

On the Molecular Structure of VO^{2+} and Ni^{2+} Complexes with Schiff Bases of Formylcamphor and Diamines

HANS PETER JENSEN

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

Previously a rather simple model, usable on transition metal complexes for the explanation of intensity in circular dichroism (CD) spectra under absorptions which may be described mainly by d -orbitals, has been proposed.¹ Although the model is not general it may well be dominating for complexes with ligands having internal transitions which in energy are not very much separated from the ligand field transitions.

Certainly the model has proven operative for complexes of Cu^{2+} with Schiff bases derived from acetylacetonone^{1,2} and formylcamphor (prepared from natural (+)-camphor)³ as well as for VO^{2+} and Ni^{2+} complexes of the former type of ligand.¹

Obviously it is important to verify as firmly as possible the suggested model. Consequently, to extend the experimental basis, various neutral inner-sphere complexes of VO^{2+} and Ni^{2+} with formylcamphor Schiff bases of 1,2-diamines have been prepared and spectroscopically investigated.

The proposed model operates in two stages which are, however, intimately related. Firstly, the absolute configuration of a given chiral complex is determined in terms of handedness of a pair of vectors representing the allowed, polarized internal ligand $\pi^* \leftarrow \pi$ transitions. Secondly, the ligand field CD-spectrum may be interpreted using simple LCAO-MO theory and the assumption that the $d \leftarrow d$ transitions borrow electric transition dipole moments for production of rotatory strength from the internal ligand transitions used in the structural assignment.

Studying complexation of formylcamphor Schiff bases it is, however, necessary to be aware of some complicating experimental facts which influence the otherwise obvious comparisons with analogous Schiff bases of acetylacetonone.

The condensation products between diamines and formylcamphor show a configuration of the ketoenamine groups which is strongly dependent on the choice of solvent. *I.e.*, in chloroform these chromophores have dominantly a *syn* (*Z*) structure with intramolecular hydrogen bonding, whereas in methanol solutions an *anti* (*E*) structure is the most abundant.^{4,5}

In preparing Cu^{2+} complexes of such ligands from methanol-water mixtures, complexation occurs with the *syn* isomer since spectra of the formylcamphor Schiff base complexes are similar to those of the corresponding acetylacetonone complexes. Furthermore, with respect to 1,2-diamines with low barrier towards rotation around the substituted ethylene bridge, the Schiff bases change configuration (handedness of the set of $\pi^* \leftarrow \pi$ transition moments) on complexation,³ just as do the acetylacetonone analogues.^{6,1}

These facts mean that the envelope of the CD spectrum in the $\pi^* \leftarrow \pi$ transition region (representing exciton coupling) of the Schiff base between *trans*-(*R,R*)-(-)-1,2-cyclohexanediamine and formylcamphor [*R*-chxn(fmch)₂] in methanol (298 nm $\Delta\epsilon = -52$, 333 nm $\Delta\epsilon = 61$)⁴ reverses in chloroform (300 nm $\Delta\epsilon = 45$, 340 nm $\Delta\epsilon = -47$)⁴ and on complexation with Cu^{2+} [*Cu R*-chxn(fmch)₂] (333 nm $\Delta\epsilon = 21$, 371 nm $\Delta\epsilon = -48$),³ whereas the envelope of the Schiff base between *R*-(+)-1,2-propanediamine and formylcamphor [*R*-pn(fmch)₂] in methanol (295 nm $\Delta\epsilon = -24$, 333 nm $\Delta\epsilon = 36$)⁴ reverses in chloroform (296 nm $\Delta\epsilon = 23$, 333 nm $\Delta\epsilon = -30$)⁴ and reverts again on complexation with Cu^{2+} [*Cu R*-pn(fmch)₂] (333 nm $\Delta\epsilon = -10$, 371 nm $\Delta\epsilon = 26$).⁴

With these points noted, we may consider ligand range CD spectra of VO^{2+} complexes of formylcamphor Schiff bases prepared according to standard procedure^{7,8} and identified through chemical analysis.

The CD envelope of *VO R*-chxn(fmch)₂ is characteristic by being similar to that of the free ligand in methanol (297 nm $\Delta\epsilon = -42$, 331 nm $\Delta\epsilon = 54$) which is opposite to the case of the corresponding Cu^{2+} complex, and since cyclohexanediamine does not allow rotation around the substituted ethylene-bridge in *R*-chxn(fmch)₂ it is concluded that the chromophoric parts of the ligand in *VO R*-chxn(fmch)₂ take on the *anti* configuration.

As far as concerns *VO R*-pn(fmch)₂, the ligand part of the CD spectrum has low intensity and is furthermore uncharacteristic in shape with respect to exciton coupling as it contains only one extremum ($\Delta\epsilon_{\text{max}} = 6$ at 330 nm). With the result presented above for *VO R*-chxn(fmch)₂ also taken into consideration, it may tentatively be concluded that *VO R*-pn(fmch)₂ exhibits an almost planar coordination of the quadridentate ligand having the chromophoric parts in *anti* configuration.

What has been said about spectra of VO^{2+} complexes of formylcamphor Schiff bases is also true for the corresponding Ni^{2+} complexes; thus *Ni R*-chxn(fmch)₂ exhibits a CD spectrum characteristic of having the chromophoric parts in *anti* configuration, and *Ni R*-pn(fmch)₂ a CD spectrum of low intensity and uncharacteristic shape.

It thus materializes that it is impossible to present a discussion concerning the electronic transitions in the ligand field range of these complexes within the model mentioned above,¹ as the molecular geometry of the ligand parts is quite different from that of acetylacetonone, *i.e.* the relative position of the exciton coupled $\pi^* \leftarrow \pi$ transitions to the substituted ethylene bridge between the two chromophoric parts is ill-defined.

A study of acetylcamphor Schiff base complexes, however, would be worthwhile, as these ligands are known to behave spectroscopically similar to acetylacetonone Schiff bases.⁹

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