Structure of an Unsymmetrical Tetradentate Schiff Base Complex of Copper(II) as Obtained from UV Absorption and Circular Dichroism Spectra

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Absorption and circular dichroism spectra from the copper(II) complex of the Schiff base derivative from (R)-1,2-propanediamine, one molecule of acetylacetone and one molecule of salicylaldehyde, have been studied. The results are interpreted by means of exciton theory in order to give stereochemical information about configurational deviations from square-planar complexation of copper(II) ions.

Through the use of exciton theory the molecular structure of various optically active Schiff bases of β-diketones and diamines, together with their transition metal complexes, have been studied extensively. As far as Schiff base derivatives of acetylacetone are concerned, the theoretical framework for a treatment within an exciton formalism was given by Larsen.[1] The $\pi \rightarrow \pi^*$ transitions, expected to be polarized in the N−O direction of the planar en-amine chromophores, may at small distances split due to a purely coulombic interaction. In the case of optically active compounds, such couplets exhibit Cotton effects (CD-bands) of numerically equal rotatory strengths, but of opposite signs. Since the absolute configuration of the rigid compound $(-)_D$-(R,R)-trans-1,2-cyclohexanediamine (R-chxn) is known, the characteristic circular dichroism envelope of the Schiff base derivative of this diamine with acetylacetone [R-chxn(acacH)$_2$] has been used in the correlation of molecular structures of similar compounds.[2−5]

Bosnich attacked the interpretation of circular dichroism spectra from optically active Schiff base derivatives of salicylaldehyde and their transition metal complexes in a similar fashion.[6] The CD

spectrum of N,N'-bis(salicylidene)-$(-)_D$-(R)-1,2-propanediamine [R-pn(salH)$_2$] exhibits two regions of interest for the present purpose, a band around 25 $\times 10^3$ cm^{-1} and a band around 30 $\times 10^3$ cm^{-1}. As indicated by Bosnich the first band may be assigned as an $n \rightarrow \pi^*$ transition, whereas the second corresponds to a $\pi \rightarrow \pi^*$ transition involving the azomethene group, a transition which is also polarized in the N−O direction of the chromophore.[7] It is, as indicated above, well known that two $\pi \rightarrow \pi^*$ transitions distributed helically possess the power of showing exciton splitting,[1,7−10] and it is immediately seen from spectra of R-pn(salH)$_2$ that such a coupling exists in the benzoic transition region,[11] analogous, by the way, to the coupling observed with enantiomers of 1,3-diphenylallene.[12]

As mentioned by Smith et al., it is puzzling that the negative circular dichroism band at 30 $\times 10^3$ cm^{-1}, assignable to $\pi \rightarrow \pi^*$ transition involving the azomethene groups of R-pn(salH)$_2$, does not show any sign of exciton coupling.[7] This may, however, as proposed by Mason et al.,[13] be a consequence of configuration interaction. Under absorptions exhibiting exciton coupling, two bands in the circular dichroism spectrum are expected of equal magnitude, but of opposite signs.[1] However, inequality in the areas of the two bands may arise from the mixing with excited states. Thus configuration interactions will mix out-of-phase (antisymmetric, B) transitions and in-phase (symmetric, A) transitions among themselves. Accordingly it is conceivable, as may also be seen from the formulas presented by Mason et al.,[13] 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 a single negative CD-band is observed. In the case of complexation, however, configurational interactions are of lesser importance as may be seen from the spectra of the Zn(II) complex of N,N'-bis(salicylidene)-$(-)_D$-(R)-1,2-propanediamine [Zn R-pn(sal)$_2$], which clearly exhibit exciton splitting under the $\pi \rightarrow \pi^*$ transition band.[6]

In this paper we shall, observing the points of view presented above, discuss and interprete spectra of the compound R-pn(acacH)(salH), *i.e.* the Schiff base derived from one molecule of $(-)_D$-(R)-1,2-propanediamine, one molecule of acetylacetone and one molecule of salicylaldehyde together with the inner-sphere Cu(II) complex of this particular ligand.

EXPERIMENTAL

The ligand R-pn(acacH)(salH) was prepared according to a modification of a procedure described earlier for R-pn(acacH)$_2$ by Martell *et al.*[14] To a mixture of 1 mol of salicylaldehyde and 1 mol of acetylacetone, 1 mol of $(-)_D$-(R)-1,2-propanediamine was added slowly and with stirring. After evolution of heat had ceased, stirring was continued for another hour and the reaction mixture finally dissolved in acetone. On addition of water in which solvent R-pn(acacH)$_2$ is soluble[14] an oil is developed and subsequently separated. According to the procedure published by Kwiatkowski and Kwiatkowski[15] the oil is then extracted several times with hot n-hexane in which solvent R-pn(salH)$_2$ is fairly insoluble. The collected extracts yield on standing R-pn(acacH)(salH) as an oil, which crystallizes below temperature (m.p.: 5 °C). The identity of the compound has been confirmed through chemical analysis. (Calc. for $C_{15}H_{20}N_2O_2$: C, 69.23%; H, 7.70%; N, 10.76%. Found: C, 69.50%; H, 7.38%; N, 10.24%). The copper(II) complex Cu R-pn(acac)(sal) may be prepared from solutions of the ligand and a convenient copper(II) salt, either acetate or carbonate.[16,17] The identity of the compound has been confirmed through chemical analysis. (Calc. for $C_{15}H_{18}N_2O_2Cu,H_2O$: C, 53.01%; H, 5.93%; N, 8.23%. Found: C, 53.73%; H, 6.01%; N, 8.07%).

RESULTS AND DISCUSSION

We may start by considering the spectra of the free ligand R-pn(acacH) (Fig. 1). Two bands in the non-benzoic transition region and of negative rota-
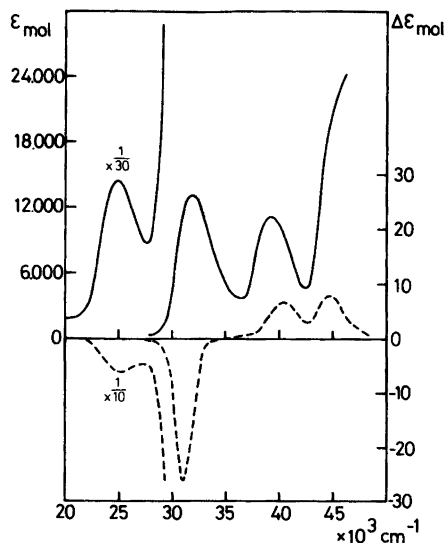

Fig. 1. Molar absorption ($-$) and circular dichroism spectra ($---$) of R-pn(acacH)(salH) dissolved in CH_3OH.

tional strength are observed in the CD spectrum. It is obvious that the spectrum resembles that of R-pn(salH)$_2$ (Fig. 1 of Ref. 6), and may be assigned similarly, *i.e.* the peak at 25×10^3 cm^{-1} to a $n \rightarrow \pi^*$ transition and the band at 31×10^3 cm^{-1} as an enforced out-of-phase exciton couplet from $\pi \rightarrow \pi^*$ transitions in the two chromophoric parts of R-pn(acacH)(salH). Thus the negative sign of this peak in the circular dichroism spectrum reflects stereochemical dominance from the R-1,2-propanediamine bridge.[1-5]

Turning our attention to the copper(II) complex it might first of all be appropriate to recollect the spectra of Cu R-pn(acac)$_2$ and Cu R-pn(sal)$_2$. The former shows in the internal ligand transition region an exciton couplet with a positive rotational strength and a circular dichroism maximum of ~ 60 M^{-1} cm^{-1} at 30×10^3 cm^{-1}.[18] The latter shows in the same region a circular dichroism maximum of ~ 15 M^{-1} cm^{-1} at 25×10^3 cm^{-1}.[19] From this information it is easily seen, in comparison with the circular dichroism spectrum of Cu R-pn(acac)(sal) Fig. 2), that we are not dealing with just a mixture of Cu R-pn(acac)$_2$ and Cu R-pn(sal)$_2$. We furthermore notice that the $\pi \rightarrow \pi^*$ transition region of the mixed-ligand complex shows circular dichroism bands of relatively low intensity. It is true, however, as may be seen from the $d \rightarrow d$ transition region of the mixed-
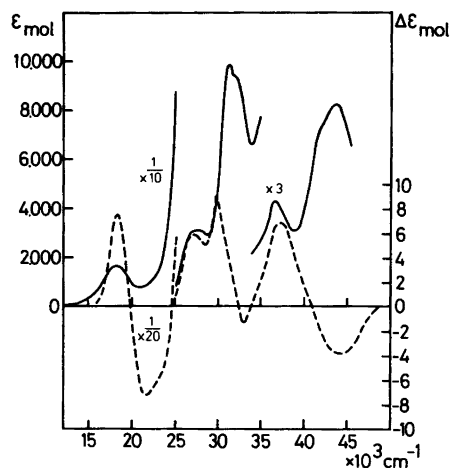
Fig. 2. Molar absorption (—) and circular dichroism spectra (---) of Cu *R*-pn(acac)(sal) dissolved in CH_3OH.

ligand complex that the two possible isomers of formula Cu *R*-pn(acac)(sal) are non-planar and that the configurational deviation from planarity must be of the same sign as that of Cu*R*-pn(acac)$_2$ (*cf.* Fig. 2 of Ref. 18).

As mentioned, the $\pi \rightarrow \pi^*$ transition region in the circular dichroism spectrum of the mixed-ligand complex does not distinctly show the characteristics of exciton couplets. This is due to the relatively large energy separation of the $\pi \rightarrow \pi^*$ transitions of salicylaldehyde and acetylacetone, respectively, occurring by complexation. It is known that the $\pi \rightarrow \pi^*$ transition of an acetylacetone Schiff base is found at 32×10^3 cm^{-1} with a shift towards 32.5 $\times 10^3$ cm^{-1} by complexation to a Cu(II) ion,[1,18] whereas a Schiff base of salicylaldehyde shows its $\pi \rightarrow \pi^*$ transition at 31.5×10^3 cm^{-1} with a shift towards 28.5×10^3 cm^{-1} by complexation.[6,19] Thus the two $\pi \rightarrow \pi^*$ transitions interact only to a minor extent in the mixed-ligand complex and will accordingly not give rise to strong exciton bands in absorption and circular dichroism spectra.

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