

Structure of Copper (II) Complexes with Schiff Bases Derived from Reaction of Diamines with Dihydroxybenzophenone & Dihydroxyacetophenone

H P JENSEN

Chemistry Department, A Building 207, Technical University of Denmark, DK-2800 Lyngby, Denmark

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Quadridentate schiff bases formed by condensing 1,2-diamines with 2,4-dihydroxybenzophenone and 2,5-dihydroxyacetophenone form 1:1 complexes with Cu(II) ions. Circular dichroism spectral data indicate that these complexes have a non-planar structure in solution which contradicts the square planar geometry suggested earlier.

Some years ago Dave *et al.* described divalent metal ion complexes of quadridentate schiff base ligands derived from the reaction of diamines with 2,5-dihydroxyacetophenone, 2,5-dihydroxypropio-phenone and 2,5-dihydroxybenzophenone¹. In their work these authors concluded from magnetic susceptibilities, ESR, IR and electronic spectra that 1:1 Cu(II) complexes of the ligands exhibit square planar structure.

This statement may be checked making the diamine involved in the schiff base condensation optically active, since $\pi \rightarrow \pi^*$ transitions in the chromophoric part of the ligands may couple and produce exciton components of opposite handedness in case of deviation from planarity of the coordination sphere in the complexes²⁻⁴.

It may be noticed from the circular dichroism (CD) spectrum of the schiff base derived from (R)-(-)-1,2-propanediamine and 2,4-pentadione² and that of its copper (II) complex³ that the ligand chirality, defined in terms of handedness of the pair of lines connecting the ligator atoms of each chromophore, change sign on complexation.

This is typical feature of open-ended β -diketone schiff base ligands with non-rigid backbones as shown experimentally in a series of papers by the present author^{5,13} and as argued for by Maeda and Tsuji¹⁴.

Accordingly we have a procedure for elucidation of deviation from planarity with sign ($\Delta \log \Lambda$)¹⁵ in terms of handedness of the pair of lines connecting the ligator atoms of each chromophore and simultaneously representing $\pi \rightarrow \pi^*$ transition dipole moments^{3,10,12} which has been used on the compounds described by Dave *et al.*¹.

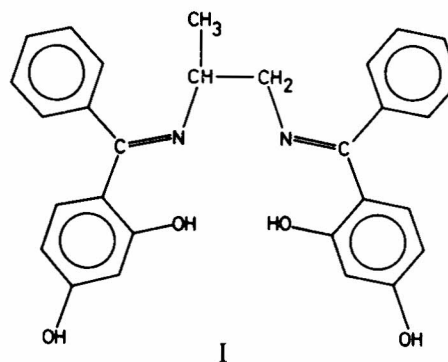
Materials and Methods

1,2-Propanediamine was resolved by standard procedure¹⁶. Schiff bases between (R)-(-)-1,2-

propanediamine (R-pn) and dihydroxybenzophenone [bp(OH)₂] and dihydroxyacetophenone [ap(OH)₂] together with their copper (II) complexes [Cu R-pn(bp(O)(OH))₂ and Cu R-pn(ap(O)(OH))₂] were prepared either according to the procedures described by Dave *et al.*¹ or by Pfeiffer *et al.*¹⁷. The identity of the compounds was established by chemical analyses. CD spectra were recorded on a Roussel-Jouan Dichrographe II.

Results and Discussion

The structure (I) for the ligand R-pn(bp(OH))₂ points to the fact that this compound is non-planar with chromophoric planes situated either *gauche* or *trans* to each other. In case of a *trans* conformation around the ethylene bridge of the dimeric schiff base one should not expect pronounced exciton coupling, since this coupling is proportional to a factor $1/r^3$ (r is the distance between the centers of gravity of the two chromophores²).



The CD spectrum of R-pn(bp(OH))₂, shown in Fig. 1, is typical of exciton coupling in a *gauche* conformation with negative optical factor for the low-energy (out of phase) component^{2,18}. The observed fine structure in the CD spectrum may be due to an overlaid $n \rightarrow \pi^*$ transition⁴ and/or a tautomeric

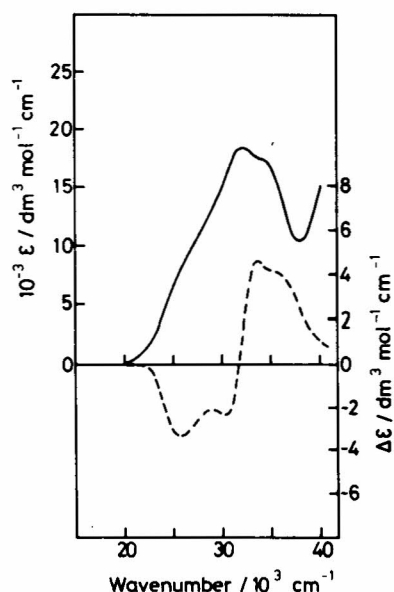


Fig. 1—Molar absorption (—) and CD-spectra (---) of free ligand R-pn(bp(OH)₂)₂ in methanol.

distribution^{5,6} on various forms of R-pn(bp(OH)₂)₂. In the copper(II) complex of R-pn(bp(OH)₂)₂ the $\pi \rightarrow \pi^*$ transition region of the $-\text{N}=\text{C}-\text{C}=\text{C}-\text{OH}$ chromophore is observed at the same energy level as in the free schiff base ($\sim 30,000 \text{ cm}^{-1}$) and furthermore it exhibits a CD spectrum typical of exciton coupling (Fig. 2). This indicates a tetrahedral distortion of the copper (II) coordination sphere.

The absolute configuration of the ligand part in the complex is seen to be the opposite of the free ligand, since the low-energy exciton component has a positive optical factor.

The attention should finally be drawn to the $d \rightarrow d$ transition region of the copper (II) ion which turns out to be similar to that of Cu R-pn(fsacH)₂ (cf. Fig. 6 of ref. 9), i.e. a copper (II) complex of a schiff base derived from 1,2-propanediamine and 3-formylsalicylic acid⁹. This is a comforting observation since the chromophoric sites in the two types of complexes are analogous. As far as transitional assignments of the bands are concerned we may, with reference to the arguments presented in connection with Cu R-pn(fsacH)₂, suggest the positive band in the ligand field range to be of $(x^2 - y^2) \rightarrow (xy)$ origin and the negative of $(xz) \rightarrow (xy)$ origin.

In conclusion it should be mentioned that the CD spectrum of Cu R-pn(ap(O)(OH))₂ shows an envelope

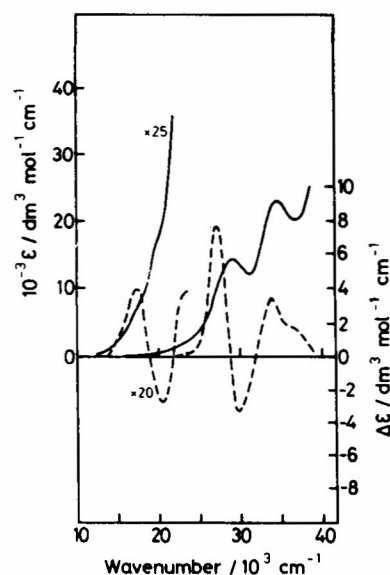


Fig. 2—Molar absorption (—) and CD-spectra (---) of copper(II) complex Cu R-pn(bp(O)(OH))₂ in methanol.

in the $\pi \rightarrow \pi^*$ transition region analogous to that of Cu R-pn(bp(O)(OH))₂. Thus also Cu Rpn(ap(O)(OH))₂ may be claimed non-planar.

Acknowledgement

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