Letters

Structural information from optical spectral properties of copper(II) complexes with Schiff-base ligands

Waters and co-workers[1] discussed the optical and e.s.r. parameters of copper(II) complexes with Schiff bases formed from *o*-aminobenzaldehyde and various diamines, and concluded that they are consistent with planar co-ordination around the copper(II) ion, except for *NN'*-1,3-propylenebis(*o*-aminobenzylideneiminato)copper(II), [Cu(abtn)], in which a small tetrahedral distortion of the co-ordination sphere is indicated. This conclusion is inconsistent with expectation for copper(II) complexes of Schiff bases derived from 1,2-propanediamine, which in several cases have been found to exhibit a marked tetrahedral distortion, as evidenced by circular dichroism (c.d.) spectroscopy.[2-5]

It was of interest therefore to prepare the optically active Schiff base derived from one molecule of enantiomeric 1,2-propanediamine and two molecules of *o*-aminobenzaldehyde and subsequently investigate it and the corresponding copper(II) complex [Cu(ab-*R*-pn)] by c.d. spectroscopy.

As pointed out by Waters and co-workers,[1] the similarity of the spectra of *o*-aminobenzylideneimine and salicylideneimine ligands is helpful in band assignments. Thus, a band at *ca.* 29 000 cm^{-1} in the absorption spectrum of *o*-aminobenzylideneimines is attributed to a $\pi \rightarrow \pi^*$ transition involving molecular orbitals which originate from the azomethene group and benzene ring. In the case of the optically active dimer derived from $(-)_{589}$-(*R*)-1,2-propanediamine (*R*-pn), also the presence of a negative band at *ca.* 29 000 cm^{-1} in the c.d. spectrum (*cf.* Figure 1) is analogous to the spectral behaviour of (*R*)-*NN'*-1,2-propylenebis(salicylideneimine) (H_2sal-*R*-pn).[6] As mentioned by Smith *et al.*,[7] it is puzzling that this negative c.d. band, assignable to a $\pi \rightarrow \pi^*$ transition polarized approximately in the N–N direction of the chromophore, does not show any sign of exciton coupling. Indeed, exciton coupling is possible and is observed in the benzoic transition region (*cf.* the coupling observed with enantiomers of 1,3-diphenylallene[8]).

Under absorptions exhibiting exciton coupling, ideally two bands of equal magnitude, but of opposite signs, are expected in the c.d. spectrum.[9] However, inequality in the areas of the two bands may arise from mixing with excited states. Thus configurational interactions will result in mixing of out-of-phase (*B*) transitions and also of in-phase transitions (*A*). Accordingly, it is conceivable, as also demonstrated by Mason and co-workers,[10] that configurational interactions may increase the absolute magnitude of the *B* transition mode, and decrease the magnitude of the *A* transition mode to such an extent that only the negative c.d. band is observed. In the case of complexation, however, configurational interactions are of less importance as may be seen, *e.g.*, from the spectrum of the zinc(II) complex of sal-*R*-pn which shows exciton coupling in the $\pi \rightarrow \pi^*$ transition region.[11]

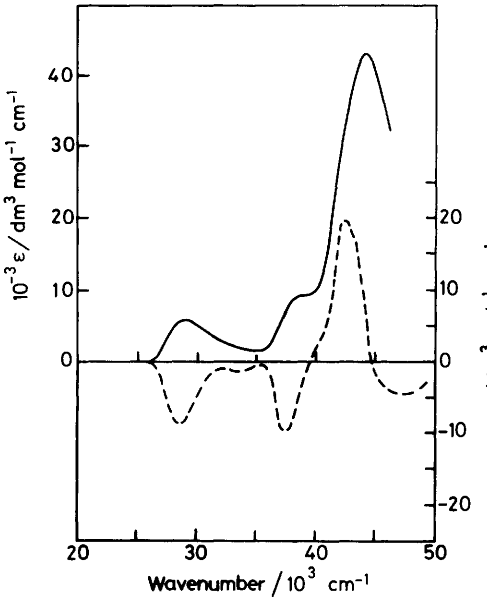

Figure 1. Molar absorption (——) and c.d. spectra (- - - -) of H_2ab-*R*-pn dissolved in CH_3OH

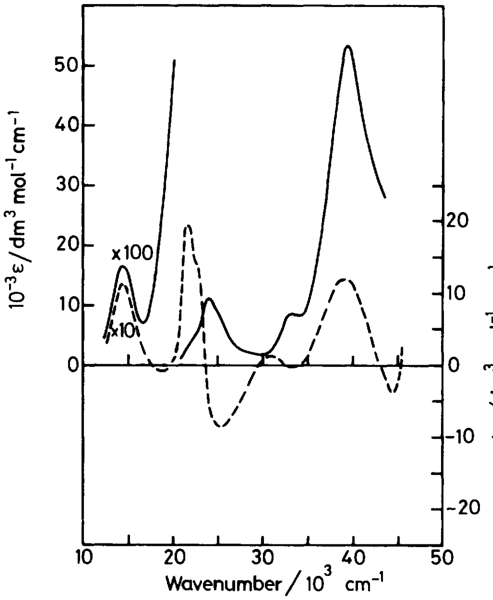

Figure 2. Molar absorption (——) and c.d. spectra (- - - -) of [Cu(ab-*R*-pn)] dissolved in $CHCl_3$

The complex [Cu(ab-*R*-pn)] shows a similar pattern in that part of the c.d. spectrum which is due to $\pi \rightarrow \pi^*$ transitions involving the azomethene group (*cf.* Figure 2). This indicates a tetrahedral distortion of the complex; further, the absolute configuration of the complex may be indicated[12] as Λ in terms of handedness of the pair of lines connecting the N atoms of each chromophore and thus simultaneously representing the $\pi \rightarrow \pi^*$ transition dipole moments of the chromophores (*cf.* Figure 3).

Within the exciton formulations, and provided that the two transition moments are perpendicular to the line which connects their centres, the expected energy splitting can be calculated from [see equation (6) of ref. 9]: $\Delta E = 2r^{-3}D_{\text{monomer}} \cos\theta$; where *r* is the distance between the transition moments

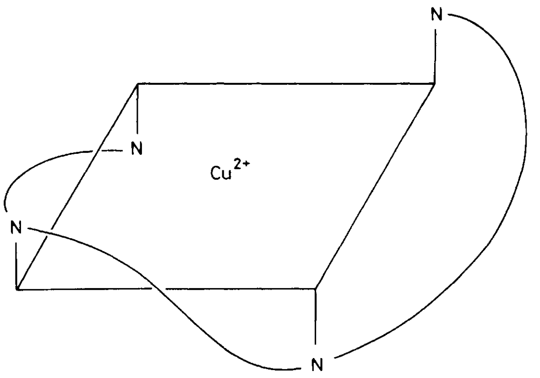

Figure 3. Representation of the structure and absolute configuration of the chiral compound [Cu(ab-*R*-pn)]

of the two $\pi \rightarrow \pi^*$ transitions, D is the dipole strength of half the quadridentate ligand, and θ the angle between the two transition moments.[2] Using the experimental values $D^{\mathrm{complex}}_{\mathrm{dimer}} = 2D_{\mathrm{monomer}} = 0.85 \times 10^{-19}$ cm^3·cm^{-1}, $\theta = 50°$, and $\Delta E = 2\,000$ cm^{-1}, the value of r is found to be *ca.* 3 Å in agreement with assumed intramolecular distances.

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Waters replies. The feeling that the more advanced analysis undertaken by Jensen should be accepted as correcting and replacing the deductions of our paper[1] is tempered by the internal consistency of the earlier observations. In 1972 Higson and McKenzie[2] noted that cobalt(II), nickel(II), and copper(II) complexes of the same *o*-aminobenzaldehyde ligand, including the *NN'*-1,2-propylenebis(*o*-aminobenzylideneimine) under discussion, were isomorphous in the solid state and that their electronic absorption spectra were similarly almost identical in solid and solution (chloroform and pyridine as solvents). Subsequent *X*-ray structural analyses of [Ni(abpn)][3] and [Cu(aben)][4] [aben = *NN'*-ethylenebis(*o*-aminobenzylideneiminate)] showed planar but 'umbrella-shaped' molecules in the crystalline state. In 1973 we reported the crystal structure of [Cu(abpn)][4] confirming the planarity and umbrella conformation of this molecule and showing that there were no intermolecular approaches less than 3.4 Å; the nearest axial approach to the copper was 3.95 Å. Our interpretation of spectroscopic data, admittedly simplistic and based on comparison between a number of ligands and complexes, was therefore not only internally consistent but also in accord with some persuasive supporting evidence.

Since the *X*-ray results are presumably not in question any argument concerns a possible change in structure on dissolution. It is here contended, as implied above, that this should be evident in spectral changes {as occurs to a small degree in [Cu(abtn)]}. That it is not, it is also contended, reflects the stereochemical difficulty, not to mention the lack of 'incentive' with copper(II) as cation, that these particular quadridentate ligands would have in adopting the degree of tetrahedral co-ordination deduced from the c.d. measurements. Exactly the same conflict was noted earlier by Jensen and Larsen[5] in connection with [Cu(acacpn)] [acacpn = 1,2-propylenebis(acetylacetoneiminate)] in which an *X*-ray result disagreed with spectral studies in solution. Although ligands of this type, *i.e.* with two bridging methylene groups, can co-ordinate to four adjacent octahedral sites,[6] the adoption of tetrahedral, or partially tetrahedral, structures normally occurs where the link contains three methylenes.[7] Furthermore, with copper(II) as the metal ion, there seems no reason to expect that the complexes would be other than planar, especially in chloroform. It can be added that with *o*-phenylene as the bridge, presumably even more likely to give a planar complex because of its steric requirements, the lowest energy ligand-field band at 14 800 cm^{-1} in chloroform is almost the same as that of [Cu(abpn)].[1] It must be added, however, that in presenting the *X*-ray crystal structure of [Ni(abtn)], Bailey *et al.*[8] note an *increase* in energy of the lowest *d-d* band on dissolution of the isomorphous [Co(abtn)] {but apparently not for [Ni(abtn)][2]}. The molecules are again planar, although substantially umbrella-shaped, and the authors argue for 'a fast interconversion of conformers' in solution.

That there is a small tetrahedral distortion in [Cu(abpn)], of the order of 5–10°, is not disputed. The burden of proof that in solution it approaches 50° (in the tetrahedral sense) still lies, it is here claimed, with the spectroscopic analysis.

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