# Changeover in a multimodal copper(II) catenate as monitored by EPR spectroscopy

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**The electrochemically triggered rearrangement of a copper catenate is monitored by EPR spectroscopy; the initially generated tetrahedral copper(II) complex (with higher *g*-factor components and lower metal hyperfine splitting) is converted to a stable five-coordinate copper(II) species, within a few minutes at room temperature, in anhydrous MeCN.**

Molecular systems whose shape and internal motions can be controlled externally by applying a chemical or physical signal are fascinating.[1] They can be regarded as mimics of metalloproteins which may undergo drastic conformational changes (folding–unfolding), triggered by electron transfer from or onto an electrophore of the enzyme.[2]

Some of us have recently described a copper catenate which can experience a substantial yet controlled conformational change (gliding of one ring within the other), the process being induced electrochemically.[3] Indeed, transition-metal complexes are particularly suited for the design of such systems, since changes in the metal oxidation state can, at least in some cases, cause its coordination geometry to rearrange significantly.[4] The principle of the presently studied system is indicated in Fig. 1.

The square scheme of Fig. 1 contains alternating electrochemical steps and rearrangements, the latter steps leading to the most stable geometry of each oxidation state: four-coordinate for $Cu^I$ ($CuN_4^+$) and five-coordinate for $Cu^{II}$ ($CuN_5^{2+}$).

The isomerization of the compound from the $CuN_4^{2+}$ form to the $CuN_5^{2+}$ form involves an intramolecular change of the coordination number of the central metal ion from four to five. Such a change necessarily implies an altered coordination geometry and thus a modification of the d-orbital splitting pattern. For $Cu^{II}$ as the central ion, such a change may easily be monitored by EPR spectroscopy, considering the well established correlations[5] between crystallographically determined structures and the d-orbital situation as deduced from EPR data, in particular *g* factors and $^{63,65}Cu$ hyperfine coupling constants.

In the present EPR monitoring experiment (Fig. 2), the copper(I) form, $CuN_4^+$, with four-coordinate $d^{10}$ metal (distorted tetrahedral)[3] was oxidized to the paramagnetic copper(II) state $CuN_4^{2+}$ ($d^9$ configuration) in an electrolysis cell for EPR measurements (platinum anode in 2 mm capillary for EPR measurements; $CaH_2$-dried acetonitrile–0.1 m $NBu_4PF_6$). Following brief electrolysis at 293 K (5 min), the mixture was

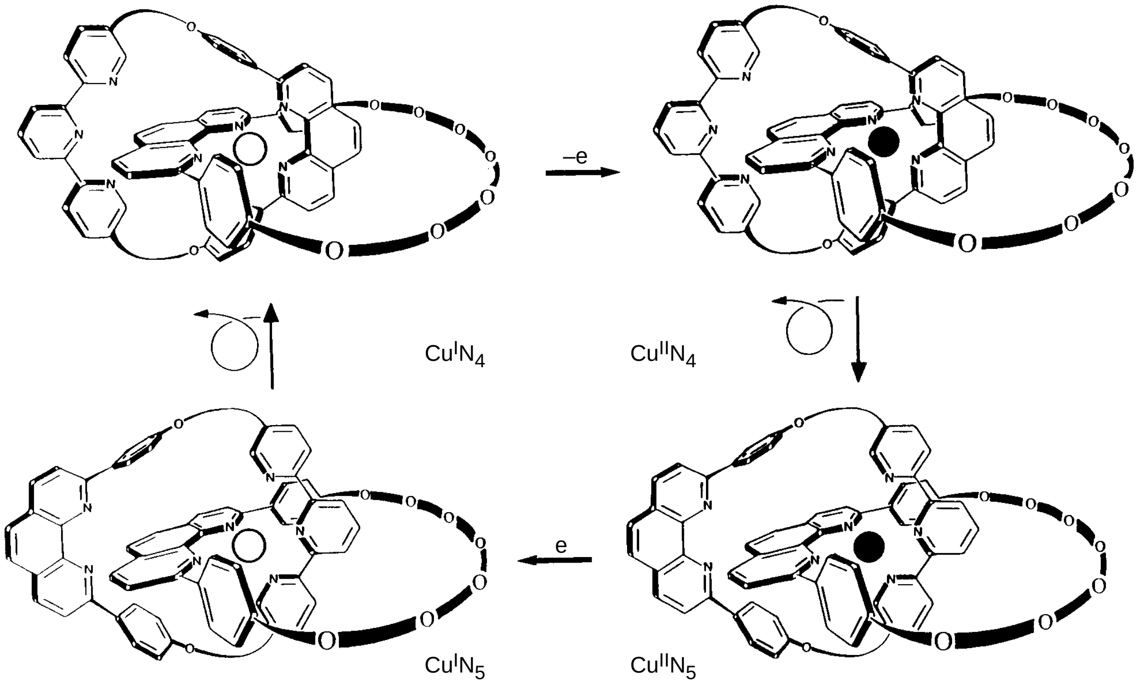

**Fig. 1** Electrochemically induced molecular rearrangements undergone by the copper catenate. The subscript 4 or 5 indicates the number of nitrogen atoms coordinated to the metal. White circles represents $Cu^I$ and black circles $Cu^{II}$. The organic backbone is a [2]catenate, consisting of two different interlocking rings. One ring incorporates a single chelate unit dpphen, whereas the other cycle contains two coordinating fragments (a dpphen unit and a terpy moiety; terpy = 2,2′:6′,2″-terpyridine).

immediately cooled to 110 K to form a glassy frozen solution. The initial anisotropic EPR spectrum is characterized by a relatively small $A_{\parallel}$ value of 12.1 mT and comparatively high $g$ components $g_{\parallel} = 2.276$ and $g_{\perp} = 2.0735$; $a_{\perp}$ and possible $^{14}$N superhyperfine splitting could not be determined due to the linewidth. These values, corresponding to the 'metastable' form $CuN_4^{2+}$, are characteristic of four-coordinate Cu$^{II}$ in a distorted tetrahedral arrangement; similar numbers were measured for related complexes consisting of the same chelating units such as 2,9-diphenyl-1,10-phenanthroline (dpphen): the copper(ii) state of catenate $[Cu(Cat_{30})]^{2+}$ ($g_{\parallel} = 2.282$, $g_{\perp} = 2.075$, $A_{\parallel} = 11.9$ mT) and the non-catenate species $[Cu(dpphen)_2]^{2+}$ ($g_{\parallel} = 2.283$, $g_{\perp} = 2.067$, $A_{\parallel} = 12.2$ mT).[6] In repeated cooling (110 K, EPR measurement) and warming cycles (308 K, 30 s, rearrangement reaction), there was a clear change in the EPR spectrum (Fig. 2), indicating the gradual formation of a new copper(ii) species with quite different EPR characteristics. The hyperfine coupling component $A_{\parallel} = 16.6$ mT is much larger than the value of 12.1 mT observed for the initial $CuN_4^{2+}$ form, whereas the $g$ components $g_{\parallel} = 2.233$ and $g_{\perp} = 2.045$ are smaller. These numbers are more in the typical range for geometrically relaxed copper(ii) complexes,[5] which implies close to square-planar or, more likely, square-pyramidal geometry ($CuN_5^{2+}$). A structurally relevant five-coordinate complex, $[Cu(\eta^3\text{-L})(\eta^2\text{-L})][ClO_4]_2$, containing the potentially terdentate 2,6-bis(benzimidazol-2′-yl)pyridine ligand L and showing square-pyramidal configuration at the metal ion, has $g_{\parallel} = 2.23$, $g_{\perp} = 2.03$ and $A_{\parallel} = 16.7$ mT.[7]

The EPR response illustrated in Fig. 2 thus supports the interpretation of a slow geometrical relaxation, $CuN_4^{2+} \rightarrow CuN_5^{2+}$, following the rapid heterogeneous oxidation of the copper(i) form (with preferred four-coordination), leading to the copper(ii) state with its preferred five-coordinate geometry. The observed spectral differences are not only obvious (Fig. 2), they can also be rationalized straightforwardly, at least in a qualitative way. Both the $A_{\parallel}$ and $g$ value differences between the two copper(ii) states support the above interpretation. According to eqn. (1) (where $j = x, y$ or $z$ coordinate, $\lambda$ is the spin–orbit coupling constant, $\Delta E_i$ is the energy separation between ground state $y_0$ and excited state $y_i$, and $L_j$ is a spin–orbit operator) and similar such approximations, high $g$ factors imply a small energy difference between the singly occupied molecular orbital (SOMO) and close-lying fully occupied MOs. Such a situation may be expected for a coordination geometry derived from the tetrahedron ($CuN_4^{2+}$) where the set of triply degenerate ($t_2$) or at least three close-lying uppermost d orbitals are occupied by five d electrons in a d$^9$ situation. On the other hand, the square or square-pyramidal geometry causes a large energy splitting between the SOMO ($d_{x^2-y^2}$) and the close-lying occupied d orbitals;[5] this splitting reduces the total energy of the system (Jahn–Teller effect) and leads to $g$ factors closer to the free electron value of $g_e = 2.0023$, as observed here for the $CuN_5^{2+}$ state of the bimodal system.

$$g = g_e + 2\lambda \sum_i \frac{<\psi_0 \,|\, L_j \,|\, \psi_i><\psi_i \,|\, L_j \,|\, \psi_0>}{\Delta E_i} \qquad (1)$$

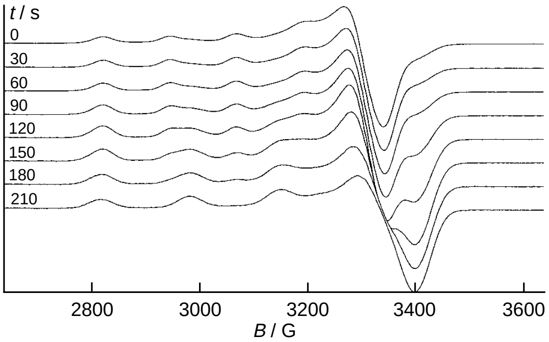

**Fig. 2** EPR spectra at 9.5938 GHz of the electrogenerated copper(ii) state in acetonitrile–0.1 m $NBu_4PF_6$, following repeated cycling between cooling to 110 K (EPR measurements) and warming to 308 K (30 s, rearrangement reaction)

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