

Structure of Mono- and Binuclear Complexes of Schiff Bases Derived from Diamines and 3-Formylsalicylic Acid as Obtained from UV Absorption and Circular Dichroism Spectra

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Absorption and circular dichroism spectra of the internal ligand $\pi^* \leftarrow \pi$ transition in compounds such as the mononuclear and dinuclear copper(II) complexes of the Schiff base derivative from (*R,R*)-1,2-cyclohexanediamine and two molecules of 3-formylsalicylic acid have been studied. The results are interpreted by means of exciton theory in order to give stereochemical information and comments to the square-planar complexation of copper(II) ions.

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.^{1–6} Further, especially copper(II) complexes of these types of ligand have been studied and interpreted similarly.^{6–8} The stereochemical results thus obtained have been checked by independent means for the ligands as well as for the complexes.^{6,9} Assignments of ligand field CD spectra have been performed using simple LCAO-MO theory and the assumption that the $d \leftarrow d$ transitions borrow electric dipole moment for production of rotatory strength from the nearest allowed transitions, the ligand $\pi^* \leftarrow \pi$.^{7,8} These assignments have been checked through measurements of transition polarization directions *via* phase modulation spectroscopy.^{10,11}

We thus have a method capable of making stereochemical predictions which we wished to apply to Schiff base complexes derived from 3-formylsalicylic acid and diamines, the preparation and properties of which have been described lately by Okawa, Kida *et al.*^{12–21}

EXPERIMENTAL

3-Formylsalicylic acid (fsacH₂) was prepared according to the method of Duff and Bills,²² and Schiff bases with methylamine (ma), 1,2-propanediamine (pn) and 1,2-cyclohexanediamine (chxn) according to the method of Poddar.²³ Schiff bases are abbreviated as ma(fsacH₂), pn(fsacH₂)₂ and chxn(fsacH₂)₂. Furthermore, the following abbreviations will be used: acacH = 2,4-pentanedione and fmcH = 3-formylcamphor.

Mononuclear complexes of copper(II) (*e.g.* Cu pn(fsacH₂)₂) may be prepared from the free ligand and copper(II) acetate²³ or by mixing 3-formylsalicylic acid, copper(II) acetate and the appropriate diamine.¹⁶ Dinuclear complexes (*e.g.* Cu₂ pn(fsac)₂) were prepared from the corresponding mononuclear complex as described by Okawa, Kida *et al.*¹⁶ The identity of the compounds was established through chemical analyses.

The diamines pn and chxn were resolved into enantiomers by well established procedures.³

A Cary 11 spectrophotometer, a Roussel-Jouan Dichrographe II and a Jobin-Yvon Dichrographe III were used for the measurements of optical spectra. All spectra were recorded with dimethylsulfoxide as the solvent. The dimension of absorptivities is M⁻¹ cm⁻¹.

RESULTS AND DISCUSSION

Molecular structures. Salicylaldehyde²⁴ and 3-formylsalicylic acid (Fig. 1) show additional bands above 300 nm in the UV spectral region as compared with salicylic acid.²⁴ These additional bands may be assigned as an electric-dipole allowed $\pi^* \leftarrow \pi$ transition in the (CHO)–C=C–OH part (protonated

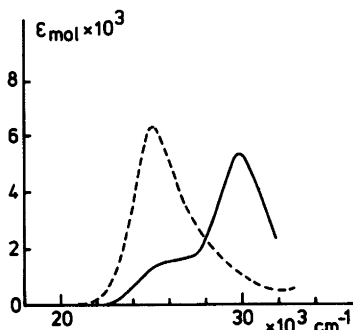


Fig. 1. Molar absorption spectra in the chromophoric $\pi^* \leftarrow \pi$ transition region of 3-formylsalicylic acid (—) and of ma(fsacH) (---).

as well as deprotonated) of salicylaldehyde and 3-formylsalicylic acid,^{25,26} and thus we have a transition in the molecular plane polarized towards the oxygen-oxygen direction, *i.e.* we have a chromophoric system somewhat analogous to acetylacetone.¹

In the Schiff base condensate between methylamine and 3-formylsalicylic acid we observe a red-shift of the $\pi^* \leftarrow \pi$ transition (Fig. 1) in analogy with observations for condensates of acetylacetone and amines.¹

Condensing a diamine with two molecules of 3-formylsalicylic acid we obtain a compound with a dipole strength approximately the double of the monomeric Schiff base ma(fsacH) (Fig. 2). We thus assume strong coupling of the electronic motions

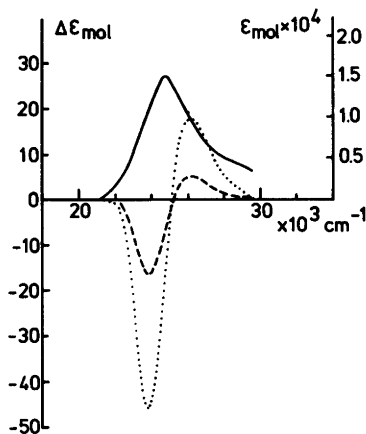


Fig. 2. Molar absorption (—) and circular dichroism spectra of $R\text{-chxn}(\text{fsacH}_2)_2$ (···) and of $R\text{-pn}(\text{fsacH}_2)_2$ (---).

in the two chromophoric parts of the compound as we, for such cases, should expect the following relation to hold: $D_{\text{dimer}} = 2D_{\text{monomer}}$.¹

An exciton splitting, however, is not obvious from the absorption spectrum, but is clearly visible in the CD spectra. The spectrum of $R\text{-chxn}(\text{fsacH}_2)_2$ is analogous to that of $R\text{-chxn}(\text{acaH})_2$ ¹ and that of $R\text{-chxn}(\text{fmcH})_2$,^{3,4} provided the latter have the chromophoric part in *syn* (*E*) configuration, and thus we may conclude that also in $R\text{-chxn}(\text{fsacH}_2)_2$ the two $\pi^* \leftarrow \pi$ transition dipole moments define a left-handed skew pair of vectors. We may estimate the angle between the two vectors using eqn. 6 of Ref. 1. From the following values: $\Delta E = 2500 \text{ cm}^{-1}$, $D_{\text{monomer}} = 0.6 \times 10^{-19} \text{ cm}^3 \text{ cm}^{-1}$, $r_{AB} = 3 \times 10^{-8} \text{ cm}$, $\cos \phi_B = 0$ we obtain the angle $\theta \approx 56^\circ$, a value in accordance with the fact that the two chromophoric parts are held in position by *trans*-1,2-cyclohexanediamine. Furthermore, on the basis of Fig. 2 we may conclude that the structure of $R\text{-pn}(\text{fsacH}_2)_2$ and that of $R\text{-chxn}(\text{fsacH}_2)_2$ is analogous, just as is the case for the corresponding acetylacetone¹ and formylcamphor^{3,4} Schiff base derivatives.

According to Okawa, Kida *et al.*¹²⁻²¹ we have the option of producing mono- and binuclear complexes of $R\text{-chxn}(\text{fsacH}_2)_2$ and $R\text{-pn}(\text{fsacH}_2)_2$. Considering the former ligand we see from Fig. 3 (CD in the $\pi^* \leftarrow \pi$ transition region) that the copper(II) ion, bonded to the quadridentate inside* coordination site, is surrounded by the ligators in such a way that there is a rather big deviation from planarity, a deviation which we may indicate by sign. Due to the formalism of the exciton procedure used we may conclude that the two chromophoric $\pi^* \leftarrow \pi$ transition moments and thus the chromophoric planes in the compound $\text{Cu } R\text{-chxn}(\text{fsacH})_2$ define a Δ configuration.^{7,8}

We also succeeded in producing the binuclear compound $\text{Cu}_2 R\text{-chxn}(\text{fsac})_2$ the spectra of which are given in Fig. 5. It is obvious from the CD spectrum that second (outside) copper(II) ion is not capable of forcing the two chromophoric parts into a planar configuration. This is beyond doubt due to the strain in the cyclohexane ring. When such strain, however, is not present, the second metal ion may force the two chromophoric parts towards a planar configuration as it was recently demonstrated

* The word "inside" will in this context be used as opposed to "outside" with respect to the diamine backbone (*cf.* Fig. 4).

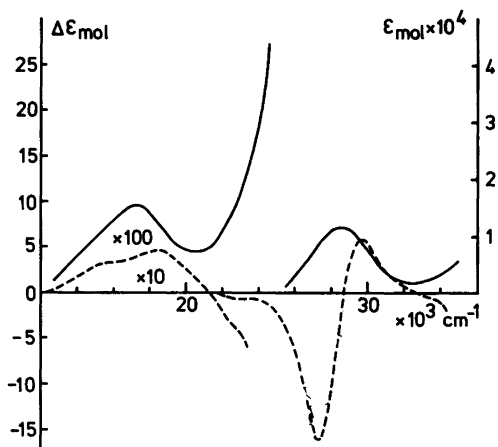


Fig. 3. Molar absorption (—) and circular dichroism (---) spectra of Cu *R*-chxn(fsacH)₂.

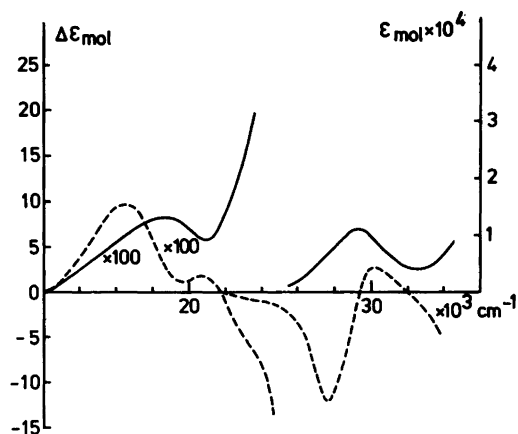


Fig. 5. Molar absorption (—) and circular dichroism (---) spectra of Cu₂ *R*-chxn(fsac)₂.

in the cases of CuCo en(fsac)₂¹⁸ (en=1,2-ethanediamine) and CuMg en(fsac)₂²⁷ by X-ray structural determinations.

In Fig. 6 is given the spectra of Cu *R*-pn(fsacH)₂. We see in the internal ligand transition region a CD spectrum less characteristic of excitation coupling than the one observed for Cu *R*-chxn(fsacH)₂, and may conclude that although Cu *R*-pn(fsacH)₂ shows deviation from planarity around the copper(II) ion coordinated to the quadridentate inside coordination site, this deviation is less than that found with Cu *R*-chxn(fsacH)₂. However, the fact that the flexibility of the ligand *R*-pn(fsacH)₂ is greater than that of *R*-chxn(fsacH)₂ (Fig. 2) may also be the cause of the less characteristic CD spectrum as this could be the sum of CD spectra of several conformers.

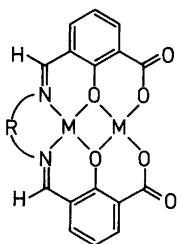


Fig. 4. Structure of the dinuclear complex M₂ diamine(fsac)₂ showing the inside and outside coordination sites.

As seen from the $\pi^* \leftarrow \pi$ transition region in the CD spectra (Figs. 3 and 6), the deviation from planarity of the most abundant conformer is the opposite for the *R*-pn derivative complex in comparison with the *R*-chxn derivative complex, *i.e.* the absolute configuration of Cu *R*-pn(fsacH)₂ may be indicated by Λ .

Preparing the dinuclear compound Cu₂ *R*-pn(fsac)₂, the spectra of which are given in Fig. 7, we have a compound with virtually no CD spectrum, thus demonstrating the planarity of the inside as well as of the outside coordination site.

Electronic structures. We may start by considering the CD spectrum of Cu₂ *R*-pn(fsac)₂ (Fig. 7), a compound which as demonstrated in the previous section is expected to exhibit nearly planar coordination around the two involved copper(II) ions.

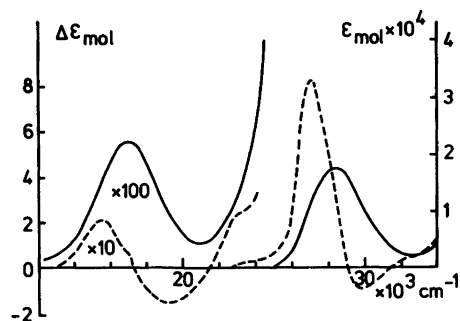


Fig. 6. Molar absorption (—) and circular dichroism (---) spectra of Cu *R*-pn(fsacH)₂.

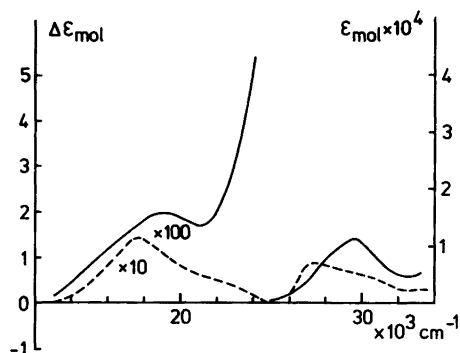


Fig. 7. Molar absorption (—) and circular dichroism (---) spectra of $\text{Cu}_2 R\text{-pn}(\text{fsac})_2$.

However, as the dissymmetric center of the molecule is situated on the backbone of the ligand we expect chiral interferences only with the copper(II) ion bound to the inside coordination site. This copper(II) ion will furthermore be characterized as being situated in a D_2 environment so that comparisons with earlier work on the origin of rotatory strength in the ligand field region^{7,8} may be performed.

Obviously for $\text{Cu}_2 R\text{-pn}(\text{fsac})_2$ the internal ligand transition part ($26.000\text{--}32.000\text{ cm}^{-1}$) of the CD spectrum must be due to transitions from former non-bonding σ^n orbitals to π^* orbitals ($\pi^* \leftarrow n$), i.e. transitions with polarisation direction perpendicular to the chromophoric and accordingly to the molecular plane. Thus we may, with reference to the coordinate system indicated in Fig. 2 of Ref. 7 (z -axis perpendicular on the ligand plane) and to our borrowing mechanism presented earlier, expect rotatory strength connected with three transitions involving $3d$ orbitals on the copper(II) ion, namely: $(xy) \leftarrow (x^2 - y^2)$, $(xy) \leftarrow (z^2)$ and $\pi^* \leftarrow (xy)$ all of z polarisation. As $(xy) \leftarrow (z^2)$ must be of lower intensity than the two others in a CD spectrum⁷ (and is probably also found at lower energy than 23.000 cm^{-1} ^{7,8}) we assign the 18.000 cm^{-1} peak to the $(xy) \leftarrow (x^2 - y^2)$ transition, the 23.500 cm^{-1} shoulder to the $\pi^* \leftarrow (xy)$ transition and expect the $(xy) \leftarrow (z^2)$ transition to be situated somewhere in between.

Considering CD spectra of those complexes which do not have planar configuration of the inside coordination site (Figs. 3, 5, 6) we find in all three cases bands around 23.000 cm^{-1} of the same magnitude and sign for the same absolute configuration. Thus the assignment to these bands as

being due to $\pi^* \leftarrow (xy)$ transitions seems reasonable.

The remaining region ($12.000\text{--}22.000\text{ cm}^{-1}$) is rather uncharacteristic for the three compounds $\text{Cu } R\text{-pn}(\text{fsacH})_2$, $\text{Cu}_2 R\text{-pn}(\text{fsac})_2$ and $\text{Cu}_2 R\text{-chxn}(\text{fsac})_2$, except for the fact that we obviously have three bands for each compound to account for. This number of bands is in agreement with our proposed model which mixes $\pi^* \leftarrow \pi$ and $d \leftarrow d$ transitions of the same symmetry giving in the D_2 point group three possible transitions with rotatory strength, namely: $(xy) \leftarrow (x^2 - y^2)$, $(xy) \leftarrow (xz)$ and $(xy) \leftarrow (z^2)$.

As we want to give a tentative assignment to bands in the ligand field region CD spectra presented in Figs. 3, 5, 6, it is appropriate first of all to look for the $(xy) \leftarrow (z^2)$ transition. This transition is, as indicated above, of low intensity since the magnetic as well as the dipole transition moment needed for production of rotatory strength have to be borrowed.⁷ The transition may thus be assigned as follows: For $\text{Cu } R\text{-pn}(\text{fsacH})_2$ the shoulder at 16.500 cm^{-1} , for $\text{Cu } R\text{-chxn}(\text{fsacH})_2$ the plateau at 16.500 cm^{-1} and for $\text{Cu}_2 R\text{-chxn}(\text{fsac})_2$ the peak at 21.500 cm^{-1} . The two first assignments agree reasonably well with the postulated positions of the same band in copper(II) complexes of Schiff bases derived from diamines and formylcamphor.⁸ The latter assignment agrees with the expected position of the same band in the planar compound $\text{Cu}_2 R\text{-pn}(\text{fsac})_2$. Although the strain in the cyclohexane backbone of $\text{Cu}_2 R\text{-chxn}(\text{fsac})_2$ would prevent the compound from having a completely planar configuration we argued in the previous section that $\text{Cu}_2 R\text{-chxn}(\text{fsac})_2$ might well be more planar than the two mononuclear complexes $\text{Cu } R\text{-pn}(\text{fsacH})_2$ and $\text{Cu } R\text{-chxn}(\text{fsacH})_2$.

Carrying the comparison between $\text{Cu}_2 R\text{-chxn}(\text{fsac})_2$ and $\text{Cu}_2 R\text{-pn}(\text{fsac})_2$ a little further we might expect the $(xy) \leftarrow (x^2 - y^2)$ transition for both compounds to be situated at almost the same energy, and thus the 17.000 cm^{-1} band of the former compound is assigned accordingly. Consequently, the slight indication of a negative deflection in the CD spectrum of Fig. 5 must be assigned to the $(xy) \leftarrow (xz)$ transition. This assignment is in accordance with our earlier findings that the high energy Cotton effect under the $\pi^* \leftarrow \pi$ transition and the Cotton effect under $(xy) \leftarrow (xz)$ are interrelated so as to have opposite signs.^{7,8}

We are now left with the problems present by the envelopes of the CD spectra of the two mononuclear compounds (Figs. 3 and 6). It seems noteworthy that

the ligand field CD spectra of these compounds are of the same overall magnitude as that of $\text{Cu}_2\text{R-pn(fsac)}_2$ which we assigned as due to borrowed intensity from $\pi^* \leftarrow n$ transitions. Thus we are obviously not in a position to say anything reasonably qualified about further assignments to the ligand field range CD spectra as these most probably reflect interactions between states whose rotatory strength has origin in both $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transitions. However, we have observed that the $(xy) \leftarrow (x^2 - y^2)$ transition is situated at lower energy than the $(xy) \leftarrow (xz)$ transition which means that the positive bands at 15.000 cm^{-1} in the mononuclear compounds supposedly are of $(xy) \leftarrow (x^2 - y^2)$ origin whereas the bands at 19.000 cm^{-1} are of $(xy) \leftarrow (xz)$ origin.

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