

Structure of Schiff Bases Derived from Heptane-2,4,6-trione and Diamines as Obtained from UV Absorption and Circular Dichroism Spectra

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Absorption and circular dichroism spectra of the $\pi^* \leftarrow \pi$ transitions in Schiff bases derived from heptane-2,4,6-trione and $(-)_D$ -(R)-1,2-propanediamine, together with their mono- and dinuclear copper(II) inner sphere complexes, have been studied. The results are interpreted by means of exciton theory to give stereochemical information.

Over the years absorption and circular dichroism (CD) spectra of internal ligand $\pi^* \leftarrow \pi$ transitions in dimeric Schiff base derivatives of various β -diketones and diamines have been studied and interpreted to give information about stereochemistry by use of exciton theory.^{1–5} Further, especially copper(II) complexes of these types of ligand have been studied and interpreted similarly.^{5–8} The stereochemical results thus obtained have been checked by independent means both for the ligands⁵ and for the complexes.⁹

Assignments of the ligand field CD spectra have been performed using simple LCAO–MO theory and the assumption that the $d-d$ transitions borrow electric dipole moment for production of rotatory strength from the nearest allowed transitions, the internal ligand $\pi^* \leftarrow \pi$ transitions.^{6–8} It has, in the case of acetylacetonate derivatives, been possible to check these assignments through determination of transition polarization directions from linear dichroism measurements.^{10,11}

We thus, as demonstrated before,^{1–8} have a method of providing stereochemical assignments in solution, which in this paper will be exploited to gain information about Schiff bases of heptane-2,4,6-

trione (diacetylacetonate) and diamines, the preparation and properties of which have been recently described.^{12–20}

EXPERIMENTAL

Heptane-2,4,6-trione (dacacH₂) was prepared from dehydroacetic acid by the method of Bethell and Maitland,²¹ a procedure analogous to the original one by Feist.²²

Synthesis of the macrocyclic Schiff base between two mol of heptane-2,4,6-trione and two mol of $(-)_D$ -(R)-1,2-propanediamine [(R)-pn₂(dacacH₂)₂] was accomplished by the method of Yano *et al.*¹² This type of macrocyclic Schiff base has been shown to undergo partial hydrolysis on reaction with copper(II) acetate in *e.g.* aqueous ethanol to give the copper(II) complex of the acyclic Schiff base: diamine(dacacH₂)₂^{12–17} [*i.e.* in this case (R)-pn(dacacH₂)₂].

1,2-Propanediamine was resolved into enantiomers by established procedures.²

The identity of the compounds was verified by chemical analysis. A Cary 11 spectrophotometer, a Roussel-Jouan Dichrographe II and a Jobin-Yvon Dichrographe III were used for the measurements of optical spectra. The dimension of absorptivities is M⁻¹ cm⁻¹.

RESULTS AND DISCUSSION

It is well-known that the absorption band of the acetylacetonate anion at 34.300 cm⁻¹ is due to a $\pi^* \leftarrow \pi$ transition with the moment oriented along the oxygen–oxygen direction and with a dipole strength of 0.7×10^{-19} cm⁻¹ cm³.^{1,23}

In Fig. 1 absorption and circular dichroism spectra of the macrocyclic Schiff base (*R*)-pn₂(dacacH₂)₂ dissolved in chloroform are reproduced. It is seen that the spectra observed several days after the macrocyclic compound was dissolved in chloroform are quite analogous to the spectra of the Schiff base between (*R*)-1,2-propanediamine and acetylacetonone [(*R*)-pn(acacH)₂], both with respect to dipole strength and with respect to envelope and magnitude of the circular dichroism. (cf. Fig. 2 of Ref. 1). Accordingly, it is obvious that an old solution in chloroform, of what was initially the macrocyclic species (*R*)-pn₂(dacacH₂)₂, contains a Schiff base derivative of two molecules of the monoenol form (II) of heptane-2,4,6-trione and one molecule of diamine the production of which is probably catalyzed by hydrochloric acid from the chloroform. Thus, exciton coupling between two essentially acetylacetonone chromophores (as en-amines) brought into mutual position by a (*R*)-1,2-propanediamine bridge is the cause of the observed CD spectrum. This conclusion is also supported by the observation that when the macrocyclic Schiff base is dissolved in chloroform, with the purpose of preparing its copper(II) complex, an opening of the macrocycle is observed in combination with precipitation of a 1:1 chelate of the resultant Schiff base from one molecule of diamine and two molecules of the triketone.^{12,13}

The initial spectra of (*R*)-pn₂(dacacH₂)₂ in chloroform are somewhat more complicated than the final ones, as may be seen from Fig. 1. First of all it is obvious that the initial dipole strength in the chloroform solution is almost twice the final dipole strength (3.1 against $1.9 \times 10^{-19} \text{ cm}^3$) which suggests the number of excited electrons in the macrocycle more likely to be four as compared with two in (*R*)-pn(acacH)₂ and (*R*)-pn(dacacH₂)₂. Furthermore, the absorption maximum is found at lower energy for the macrocycle in comparison with (*R*)-pn(dacacH₂)₂, as we observe the major peak at 28.500 cm^{-1} and the minor at 26.500 cm^{-1} . These two peaks are distributed in the same spectral region as the peak at 27.800 cm^{-1} found for heptane-2,4,6-trione in alkaline solution, assignable as mentioned above to a $\pi^* \leftarrow \pi$ transition in a dianionic structure derived from the dienol (III). From these observations it is deduced that the initial UV spectra are mainly caused by exciton coupling between two $\pi^* \leftarrow \pi$ transitions in the two conjugated parts of structure IV, where the

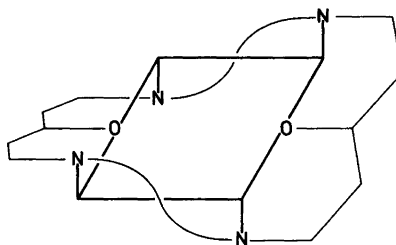


Fig. 2. (*R*)-pn₂(dacacH₂)₂. An indication of the structure and the absolute configuration of the chiral system formed by the conjugated ligand parts.

transitions for symmetry reasons have to be directed in the nitrogen–nitrogen direction of the same conjugated part. Thus the CD spectrum with a positive peak at low energy reflects, according to our adopted method,^{1,33} a right-handed distribution (*i.e.* positive optical factor) of the two out-of-phase $\pi^* \leftarrow \pi$ transitions in the conjugated diacetylacetonone backbones (Fig. 2). It is further clear that our assignment of the spectra as due to exciton coupling with a splitting between the excited states of 2.000 cm^{-1} gives molecular parameters of reasonable magnitude [cf. eqn. (6) of Ref. 1].

The structure of a conjugated macrocyclic Schiff base cannot be very flexible and thus the CD spectrum of (*R*)-pn(dacacH₂)₂ has appreciable magnitude in comparison with that of *e.g.* (*R*)-pn(acacH)₂.

From the initial CD spectrum and dipole strength it is further concluded that the macrocyclic molecules present in solution do not all take a structure as represented in Fig. 2. There is, as seen from Fig. 1, another pattern characteristic of exciton coupling around 31.000 cm^{-1} represented by the positive peak at 33.000 cm^{-1} and the negative shoulder at 30.000 cm^{-1} . The shape is the same as in the CD spectrum of (*R*)-pn(acacH)₂, and thus part of the macrocyclic molecules, when dissolved in chloroform, has the diacetylacetonone backbone represented by the monoenolic structure (II). This part of the macromolecules are accordingly only capable of showing exciton coupling of transitions in acetylacetonone chromophoric parts obviously distributed so as to give negative optical factor for the out-of-phase $\pi^* \leftarrow \pi$ couplet.^{1,33} Again the rigidity of the macrocycle makes the CD peaks fairly intense.

From (*R*)-pn₂(dacacH₂)₂ the complex Cu(*R*)-pn(dacacH)₂ was prepared. The absorption and

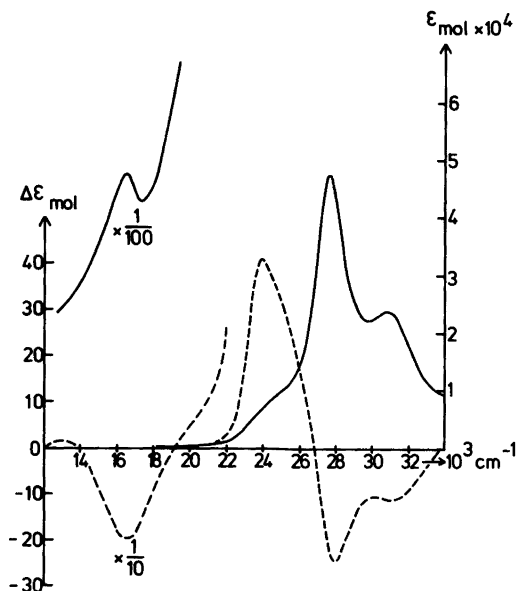


Fig. 3. Molar absorption (—) and circular dichroism spectra (---) of $\text{Cu}_2(\text{R})\text{-pn}(\text{dacac})_2$ dissolved in $(\text{CH}_3)_2\text{SO}$.

circular dichroism spectra of this complex are analogous to those of $\text{Cu}(\text{R})\text{-pn}(\text{acac})_2$ with respect to positions of maxima and magnitudes as well as to envelopes (Fig. 1 of Ref. 6). Accordingly the compound $\text{Cu}(\text{R})\text{-pn}(\text{dacacH})_2$ has an N_2O_2 tetracoordinated copper(II) ion, as also postulated by Yano *et al.*,⁵ around which the distribution of the ligands are as shown in Fig. 2 of Ref. 6.

From the mononuclear compound the dinuclear species $\text{Cu}_2(\text{R})\text{-pn}(\text{dacac})_2$ was prepared according to methods of the literature.¹⁴ The spectra of this compound is given in Fig. 3 and it is interesting to note that the exciton coupled internal ligand $\pi^* \leftarrow \pi$ transitions in this case are positioned around 26.000 cm^{-1} , *i.e.* in a spectral range which corresponds to conjugation in the two diacetylacetone backbones. The CD spectrum in this region is fairly intense since it corresponds to a four-electron transition. However, the ligand set N_2O_2 has to be twisted towards a fairly planar configuration in comparison with the mononuclear compound in order also to provide binding within an O_2O_2 ligand set (*cf.* Ref. 8).

A discussion of the Cotton effects of the $d-d$ transitions in the dinuclear complex is difficult since the rather intense internal ligand absorption hides

two bands⁶ and only the third, a negative band at 16.000 cm^{-1} probably assignable to the transition $(xy) \leftarrow (x^2 - y^2)$, can be seen.

Acknowledgements. The author wishes to acknowledge the skilful technical assistance of Mrs. L. Penzien.

The dichrographs were provided by the Danish Natural Science Research Council.

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Received June 12, 1981.