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Conformation and Optical Activity of Copper(II) Complexes with L-aminoacids in the Visible Region

A. DECINTI and G. LARRAZÁBAL
Departamento de Química Inorgánica y Analítica, Facultad de Ciencias Químicas, Universidad de Chile, Chile

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The Cotton effect of d–d transitions of copper(II) complexes with optically active aminoacids in aqueous media is qualitatively analyzed in terms of conformational models by means of a simple one-electron MO treatment. The results are dependent on the kind of puckering through which the chelate ring attains a definite conformation (k or k′).

Introduction

In 1967 Wellman and coworkers proposed that the Cotton effect of copper(II) chelates with optically active aminoacids can be correlated to their molecular conformation. On the basis of assumed kinds of puckering of the chelate ring, they found that a simple octant rule can be successfully applied to a number of bidentate and tridentate chelates with L-α-aminoacids and L-α-substituted ethylenediamines[1,2]. Subsequently, on the basis of x-ray diffraction data and conformational analysis, Hawkins and Wong[3] questioned the relevance of molecular conformation on optical activity of copper complexes with aminoacids, pointing out that there should be no significant preference for one particular chirality in aqueous solution. However, detailed information about geometry and conformation of these species under solvation effects is not available at present.[4]

Although the molecular conformation cannot be considered as the only and most relevant source of induced optical activity in copper(II) complexes with L-aminoacids, the study of the contribution to the rotational strength of such structural features would be of some interest for the investigation of the other possible mechanisms. In this work the effect of the conformation of chelate rings on the rotatory strength of the magnetic dipole allowed *d–d* transitions of *trans* and *cis*-bis(L-α-aminoacidato)copper(II) was qualitatively analyzed by means of a simple one-electron LCAO–MO approach.

Rotatory Strengths and Conformational Models

The ideal species *trans*-Cu(L-amac)$_2$X$_2$ and *cis*-Cu(L-amac)$_2$X$_2$, where X is an axial ligand (coordinating solvent), were taken as starting point to define molecular orbitals and to build up molecular models involving the conformations k and k′. The suggestion of Wilson and Martin[5] that π-bonding could be considered as a mechanism of transmission of asymmetry to the transition metal ion was followed, but the effects of the asymmetric centre were regarded as favoring a definite conformation of the chelate ring.

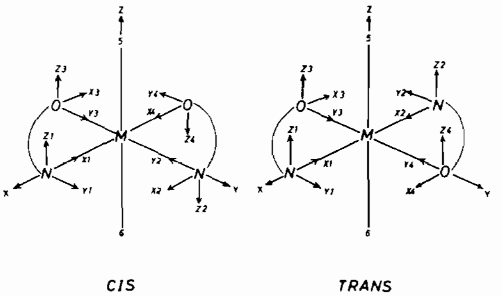

Figure 1. Metal-centered coordinate system and local ligand coordinate systems of *cis* and *trans* complexes.

In order to develop expressions for the rotatory strengths, molecular orbitals were defined under C$_2$ symmetry. For the *trans* complex, as it appears in Figure 1, these are:

$$\Psi_{xy}(A) = a_1 d_{xy} + a_2(p_{x3} + p_{x4}) + a_3(p_{z3} + p_{z4}) + \text{other terms}$$

$$\Psi_{yz}(B) = b_1 d_{yz} + b_2(p_{x3} - p_{x4}) + b_3(p_{z3} - p_{z4}) + \text{other terms}$$

$$\Psi_{xz}(B) = c_1 d_{xz} + c_2(p_{x1} - p_{x2}) + c_3(p_{z1} - p_{z2}) + \text{other terms}$$

$$\Psi_{x^2-y^2}(A) = f_1 d_{x^2-y^2} + f_2(\sigma_1 + \sigma_2) + f_3(\sigma_3 + \sigma_4) + \text{other terms}$$

The magnetic dipole transition moments were taken as:

$$\langle d_{x^2-y^2} | \bar{M} | d_{xy} \rangle = -ehi\,(2\pi m_e c)^{-1} k$$

$$\langle d_{x^2-y^2} | \bar{M} | d_{yz} \rangle = ehi(4\pi m_e c)^{-1} i$$

$$\langle d_{x^2-y^2} | \bar{M} | d_{xz} \rangle = ehi(4\pi m_e c)^{-1} j$$

Hence, selecting the terms of appropriate polarization and neglecting the two-center ligand–ligand terms, the electric dipole transition moments turned out to be:

$$\langle \Psi_{xy}(A) | \bar{R}(k) | \Psi_{x^2-y^2}(A) \rangle \approx -2e(f_1E_O - \lambda_O f_3 F_O)a_3$$

$$\langle \Psi_{yz}(B) | \bar{R}(j) | \Psi_{x^2-y^2}(A) \rangle \approx 2e(f_1D_O - \lambda_O f_3 F_O)b_2$$

and

$$\langle \Psi_{xz}(B) | \bar{R}(j) | \Psi_{x^2-y^2}(A) \rangle \approx 2e(f_1D_N + \lambda_N f_2 F_N)c_2$$

In these expressions e is the electron charge; E_O, D_O, D_N, F_O and F_N are the scalar part of electric moment integrals, whose details are included in the appendix; λ_O is the coefficient of the 2s orbital on the chelated oxygen σ-orbital and λ_N is the coefficient of the 2s orbital on the nitrogen σ-orbital. Furthermore, on the assumption that the amino group should be a very weak π-donor, in the case of the k-polarized terms the nitrogen contributions were considered negligible as compared to the coordinated oxygen ones. However, they were further included in discussing the intensity of the Cotton effect of the long wavelength transition.

According to classic relations the expressions for the rotatory strengths turn out to be:

$$R(d_{xy} \rightarrow d_{x^2-y^2}) \approx e^2h(\pi m_e c)^{-1}(f_1E_O - \lambda_O f_3 F_O)a_3$$

$$R(d_{yz} \rightarrow d_{x^2-y^2}) \approx e^2h(2\pi m_e c)^{-1}(f_1D_O - \lambda_O f_3 F_O)b_2$$

$$R(d_{xz} \rightarrow d_{x^2-y^2}) \approx e^2h(2\pi m_e c)^{-1}(f_1D_N + \lambda_N f_2 F_N)c_2$$

where the coefficients a_3, b_2 and c_2 are functions of the conformation.

For the *cis* complex, the essentially 3d MO's are:

$$\Psi_{xy}(A) = a_1d_{xy} + a_2(p_{x3} + p_{y4}) + a_3(p_{z3} + p_{z4}) + \text{other terms}$$

$$\Psi_{xz-yz}(A) = b_1(d_{xz} - d_{yz}) + b_2(p_{x3} + p_{y4}) + b_3(p_{z3} + p_{z4}) + \text{other terms}$$

$$\Psi_{xz+yz}(B) = c_1(d_{xz} + d_{yz}) + c_2(p_{x3} - p_{y4}) + c_3(p_{z3} - p_{z4}) + \text{other terms}$$

$$\Psi_{x^2-y^2}(B) = f_1d_{x^2-y^2} + f_2(\sigma_1 - \sigma_2) + f_3(\sigma_3 - \sigma_4) + \text{other terms}$$

The magnetic dipole moments were taken as:

$$\langle d_{x^2-y^2} | \bar{M} | d_{xy} \rangle = -ehi(2\pi m_e c)^{-1}k$$

$$\langle d_{x^2-y^2} | \bar{M} | 2^{-1/2}(d_{xz} - d_{yz}) \rangle = -2^{1/2}ehi(4\pi m_e c)^{-1}(i-j)$$

$$\langle d_{x^2-y^2} | \bar{M} | 2^{-1/2}(d_{xz} + d_{yz}) \rangle = 2^{1/2}ehi(4\pi m_e c)^{-1}(i+j)$$

Selecting the terms of appropriate polarization and neglecting the two-center ligand–ligand terms and Cu–N π-bonding, the electric dipole moments turned out to be:

$$\langle \Psi_{xy}(A) | \bar{R}(k) | \Psi_{x^2-y^2}(B) \rangle \approx -2e(f_1E_O - \lambda_O f_3 F_O)a_3(k)$$

$$\langle \Psi_{xz-yz}(A) | \bar{R}(i,j) | \Psi_{x^2-y^2}(B) \rangle \approx 2e(f_1D_O - \lambda_O f_3 F_O)b_2(i-j)$$

$$\langle \Psi_{xz+yz}(B) | \bar{R}(i,j) | \Psi'_{x^2-y^2}(B) \rangle \approx 2e(f_1D_O - \lambda_O f_3 F_O)c_2(i+j)$$

Hence:

$$R(d_{xy} \rightarrow d_{x^2-y^2}) \approx e^2h(\pi m_e c)^{-1}(f_1E_O - \lambda_O f_3 F_O)a_3$$

$$R(d_{xz-yz} \rightarrow d_{x^2-y^2}) \approx -e^2h(2^{1/2}\pi m_e c)^{-1}(f_1D_O - \lambda_O f_3 F_O)b_2$$

$$R(d_{xz+yz} \rightarrow d_{x^2-y^2}) \approx e^2h(2^{1/2}\pi m_e c)^{-1}(f_1D_O - \lambda_O f_3 F_O)c_2$$

According to the reference coordinates system selected and the nodal properties of the mainly $d_{x^2-y^2}$ MO, both f_1 and f_3 are positive and f_2 is negative. In order to obtain the net sign of the terms involving these coefficients, the E, D and F type integrals were computed by employing 3d functions of Richardson[6] and 2s and 2p single exponential functions of Clementi[7]. The value calculated by Fujimoto and Janecka for the *trans*-L-alanine–copper(II) complex from paramagnetic resonance spectra[8] was taken for f_1; f_3 was evaluated from the normalization condition neglecting ligand–ligand overlap and taking $f_2 = f_3$. The overlap integrals were computed by using $\lambda_O = 3^{-1/2}$ and $\lambda_N = 2^{-1}$. From these approximations, $f_1E_O - \lambda_O f_3 F_O$, $f_1D_O - \lambda_O f_3 F_O$ and $f_1D_N + \lambda_N f_2 F_N$ turned out to be $\langle 0$. Moreover, if λ_O and λ_N are obtained by minimizing $VSIE(\Theta)/S(\Theta)$, the above results are still valid.

Three dihedral angles were considered to build up molecular frameworks involving both k and k′ conformations. These were the dihedral angle between planes NCuO and CuOC (ϱ), the dihedral angle between planes CuOC and OCO (ω) and the dihedral angle between planes NCuO and CuNC (Φ). For the sake of simplicity, three kinds of puckering were considered: I) $\varrho \neq 0$, $\omega = 0$; II) $\varrho = 0$, $\omega \neq 0$ and III) $4\varrho = -\omega$; Φ being implicitly established in each case. As is shown in Figure 2, the first molecular model implies the chelate ring to be puckered around the chelated oxygen–nitrogen internuclear axis. In the case of k′ conformation, this particular type of puckering forces the carbonyl group to lie in a positive Wellman octant. The second scheme involves a puckering around the carbonylic carbon–nitrogen internuclear axis. In this case, for k′ conformation the carbonylic oxygen lies in a negative octant. Finally, the third model implies the chelate ring to be simultaneously and oppositely puckered around the chelated oxygen–nitrogen and carbonylic carbon–nitrogen internuclear axes. In this case for k′ conformation the carbonyl group lies in a negative octant. The diedral angle ϱ was measured in a clockwise sense, looking from the metal ion towards the coordinated oxygen. The dihedral angle ω was also measured in a clockwise sense looking from the coordinated oxygen towards the carbonylic carbon. Thus, in model I the conformation k requires $\varrho > 0$ and the conformation k′ $\varrho < 0$. In model II $\omega > 0$ is required for k conformation and $\omega < 0$ for k′. In model III, however, $\varrho < 0$ is required for k conformation and $\varrho > 0$ for k′. The dihedral angle Φ is dependent only

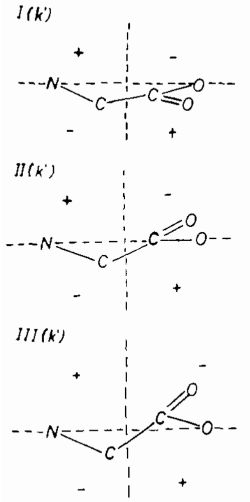

Figure 2. Conformational models of chelate ring in k′ disposition and octant rule. Only back octants are shown (left ring of Figure 1). The metal ion has been omitted.

on the arrangement of the asymmetric carbon, therefore for a particular conformation (k or k′) it takes the same sign for the three conformational models. This angle was measured in a counter-clockwise sense looking from the metal ion towards the nitrogen atom.

Rotatory Strength Sign Rules of *trans* Species

Sign rules for a_3, b_2 and c_2 were obtained on each conformational scheme from over-simplified extended Hückel matrices which include the appropriate dihedral angles. The atomic orbital basis consisted of the $3d\pi$ metal orbitals, the $2p\pi$ orbitals of the coordinated ligand atoms, the σ orbitals of the ligand atoms directly linked to the coordinated atoms and the π orbitals of the carbonyl groups. However, the carbonylic carbon σ-orbitals pointing towards the coordinated oxygens were excluded from model II, because in this case the arrangement of the carboxylate carbon is the same for both k and k′ conformation. The generalized transformation matrices of I and III are given in the appendix.

For model I, from row–row operations on the $\Gamma_A(d_{xy})$ matrix the following expression was derived:

$$a_3 = 2^{-1/2}(2A_{12}^{2} + H_aA_{11})(A_{12}H_a)^{-1}a_1\cos^{-1}\varrho\,\mathrm{sen}\,\varrho \qquad (1)$$

where:

$\varrho \neq 0$; $H_a = A_{25}^{2}A_{66}(A_{55}A_{66}-A_{56}^{2})^{-1}-A_{22}$

$A_{11} = \langle 3d|H|3d\rangle - E_{xy}$
$A_{12} = \langle 3d(\pi)|H|2p_o(\pi)\rangle - S(2p_o\pi,3d\pi)E_{xy}$
$A_{22} = \langle 2p_o|H|2p_o\rangle - E_{xy}$; $2p_x$ and $2p_z$ orbitals of chelated oxygen
$A_{25} = \langle 2p_o(\pi)|H|2p_c(\pi)\rangle - S(2p_o\pi,2p_c\pi)E_{xy}$; $R_{c-o} = 1.28\,\text{Å}$
$A_{55} = \langle 2p_c|H|2p_c\rangle - E_{xy}$; $2p\pi$ orbital of carbonylic carbon
$A_{56} = \langle 2p_c(\pi)|H|2p_o(\pi)\rangle - S(2p_c\pi,2p_o\pi)E_{xy}$; $R_{c-o} = 1.22\,\text{Å}$
$A_{66} = \langle 2p_o|H|2p_o\rangle - E_{xy}$; $2p\pi$ orbital of carbonylic oxygen
E_{xy} = essentially $3d_{xy}$ MO energy.

Since $S(2p_o\pi,3d\pi)$ is small, it can be shown from the usual parametrization of the angular overlap and Wolfsberg–Helmholz methods[10, 15] that all the A_{ij} terms are negative, excepting A_{55}. Therefore $A_{12}H_a < 0$. In order to obtain the sign of the term $2A_{12}^{2} + H_aA_{11}$, A_{12} and A_{11} were expressed by means of Jørgensen's approximations for metal–ligand non-diagonal elements and antibonding energies respectively[9], neglecting Cu–N π-bonding and taking $A_{22} \approx H_X - H_M$:

$$A_{12} \approx (A_{22} + E_{xy})S(2p_o\pi,3d\pi) \qquad (2)$$

$$A_{11} \approx 2(A_{22} + E_{xy})A_{22}^{-1}[S'(2p_o\pi,3d\pi)]^{2} \qquad (3)$$

where $S'(2p_o\pi,3d\pi)$ is a reduced overlap integral, since $2p_{x3}$ and $2p_{x4}$ are strongly involved in C–O σ-bonding. For the sake of simplicity the essentially $3d_{xy}$ MO was regarded as a combination of the $3d_{xy}$ orbital and the oxygen hybrid orbitals:

$$3^{-1/2}(2s_3) + 2^{-1/2}(2p_{x3}\cos\varrho - 2p_{z3}\,\mathrm{sen}\,\varrho) - 6^{-1/2}(2p_{y3})$$

$$3^{-1/2}(2s_4) + 2^{-1/2}(2p_{x4}\cos\varrho - 2p_{z4}\,\mathrm{sen}\,\varrho) - 6^{-1/2}(2p_{y4})$$

Hence, $S'(2p_o\pi,3d\pi) = 2^{-1/2}S(2p_o\pi,3d\pi)\cos\varrho$. Using these assumptions and defining $k = A_{66}/A_{22}$, the sum $2A_{12}^{2} + H_aA_{11}$ becomes:

$$(A_{22} + E_{xy})^{2}[S(2p_o\pi,3d\pi)]^{2}[1 + kA_{25}^{2}(A_{55}A_{66} - A_{56}^{2})^{-1}\cos^{2}\varrho + \mathrm{sen}^{2}\varrho]$$

where: $0 < k \leqslant 1$ and $|A_{56}| \geqslant |A_{25}|$. Therefore, $(2A_{12}^{2} + H_aA_{11}) > 0$, and (1) may be written as:

$$a_3 = -|a_3\,\mathrm{sen}^{-1}\varrho|\,\mathrm{sen}\,\varrho$$

Hence, $R(d_{xy} \rightarrow d_{x^2-y^2})_1 \approx e^{2}a_oh(\pi m_ec)^{-1}|f_1E_O - \lambda_Of_3F_O||a_3\,\mathrm{sen}^{-1}\varrho|\,\mathrm{sen}\,\varrho$ and is positive for the conformation k and negative for the conformation k′.

Analogously, from the $\Gamma_B(d_{yz})$ matrix of I it was derived:

$$b_2 = -2^{-1/2}(2B_{12}^{2} + H_bB_{11})(B_{12}H_b)^{-1}b_1\cos\varrho\,\mathrm{sen}^{-1}\varrho$$

where $\varrho \neq 0$ and the B_{ij}'s and H_b have the same meaning as the A_{ij}'s and H_a, but replacing E_{xy} by E_{yz}. As in the case of the A_{ij}'s, all the B_{ij} terms are negative, excepting B_{55}. Therefore $B_{12}H_b$ is negative. Using the same approximations which led to (2) and (3), and regarding the essentially $3d_{yz}$ MO as a combination of the $3d_{yz}$ orbital and the higher energy filled MO of the carboxylate anions:

$$2B_{12}^2 + H_bB_{11} \approx (B_{22} + E_{yz})^2[S(2p_o\pi, 3d\pi)]^2 \\ [1 + kB_{25}^2(B_{55}B_{66} - B_{56}^2)^{-1}\cos^2\varrho + \mathrm{sen}^2\varrho]$$

where: $0 < k = B_{66}/B_{22} \leqslant 1$ and $|B_{56}| \geqslant |B_{25}|$
Hence: $b_2 = |b_2\mathrm{sen}^{-1}\varrho|\,\mathrm{sen}\varrho$
and $R(d_{yz} \rightarrow d_{x^2-y^2})_\mathrm{I} \approx$

$$-e^2a_oh(2\pi m_ec)^{-1}|f_1D_O - \lambda_Of_3F_O||b_2\mathrm{sen}^{-1}\varrho|\,\mathrm{sen}\varrho$$

Therefore, $R(d_{yz} \rightarrow d_{x^2-y^2})_\mathrm{I}$ and $R(d_{xy} \rightarrow d_{x^2-y^2})_\mathrm{I}$ have opposite signs for the same conformation.

It can be shown that these results are still valid when 4s, 4p and metal–ligand σ terms (including σ-nitrogen) are considered.

In the case of model II, by performing the appropriate row–row operations on the $\Gamma_A(d_{xy})$ matrix, the following expression was obtained:

$$a_3 \approx 8^{-1/2}A_{11}A_{66}A_{25}^2A_{12}^{-1}[A_{25}^2A_{66}\cos^2\omega - (A_{55}A_{66} \\ - A_{56}^2)A_{22}]^{-1}a_1\cos\omega\,\mathrm{sen}\omega$$

and in a similar way from the $\Gamma_B(d_{yz})$ matrix it was found that:

$$b_2 \approx -2^{-1/2}B_{11}B_{66}B_{25}^2B_{12}^{-1}[2^{-1}B_{25}^2B_{66}\mathrm{sen}^2\omega \\ -2(B_{55}B_{66} - B_{56}^2)B_{22}]^{-1}b_1\cos\omega\,\mathrm{sen}\omega$$

the A_{ij} and B_{ij} terms having been already defined.

Therefore rotatory strengths become:

$$R(d_{xy} \rightarrow d_{x^2-y^2})_\mathrm{II} \approx -e^2a_oh(\pi m_ec)^{-1}|f_1E_O - \lambda_Of_3F_O \\ ||a_3\mathrm{sen}^{-1}\omega|\,\mathrm{sen}\omega$$

and

$$R(d_{yz} \rightarrow d_{x^2-y^2})_\mathrm{II} \approx e^2a_oh(2\pi m_ec)^{-1}|f_1D_O - \lambda_Of_3F_O \\ ||b_2\mathrm{sen}^{-1}\omega|\,\mathrm{sen}\omega$$

Therefore, they have opposite signs for the same conformation.

From the $\Gamma_A(d_{xy})$ matrix of III the following expression was derived:

$$a_3 = 2^{-1/2}(2A_{12}^2 - K_aA_{11})(A_{12}L_a)^{-1}a_1\cos^{-1}\varrho\,\mathrm{sen}\varrho$$

where:

$$K_a = A_{25}^2A_{66}(A_{55}A_{66} - A_{56}^2)^{-1}(\cos2\varrho + \mathrm{sen}^22\varrho) \\ \cos^24\varrho + A_{22}$$

$$L_a = A_{25}^2A_{66}(A_{55}A_{66} - A_{56}^2)^{-1}(\cos2\varrho - \mathrm{sen}^22\varrho) \\ \cos^24\varrho - A_{22}$$

the terms A_{ij} having the meaning already defined.

On employing the same approximations as for I, it can be shown that

$$a_3 = -|a_3\mathrm{sen}^{-1}\varrho|\,\mathrm{sen}\varrho$$

In the same way, from $\Gamma_B(d_{yz})$ it was derived:

$$b_2 = 2^{-1/2}(2B_{12}^2 + L_bB_{11})(B_{12}K_b)^{-1}b_1\cos\varrho\,\mathrm{sen}^{-1}\varrho$$

where B_{ij}, K_b and L_b have the same meaning as A_{ij}, K_a and L_a, but replacing E_{xy} by E_{yz}.

In this case: $b_2 = |b_2\mathrm{sen}^{-1}\varrho|\,\mathrm{sen}\varrho$

Hence, the rotatory strength expressions for model I are valid in the case of model III but with an opposite requirement of ϱ for the same conformation. It should be pointed out that taking $2\varrho = -\omega$ or $\varrho = -\omega$ the same sign rules as for model III are obtained.

Finally, on performing the appropriate row–row operations on the $\Gamma_B(d_{xz})$ matrix it was obtained

$$c_2 = -2^{-1/2}C_{12}^{-1}(2C_{12}^2 - H_cC_{11})H_c^{-1}c_1\cos\Phi\,\mathrm{sen}^{-1}\Phi$$

where: $\Phi \neq 0$

$$H_c = C_{22} - (4/3)C_{25}^2C_{55}^{-1}$$

$C_{11} = \langle 3d|H|3d\rangle - E_{xz}$
$C_{12} = \langle 3d(\pi)|H|2p_N(\pi)\rangle - S(2p_N\pi, 3d\pi)E_{xz}$
$C_{22} = \langle 2p_N|H|2p_N\rangle - E_{xz}$
$C_{25} = \langle 2p_N|H|1s\rangle - S(1s, 2p_N)E_{xz}$
$C_{55} = \langle 1s|H|1s\rangle - E_{xz}$

From the ordinary extended Hückel and angular overlap[10] parametrization, $H_c > 0$. Therefore:

$$R(d_{xz} \rightarrow d_{x^2-y^2}) \approx -e^2h(2\pi m_ec)^{-1}|f_1D_N + \lambda_Nf_2F_N| \\ |c_2\mathrm{sen}^{-1}\Phi|\,\mathrm{sen}\Phi$$

The above considerations were based on the assumption that[10] $H_{3d3d} > H_{2p_N2p_N}$, and were checked by means of Hückel calculations neglecting $G_{ij}E$ in the off-diagonal terms. However if $H_{3d3d} < H_{2p_N2p_N}$ is taken, they are no longer valid.

Rotatory Strength Sign Rules of *cis* Species

In order to obtain sign rules for the coefficients a_3, b_2 and c_2 of the *cis* complex the same procedures as above were followed. In this case, the results are dependent on the energy level sequence of the mainly 3d π MO's. The 3d π orbital splitting was considered to arise mainly from the suitable crystal field potential. Hence, the energy level sequence $E_{xy} > E_{xz-yz}$ in the Γ_A representation was assumed. Only models I and III were analyzed, and the following sign rules were derived:

$$a_3 = -|a_3\mathrm{sen}^{-1}\varrho|\,\mathrm{sen}\varrho$$

$$b_2 = -|b_2\mathrm{sen}^{-1}\varrho|\,\mathrm{sen}\varrho$$

and

$$c_2 = |c_2\mathrm{sen}^{-1}\varrho|\,\mathrm{sen}\varrho$$

These expressions are valid for both models. If $E_{xy} < E_{xz-yz}$ were taken, the sign of a_3 is reversed.

Discussion

The sign patterns of the rotatory strengths for k′ conformation are given in Tables 1 and 2, where the transitions are listed from lower to higher energy, according to recent crystal field calculations on the diaquo species[11]. As can be seen, they agree with Wellman's octant rule.

From these results, both *trans*-II(k') and *trans*-III(k') lead to sign patterns that correspond to most of the available CD data for the region 400–800 nm of 1:2 copper L-α-aminoacids complexes[3,12]. Therefore, if the conformational effects were the determining factor in the *trans* complexes in aqueous solution, the chelate ring should be predominantly puckered according to II(k') or III(k'). However *trans*-I(k) would be also acceptable. For that reason, a further comment on the intensity of the long wavelength band is required. Since the contribution of the terms involving nitrogen orbitals to the k-polarized electric-dipole moment transition is dependent only on the arrangement of the asymmetric carbon, they should make a contribution of the same sign to the rotatory strengths of all the conformational models of a particular conformation. From similar approximations as for the j-polarized magnetically allowed transition, this contribution was found to be positive for the conformation k and negative for the conformation k'. This indicates that the rotatory strength of the long wavelength transition is reinforced in the case of I and weakened in the case of II, on account of Cu–N π-bonding. Furthermore, if $\omega \neq 0$ and the nodal plane of the carboxylate π-system was conserved, the coordinated oxygen σ-orbitals should be deviated out of the plane NCuO, and a $(p_{z3} + p_{z4})$ component would arise on the essentially $d_{x^2-y^2}$ MO. In the case of model II, the symmetry combination of rotated σ-orbitals become:

$$\sigma'_3 + \sigma'_4 = 3^{-1/2}(s_3 + s_4) + 8^{-1/2}(1-\cos\omega) \\ (p_{x3} + p_{x4}) + 24^{-1/2}(1 + 3\cos\omega)(p_{y3} + p_{y4}) \\ + 2^{-1/2}(p_{z3} + p_{z4})\mathrm{sen}\,\omega$$

Regarding the mainly d_{xy} MO as $a_1(d_{xy}) + a_2(n_3 + n_4)$, where n_3 and n_4 are sp^2 hybrid orbitals describing the unshared electron pairs on the coordinated oxygen atoms, and adding up the new electric-dipole moment one-center term, the expression of the rotatory strength becomes:

$$R(d_{xy} \rightarrow d_{x^2-y^2})_{II} \approx -e^2h(2\pi m_e c)^{-1}(|f_1E_O - \lambda_O f_3 F_O| \\ |a_3\mathrm{sen}^{-1}\omega| - |18^{-1/2}a_2 f_3 F_O|)\mathrm{sen}\,\omega$$

Hence, the rotatory strength should be also weakened on account of the Cu–O σ-bonding distortion, which is inherent to the models II and III.

Taking into account these considerations, Cotton effects arising mainly from $d_{xz} \rightarrow d_{x^2-y^2}$ (+) and $d_{yz} \rightarrow d_{x^2-y^2}$ (–) transitions are predicted for the *trans* L-alanine complex in aqueous solution, the forms II(k') and III(k') being predominant. This assignment appears to be consistent with crystal field calculations[11], which show that the $d_{xz} \rightarrow d_{x^2-y^2}$ transition tend to be near the lowest energy magnetically allowed *d–d* transition. On the other hand, if the conformational effects were relevant, the Cotton effects observed for the L-proline complex in water solution would have to arise from the $d_{xy} \rightarrow d_{x^2-y^2}$ (+), $d_{xz} \rightarrow d_{x^2-y^2}$ (–) and $d_{yz} \rightarrow d_{x^2-y^2}$(–) transitions, the form *trans*-I(k) being predominant. From molecular models it appears that this conformation favours the coordination of the solvent at position 5.

TABLE I. Sign Patterns of *trans* Complexes: Conformation k'.

	I	II	III
$d_{xy}(A) \rightarrow d_{x^2-y^2}(A)$	–	+	+
$d_{xz}(B) \rightarrow d_{x^2-y^2}(A)$	+	+	+
$d_{yz}(B) \rightarrow d_{x^2-y^2}(A)$	+	–	–

TABLE II. Sign Patterns of *cis* Complexes: Conformation k'.

	I	III
$d_{xy}(A) \rightarrow d_{x^2-y^2}(B)$	–	+
$(d_{xz}-d_{yz})(A) \rightarrow d_{x^2-y^2}(B)$	+	–
$(d_{xz}+d_{yz})(B) \rightarrow d_{x^2-y^2}(B)$	+	–

The above results can be also extended to the visible CD spectra of the copper complexes with N,N-dialkylated-α-aminoacids in aqueous solution. *Trans*-bis(L-N,N-dimethyl-α-alaninato)copper(II) and *trans*-bis(L-N,N-diethyl-α-alaninato)copper(II) exhibit Cotton effects with opposite sign patterns, although for both species the conformation k' is sterically favored[13]. The crystal structure of the copper complex with L-N,N-diethyl-α-alanine shows that the carbonyl group lies on the same side of the coordination plane as the asymmetric carbon[14], which implies that the chelate ring should be puckered according to model I. Hence, if in aqueous solution this type of puckering was preserved, the sign pattern from *trans*-I(k') would be in agreement with the experimental data, whereas in aqueous solution the chelate ring of *trans*-bis(L-N,N-dimethyl-α-alaninato)copper(II) would be predominantly in the forms II(k') or III(k'). The form I(k') for the complex of copper(II) and L-N,N-diethyl-alanine seems to be consistent with the shortened Cu–O distance[14] which makes the Cu–O σ-bonding distortion unlikely.

Finally, the results from the *cis*-species are also in agreement with most CD data for the visible region of copper complexes with L-aminoacids, when the form III(k') or, probably, II(k') are assumed to be predominant. In this case, the typical net negative Cotton effect of copper complexes with L-aminoacids, others than L-proline, is best reproduced.

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Appendix

Transition Moment Integrals[16]

$$\begin{array}{lll}
D_N = \langle p_{y1}|y|d_{x^2-y^2}\rangle & = -\langle p_{y2}|y|d_{x^2-y^2}\rangle & = P_N-3Q_N \\
E_N = \langle p_{z1}|z|d_{x^2-y^2}\rangle & = \langle p_{z2}|z|d_{x^2-y^2}\rangle & = P_N-Q_N \\
F_N = \langle p_{y1}|y|s_1\rangle & = -\langle p_{y2}|y|s_2\rangle & \\
 = \langle p_{z1}|z|s_1\rangle & = \langle p_{z2}|z|s_2\rangle & \\
D_O = \langle p_{x3}|x|d_{x^2-y^2}\rangle & = -\langle p_{x4}|x|d_{x^2-y^2}\rangle & = P_O-3Q_O \\
E_O = -\langle p_{z3}|z|d_{x^2-y^2}\rangle & = -\langle p_{z4}|z|d_{x^2-y^2}\rangle & = P_O-Q_O \\
F_O = -\langle p_{x3}|x|s_3\rangle & = \langle p_{x4}|x|s_4\rangle & \\
 = \langle p_{z3}|z|s_3\rangle & = \langle p_{z4}|z|s_4\rangle &
\end{array}$$

$$P = (R/2)S(2p\pi,3d\pi)-(3/8)^{1/2}(a_o/\mu_a)S(3d\pi,3d\pi)$$

$$Q = (3/8)^{1/2}(a_o/\mu_a)S(3d\delta,3d\delta)$$

$$F = (160a_o)(3)^{-1/2}(\mu_{2s}\mu_{2p})^{5/2}(\mu_{2s}+\mu_{2p})^{-6}$$

Where: a_o = Bohr radius for $n = 1$
μ_a = 2p orbital exponent
R = Cu–N or Cu–O internuclear distance

Generalized Transformation Matrices of the trans Complex

In the forthcoming tables, the labeling of the A_{ij} and B_{ij} terms was chosen so as to reflect the analogy of some elements inside a particular matrix, besides correlating some elements of both transformation matrices. Therefore, on obtaining the matrices $\Gamma_A(xy)$ and $\Gamma_B(yz)$ for model II, the same labeling as for models I and III was conserved, although on omiting the H_{i4} (and H_{4j}) elements they become 5×5 matrices.

$\Gamma_A(xy)$
$M_{11} = A_{11}$
$M_{12} = 2^{-1/2}A_{12}$
$M_{22} = A_{22}$
$M_{24} = -(3/4)^{1/2}A_{24}\cos\varrho$
$M_{25} = A_{25}(2^{-1}\cos\varrho\,\mathrm{sen}\,\omega + \mathrm{sen}\,\varrho\cos\omega)$
$M_{33} = A_{22}$
$M_{34} = (3/4)^{1/2}A_{24}\mathrm{sen}\,\varrho$
$M_{35} = A_{25}(\cos\varrho\cos\omega - 2^{-1}\mathrm{sen}\,\varrho\,\mathrm{sen}\,\omega)$
$M_{44} = A_{44}$
$M_{55} = A_{55}$
$M_{56} = A_{56}$
$M_{66} = A_{66}$

$\Gamma_B(yz)$
$M_{11} = B_{11}$
$M_{13} = -2^{-1/2}B_{12}$
$M_{22} = B_{22}$
$M_{24} = -(3/4)^{1/2}B_{24}\cos\varrho$
$M_{25} = B_{25}(2^{-1}\cos\varrho\,\mathrm{sen}\,\omega + \mathrm{sen}\,\varrho\cos\omega)$
$M_{33} = B_{22}$
$M_{34} = (3/4)^{1/2}B_{24}\mathrm{sen}\,\varrho$
$M_{35} = B_{25}(\cos\varrho\cos\omega - 2^{-1}\mathrm{sen}\,\varrho\,\mathrm{sen}\,\omega)$
$M_{44} = B_{44}$
$M_{55} = B_{55}$
$M_{56} = B_{56}$
$M_{66} = B_{66}$

$\Gamma_B(xz)$
$M_{11} = C_{11}$
$M_{12} = 2^{-1/2}C_{12}$
$M_{22} = C_{22}$
$M_{24} = -(8/9)^{1/2}C_{24}\cos\Phi$
$M_{25} = (2/9)^{1/2}C_{25}(\cos\Phi + 3^{1/2}\mathrm{sen}\,\Phi)$
$M_{26} = (2/9)^{1/2}C_{25}(\cos\Phi - 3^{1/2}\mathrm{sen}\,\Phi)$
$M_{33} = C_{22}$
$M_{34} = (8/9)^{1/2}C_{24}\mathrm{sen}\,\Phi$
$M_{35} = (2/9)^{1/2}C_{25}(3^{1/2}\cos\Phi - \mathrm{sen}\,\Phi)$
$M_{36} = -(2/9)^{1/2}C_{25}(3^{1/2}\cos\Phi + \mathrm{sen}\,\Phi)$
$M_{44} = C_{44}$
$M_{55} = C_{55}$
$M_{66} = C_{55}$

In these tables:

$A_{24} = \langle 2p_o|H|\sigma_c\rangle - S(\sigma_c, 2p_o)E_{xy}$
$A_{44} = \langle \sigma_c|H|\sigma_c\rangle - E_{xy}$
$C_{24} = \langle 2p_N|H|\sigma_{c(\alpha)}\rangle - S(\sigma_{c\alpha}, 2p_N)E_{xz}$
$C_{44} = \langle \sigma_{c(\alpha)}|H|\sigma_{c(\alpha)}\rangle - E_{xz}$

B_{24} and B_{44} having the same meaning as A_{24} and A_{44} on replacing E_{xy} by E_{yz}. The remaining A_{ij}, B_{ij} and C_{ij} have already been defined.

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