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The Possibility of an Electronic Criterion of Stereochemistry of Bis(chelate)Copper(II) Complexes

ANTHONY O'LEARY, S. TYAGI and B. J. HATHAWAY*

The Chemistry Department, University College, Cork, Ireland

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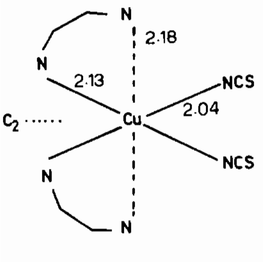
In several early [1] and more recent papers [2] it has been suggested that the electronic spectra of copper(II) complexes may be used as a criterion of stereochemistry, but only if as wide a range of physical properties as possible are used to complement the electronic spectra [3] such as e.s.r., and infrared spectra. This suggestion has been criticised in the past [4] and more recently [5] in respect to the reported electronic spectra and crystal structure of two [Cu(phen)$_2$(NCS)$_2$], (1) and [Cu(phen)$_2$(NCSe)$_2$], (2) complexes, where phen = 1,10-phenanthroline. The electronic spectra of (1) and (2) were both reported [5] to have a single peak at 12900 cm^{-1} and to involve a *cis*-octahedral CuN$_4$N$_2$ chromophore stereochemistry, (1), with a *trans* elongated distortion. As it was previously suggested [1] that the electronic criterion of a *cis*-octahedral stereochemistry was that the electronic spectrum would involve a splitting of 5000 cm^{-1}, the above spectrum conflicts with this prediction.



(1) [Cu(phen)$_2$(NCS)$_2$]

In order to check this contradiction the preparation [6] of (1) has been repeated and its electronic spectra, Fig. 1, and e.s.r. spectra, Fig. 2, reported as polycrystalline samples and for the copper(II) complex doped in [Zn(phen)$_2$(NCS)$_2$] as a diamagnetic host lattice. As only microcrystalline samples could be prepared no single-crystal electronic or X-ray properties were obtainable. The pure copper(II) and zinc(II) complexes were shown to be isomorphous from their X-ray powder photographs, but this does not mean that the MN$_4$N$_2$ chromophores are isostructural.

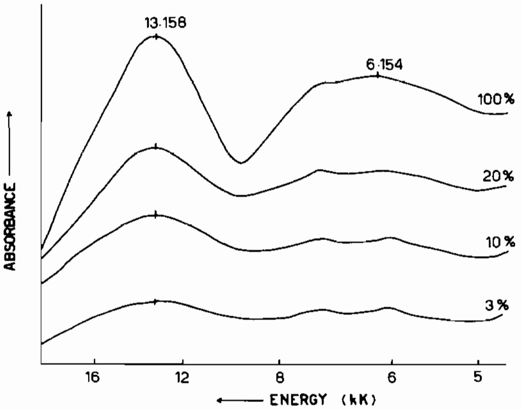


Fig. 1. The electronic reflectance spectra of copper(II) doped [Zn(phen)$_2$(NCS)$_2$], 3–100%.

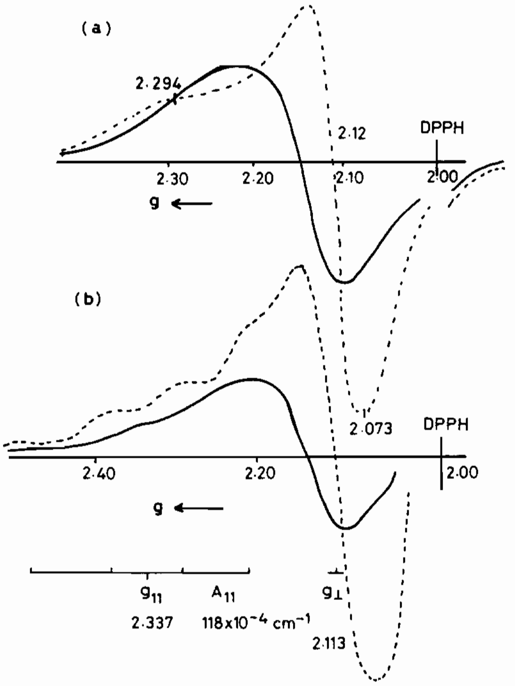


Fig. 2. The polycrystalline e.s.r. spectra of (a) [Cu(phen)$_2$(NCS)$_2$] and (b) 3% copper(II) doped [Zn(phen)$_2$(NCS)$_2$]. (——) room temperature, (-----) liquid nitrogen temperature.

The electronic reflectance spectra of the pure (1) involves two clear peaks, the most intense at 13158 cm^{-1} with a less intense broad band at 6154 cm^{-1}, a difference in energy of 7000 cm^{-1}, which is consistent with the *cis*-octahedral stereochemistry of (1),

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*Author to whom correspondence should be addressed.

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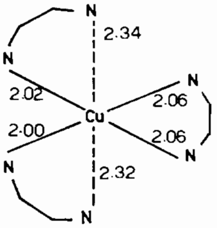
and with the criterion of stereochemistry previously established [1]. The spectrum of (1), Fig. 1, contrasts with the single peak at 129000 cm^{-1} previously reported [5] for (1) and suggests that this spectrum was, previously, only recorded over a restricted range of energy. The need to record the electronic reflectance spectra of copper(II) complexes over the energy range 5–30000 cm^{-1} has been emphasised earlier [3] and two recent examples have highlighted the limitations introduced, when spectra are restricted to measurement in the visible region only. These have been described recently for the $Cu(bipy)_1(C_2O_4)_1 \cdot xH_2O$ [7] (X = 2, 3) and $K_3Cu(NO_2)_5$ [8] complexes. The characteristic two peaked spectrum of (1) is closely comparable [9] to that of $[Cu(phen)_3][ClO_4]_2$, 7600 and 15000 cm^{-1}, consistent with the static elongated rhombic *cis*-octahedral stereochemistry of the CuN_4N_2 chromophore of the latter (3). The invariance of the electronic energies of (1) with concentration [11], when doped in the zinc(II) complex, Fig. 1, suggests that the CuN_4N_2 chromophore stereochemistry is the same in both the concentrated and dilute systems and that the stereochemistry in the zinc complex must be at least near *cis*-octahedral, if not isostructural with the CuN_4N_2 stereochemistry of (1).



(3) $[Cu(phen)_3][ClO_4]_2$

The room temperature polycrystalline e.s.r. spectrum of (1), Fig. 2(a), is near isotropic, with broadness on or near the high g-value side. At liquid nitrogen temperature the spectrum becomes clearly axial with $g_\parallel \gg g_\perp > 2.0$ suggesting a $d_{x^2-y^2}$ (or d_{xy}) ground state [12] consistent with the elongated tetragonal octahedral stereochemistry of (1). As the electronic reflectance spectra of (1), Fig. 1, are independent of the copper(II) concentration, this suggests that the e.s.r. spectra of the copper(II) doped $[Zn(phen)_2(NCS)_2]$ complex may be equated with the CuN_4N_2 structure of (1). The doped polycrystalline e.s.r. spectrum, $g_\parallel = 2.337$, $A_\parallel = 118 \times 10^{-4}$ cm^{-1} and $g_\perp = 2.113$, is considered more accurate than that of the concentrated (1) polycrystalline e.s.r. spectrum and is also consistent with the $d_{x^2-y^2}$ (or d_{xy}) ground state suggested above, with the low $A_\parallel$ value associated with the relatively low tetragonal elongation present [12].

The infrared spectrum of (1) shows two barely resolved CN stretching frequencies at 2060 and 2080 cm^{-1} consistent [13] with nitrogen bonded thiocyanate groups and a *cis*-coordination of these ligands, consistent with the crystallographic evidence and the above prediction from the electronic spectra.

Taken together the above physical properties do suggest that the correct *cis*-**octahedral structure** for (1) could have been predicted.

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