Electron Spin Resonance Spectrum of Bis(4-phenylamino-2-phenyliminopent-3-enato-*NN'*)copper(II); A Complex Having Both a Low A_{zz} and Low-energy *d-d* Band

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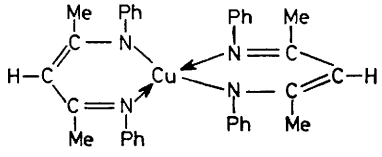
Summary Bis(4-phenylamino-2-phenyliminopent-3-enato-*NN'*)copper(II) (I), having a low energy *d–d* band characteristic of near-tetrahedral stereochemistry, shows an e.s.r. spectrum (as a doped sample of the zinc analogue) with a low $A_{\|}$(Cu) (107×10^{-4} cm^{-1}); the relevance of this spectrum to the stereochemistries proposed for 'blue' copper proteins is discussed.

THERE have been several reports recently on the geometry of the active site in the 'blue' copper proteins (e.g., stellacyanin and azurin). Trigonal bipyramidal,[1] 'square planar' [CuS_4],[2] and various tetrahedral chromophores, *e.g.*, [CuS_2NL],[3] [$CuSN^*N_2$],[4] and [CuS_4],[5] have been suggested. The tetrahedral model proposed by Gray *et al.*[4] is attractive, being based on more complete spectral data on the proteins themselves, especially the presence of a near-i.r. band at *ca.* 5500 cm^{-1}. A band at such low energy is difficult to rationalise on the basis of most other geometries for Cu^{II} complexes.[6] It is difficult to obtain support for this model from low molecular weight complexes because near-tetrahedral Cu^{II} complexes are not easily obtained (as opposed to slightly distorted D_{2d} complexes).[7]

We report preliminary results (*i.e.*, on powders) of the e.s.r. study of a complex giving both a low A_{zz} and a low-energy band in the electronic spectrum (the two most important spectral features of 'blue proteins'[4,8]).



(I)

Dark green complex (I) and the mixed crystal ^{63,65}Cu (3% nominal)–Zn analogue were prepared as described previously.[9] At that time it was not realised that their electronic spectra were unique in having a very low energy *d–d* band (at 6000 cm^{-1}, in reflectance). Molecular models show that the steric hindrance between the phenyl groups leads to a near-tetrahedral stereochemistry.† The only other 'squashed tetrahedral' *N*-bonded copper complex with resolved *d–d* bands, Cu(di-2-pyridylamine)$_2$(ClO$_4$)$_2$, with a dihedral angle of 55·6° between the ligand planes, has the first band at 10,400 cm^{-1}.[10]

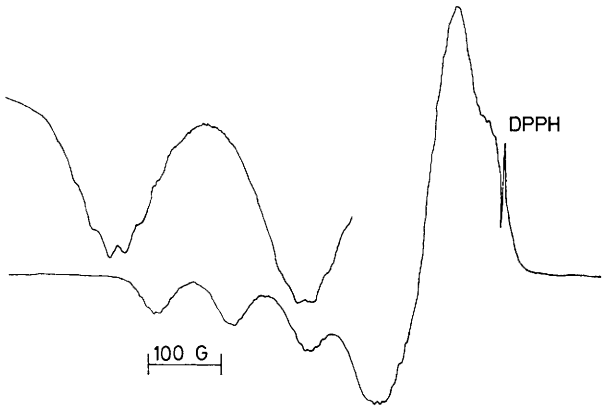


FIGURE. E.s.r. spectrum of ^{63,65}Cu–Zn analogue of (I) as a powder at 120 K (insert: low-field components × 4). The frozen solution spectrum at 120 K was identical, but without ^{14}N h.f.s. DPPH = Diphenylpicrylhydrazyl.

The relevance of this compound to structural models for 'blue' proteins is apparent from its e.s.r. spectrum (Figure). The spectrum has $g_{\|} = 2{\cdot}218$ and $g_{\perp} = 2{\cdot}070$, with clear hyperfine structure on $g_{\|}$ (that on $g_{\perp}$ can be resolved only after single crystal studies are completed). In addition, ligand hyperfine splitting (h.f.s.) apparently derived from four equivalent ^{14}N nuclei, is visible (the first time this is observed for a tetrahedral Cu^{II} complex). The A_{zz}(Cu) is very low for *N*-bonding ligands (107×10^{-4} cm^{-1}), which may be compared with that of Cu(phthalocyanine)$_2$ [$A_{\|}$(Cu) = 219×10^{-4} cm^{-1}].[11] The frozen solution spectrum was identical.

Some time ago, Bates *et al.* calculated that in tetrahedral Cu^{II} complexes, $A_{\|}$ could be reduced to < 20 G by admitting an admixture of *ca.* 30% 4*p* character into the 3*d* orbitals (*via* mixing of the $3d_{xy}$ and p_z orbitals in tetrahedral or near-tetrahedral symmetry, forbidden in most other symmetries).[12] However, their measurements were carried out on undiluted crystals of Cu(α,α'-dibromodipyrromethene)$_2$ so that an experimental estimate of $A_{\|}$ was not possible, and *d–d* transitions could not be located with certainty. To our knowledge, (I) is therefore the only *N*-bonded Cu^{II} complex having both a low $A_{\|}$ and low-energy *d–d* band, as have the 'blue' proteins. To date none of the other low molecular weight models have succeeded in simulating both spectra.

We do not suggest that (I) is a suitable model for 'blue' proteins, since we have yet to introduce an S$^-$ (or sulphide

† Preliminary crystal structure data confirm this; the dihedral angle is *ca.* 68° (G. Dessy and V. Fares, personal communication).

S) donor atom.[4] However, the dearth of information on tetrahedral d^9 systems makes its e.s.r. spectrum of importance since it provides evidence for the tetrahedral stereochemistry of the active site and contradicts the suggestion that the unique spectral properties of 'blue' Cu^{II} proteins are mainly due to electronic effects of the donor(s) rather than to geometric factors.[2]

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