

Molecular and Electronic Structure in Copper(II) Complexes with Schiff Bases of β -Diketones and Diamines, and a Comparison with the Corresponding Vanadyl and Nickel(II) Complexes. A Study of the Absorption and Circular Dichroism Spectra

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Absorption and circular dichroism spectra of the internal ligand $\pi \rightarrow \pi^*$ transitions in complexes such as the copper(II) complex of the Schiff base from (*R*)-1,2-propanediamine and two molecules of acetylacetone have been studied. The results have been interpreted by means of exciton theory to give information about stereochemistry. It is found that this complex in solution has a structure halfway between tetrahedral and planar arrangement. The corresponding oxovanadium(IV) complex is closer to planarity, and the nickel(II) complex is found to be planar. Interpretations of the circular dichroism spectra of these complexes are based upon simple LCAO-MO theory and the assumption that the $d \rightarrow d$ transitions borrow electric transition dipole moments from the nearest allowed transitions: the ligand $\pi \rightarrow \pi^*$ transitions. The level order for the d -orbitals in the copper complex seems to be $(xy) > (x^2 - y^2) > (xz)$, $(yz) > (z^2)$.

In the crystalline state, many copper(II) complexes are found to have varying coordination numbers. For example, several adducts of tetra-coordinated complexes exist, such as the anhydrate, the hemihydrate, and the monohydrate of the copper(II) complex with 4,4'-(ethylenediimino)-di(3-penten-2-one).¹⁻³ Also, in the molecular structures of copper complexes, a profound irregularity has been found. Thus bis(ethylenediamine) copper(II) complexes are strongly distorted⁴ relative to the structure of, for example, *trans*-di-bromo-bis(ethylenediamine) cobalt(III).⁵ From crystal structures in general it appears that copper(II) complexes are less regularly

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built than the corresponding cobalt(III) and nickel(II) complexes. Although already in 1942 it was asserted⁶ that $\text{Ni en}(\text{fmc})_2^*$ was highly distorted from planarity because of the appreciable magnitude of the optical rotatory dispersion, very little information about the molecular structure of complexes in solution exists. In this paper, use will be made of the internal ligand transitions in some copper, nickel, and oxovanadium(IV) complexes analogous to copper acetylacetonate to give information on the relative orientation of the two conjugated planar ligands in solution. The pertinent $\pi \rightarrow \pi^*$ ligand transitions in dimeric molecules such as $R\text{-pn}(\text{acacH})_2^7$ have been rationalized by exciton theory.

Geometry of Cu R-pn(acac)₂ in solution. The absorption spectrum of Cu $R\text{-pn}(\text{acac})_2$ shown together with the circular dichroism in Fig. 1 have some

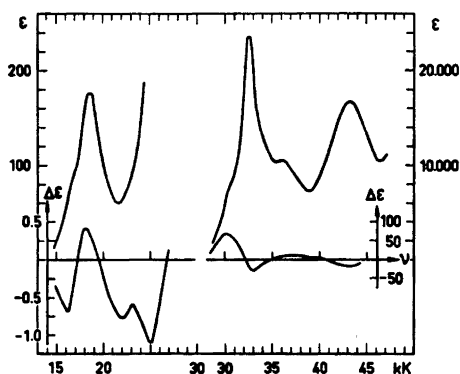


Fig. 1. Molar absorption and circular dichroism spectra of Cu $R\text{-pn}(\text{acac})_2$ in methanol solution.

characteristic regions. In the range 15–23 kK are the “ $d \rightarrow d$ ” transitions, and at 29–35 kK are bands which are attributed to the essentially internal ligand transitions because they are found in the same wavelength range as in the free ligand. At higher energy, more bands are observed. They may be due to allowed charge transfer transitions.

The transition dipole strength of the bands assigned as due to the $\pi \rightarrow \pi^*$ transition on the ligand is $1.3 \times 10^{-19} \text{ cm}^{-1} \text{ cm}^3$ compared with $2.2 \times 10^{-19} \text{ cm}^{-1} \text{ cm}^3$ in the free ligand.⁷ The relatively good agreement is taken as an additional indication of the correct assignment to this band, since both σ and π bonding to the metal may influence the intensity. The band is split into two apparent components with an energy separation of $\sim 3.5 \text{ kK}$. The origin of this splitting could be π bonding in a planar complex, as Cotton *et al.*¹⁴ have shown by an extended Hückel calculation. Or, the origin of the splitting could be exciton splitting of the excited states in a nonplanar (screwed) complex. The latter explanation will be used here, because Cu $R\text{-pn}(\text{acac})_2$ exhibits large Cotton

* The abbreviations used are: en for ethylenediamine, pn for 1,2-propanediamine, tn for 1,3-propanediamine, chxn for *trans*-1,2-cyclohexanediamine, acacH for acetylacetonate, fmcH for formylcamphor (from natural (+)_D-camphor), sal for salicylaldehyde, and combinations as en(acacH)₂ for the “Schiff base” formed from one molecule of diamine and two molecules of the diketone (really enamines).

effects in the range of the $\pi \rightarrow \pi^*$ transitions, and this means that these transitions cannot take place in the same plane. As a consequence of the claimed large distortion from planarity it follows, that the π bonding between metal and ligand in this complex is small.

Following the procedure given previously⁷ the angle θ between the two transition moments is calculated from

$$\tan^2 \theta / 2 = D_- / D_+$$

where D_- and D_+ are the integrated intensities of the low and high energy components, respectively. These magnitudes are not accurately determined because of overlap of the bands. Thus an experimentally estimated θ value of 45° is uncertain by as much as $\pm 50\%$.

Within the exciton formulations, and provided that the two transition moments both are perpendicular to the line which connects their centers, the energy splitting can be calculated from (see eqn. 6, Ref. 7)

$$\Delta E = 2r^{-3} D_{\text{monomer}} \cos \theta$$

where r is the distance between the transition moments of the two $\pi \rightarrow \pi^*$ transitions, and D is the dipole strength of half the quadridentate ligand.

Using the experimental values $D_{\text{dimer}} = 2D_{\text{monomer}} = 1.3 \times 10^{-19} \text{ cm}^{-1} \text{ cm}^3$, $\theta = 45^\circ$ and $\Delta E = 3.5 \text{ kK}$, the value for r in the above equation is found to be 3.0 \AA in agreement with assumed intramolecular distances.

The circular dichroism spectrum in the $30 - 35 \text{ kK}$ range exhibits two Cotton effects, coming from the two resultant exciton transitions. The positive sign of the low energy component must originate from a right handed helical transition. Thus the deviation from planarity has been found with sign as shown in Fig. 2.

The experimental rotatory strength, R_+ , for this band is $4.6 \times 10^{-23} \text{ cm}^{-1} \text{ cm}^3$, which is reasonably close to the value 15×10^{-23} calculated, using the above found geometrical parameters θ and r :⁷

$$R_+ = -\pi E_+(P_1 \times P_2) \frac{r}{2} = \pi E_+ D_+ \frac{r}{2} \sin \theta = \frac{46.2 \times 10^{-24}}{4} \int \frac{\Delta \epsilon}{\nu} d\nu \text{ cm}^{-1} \text{ cm}^3$$

The cancellation of the two circular dichroism components seems more important in the complex than for the free ligand where $R_- = 12 \times 10^{-23} \text{ cm}^{-1} \text{ cm}^3$ (the $\Delta \epsilon$ curves in Figs. 1 and 2 of Ref. 7 should be multiplied with 10).

It is often valuable in stereochemical work to make compounds of high rigidity, and, for example, (*R,R*)-chxn(acacH)₂ was used when the free ligands were considered. It would indeed be desirable to use this as a ligand in a copper complex. However, we have been unable to prepare Cu (*R,R*)-chxn(acac)₂. Also Schwarzenbach has reported such negative attempts.⁸ A negative result seems predictable from considerations on stereochemical models; it is remarkable that (*R,S*)-chxn(acacH)₂ forms a complex.⁸

It has been noted⁷ that in the comparatively rigid molecule *R*-pn(acacH)₂, the dissymmetric configuration of the pair of skew lines formed by the electric transition dipole moments was determined by the methyl group on the diamine bridge. However, in *R*-pn(fmch)₂, the bulk of the asymmetric camphor groups was

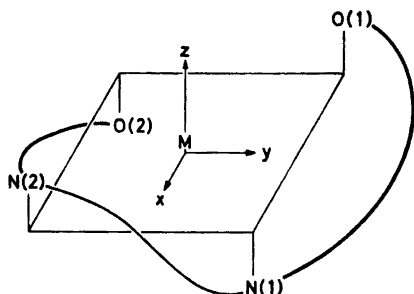


Fig. 2. Cu *R*-pn(acac)₂. An indication of the structure and the absolute configuration of the chiral system, formed by the conjugated ligand parts.

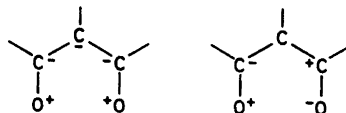


Fig. 3. Sign of the eigenvectors in 3π and 4π orbitals in acac⁻, respectively.

the dominating factor, since en(fmcH)₂ and *R*-pn(fmcH)₂ gave nearly identical UV circular dichroism of opposite sign to that of *R*-pn(acacH)₂. The complexes Cu en(fmc)₂ and Cu *R*-pn(fmc)₂ exhibit circular dichroism of opposite sign in the 30–35 kK range, and the curve for the latter complex is similar to that of Cu *R*-pn(acac)₂. Therefore, in the complexes, a methyl group on the diamine bridge is the determining steric factor.

Comparison with crystal structures. A number of Schiff base complexes have been investigated by X-ray crystallography. The only obviously pertinent examples are those provided by Hall and Waters,¹⁻³ of Cu en(acac)₂ with 0, 1/2, and 1 H₂O. The molecular structures are irregular but much more planar than claimed here for the structure in solution. However, when the deviation of the donor atoms from their mean plane is calculated, the screwed structure is definitely demonstrated as shown in Table 1. A large number of complexes of Schiff bases of salicylaldehyde have been investigated in the crystalline

Table 1. Literature values for the atomic coordinates have been used to insert an orthogonal coordinate system such that (a) the ligators define the *x,y* plane (least mean squares), (b) the *x* axis is the projection in this plane of the line passing the midpoints between the two oxygens and the two nitrogens, respectively, (c) the *z* axis is normal to the *x,y* plane and passes through the metal ion. The *z* coordinate for copper is given to demonstrate the irregularities far beyond experimental uncertainty.

| Compound | Ref. | <i>z</i> -coordinates in Å of | | | | Cu |
|---|------|-------------------------------|-------|--------------------|--------|-------|
| | | O (1) | O (2) | N (1) | N (2) | |
| Cu en(acac) ₂ | 1 | -0.019 | 0.018 | 0.009 ^a | -0.008 | 0.028 |
| Cu en(acac) ₂ , 1/2 H ₂ O | 2 | -0.056 | 0.056 | 0.047 | -0.046 | 0.005 |
| Cu en(acac) ₂ , H ₂ O | 3 | -0.033 | 0.030 | 0.030 | -0.033 | 0.186 |
| Cu en(sal) ₂ | 11 | -0.035 | 0.031 | 0.033 | -0.037 | 0.158 |

^a The computed *x,y* coordinates for this atom seem to be wrong and it is supposed that the original paper¹ contains a misprint for the coordinates to this atom.

state as well as in solution. The geometry of such complexes varies from planarity to nearly tetrahedral structures.^{9,10} The geometrical arrangement of Cu en(sal)₂¹¹ is analogous to that of Cu en(acac)₂ (see Table 1).

Electronic structure. The main object for the following discussion is the origin to the circular dichroism bands observed under the absorption due to ligand field transitions. These transitions are forbidden to the first order in electric dipole excitation. However, in the low symmetry of Cu en(acac)₂, *d*→*d* transitions mix with allowed transitions of the same symmetry. The 29–35 kK transitions are the nearest source, and we shall, in what follows, adopt the working hypothesis that the electronic spectrum in the 15–23 kK region predominantly is produced by those *d*→*d* transitions which gain their intensity from the 29–35 kK π → π^* ligand transitions. The mixing will be described within an LCAO-MO formulation, using a simplified modification of the scheme outlined by Liehr.¹²

Referring to the above found geometry for Cu R-pn(acac)₂ we note that the chromophoric symmetry cannot be higher than *C*₂, but we shall characterize the orbitals and the states by the irreducible representations belonging to the *D*₂ point group. Since we are mainly interested in the π orbitals, where empirical Hückel parameters are not very different for N and O,¹³ this is a less drastic restriction than it would be for complexes with only σ ligands. Thus the basis orbitals in the discussion are:

(1) the ligand p_π orbitals directed along *z'* which may or may not be parallel to the *xz* plane (Fig. 2). Each (1 and 2) conjugated ligand skeleton forms the basis for the five ligand orbitals of the form $n\pi = \sum_{i=1}^5 c_{i,n} p_{z',i}$.

The highest occupied (3 π) orbital and the lowest unoccupied (4 π) orbital have the forms sketched in Fig. 3. From these orbitals are formed composite molecular orbitals which transform as the irreducible representations of the *D*₂ point group. Using the coordinate system of Fig. 2, these composite MO's are:

$$\begin{aligned} 4\pi(b_2) &= (4\pi_1 - 4\pi_2)/\sqrt{2} \\ 4\pi(a) &= (4\pi_1 + 4\pi_2)/\sqrt{2} \\ 3\pi(b_1) &= (3\pi_1 + 3\pi_2)/\sqrt{2} \\ 3\pi(b_3) &= (3\pi_1 - 3\pi_2)/\sqrt{2} \end{aligned}$$

The ligand π orbitals combine in molecular orbitals with some of

(2) the metal 3*d* orbitals.

The transformation properties of the basis orbitals are given in Table 2. The relative energies of the *d* orbitals and the π orbitals are important for the form of the molecular orbitals. Extended Hückel MO calculations indicate the relative energies $3\pi \approx 3d < 4\pi$ for a similar system but with a different (planar) symmetry.¹⁴ However, there seem to be rather small spectral differences between crystalline Cu acac₂ and dissolved Cu en(acac)₂; therefore we assume a qualitatively similar structure with the *b*₁(*xy*) orbital less stable than the 3 π orbitals. Then the molecular orbitals are of the form given in Table 3 in the order of increasing stability. The ground state becomes

$${}^2B_1 = |\bar{b}_1^+ \bar{b}_1^- \bar{b}_3^+ \bar{b}_3^- a^+ a^- \bar{b}_2^+ \bar{b}_2^- \bar{b}_3^+ \bar{b}_3^- a^+ a^-|$$

where the + or - denote α and β spin, respectively, and arbitrarily the $3d(a)$ orbitals are differentiated by an asterisk.

The 29–35 kK transitions may now be described as being due to excitation of an electron in the “ 3π ” orbitals b_1' or b_3' to the “ 4π ” orbitals a' or b_2' . In the exciton formulations of Ref. 7, the pertinent transitions are to the two doublet states

$${}^2B_2\pi = \frac{1}{2} \left[|\bar{b}_1^{\dagger} \bar{b}_2^{\dagger} \bar{b}_3^{\dagger} \bar{b}_3' \bar{b}_1^{\dagger}| - |\bar{b}_1^{\dagger} \bar{b}_2^{\dagger} \bar{b}_3^{\dagger} \bar{b}_3' \bar{b}_1^{\dagger}| + |\bar{b}_1^{\dagger} \bar{b}_1^{\dagger} \bar{b}_3^{\dagger} \bar{a}' \bar{b}_1^{\dagger}| \right. \\ \left. - |\bar{b}_1^{\dagger} \bar{b}_1^{\dagger} \bar{b}_3^{\dagger} \bar{a}' \bar{b}_1^{\dagger}| \right]$$

$${}^2A\pi = \frac{1}{2} \left[|\bar{b}_1^{\dagger} \bar{a}' \bar{b}_3^{\dagger} \bar{b}_3' \bar{b}_1^{\dagger}| - |\bar{b}_1^{\dagger} \bar{a}' \bar{b}_3^{\dagger} \bar{b}_3' \bar{b}_1^{\dagger}| + |\bar{b}_1^{\dagger} \bar{b}_1^{\dagger} \bar{b}_3^{\dagger} \bar{b}_2' \bar{b}_1^{\dagger}| \right. \\ \left. - |\bar{b}_1^{\dagger} \bar{b}_1^{\dagger} \bar{b}_3^{\dagger} \bar{b}_2' \bar{b}_1^{\dagger}| \right]$$

where the filled $3d$ orbitals are omitted for convenience.

Two of the d -excited states have the same symmetries as these π -excited states (see Table 2), and following our working hypothesis, we shall now investigate if it is possible to explain the ligand field part of the absorption and circular dichroism spectra by considering only these two d -excited states.

Table 2. The table shows how the basis ligand π orbitals and the metal $3d$ orbitals transform in the point group D_2 . The subscripts to the π orbitals refer to the ligand part with positive (1) or negative (2) y coordinates (see Fig. 2). To the right, the assignments of the Cotton effects observed for Cu R -pn(acac) $_2$.

| Orbital levels | | Doublet states | | | |
|----------------|---|--|--------------------------|-----------|----------------------|
| Type | Representations in D_2 | Type | Representations in D_2 | Energy kK | Sign (Cotton effect) |
| 4 π | $b_2 = (4\pi_1 - 4\pi_2)/\sqrt{2}$, $a = (4\pi_1 + 4\pi_2)/\sqrt{2}$ | π -Excited states | $B_2\pi$ | 32.6 | — |
| 3 d | b_1 $\begin{cases} (xy) \\ (x^2 - y^2) \end{cases}$ | | $A\pi$ | 30 | + |
| | a $\begin{cases} (x^2 - y^2) \\ (xz), (yz) \end{cases}$ | $A(?)$ | 22 | — | |
| | b_2, b_3 $\begin{cases} (xz), (yz) \\ (z^2) \end{cases}$ | d -Excited states $\begin{cases} B_2, B_3(?) \\ A \end{cases}$ | 18.5 | + | |
| 3 π | $b_1 = (3\pi_1 + 3\pi_2)/\sqrt{2}$, $b_3 = (3\pi_1 - 3\pi_2)/\sqrt{2}$ | Ground state | B_1 | 0 | — |

Table 3. Unnormalized molecular orbitals for the copper(II) complex arranged in three groups after energy. All mixing coefficients are positive, except c_6 (see text). The a molecular orbital represents the essentially $(x^2 - y^2)$ orbital, and (z^2) is omitted for convenience. Primed orbitals are essentially ligand π orbitals.

$$a' = 4\pi(a) - c_1 3d(a)$$

$$b_2' = 4\pi(b_2) - c_2 3d(b_2)$$

$$b_1 = 3d(b_1) - c_3 3\pi(b_1)$$

$$b_1' = 3\pi(b_1) + c_4 3d(b_1)$$

$$b_3' = 3\pi(b_3) \pm c_5 3d(b_3)$$

$$a = 3d(a) + c_6 4\pi(a), \quad b_2 = 3d(b_2) + c_7 4\pi(b_2), \quad b_3 = 3d(b_3) \mp c_8 4\pi(b_3)$$

Introducing the molecular orbitals of Table 3 it is found that the pertinent matrix elements for the electric and magnetic transition moments P and M , respectively, for the x (Fig. 2) polarized transitions are:

$$\begin{aligned}
 P_{\pi}^x &= \langle {}^2B_1 | er | {}^2B_2^{\pi} \rangle = \langle b_1' | ex | b_2' \rangle + \langle b_3' | ex | a' \rangle \sim \\
 &\quad \langle 3\pi_1 | ex | 4\pi_1 \rangle - \langle 3\pi_2 | ex | 4\pi_2 \rangle = P_x \hat{\mathbf{i}} \\
 P_d^x &= \langle {}^2B_1 | er | {}^2B_2^d \rangle = \langle b_2 | ex | b_1 \rangle \simeq -c_3 c_7 \langle 4\pi(b_2) | ex | 3\pi(b_1) \rangle = \\
 &\quad -\frac{1}{2} c_3 c_7 P_x \hat{\mathbf{i}} \\
 M_{\pi}^x &= \frac{e}{2mc} \langle {}^2B_2^{\pi} | L | {}^2B_1 \rangle = \frac{e}{2mc} [\langle b_2' | L_x | b_1' \rangle + \langle a' | L_x | b_3' \rangle] \sim \\
 &\quad \frac{e}{2mc} [\langle 4\pi_1 | L_x | 3\pi_1 \rangle - \langle 4\pi_2 | L_x | 3\pi_2 \rangle] = -M_x \beta_M \hat{\mathbf{i}} \\
 M_d^x &= \frac{e}{2mc} \langle {}^2B_2^d | L | {}^2B_1 \rangle = \frac{e}{2mc} \langle b_1 | L_x | b_2 \rangle \simeq \\
 &\quad \frac{e}{2mc} \langle xy | L_x | xz \rangle = -i \beta_M \hat{\mathbf{i}}
 \end{aligned}$$

and for the z polarized transitions:

$$\begin{aligned}
 P_{\pi}^z &= \langle {}^2B_1 | er | {}^2A^{\pi} \rangle = \langle b_1' | ez | a' \rangle + \langle b_3' | ez | b_2' \rangle \simeq \\
 &\quad \langle 3\pi_1 | ez | 4\pi_1 \rangle + \langle 3\pi_2 | ez | 4\pi_2 \rangle = -P_z \hat{\mathbf{k}} \\
 P_d^z &= \langle {}^2B_1 | er | {}^2A^d \rangle = \langle a | ez | b_1 \rangle = \frac{1}{2} c_3 c_6 P_z \hat{\mathbf{k}} \\
 M_{\pi}^z &= \frac{e}{2mc} \langle {}^2A^{\pi} | L | {}^2B_1 \rangle = -M_z \beta_M \hat{\mathbf{k}} \\
 M_d^z &= \frac{e}{2mc} \langle {}^2A^d | L | {}^2B_1 \rangle = \frac{e}{2mc} \langle b_1 | L_z | a \rangle \simeq \\
 &\quad \frac{e}{2mc} \langle xy | L_z | x^2 - y^2 \rangle = 2 i \beta_M \hat{\mathbf{k}}
 \end{aligned}$$

Thus the dipole (D) and rotatory strengths (R) for the two ligand field transitions are

$$\begin{aligned}
 D_d^x &= |P_d^x|^2 = \frac{1}{4} c_3^2 c_7^2 P_x^2 & R_d^x &= \frac{1}{2} c_3 c_7 P_x \beta_M \\
 D_d^z &= |P_d^z|^2 = \frac{1}{4} c_3^2 c_6^2 P_z^2 & R_d^z &= c_3 c_6 P_z \beta_M
 \end{aligned}$$

Both $d \rightarrow d$ transitions should accordingly exhibit positive Cotton effects, if c_3 , c_6 , and c_7 are all positive. The mixing coefficients in the molecular orbitals have signs not only dependent on the relative energies of the orbitals involved, but also dependent on the overlap integrals. The phases are chosen such that the overlap integrals between metal d orbitals and ligand π orbitals are positive

in a planar or nearplanar complex. The overlap integral between the two orbitals of A symmetry, $\langle x^2 - y^2 | 4\pi(a) \rangle$, represents a problem since it is zero in a regular planar arrangement. In the very distorted Cu R -pn(acac)₂, even the sign of the overlap integral is impossible to evaluate because the conjugated ligand parts most probably are bent relative to each other in such a way that the ligand π orbitals no longer are parallel to the xz plane (Fig. 2). Also in crystal structures are reminiscences of a bent structure in the complexes. When the distortion from planarity is as large as it is in the copper complex, it seems quite reasonable that the bending of the two acetylacetonate parts towards each other is pronounced, otherwise the ethylene bridge would not be long enough. Here, it is pertinent to notice that we have not been able to make the corresponding zinc complex which we expected to take on a tetrahedral structure.

In the region 15–19 kK is observed a negative and a positive Cotton effect. The positive Cotton effect is assigned to the ${}^2B_1 \rightarrow {}^2B_2^d$ transition, and the negative to the ${}^2B_1 \rightarrow {}^2A^d$ transition. This gives accordance between the sign of the Cotton effects and the known positive signs of c_3 and c_7 , and it follows then that c_6 and $\langle x^2 - y^2 | 4\pi(a) \rangle$ are negative.

If the observed value for the ratio $D_\pi^s/D_\pi^x \sim \frac{1}{10}$ is inserted in the expression for the calculated ratio D_d^s/D_d^x observed to be $\sim \frac{1}{4}$, $|c_6|/|c_7|$ is found to be $\sqrt{10/4}$: $D_d^s/D_d^x = c_3^2 c_6^2 D_\pi^s / (c_3^2 c_7^2 D_\pi^x) = \frac{c_6^2}{c_7^2} \frac{1}{10} = \frac{1}{4} \rightarrow \left| \frac{c_6}{c_7} \right| = \sqrt{\frac{10}{4}}$

This ratio between the eigenvectors inserted in the expression for the ratio between the numerical value of the rotatory strengths gives

$$|R_d^s|/|R_d^x| = 2 \left| \frac{c_6}{c_7} \right| \left(\frac{D_\pi^s}{D_\pi^x} \right)^{\frac{1}{2}} \sim 2 \sqrt{\frac{10}{4}} \sqrt{\frac{1}{10}} = 1$$

The experimental ratio between the rotatory strengths is estimated to 1.5 and may be too big because of cancellation of R_d^x from the Cotton effects of higher energy. Therefore, there seems to be a satisfactory numerical self-consistency.

The use of unnormalized molecular orbitals should not introduce significant numerical errors, since the mixing coefficients are small.

Such considerations lead to assignments which are summarized in Table 2. The positive Cotton effect at 18 kK is attributed to the $(xz) \rightarrow (xy)$ ($B_1 \rightarrow B_2$) transition. Of the two $d \rightarrow d$ transitions with B_1 symmetry, essentially $(x^2 - y^2) \rightarrow (xy)$ and $(z^2) \rightarrow (xy)$, only the former has a first order magnetic transition moment, and only this transition should exhibit a large Cotton effect. The negative Cotton effect at 16 kK is assigned to the $(x^2 - y^2) \rightarrow (xy)$ transition. The $(yz) \rightarrow (xy)$ ($B_1 \rightarrow B_3$) transition should not, according to the used model, give rise to any Cotton effect. However, the energy of this transition may very well be close to that of the $B_1 \rightarrow B_2^d$ transition.

The transition $(z^2) \rightarrow (xy)$ could have higher energy than the other $d \rightarrow d$ transition because of the possibility of an efficient mixing of the (z^2) with the $(4s)$ orbital. As mentioned above, this transition does not give rise to any first order magnetic moment. A Cotton effect connected to this transition must be small, since both the electric and the magnetic transition moments are borrowed. Only

a detailed numerical analysis would enable us to predict the sign for this transition. The circular dichroism curve could indicate that this transition takes place at 22–23 kK. However, the main origin of the negative circular dichroism at 21–27 kK is not assigned to a $d \rightarrow d$ transition.

It is believed that the transition producing this Cotton effect is analogous to that giving a shoulder in the absorption curve for Cu acac_2 at 26 kK. This shoulder has caused much discussion in the literature, and it is now generally accepted that it is not a $d \rightarrow d$ transition, at least. Belford and Yeranov,¹⁵ and Jørgensen¹⁶ have tentatively assigned the transition as a $3\pi \rightarrow (xy)$ transition. This assignment is in agreement with the rather low intensity. However, the symmetries of the excited states should be B_1 and B_3 . These cannot mix with the π -excited states, and so no circular dichroism is expected. If, instead, the 25 kK band is due to the transitions $(xy) \rightarrow 4\pi$, two Cotton effects are expected, because then mixing with A^π and B_2^π is possible. The observed circular dichroism could be in accordance with this assignment proposed by Cotton.¹⁷ Also the transition from the non-bonding oxygen σ^n -orbitals (as opposed to the ligand π orbitals) to the 4π orbitals yield A and B_2 states ($n \rightarrow \pi^*$ transitions). So, also this proposition seems possible, and further, with this assignment, there is no difficulty in explaining the existence of circular dichroism bands in, for example, VO $R\text{-pn}(\text{acac})_2$ and in Ni $R\text{-pn}(\text{acac})_2$ (*vide infra*) at nearly the same wavelength.

The $3\pi \rightarrow 4\pi$ transitions at 30–34 kK have been commented on.

The experimental techniques used here do not distinguish very well between the various possibilities for the origin of the bands in the UV range above 35 kK, and they will not be discussed further.

The complex Cu $\text{tn}(\text{acac})_2$ (see Fig. 4) has a third methylene group in the bridge between the π systems. The absorption spectrum of this complex is rather different from that of Cu $\text{pn}(\text{acac})_2$. The difference must be a consequence of the change in the strain of the bridge from one conjugate part to the other. It is seen from the 30–32 kK band that the $\pi \rightarrow \pi^*$ transition moments are much more co-planar than in Cu $\text{pn}(\text{acac})_2$. In the visible region the absorption is much less intense than it is for Cu $\text{pn}(\text{acac})_2$. At *ca.* 25 kK, two shoulders are clearly visible. These shoulders may be the two components of the $\sigma^n \rightarrow \pi^*$ transitions.

In a recent paper, Downing and Urbach¹⁸ have reached the qualitative result that some Schiff base complexes of copper are non-planar. These authors emphasize the role of the methyl group on the bridging diamine in, for example, Cu $R\text{-pn}(\text{acac})_2$. The tentative assignments of the ligand field transitions proposed by Downing and Urbach are very different from those reached here, using a simple LCAO-MO model. The value of our model must of course be measured by its successful use on several systems. Therefore, a discussion of the nickel and vanadyl complexes analogous to Cu $R\text{-pn}(\text{acac})_2$ is relevant.

Ni $R\text{-pn}(\text{acac})_2$. In the preceding discussion it has been demonstrated that part of the UV absorption and circular dichroism spectra can be explained satisfactorily by the combined use of exciton and simple MO theory. The corresponding nickel complex seems more complicated. The spectra are shown in Fig. 5. The circular dichroism curve is similar to the extremum values published by Downing and Urbach.¹⁹ The ultraviolet part of the absorption does contain

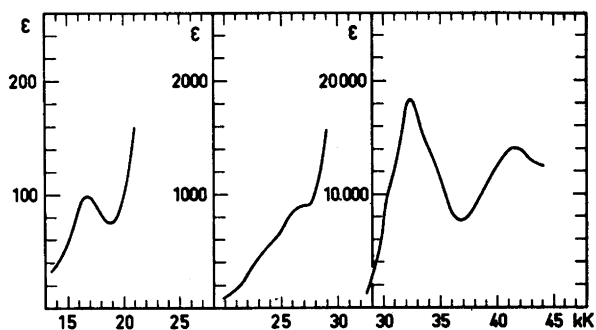


Fig. 4. Molar absorption spectrum of $\text{Cu pn}(\text{acac})_2$ in methanol solution.

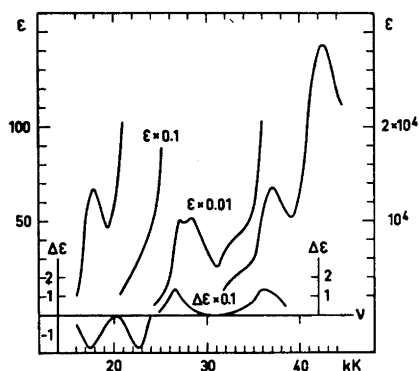


Fig. 5. Molar absorption and circular dichroism spectra of $\text{Ni R-pn}(\text{acac})_2$ in methanol solution.

a band which may be assigned as an essentially ligand $3\pi \rightarrow 4\pi$ transition, where complex formation has drastically modified both the transition energy (32 kK in both $\text{pn}(\text{acacH})_2$ and its copper complex, but 37 kK in $\text{Ni pn}(\text{acac})_2$) and the intensity (in $\text{Ni pn}(\text{acac})_2$ 0.46×10^{-19} , in $\text{Cu pn}(\text{acac})_2$ 1.3×10^{-19} , and in $\text{pn}(\text{acacH})_2$ $2.2 \times 10^{-19} \text{ cm}^{-1} \text{ cm}^3$). The absorption band contains a shoulder at the low energy side of the maximum with an apparent splitting of *ca.* 3 kK. However, the circular dichroism curve in this region is of very low intensity, and the pattern is not as expected for coupled chromophores with two Cotton effects of equal size but of opposite signs. Therefore, it is inferred that the complex (the chromophore) is very nearly planar on a time average. Thus, there may be a pronounced difference in the electronic structures of the copper and nickel complex of $\text{pn}(\text{acacH})_2$. A strong π bonding between metal and ligand is likely to exist in the nickel complex.

We may tentatively proceed a little further, using the same model as used for the copper complexes. The ionization potentials for nickel are not very different from those of copper; therefore, the same order of the molecular orbitals can be assumed with the ligand 3π orbitals lying below at least the most antibonding $3d$ orbital, and the ligand 4π orbitals at higher energy than this $3d$

orbital. When this is the case, the pertinent matrix elements are similar to those calculated for the copper complexes. Because of the symmetry, P_{π^*} is much smaller than P_{π^x} , and similarly c_6 is smaller than c_7 . Therefore, in this model, P_{d^*} becomes much smaller than P_d^x , and only one absorption band in the visible is expected. This absorption band, due to the $d \rightarrow d$ transition ($xz \rightarrow xy$), exhibits a negative Cotton effect, whereas the same transition exhibits a positive Cotton effect in Cu R -pn(acac)₂. This observation shows that Ni R -pn(acac)₂ is distorted from planarity in the direction opposite to the extremely distorted structure of the copper complex. Only one Cotton effect is observed under the absorption due to the $\pi \rightarrow \pi^*$ transitions. This seems to indicate that one of the π transition moments nearly vanishes because of an efficient mixing between the ligand π and $3d$ orbitals.

VO R -pn(acac)₂. The absorption and circular dichroism spectra have been reported previously.²¹ They show that the Schiff base complex is far from planar in solution, but less so than the copper complex. A recent crystal structure determination of VO en(acac)₂ shows that the π -system in this complex also in the crystalline state is non co-planar.²²

Table 4. Unnormalized molecular orbitals for the vanadyl complex arranged in groups after energy. All mixing coefficients are positive. The (z^2) orbital is omitted for convenience.

| | |
|------------------------------------|----------------------------------|
| $b_1 = 3d(b_1) - k_1 3\pi(b_1)$ | $b_3 = 3d(b_3) - k_3 3\pi(b_3)$ |
| $b_2 = 3d(b_2) \mp k_2 4\pi(b_2)$ | $a' = 4\pi(a) - k_5 3d(a)$ |
| $b_2' = 4\pi(b_2) \pm k_4 3d(b_2)$ | |
| <hr/> | |
| $a = 3d(a) + k_6 4\pi(a)$ | |
| <hr/> | |
| $b_1' = 3\pi(b_1) + k_7 3d(b_1)$ | $b_3' = 3\pi(b_3) + k_8 3d(b_3)$ |

There is a difference of some 35 kK in the $3d$ -ionization potentials for copper and vanadium. This enforces us to assume that even the least antibonding $3d$ orbital, ($x^2 - y^2$), is less stable than the 3π orbitals, so that the molecular orbitals for the vanadyl complex must take the forms given in Table 4. With these orbitals, the π and d transition moments of both allowed symmetries are:

$$P_{\pi^x} = \langle {}^2A | er | {}^2B_3^{\pi} \rangle = \langle b_1' | ex | b_2' \rangle + \langle b_3' | ex | a' \rangle \simeq P_x \hat{i}$$

$$P_d^x = \langle {}^2A | er | {}^2B_3^d \rangle = \langle a | ex | b_3 \rangle \simeq -\frac{1}{2} k_3 k_6 P_x \hat{i}$$

$$M_{\pi^x} = \frac{e}{2mc} \langle {}^2B_3^{\pi} | L | {}^2A \rangle = \frac{e}{2mc} [\langle b_2' | L_x | b_1' \rangle + \langle a' | L_x | b_3' \rangle] = -M_x \beta_M \hat{i}$$

$$M_d^x = \frac{e}{2mc} \langle {}^2B_3^d | L | {}^2A \rangle = \frac{e}{2mc} \langle b_3 | L_x | a \rangle \simeq -i \beta_M \hat{i}$$

$$\begin{aligned}
 P_{\pi}^z &= \langle {}^2A | er | {}^2B_1^{\pi} \rangle = \langle b_1' | ez | a' \rangle + \langle b_3' | ez | b_2' \rangle = -P_x \hat{k} \\
 P_d^z &= \langle {}^2A | er | {}^2B_1^d \rangle = \langle a | ez | b_1 \rangle \simeq \frac{1}{2} k_1 k_6 P_x \hat{k} \\
 M_{\pi}^z &= \frac{e}{2mc} \langle {}^2B_1^{\pi} | L | {}^2A \rangle = \frac{e}{2mc} [\langle a' | L_x | b_1' \rangle + \langle b_2' | L_x | b_3' \rangle] = \\
 &\quad -M_x \beta_M \hat{k} \\
 M_d^z &= \frac{e}{2mc} \langle {}^2B_1^d | L | {}^2A \rangle = \frac{e}{2mc} \langle b_1 | L_x | a \rangle \simeq 2 i \beta_M \hat{k} \\
 R_d^z &= \frac{1}{2} k_3 k_6 P_x \beta_M \\
 R_d^z &= k_1 k_6 P_x \beta_M
 \end{aligned}$$

Consequently, two allowed positive Cotton effects are expected in the range of $d \rightarrow d$ transitions if all mixing coefficients are positive. This has been observed, and this coincidence very strongly supports the empirical assignments given earlier and thus lends support to the MO scheme for oxovanadium(IV) complexes given by Ballhausen and Gray.²³ It is not surprising that the $(x^2 - y^2) \rightarrow (xz)$ (B_2) transition gives a small Cotton effect, since we have used a low but obviously too high symmetry for these contemplations.

Experimental. The properties of the complexes studied agreed closely with those reported previously.^{5,20,24} The agreement was established from melting points, chemical analyses, and ¹H NMR spectra.

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