The Correlation of the Electronic Properties and Stereochemistry of Mononuclear $\{CuN_{4-6}\}$ Chromophores

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An attempt is made to assess the value of the electronic properties of polycrystalline samples of copper(II) complexes of unknown crystal structure to predict the stereochemistry of the local copper(II) ion environment. The value of obtaining complementary data, namely, magnetic moments, e.s.r., and electronic spectra, is emphasised in order to produce the most reliable prediction of stereochemistry and is applied to systems containing the CuN_{4-6} chromophore.

The current literature [1-6] contains a number of papers attempting to show a correlation between the electronic properties of copper(II) complexes and the local stereochemistry of the copper(II) ion present. Most of these attempts [3-6] refer to a closely related series of complexes and may be justified, especially when results from a wide range of physical techniques are correlated.[7,8] Unfortunately, attempts have been made [1,2,9] to predict the stereochemistry of copper(II) complexes of unknown crystal structure, which fail to utilise all the information which could be available from physical techniques. Very often measurements involving only one electronic technique are used,[1,2,9] usually the electronic reflectance spectra and while this technique can be most informative,[7,8] the results can be in error or at best uncertain, if complementary data from the e.s.r. spectra are not utilised. The present paper attempts to summarise the type of information available from the complementary physical properties [8] of copper(II) complexes of unknown crystal structure, which may be used to predict the stereochemistry of the copper(II) ion present.

General Comments.—Before looking in detail at the way in which the data from various physical techniques can yield stereochemical information, it is worth looking at a number of generalisations which probably amount simply to common sense.

(1) Present knowledge of the stereochemistry of copper(II) complexes [8] is now probably more extensive than for any other first-row transition-metal ion.

(2) Unless four, five, or six equivalent monodentate ligands are present, an even approximately regular local stereochemistry is unlikely. With polydentate ligands, both bond-length and bond-angle distortions from a regular stereochemistry will be the normal situation.[8] With facultative polydentate ligands [1,10] different stereochemistries may also occur.

(3) It is sometimes possible to specify the co-ordination number of the copper(II) ion from the nature of the ligand present. The i.r. spectra may yield information on whether or not all the nitrogen donors in a given ligand are co-ordinated [1] and of evidence for co-ordination [11] or semi-co-ordination [7] of polyatomic anions. Unless there is a steric factor involved nitrogen donors tend to co-ordinate to the copper(II) ion in preference to oxygen donors. Co-ordination numbers of four only occur with potentially π-bonding ligands [8] and may range from strictly square-coplanar [12] to compressed tetrahedral [14] stereochemistries. In CuL_4X_2 complexes where L is a monodentate σ-bonding ligand, the co-ordination number is increased above four by semi-co-ordination [13] of the anions to give a co-ordination number of five or six. In CuL_2X_4 complexes, co-ordination numbers of four are readily obtained by bonding of the anions X, acting as monodentate ligands; higher co-ordination numbers (five and six) are then obtained by the anions acting as bridging ligands, especially halide ions, usually involving bonding at a longer bond-length than that involved in-the-plane (semi-co-ordination [14]). When X involves a planar trigonal AO_2 system, such as nitrate, nitrite, formate, or carboxylate anions, these can bond [15] through one oxygen atom in the plane, and the second terminal oxygen atom out-of-the-plane, with Cu–O bond lengths of 2·0 and 2·6 Å respectively. For geometric reasons the terminal oxygen is positioned off the z-axis with an O-$\widehat{\mathrm{Cu}}$-O angle of 50—55°. For CuL_5X_2 and CuL_6X_2 complexes,[3,4] there is little evidence of co-ordination or even semi-co-ordination of the anions X, especially where these are only weakly co-ordinating anions such as ClO_4^-, BF_4^-, or NO_3^- (see i.r. evidence). The only way in which the co-ordination number of the copper(II) ion is raised above six is when off-the-Z-axis oxygen atoms are present as in $Cu(NO_3)_2,2\cdot5\,H_2O$ [16] (co-ordination

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number seven) and in $CaCu(CH_3CO_2)_46H_2O$[17] (co-ordination number eight).

(4) It is usually possible to make a reasonable guess about the type of lattice present in a copper(II) complex of unknown crystal structure from the number and type of donors present, namely whether the lattice is a molecular lattice or an infinite lattice in one, two, or three dimensions. Complexes involving ligands containing a large number (six) of donor atoms per copper(II) ion or with large bulky groups (*i.e.* 2,2′-bipyridyl) tend to form molecular lattices. Complexes involving ligands containing a small number (two) of donor atoms per copper(II) ion, especially when the anions present are halide ions [which usually co-ordinate to more than one copper(II) ion] tend to form infinite lattice structures.[8,18]

Physical Techniques.—The most important physical techniques which can give information on the stereochemistry of the copper(II) ion present in a complex of unknown crystal structure from measurements on a polycrystalline sample are: (1) the room temperature magnetic moment; (2) the e.s.r. spectrum; (3) the electronic reflectance spectrum. The structural data[8] that is available from each technique will now be discussed.

(1) *Magnetic Moment.*—If the magnetic moment is in the region 1·80—2·00 B.M. then the complex is almost certainly magnetically dilute and there will be negligible spin–spin coupling characteristic of the type of dinuclear structure[19] found in $\{Cu(CH_3CO_2)_2H_2O\}_2$ or comparable polynuclear structures containing metal–metal bonds. A magnetic moment of 1·80—2·00 B.M. does not rule out the weak type of antiferromagnetic or, the less common, ferromagnetic interactions found in complexes containing infinite halide bridging systems,[10] such as $CuCl_2$. Further information on the possible presence of this type of weak interaction can be obtained by measuring the variation of the molar magnetic susceptibility with temperature. If the Curie–Weiss Law is obeyed, with a Weiss constant of less than 5°, then the interaction is very small and does not seriously affect the ground state.[20]

(2) *E.s.r. Spectrum.*—Two types of copper(II) ion environments can be recognised by the e.s.r. spectrum of a polycrystalline sample of a copper(II) complex of unknown structure: (*a*) Magnetically concentrated systems, such as $\{Cu(CH_3CO_2)_2H_2O\}_2$, give both low and high field spectra.[21] These characteristic e.s.r. spectra may be used as an alternative means of recognising polynuclear systems and complement the magnetic moment measurements.

(*b*) Magnetically dilute systems[8] give a rather more simple e.s.r. spectrum involving one, two, or three *g*-values in the region 2·0—2·5. The stereochemical significance of these types of e.s.r. spectra have been described elsewhere.[8] The most important single piece of information which the e.s.r. spectra may yield is the presence of a lowest *g*-value of *ca.* 2·00, which is indicative of a d_{z^2} ground state rather than a $d_{x^2-y^2}$ (or less commonly a d_{xy}) ground state. The ground states associated with the various possible stereochemistries have been discussed previously and are listed[8] in the Table.

The one-electron orbital ground states for the known stereochemistries of the copper(II) ion (for notation see ref. 8)

(1)	$d^1{}_{x^2-y^2}$	Elongated tetragonal-octahedral Elongated rhombic-octahedral Square-coplanar Square-pyramidal
(2)	$d^1{}_{z^2}$	Compressed tetragonal-octahedral Compressed rhombic-octahedral Linear Trigonal bipyramidal *cis*-Distorted octahedral
(3)	$d^1{}_{xy}$	Compressed tetrahedral Square-coplanar—$Cu(acac)_2$ type
(4)	$d^2{}_{z^2},d^1{}_{x^2-y^2}$ or $d^1{}_{z^2},d^2{}_{x^2-y^2}$	Octahedral
(5) *	$d^2{}_{xz},d^1{}_{yz}$ or $d^1{}_{xy},d^2{}_{yz}$	Trigonal Elongated tetrahedral
(6) *	$d^2{}_{xy},d^2{}_{xz},d^1{}_{yz}$ *etc.*	Tetrahedral

* These configurations are orbitally degenerate, in 5 and 6 this orbital degeneracy is removed by spin-orbit coupling, but is not removed by this mechanism in 4.

The ability to distinguish a d_{z^2} ground state is consequently of particular importance in recognising the most common of the stereochemistries associated with this ground state, namely trigonal bipyramid and in distinguishing this stereochemistry from the much more common (Table) square pyramidal structure. Nevertheless, the failure to observe a lowest *g*-value of *ca.* 2·00 does not necessarily rule out a d_{z^2} ground state as exchange coupling could well invalidate such a criteria if there is a significant misalignment of the molecular axes of the different molecules in the unit cell.[8] The effect of exchange coupling may equally reduce the amount of information obtainable from e.s.r. spectra involving the copper(II) ion in a $d_{x^2-y^2}$ or d_{xy} ground state. Extensive exchange coupling produces[8] an isotropic spectrum, or a spectrum which is nearly isotropic but has a point of inflection between the two maxima of the first derivative spectrum (Figure 7E and F; ref. 8); neither type gives any definite information on the electronic ground state present. The observation of a two or three *g*-value e.s.r. spectrum does not rule out the presence of exchange coupling. For two *g*-value spectra with the lowest *g*-value $>2·0$, if the value of $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$ is 4·0—4·5, exchange coupling is negligible, for $G = 3·5$—$5·0$ it may also be small and

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the observed g-values meaningful. For G-values outside the range 3·5—5·0 exchange coupling invalidates the observed g-values. In a three g-value spectrum with $g_1 < g_2 < g_3$ the value of $R = (g_2 - g_1)/(g_3 - g_2)$ may be significant;[22] if $R > 1$ a predominant d_{z^2} ground state is present, if $R > 1$ a predominant $d_{x^2-y^2}$ ground state is present. When $R \approx 1$ then the ground state involves an approximately equal mixture of d_{z^2} and $d_{x^2-y^2}$, a situation which is found to apply with stereochemistries which are intermediate between square pyramidal and trigonal bipyramidal,[22] particularly with facultative ligands.[1] Occasionally,[23] the e.s.r. spectrum of a polycrystalline sample of a complex which has axial or rhombic crystal g-values, may appear approximately isotropic due to the much greater intensity of the signal associated with $g_\perp$, relative to that associated with $g_\parallel$. In these cases a higher instrument sensitivity should be used to scan the region of $g_\parallel$ and the apparently isotropic spectrum ($g_\perp$) should be carefully checked for asymmetry. In the last resort the more sensitive single-crystal technique[8] may be necessary, involving the facility to rotate the crystal.

(3) *Electronic Reflectance Spectra.*—A knowledge of the electronic reflectance spectrum of a copper(II) complex of unknown crystal structure is the most informative piece of electronic data in predicting the environment of the copper(II) ion present, especially if the type of information already discussed is also available. It is important that the spectra are recorded over the full range 5—30 kK, particularly in the low-energy region as a number of copper(II) complexes[8] have a resolved band in this region. Many reflectance spectra reported in the literature fail to include this region and are consequently only of limited value.[24]

In principle the maximum number of *d–d* transitions in the electronic spectrum of a copper(II) complex is four, in practice, very few complexes give any indication of more than two bands.[1,3,4] Many complexes yield spectra involving two clear bands, but many show a main band with a low frequency shoulder only partially resolved. Many complexes involve a single broad absorption band with no indication of a second band. Four effects contribute to the ability to resolve the component bands in the electronic spectrum of a copper(II) complex; these are: (1) the separation of the excited state levels from the ground state (10 *Dq*); (2) the separation of the excited state levels; (3) the relative intensity of the individual transitions; (4) the relative half widths of the individual transitions. The structural features[8] in the local molecular stereochemistry of the copper(II) ion which may contribute to these four factors are: (*a*) a centre of inversion; (*b*) the co-ordination number and stereochemistry present; (*c*) the tetragonal distortion present; (*d*) π-bonding and rhombic ligand field.

(*a*) The presence of a non centro-symmetric copper(II) ion environment should yield a more intense *d–d* spectrum through *d–p* mixing. In practice it is difficult to pinpoint precisely what determines the 'effective' local symmetry[8]; it usually lies between the crystallographic point symmetry and the much higher CuN_x chromophore symmetry. Consequently, it is not possible to use intensity to predict the presence or absence of a centre of symmetry. Nevertheless, most obviously non-centrosymmetric stereochemistries, such as tetrahedral, trigonal bipyramidal, and square pyramidal, do tend to be slightly more intense than the *corresponding* square-coplanar, tetragonal-octahedral, or rhombic-octahedral ones.

(*b*) The effect of co-ordination number upon the energies of the *d–d* transitions of copper(II) complexes is complicated;[8] for regular stereochemistries involving n-equivalent ligands bonding at the same distance the crystal field splitting parameter 10 *Dq* would increase (in theory) in the sequence

four co-ordinate	$<$	five co-ordinate	$<$	six co-ordinate
tetrahedral		trigonal pyramidal		octahedral

and the spectra would occur at correspondingly higher energies. In general, these regular stereochemistries rarely occur in copper complexes[8] as differences in bond lengths and bond angles occur to complicate this simple picture.

(*c*) In practice it is the degree of tetragonal distortion[8,14] which has the major effect in determining the energy of the bands in the *d–d* spectrum of a copper(II) complex. This can be seen in the correlation diagrams (Figures 4—6, ref. 8) as the tetragonal distortion increases from a regular octahedral or tetrahedral stereochemistry towards the square-coplanar one, the centre of gravity of the *d–d* transitions move to higher energy. Between these extremes fit the intermediate stereochemistries, tetragonal, octahedral, square pyramidal and compressed tetrahedral.

(*d*) The presence of rhombic crystal-fields and of π-bonding primarily influences the separation and ordering of the d_{xy}, d_{xz}, and d_{yz} levels, but as neither effect amounts to more than 4·0 kK they are both second-order effects.

With the above four effects in mind, the reflectance spectrum of a copper(II) complex of unknown crystal structure contains the following information. (1) A value of the mean energy * of all four *d–d* transitions, this is taken as the band maximum when only one band is observed or the weighted mean if more than one band is observed.

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* The effect of varying ligands, *i.e.* Cl^-, O, and N on the centre of gravity is small, but significant; thus for a tetragonal-octahedral environment ($T =$ *ca.* 0·80) the centre of gravity of the *d–d* bands increases approximately in the sequence

$CuCl_6$	$<$	CuO_6	$<$	CuN_6
ca. 13·0		*ca.* 15·0		*ca.* 17·0

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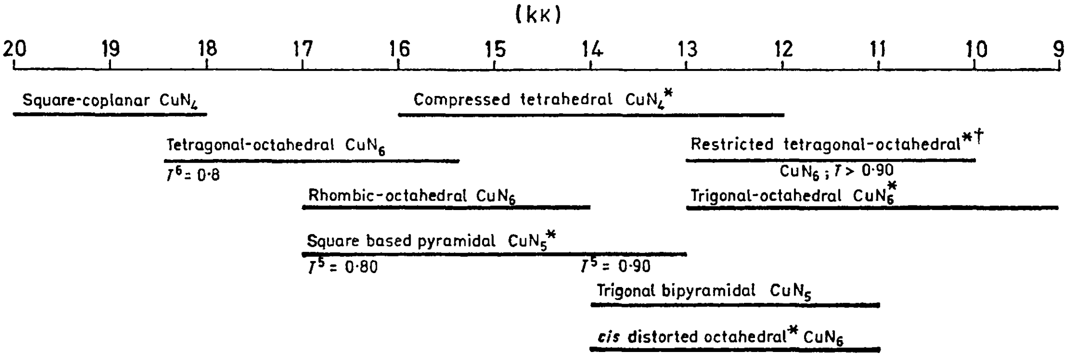
(2) The energies of those *d–d* transitions which are resolved as band maxima.

(3) An idea of the intensity of the *d–d* spectrum.

In order to show how this data can be best used it is applied to the complexes of the copper(II) ion containing the CuN_{4-6} chromophore. A significant amount of structural and electronic data[1,7,8] is now available on such systems, involving a variety of ligands such as ammonia, ethylenediamine, diethylenetriamine, 2,2′-bipyridyl. The Figure summarises the energy ranges covered by the *d–d* transition of CuN_{4-6} chromophores of different stereochemistry, including an indication of the tetragonal distortion present (for the notation used see refs. 8, 14, 25).



* Chromophores indicated with an asterisk involve a clearly resolved shoulder to low frequency. † In most cases the restriction arises through out-of-plane co-ordination by a chelate ligand.

Energies of the centre of gravity of the *d–d* transitions of the CuN_x chromophore with varying stereochemistry ($CuN_4 \longrightarrow CuN_6$)

Conclusion.—From a polycrystalline sample of a copper(II) complex of unknown crystal structure, under favourable circumstances of the arrangement of the molecules in the unit cell and a knowledge of (1) the room temperature magnetic moment, (2) the e.s.r. spectrum, (3) the electronic reflectance spectrum (5—30 kK), and (4) the i.r. spectrum (250—4000 cm^{-1}), it should be possible to make a tentative prediction of (1) the approximate copper(II) ion stereochemistry and (2) for axial systems, the degree of tetragonal distortion present.

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