

Asymmetric Spin Density Distribution in the Copper(II) Complex of N-Confused Tetraphenylporphyrin Revealed by a Multifrequency Continuous Wave and Pulse EPR Study

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During the past decades, metalloporphyrins, playing a decisive role in catalysis, biology, medicine and materials science, have been extensively studied.^[1] Recently, N-confused porphyrins (NCP), a new family of porphyrin isomers, with the same porphyrin backbone but containing a confused pyrrole ring connected through its α, β' -positions in the macrocycle, have been attracting the attention of an increasing number of scientists.^[2, 3]

It has been found that N-confused porphyrins form stable organometallic macrocycles with transition metal centers.^[4] One of the first described is copper(II) N-confused tetraphenyl-porphyrin ($\text{Cu}^{\text{II}}\text{NCTPP}$, Figure 1).^[5] This organocopper(II) species is of particular interest as model compound in studies of reaction mechanisms of metalloenzymes, since its properties are directly related to the electronic structure. Consequently, the delocalization of the unpaired electron over the complex can be used as a probe to study the reaction mechanisms.

This work focuses on the elucidation of the magnetic interactions between the unpaired electron and the nitrogen donors of the porphyrin ring of CuNCTPP . The application of pulse EPR methods (Davies ENDOR, HYSCORE) revealed a pronounced asymmetric distribution of the spin density on the three core nitrogen nuclei, in contrast to $\text{Cu}^{\text{II}}\text{TPP}$. This finding, also supported by DFT results, demonstrates the breaking of the D_{4h} symmetry due to the confusion of the pyrrole ring.^[6]

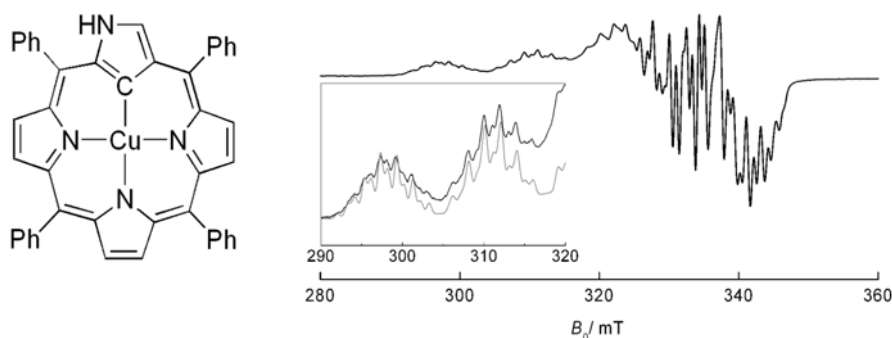


Figure 1: Chemical structure of CuNCTPP and X-band EPR spectrum of CuNCTPP diluted in ZnTPP powder ($T=150$ K). The inset shows the enlarged low-field region of the spectrum with the copper and nitrogen hyperfine couplings. Upper trace (black), experiment; lower trace (gray), simulation.

References:

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