

# Molecular and Electronic Structure in Copper(II) Complexes with Schiff Bases of Formylcamphor and Diamines as Obtained from Absorption and Circular Dichroism Spectroscopy

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Absorption and circular dichroism spectra of the internal ligand  $\pi^* \leftarrow \pi$  transitions in compounds such as the copper(II) complex of the Schiff base from (*R,R*)-1,2-cyclohexanediamine and two molecules of formylcamphor derived from natural (+)<sub>D</sub>-camphor have been studied. The results have been interpreted by means of exciton theory to give information about stereochemistry.

The Cotton effects in the ligand field range may be understood using simple LCAO–MO theory and the assumption that  $d \leftarrow d$  transitions borrow electric transition dipole moments from the nearest allowed transitions: the ligand  $\pi^* \leftarrow \pi$ .

Absorption and circular dichroism spectra of the internal ligand  $\pi^* \leftarrow \pi$  transitions in Schiff bases of acetylacetone and thioacetylacetone with diamines, <sup>1,2</sup> of formylcamphor with amines, <sup>3,4</sup> and of acetylcamphor with amines, <sup>5</sup> have been studied and interpreted by means of exciton theory to give information about stereochemistry. Also copper(II) complexes of the acetylacetone Schiff bases have been studied and the spectra interpreted similarly. <sup>2,6,7</sup> The stereochemical results have been checked by independent means. <sup>2,8</sup> Assignments of ligand field circular dichroism (CD) spectra have been performed using simple LCAO–MO theory and the assumption that the  $d \leftarrow d$  transitions borrow electric transition dipole moments from the nearest allowed transitions, the ligand  $\pi^* \leftarrow \pi$  transitions, <sup>6</sup> and the assignments have been checked through polarization spectroscopy. <sup>9,10</sup>

For the sake of further investigations of the model, copper(II) complexes of Schiff bases derived

from formylcamphor and diamines have been prepared and their absorption and circular dichroism spectra measured.

## EXPERIMENTAL

Schiff bases of formylcamphor and diamines were prepared as described earlier, <sup>3,4</sup> and neutral inner-sphere copper(II) complexes thereof according to the procedure of Pfeiffer *et al.* <sup>11</sup> The identity of the compounds have been established through chemical analyses. A Cary 11 spectrophotometer and Roussel-Jouan Dichrographs II & III were used for the measurements of optical spectra. All spectra were recorded in methanol.

**Abbreviations.** *Amines.* en = 1,2-ethanediamine, R-pn = (*R*)-(–)<sub>D</sub>-1,2-propanediamine, S-pn = (*S*)-(+) <sub>D</sub>-1,2-propanediamine, R-2,3-bn = (*R,R*)-(–)<sub>D</sub>-2,3-butanediamine, S-2,3-bn = (*S,S*)-(+) <sub>D</sub>-2,3-butanediamine, R,S-2,3-bn = *meso*-(*R,S*)-2,3-butanediamine, R-chxn = *trans*-(*R,R*)-(–)<sub>D</sub>-1,2-cyclohexanediamine, S-chxn = *trans*-(*S,S*)-(+) <sub>D</sub>-1,2-cyclohexanediamine, R,S-chxn = *meso*-(*R,S*)-1,2-cyclohexanediamine, ibn = 1,2-diamino-2-methylpropane, tn = 1,3-propanediamine.

**Dioxo compounds.** acacH = acetylacetone, fmcH = formylcamphor. en(fmcH)<sub>2</sub> *etc.* symbolize the Schiff base condensate from 1 mol of diamine and 2 mol of dioxo compound.

## THEORETICAL RESULTS

**Ligand range.** It can be assumed that the  $\beta$ -diketone chromophoric parts in the complexes take on a *syn* (*Z*) conformation and that the two

chromophoric parts linked together through the substituted ethylene bridge are in a *gauche* arrangement. If  $\pi$  bonding to the metal is negligible we may then directly determine the absolute configuration from the envelope of the CD spectrum in the  $\pi^* \leftarrow \pi$  transition range in terms of the handedness of a pair of vectors representing the allowed  $N \leftarrow O$  transitions in the conjugated parts of the ligands. Furthermore the angle  $\theta$  between the two transition moments can be estimated and checked independently through eqns. 3 and 6 of Ref. 1.

**Ligand field range.** As with Cu *R*-pn(acac)<sub>2</sub> orbitals and states will be characterized in terms of irreducible representations belonging to the point group  $D_2$ . Further it will be assumed that the relative energies of ligand and metal orbitals are  $3\pi \leq 3d < 4\pi$ , ( $xy$ ) being the un-filled  $3d$  orbital and ( $x^2 - y^2$ ) the highest filled.<sup>6</sup> With this ordering of the orbitals four electronic transitions in the ligand field range of the Cu(II)  $d^9$ -system may be expected namely: ( $xy$ ) $\leftarrow$ ( $x^2 - y^2$ ), ( $xy$ ) $\leftarrow$ ( $xz$ ), ( $xy$ ) $\leftarrow$ ( $yz$ ), and ( $xy$ ) $\leftarrow$ ( $z^2$ ) of excited state symmetries  $A$ ,  $B_2$ ,  $B_3$  and  $A$ , respectively. Since the excited state symmetries of the  $\pi^* \leftarrow \pi$  transitions are  $A$  (out-of-phase) and  $B_2$  (in-phase), three of the ligand-field transitions can gain transition intensity for CD bands through mixing with the  $\pi$ -excited states.

Also transitions from the former non-bonding oxygen  $\sigma^n$ -orbitals to  $\pi^*$ -orbitals ( $\pi^* \leftarrow n$ ) can be expected, and as such transitions have excited state symmetries  $A$  and  $B_2$  these may mix with the internal ligand transitions in producing two CD-bands.

In conclusion we expect, in the spectral range 12 000–32 000  $\text{cm}^{-1}$  of optical active copper(II) complexes of Schiff bases derived from diamines and  $\beta$ -diketones, seven CD-bands, three of mainly  $d \leftarrow d$  origin, two of mainly  $\pi^* \leftarrow n$  origin and two of mainly  $\pi^* \leftarrow \pi$  origin.

## RESULTS AND DISCUSSION

It is often valuable in stereochemical work to use compounds of high rigidity, and, *e.g.*, *R*-chxn(acacH)<sub>2</sub> was used when the spectral properties of Schiff bases of acetylacetonone were discussed.<sup>1</sup> It would indeed have been desirable to use this particular ligand in a copper complex, however, we were,<sup>6</sup> as was also Schwarzenbach,<sup>12</sup> unable to prepare Cu *R*-chxn(acac)<sub>2</sub>.

The situation is quite different with the Schiff bases of diamines and formylcamphor as Cu *R*-chxn(fmc)<sub>2</sub> and Cu *S*-chxn(fmc)<sub>2</sub> are easily prepared by standard procedures.<sup>11</sup> Spectra of these compounds are given in Fig. 1.

It is immediately obvious from Fig. 1 that the two compounds show an overall mirror image relationship. Small deviations can be attributed to the fact that the two ligands are not enantiomeric since the formylcamphor chromophore in both are derived from natural (+)<sub>D</sub>-camphor.<sup>13</sup>

It is obvious that the predicted seven CD-bands are present: three in the region 12 000–18 000  $\text{cm}^{-1}$ , two in the region 20 000–25 000  $\text{cm}^{-1}$  and two in the region 26 000–32 000  $\text{cm}^{-1}$ .

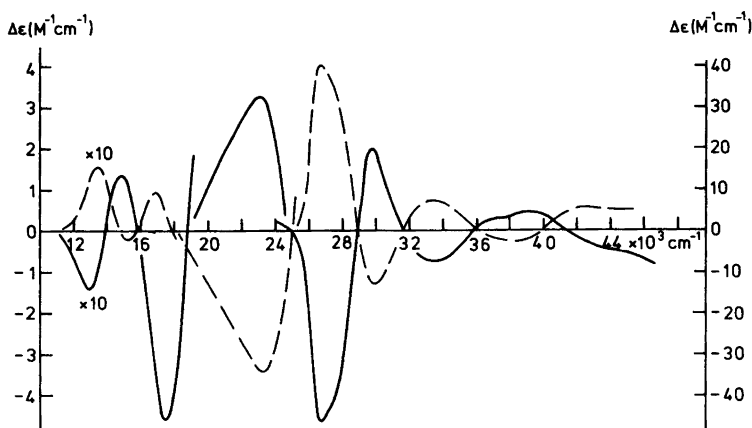


Fig. 1. CD spectra of Cu *R*-chxn(fmc)<sub>2</sub> (—) and Cu *S*-chxn(fmc)<sub>2</sub> (---).

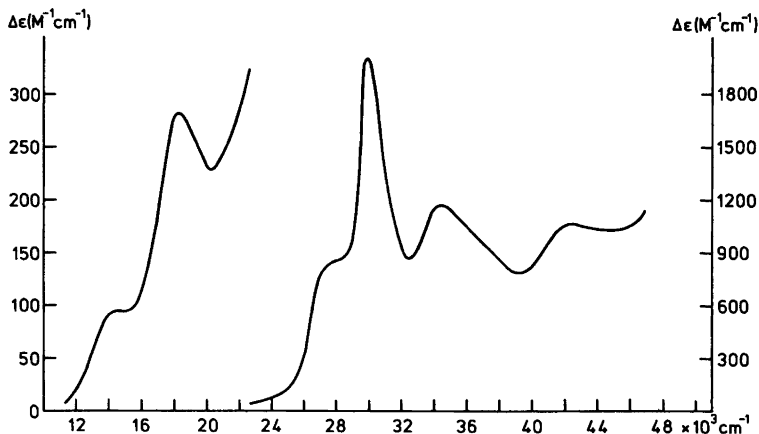


Fig. 2. Absorption spectrum of Cu en(fmc)<sub>2</sub> and all other discussed 1,2-diamine Schiff base derivatives of formylcamphor.

Let us first consider the bands in the  $\pi^* \leftarrow \pi$  region. It is, with reference to spectra of the free ligands in *syn* conformation,<sup>3,4</sup> striking that the chirality of the pair of vectors, representing the allowed polarized internal ligand transitions, does not change on complexation as is the case with, *e.g.*, R-pn(acacH). This means that the absolute configuration of Cu *S*-chxn(fmc)<sub>2</sub> is the same as that of Cu *R*-pn(acac)<sub>2</sub> (Fig. 2 of Ref. 6).

The spectra in Fig. 1 and Fig. 2 furthermore give indirect information as to the cause of the non-existence of Cu *R*-chxn(acac)<sub>2</sub> and Cu *S*-chxn(acac)<sub>2</sub>. Obviously the two chromophoric parts of the ligands are forced towards a more planar overall configuration during complexation, as may be seen from absorption spectra (Fig. 2 and Fig. 5 of Ref. 4) and through use of eqn. 3 of Ref. 1. This has, due to the cyclohexane ring, to happen through the smallest possible angle, and in the case of acetylacetonone this leads to unfavourable interactions between methyl groups and the substituted ethylene bridge with the non-existence of Cu *R*-chxn(acac)<sub>2</sub> and Cu *S*-chxn(acec)<sub>2</sub> as a consequence. However, as formylcamphor does not have a methyl group at the keto group involved in Schiff base formation, Cu *R*-chxn(fmc)<sub>2</sub> and Cu *S*-chxn(fmc)<sub>2</sub> exist. The fact that Cu *R,S*-chxn(acac)<sub>2</sub> exists<sup>12</sup> may, in combination with the other observations mentioned above and through conformational calculations, give detailed information about nonbonding interactions in this type of complexes.

Focusing now on the three CD-bands in the ligand field range we may first of all stress the agreement between the actual number of bands and the number predicted by the model in use. Secondly, we can assign transitions, and for that purpose note that of the three transitions  $(xy) \leftarrow (x^2 - y^2)$ ,  $(xy) \leftarrow (xz)$  and  $(xy) \leftarrow (z^2)$  the latter is both electric as well as magnetic dipole forbidden, whereas the two former transitions are electric dipole forbidden but magnetic dipole allowed. This means in the present model that a Cotton effect connected to the transition  $(xy) \leftarrow (z^2)$  must be small, since both electric and magnetic transition moments are "borrowed".

From earlier investigations of our model we know definitely that the high-energy Cotton effect under  $\pi^* \leftarrow \pi$  and the Cotton effect under  $(xy) \leftarrow (xz)$  are interrelated in such a way as to have opposite signs, since the phases in the construction of the molecular orbitals are chosen so that the overlap integrals between metal *d* orbitals and ligand  $\pi$  orbitals are positive in a planar or near planar complex.<sup>6</sup>

Thus in Fig. 1 the bands at  $\sim 13\,000\text{ cm}^{-1}$  are assigned as  $(xy) \leftarrow (x^2 - y^2)$ , the bands at  $15\,000\text{ cm}^{-1}$  as  $(xy) \leftarrow (z^2)$  and the bands at  $18\,000\text{ cm}^{-1}$  as  $(xy) \leftarrow (xz)$ .

Since five out of seven transitions have been assigned, the bands around  $22\,000\text{ cm}^{-1}$  are accordingly assumed to be the  $\pi^* \leftarrow \pi$  transitions.

Carrying the discussion a little further we may consider the CD-spectra of neutral inner-sphere

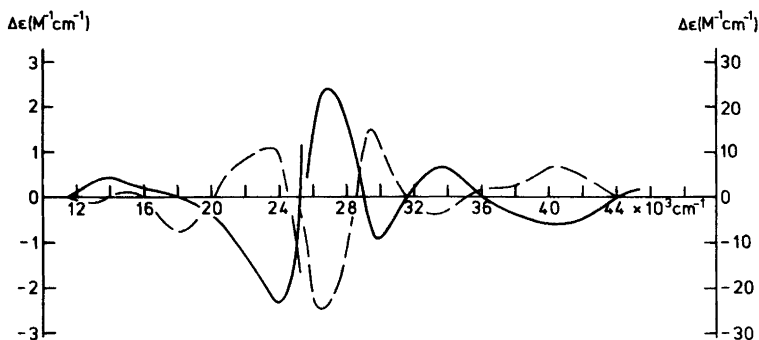


Fig. 3. CD spectra of Cu *R*-pn(fmc)<sub>2</sub> (—) and Cu *S*-pn(fmc)<sub>2</sub> (---).

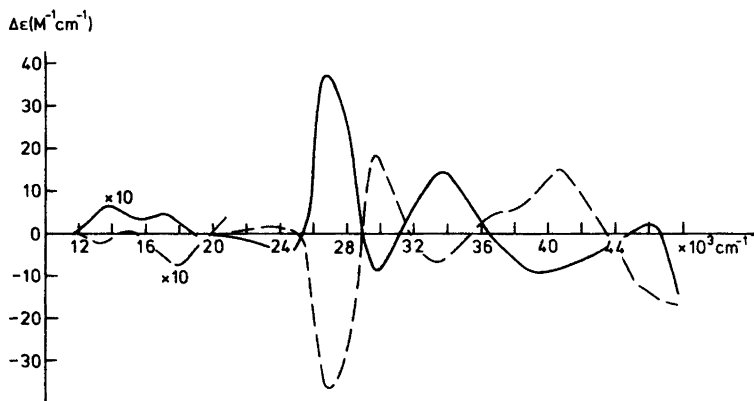


Fig. 4. CD spectra of Cu *R*-2,3-bn(fmc)<sub>2</sub> (—) and Cu *S*-2,3-bn(fmc)<sub>2</sub> (---).

copper(II) complexes of *R*- and *S*-pn(fmcH)<sub>2</sub> (Fig. 3) and of *R*- and *S*-2,3-bn(fmcH)<sub>2</sub> (Fig. 4), respectively.

Considering the  $\pi^* \leftarrow \pi$  transition region of these complexes, it is worth noting that the ligands change chirality on complexation just as it is the case with the acetylacetonone analogues,<sup>3,4,6</sup> and this is, of course, possible since the barrier towards rotation around the substituted ethylene bridge in these cases is relatively low. Suggestions as to the cause of this change in chirality as well as to the route of rotation may only be given through a detailed conformational analysis, involving also the information about non-bonding interactions which may be gathered from the experimental evidences about the copper(II) complexes of cyclohexanediamine Schiff base derivatives mentioned above.

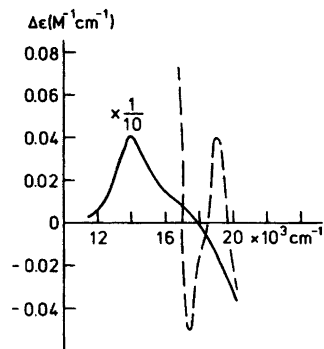


Fig. 5. CD spectra of Cu *R*-pn(fmc)<sub>2</sub> in methanol at room temperature (—) and in EPA at  $-187^\circ\text{C}$  (---).

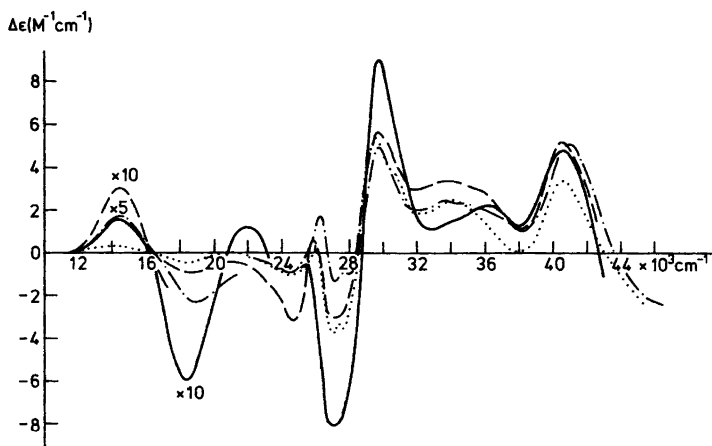


Fig. 6. CD spectra of Cu en(fmc)<sub>2</sub> (—) Cu ibn(fmc)<sub>2</sub> (---) Cu R,S-chxn(fmc)<sub>2</sub> (-·-) and Cu R,S-2,3-bn(fmc)<sub>2</sub> (···).

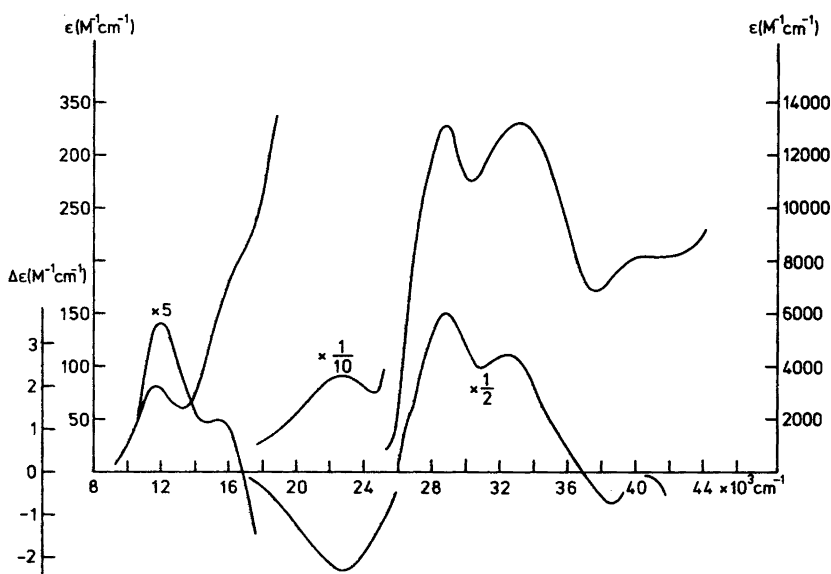


Fig. 7. Absorption and CD spectra of Cu tn(fmc)<sub>2</sub>.

With this point noted we may from the spectra conclude that Cu *R*-pn(acac)<sub>2</sub>, Cu *R*-2,3-bn(fmc)<sub>2</sub> and Cu *R*-pn(fmc)<sub>2</sub> have the same absolute configuration ( $\Lambda$ )<sup>14</sup> and the corresponding compounds of *S* configuration the opposite ( $\Delta$ ).<sup>14</sup>

The ligand field ranges of Figs. 3 and 4 are seen to be in accordance with the assignments given above

in the case of cyclohexanediamine derivative complexes, although the three ligand field bands as far as concerns Cu *R*-pn(fmc)<sub>2</sub> are only visible on cooling (Fig. 5), and although the (*xy*)←(*z*<sup>2</sup>) band (presumably negative) in the case of Cu *R*-2,3-bn(fmc)<sub>2</sub> seems to be cancelled to a major extent by the two visible positive components.

The stereochemical induction from the camphor group itself may also be studied in this type of complexes preparing Schiff bases with optically inactive diamines, examples of which are given in Fig. 6. Obviously the predominating absolute configuration in these compounds are the same ( $\Delta$ ), and it is especially interesting to note that contrary to the case of complexes with optically active diamines we here observe no difference between the chirality of the derivative of cyclohexanediamine and the other substituted ethylenediamine derivatives.

Generally, however, the Cotton effects are rather small and furthermore only four bands are clearly visible in the range  $12\,000\text{--}26\,000\text{ cm}^{-1}$ . The "missing" band seems to be in the ligand field range, and this is not surprising as we already have argued for the  $(xy)\leftarrow(z^2)$  transition to be of small intensity.

It has earlier been demonstrated that the introduction of a three-membered chain between the two chromophoric parts instead of the ethylene bridge changes the spectral properties radically as, e.g., the  $\pi^*\leftarrow\pi$  transition region of  $\text{Cu tn}(\text{acac})_2$  shows the transition moments to be much more co-planar than in, e.g.,  $\text{Cu pn}(\text{acac})_2$ .<sup>6</sup>

We may with formylcamphor as chromophoric part investigate this point a little further, since the ligand  $\text{tn}(\text{fmcH})_2$  is optically active, and spectral properties of the copper(II) complex are shown in Fig. 7.

As is seen, neither the absorption nor the CD-spectra show properties typical of exciton coupling which demonstrates the postulated planarity of the compound.

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

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Received May 22, 1978.