecular electron transfer processes, the eventual formation of the dicopper(I) double-helix complex with the ligand **2**.



In the course of an investigation of the solution behaviour of copper(II) complexes with sterically constrained poly-aza chelating agents, titration with base of the  $[\text{Cu}^{\text{II}}(\mathbf{1})]^{2+}$  complex, dissolved as triflate salt, in a dioxane–water mixture (4 : 1 v/v), under a dinitrogen atmosphere, disclosed the occurrence of a deprotonation process at  $\text{pH} = \text{p}K_{\text{A}} = 9.98 \pm 0.02$ . The acid–base process, which is accompanied by a shift of the d–d absorption band from 642 to 613 nm (colour change from blue–green to greenish), is ascribed to the deprotonation of a water molecule coordinated to the metal centre, according to the equilibrium:



The same process is typically observed to occur for  $\text{Cu}^{\text{II}}$  complexes with a variety of tetra-aza ligands over a wide pH range.<sup>1</sup> The crystal and molecular structure of the  $[\text{Cu}^{\text{II}}(\mathbf{1})(\text{Cl})]^{2+}$  complex has been recently reported,<sup>2</sup> showing a square pyramidal geometry, with the four nitrogen atoms occupying the basal plane. It is hypothesised that the  $[\text{Cu}^{\text{II}}(\mathbf{1})(\text{H}_2\text{O})]^{2+}$  and  $[\text{Cu}^{\text{II}}(\mathbf{1})(\text{OH})]^{2+}$  complexes involved in the acid–base equilibrium exhibit a similar coordination geometry, with the chloride ion replaced by  $\text{H}_2\text{O}$  and  $\text{OH}^-$ , respectively, in the apical site of the square pyramid. Successive addition of standard base up to  $\text{pH} = 12$  did not cause any further deprotonation process, as shown by potentiometric and spectrophotometric measurements. However, when the titration with standard base was carried out in the presence of air, a red–violet colour was observed to develop in the solution at  $\text{pH} \geq 10$ . In particular, an intense absorption band formed with a maximum at 530 nm.

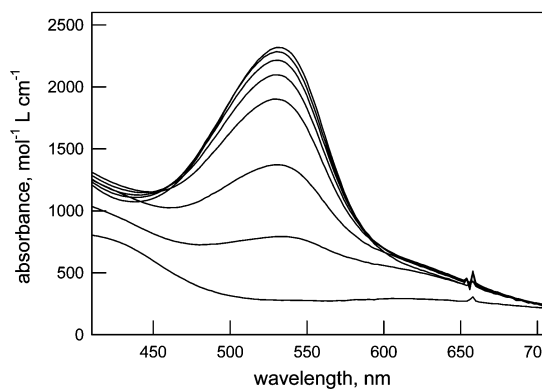
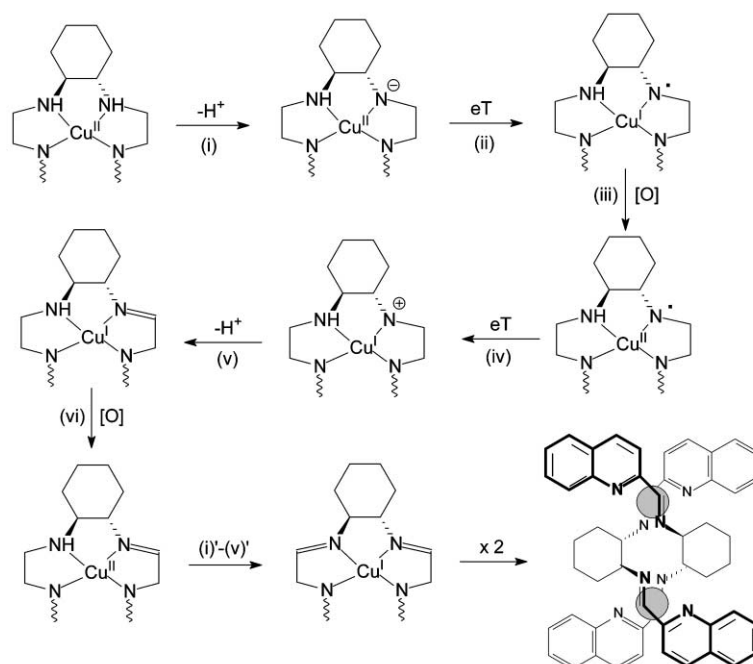


Fig. 1 Spectra of a  $10^{-3}$  M dioxane–water (4 : 1 v/v) solution of  $[\text{Cu}^{\text{II}}(\mathbf{1})]^{2+}$ , adjusted to pH 12. Data recorded every 15 minutes. The intense band that develops at 530 nm corresponds to the double-helix complex  $[\text{Cu}_2^{\text{I}}(\mathbf{2})_2]^{2+}$ .

The temporal development of the band at 530 nm for a solution adjusted to  $\text{pH} = 12$  is shown in Fig. 1. In particular, it was observed that the band reached a limiting value of  $2320 \text{ mol}^{-1} \text{ L cm}^{-1}$ . Such an intense band should have a charge transfer character and is reminiscent of an MLCT transition from a  $\text{Cu}^{\text{I}}$  centre to an aza ligand displaying  $\pi$  features. In particular, we had previously observed that the dicopper(I) complex of the parent unsaturated ligand **2**,  $[\text{Cu}_2^{\text{I}}(\mathbf{2})_2]^{2+}$ , shows an absorption band at 530 nm with a molar absorbance  $\epsilon = 10150 \text{ mol}^{-1} \text{ L cm}^{-1}$ .<sup>3</sup> X-Ray diffraction studies have shown that in the  $[\text{Cu}_2^{\text{I}}(\mathbf{2})_2]^{2+}$  complex the two ligand molecules exhibit a double-helix arrangement.<sup>3</sup> Quite interestingly, an ESI mass investigation on the red–violet solution of the original  $[\text{Cu}^{\text{II}}(\mathbf{1})]^{2+}$  complex, at pH 12 under air, showed a dominant peak at  $m/z$  1061, corresponding to the  $[\text{Cu}_2^{\text{I}}(\mathbf{2})_2](\text{CF}_3\text{SO}_3)^+$  species. The above evidence indicates that the  $[\text{Cu}^{\text{II}}(\mathbf{1})]^{2+}$  complex reacts with  $\text{OH}^-$  and  $\text{O}_2$  to give the  $[\text{Cu}_2^{\text{I}}(\mathbf{2})_2]^{2+}$  helicate complex: the reaction is not quantitative, as judged from the values of the absorbance of the solution at pH 12, which is approximately  $1/4$  of the molar extinction coefficient of the  $[\text{Cu}_2^{\text{I}}(\mathbf{2})_2]^{2+}$  complex. Moreover, it has to be noted that prolonged exposure of the solution to air caused a decrease of the band intensity at 530 nm, indicating decomposition of the dicopper(I) complex. Extended decomposition was also observed at  $\text{pH} > 12$ .

Ligand dehydrogenation through consecutive reactions with  $\text{OH}^-$  and  $\text{O}_2$  has been observed for  $\text{Fe}^{\text{II}}$  complexes of 14-membered tetra-aza macrocycles.<sup>4</sup> Amine dehydrogenation of  $\text{Ni}^{\text{II}}$  tetra-aza macrocyclic complexes required a stronger oxidising agent than dioxygen, *i.e.* nitric acid.<sup>5</sup> The reaction involves a multi-step process at a coordinated amine group, according to a complex mechanism, which includes an  $\text{M}^{\text{II}}/\text{M}^{\text{III}}$  redox change.<sup>6</sup> A similar mechanistic pathway can be proposed for the  $[\text{Cu}^{\text{II}}(\mathbf{1})]^{2+}$  complex, as shown in Scheme 1.

In particular, in step (i), a coordinated secondary amine group of **1** deprotonates at  $\text{pH} \geq 10$ : it is possible that the deprotonation process is made easier by an intramolecular proton transfer from the secondary amine group to the  $\text{OH}^-$  ion coordinated to the metal centre. Then, in step (ii), an



**Scheme 1** Stepwise formation of the the dimeric  $[\text{Cu}_2^{\text{I}}(\mathbf{2})_2]^{2+}$  helicate complex from the monomeric species  $[\text{Cu}^{\text{II}}(\mathbf{1})]^{2+}$ .

intra-complex electron transfer (eT) process from the negatively charged nitrogen atom to the  $\text{Cu}^{\text{II}}$  centre takes place with formation of a  $\text{Cu}^{\text{I}}$ -radical nitrogen atom species. In step (iii), oxygen oxidises  $\text{Cu}^{\text{I}}$  to  $\text{Cu}^{\text{II}}$ , and, following a second internal eT process (iv), a  $\text{Cu}^{\text{I}}$ -nitrenium species is formed. Deprotonation of the adjacent  $-\text{CH}_2-$  group, step (v), leads to a  $\text{Cu}^{\text{I}}$  complex with a ligand in which an amine group has been dehydrogenated to an imine. Then, in step (vi), oxygen oxidises  $\text{Cu}^{\text{I}}$  to  $\text{Cu}^{\text{II}}$ . At this stage, the  $\text{Cu}^{\text{II}}$  complex of the mono-imine ligand undergoes an analogous sequence of reactions with  $\text{OH}^-$  and oxygen, indicated as (i)'–(v)' in Scheme 1, to give the  $\text{Cu}^{\text{I}}$  complex of the di-imine ligand **2**. Finally, the  $[\text{Cu}^{\text{I}}(\mathbf{2})]^+$  complex dimerises to give the helicate  $[\text{Cu}_2^{\text{I}}(\mathbf{2})_2]^{2+}$ , whose red–violet colour is visually perceived. It has to be noted that the multistep mechanism illustrated in Scheme 1 is very speculative, and cannot be substantiated step by step. Alternative pathways are therefore possible: for instance, it may happen that a dinuclear species forms at an earlier stage than suggested in Scheme 1, after the formation of the first  $\text{Cu}=\text{N}$  bond, *i.e.* after step (v).

Oxidative dehydrogenation of the secondary amine ( $-\text{CH}_2-\text{NH}-$ ) to imine ( $-\text{CH}=\text{N}-$ ) functions, through the  $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$  couple, is a rather unusual and rare phenomenon. In this connection, it has to be noted that copper(II) complexes with tren derivatives [ $\text{Bz}_3\text{tren}$ : tris(2-benzylaminoethyl)amine, and  $\text{py}_3\text{tren}$ : tris(2-pyridin-2-ylmethylamino-ethyl)amine] undergo fast hydrolysis of the  $-\text{CH}_2-\text{NH}-$  bonds, with formation of the tetramine tren and of the corresponding aldehyde, benzaldehyde and pyridine-2-aldehyde, respectively.<sup>7,8</sup> It has been suggested that a sequence of deprotonation and oxidation steps, like that illustrated in Scheme 1, takes place, which eventually leads to the formation of the  $\text{Cu}^{\text{II}}$  complex with the imine ligand: however, this species is highly unstable and the  $-\text{CH}=\text{N}-$  bond instantaneously hydrolyses to give tren and aldehyde molecules. This is not the case of the system investigated here: the  $\text{Cu}^{\text{I}}$  complex with the imine ligand,  $[\text{Cu}^{\text{I}}(\mathbf{2})]^+$ , which is formed according to steps (i)–(v)' of Scheme 1, immediately dimerises to give the double-helix complex  $[\text{Cu}_2^{\text{I}}(\mathbf{2})_2]^{2+}$ . This coordinative arrangement is especially stable and allows the  $\text{Cu}^{\text{I}}$  centre to resist to the oxidation by oxygen to  $\text{Cu}^{\text{II}}$ , preventing hydrolysis. Thus, it was the use of a chelating agent sterically organized to give an especially favourable coordinative arrangement—the double helix—that enabled trapping of the  $\text{Cu}^{\text{I}}$  state, which precluded (or slowed) ligand decomposition (to *trans*-1,2-

cyclohexanediamine and quinoline-aldehyde). We believe that formation of the  $[\text{Cu}^{\text{II}}(\mathbf{1})(\text{OH})]^+$  hydroxo complex is an essential prerequisite for the occurrence of the multistep process of Scheme 1. This is suggested by the following evidence: (i) the process occurs at  $\text{pH} \geq 10$ , *i.e.* at a pH higher than the  $\text{p}K_{\text{A}}$  associated with deprotonation of the  $[\text{Cu}^{\text{II}}(\mathbf{1})]^{2+}$  complex; (ii) presence of chloride ions prevents the appearance of the red–violet colour, which is delayed until  $\text{pH} > 12$ : it is possible that the  $\text{Cl}^-$  anion firmly coordinates the metal in the apical position of the square pyramid, being replaced by  $\text{OH}^-$  only at a higher hydroxide concentration.

Oxidative dehydrogenation of polyamines had been previously observed for a number of transition metal complexes, including ruthenium and osmium.<sup>9</sup> In all cases, the reaction proceeded through the achievement of high oxidation states, *e.g.*  $\text{M}^{\text{III}}$  (Fe, Ni, Cu) and  $\text{M}^{\text{IV}}$  (Ru, Os), in a variety of stereochemistries.<sup>9</sup> This work has demonstrated that the  $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$  couple can be effective too, taking profit from an unusual geometrical arrangement: the double helix. Such an arrangement is essential for stabilising the lower oxidation state and for preventing decomposition.

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## Notes and references

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