Contribution of the Laboratorio de Quìmica General e Inorgánica, and Centro de Investigaciones Quìmicas, Facultad de Quìmica y Farmacia, Universidad da Chile, Chile.

Optical Activity of Nickel(II) and Copper(II) Complexes with L-Aminoacids in the UV Spectral Region

C. Ibarra, R. Soto, L. Adán, A. Decinti, and S. Bunel

Complexes of Cu^{II} and Ni^{II} with L-aminoacids have been prepared and their UV spectra and optical activity studied.

The results are interpreted in terms of the conformation of the chelated rings. A molecular orbital treatment leads to results agreeing with experimental facts.

Introduction

The induced optical activity of metal ion complexes with optically active ligands in the visible region of the spectrum is well known; but their optical behaviour in the UV has not been widely studied.

In this work the optical activity of complexes of Ni^{II} with several aminoacids is discussed. The origin of the Cotton effect observed in the region of the charge transfer absorption band of the Cu^{II} complexes with several L-aminoacids is also analyzed.[1,2]

In both groups of complexes, the optical behaviour is different from that of the free aminoacids.[3,5]

The compounds have been prepared and characterized by elementary analyses and their absorption, circular dichroism and rotatory dispersion spectra have been measured (Tables I to III, Figures 1 and 2).

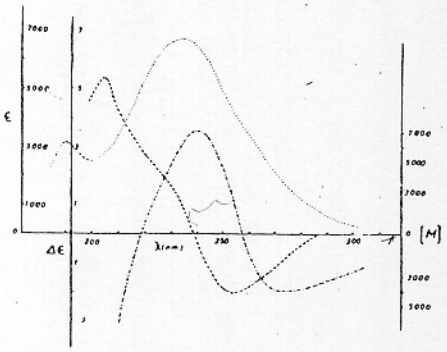

Figure 1. Absorption spectrum (.....), rotatory dispersion (.—.—.) and circular dichroism (-----) of $Cu(L\text{-isoleu})_2H_2O$ aq. solution.

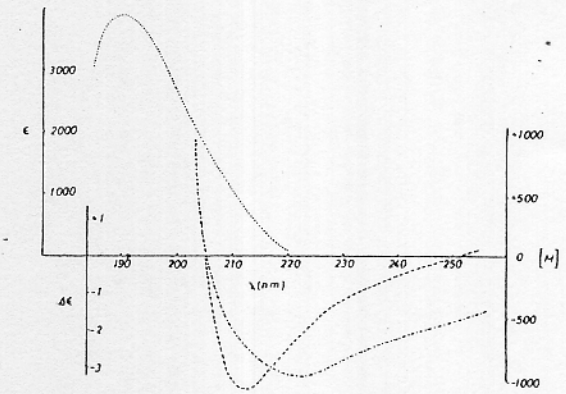

Figure 2. Absorption spectrum (.....), rotatory dispersion (.—.—.) and circular dichoism (-----) of $Ni(L\text{-threo})_2(H_2O)_2$ aq. solution.

A spatial model having a particular conformation of the chelated rings is proposed. This model, in turn, constitutes the basis of a molecular orbital treatment which accounts for the optical properties.

Experimental Section

The copper(II) complexes with L-alanine, L-serine, L-threonine, L-valine and L-isoleucine and the nickel(II) complexes with L-alanine, L-serine and L-threonine were prepared. Bis-ethylene-diamine Cu^{II} perchlorate and copper malonate were prepared as reference compounds.

In the synthesis of the complexes of Cu^{II} and Ni^{II} with aminoacids, a method similar to that of Abderhalden and Schnitzer[6] was followed: the solution of an aminoacid was saturated with freshly prepared. electrolite-free nickel or copper hydroxide at a temperature of 40°C. After filtration, water was partially evaporated at room temperature under vacuum. The crystalline product thus obtained was then recrystallized from water. A similar technique was

(1) K.M. Wellman, S. Bogdansky, W. Mungall, T.G. Mecca, and C.R. Hare *Tetrahedron Letters*, 37, 3607 (1967).
(2) J.M. Tsangaris, Y. Wen Chang, and R.B. Martin, *J. Am. Soc.*, *91*, 726 (1969).
(3) J.P. Jennings, W. Klyne, P.M. Scopes, *J. Chem. Soc.*, 924 (1965).
(4) L.I. Katzin and E. Gulyas, *J. Am. Chem. Soc.*, *90*, 247 (1968).
(5) C. Tonfolo, *J. Phys. Chem.*, *74*, 1390 (1970).
(6) E. Abderhalden and E. Schnitzler, Z. *Physiol. Chem.*, *94*, 1963 (1927).

Table I. Chemical analyses of metal complexes.

Complexes*	C % Found	C % Calcd.	H % Found	H % Calcd.	N % Found	N % Calcd.	metal % Found	metal % Calcd.
	30.50	30.04	5.10	5.04	11.80	11.68	26.36	26.51
	26.85	26.50	4.51	4.45	10.40	10.31	23.07	23.33
$Cu(L\text{-threo})_2H_2O$	30.39	30.21	5.68	5.71	9.06	8.81	20.55	19.99
$Cu(L\text{-val})_2H_2O$	39.01	38.24	7.11	7.07	9.28	8.92	20.09	20.25
$Cu(L\text{-isoleu})_2H_2O$	42.70	42.12	7.80	7.67	8.40	8.19	18.73	18.58
$Ni(L\text{-ala})_2(H_2O)_4$	23.50	23.48	6.60	6.57	9.20	9.13	18.75	19.13
$Ni(L\text{-ser})_2(H_2O)_2$	23.71	23.77	5.50	5.29	9.40	9.24	19.25	19.38
$Ni(L\text{-threo})_2(H_2O)_2$	29.20	29.00	6.20	6.06	8.20	8.46	17.73	17.74

* ala = alaninate; ser = serinate; threo = threoninate; val = valinate; isoleu = isoleucinate.

Table II. Spectral and optical activity data of nickel complexes.

Compounds	$[M]_{max}$	λ_m	λ_o	$\Delta\varepsilon$	λ_{CD}	λ_a	ε_λ
$Ni(L\text{-ala})_2(H_2O)_4$	−209	235	217	−1.10	218	190	3971
$Ni(L\text{-ser})_2(H_2O)_2$	−586	222	212	−2.22	215	190	3440
$Ni(L\text{-threo})_2(H_2O)_2$	−980	222	207	−3.56	212	190	3900

[M] is in (degree $cm^{-1}mole^{-1}$ $ml\times10^{-1}$) units $\Delta\varepsilon$ is in (degree $cm^{-1}mole^{-1}$ $ml\times10^{-1}$) units

Table III. Spectral and optical activity of copper complexes.

Compounds	$[M]_{max}$	λ_m	λ_o	$\Delta\varepsilon$	λ_{CD}	λ_a	ε_λ
$Cu(L\text{-ala})_2$	+3920	220	210	+1.891	205	230	2540
	−5360	267	236	−1.6	242		
$Cu(L\text{-ser})_2$	+1680	240	235	+1.261	225	230	4080
	−4320	282	254	−0.970	260		
$Cu(L\text{-threo})_2H_2O$	+8727	240	212	+3.75	205	232	4508
	−3272	285	262	−2.92	257		
$Cu(L\text{-var})_2H_2O$	+4860	235	220	+4.984	205	232	6540
	−8300	272	250	−2.832	255		
$Cu(L\text{-isoleu})_2H_2O$	+7058	240	219	+5.70	205	235	6678
	−4118	272	257	−2.138	255		

followed to prepare copper malonate, starting from malonic acid (Merck).

The nickel hydroxide was prepared from $Ni(ClO_4)_2{\cdot}6H_2O$ (J. Frederick Smith Chemical Co.) and the copper hydroxide from $CuSO_4.5H_2O$ (Merck) and both were washed many times with water until they became colloidal. The aminoacids were obtained from General Biochemicals. Ethylenediamine (Matheson Coleman Bell) was used to prepare the $[Cu(en)_2](ClO_4)_2$ complex by a standard method.[7]

The elementary analyses were performed in the Organic Milcroanalyses Laboratory in the Faculty. The nickel and copper content of the complexes was determinated by titration with EDTA after destruction of the organic matter using a mixture of concentrated hydrochloric and nitric acid.

The absorption spectra of aqueous solutions of the complexes were measured using a Zeiss PMQ II spectrometer in the range 300-185 nm. in a nitrogen atmosphere. The spectra of Cu-aminoacid complexes in aqueous solution containing an excess of ammonia with respect to the copper content, were also run.

The rotatory dispersion and circular dichroism measurements obtained using a Cary 60 spectropolarimeter equipped with circular dichroism attachment.

(7) Inorganic Synthesis. McGraw Hill Ed. 1960. Vol VI. pag. 200.

Results and Discussion

The complexes of Cu^{II} and aminoacid anions show a band due to charge transfer transitions in the UV region of the spectrum, with maximum around 230 nm. and a shoulder or a peak at 190 nm.

Two circular dichroism peaks of opposite sign, separated by approximately 9 kK, appear in the region of the charge transfer bands of the copper complexes. The optical rotatory dispersion curves show two points of zero rotation corresponding to the circular dichroims peaks. The absorption, circular dichroism and optical rotatory dispersion spectra of $Cu(L\text{-isoleu})_2H_2O$ appearing in Figure 1 are given as an example of the behaviour described for copper complexes.

The complexes of Ni^{II} with aminoacid anions exhibit an absorption band at 190 nm, and a single negative circular dichroism peak near the low frequency edge of the absorption band, its position coinciding with the location of one of the $n\rightarrow\pi^*$ transitions of the aminoacids.[5] The rotatory dispersion curves show only one point of zero rotation, which is at a wavelength very close to the zero rotation point of the corresponding aminoacids. Figure 2, corresponding to $Ni(L\text{–threo})_2(H_2O)_2$, illustrates the behaviour of this series of complexes.

When analysing the optical behaviour of the com-

plexes of Ni^{II} and aminoacids one should consider that the L-aminoacids, as in the cases of the α-halocarboxylic acids,[8] the aminoacid esters[5] and the L-lactic acid,[9,10] have two circular dichroism bands in the UV region: a positive one at 210 nm and a negative one near 240 nm.

Anand and Hargreaves[10] interpret these results assuming that the band at 210 nm corresponds to a $\pi \rightarrow \pi^*$ transition of the carboxylate group and that the band at 240 nm is due to an $n \rightarrow \pi^*$ transition. It is difficult to support this assignation in view of the fact that the absorption band of protonated aminoacids at 210 nm has a molar extintion of nearly 50[4], which is a characteristic extintion value of an $n \rightarrow \pi^*$ transition. Moreover, the $\pi \rightarrow \pi^*$ band of acetic acid, for example, has an extintion of nearly 400 and is placed at 160 nm.[11]

Djerassi[9] ascribes the bands of L-aminoacids to $n \rightarrow \pi^*$ transitions associated with chemical species possessing different conformations. The behaviour of the nickel-aminoacid complexes is consistent with this conclusion. The only negative circular dichroism maximum at 215 nm might correspond to an $n \rightarrow \pi^*$ transition of the aminoacid maintained in a fixed disposition in the complex. It should be borne in mind at this point that the protonated aminoacids may originate three rotamers. Only one of them has a structure around the CO group that can be compared to that of the chelated compound.

The experimental results obtained with copper complexes can be interpreted through an analysis of the charge transfer bands appearing when water molecules, amino or carboxylate groups surround the Cu^{II} ion.

Cu-malonate and Bis-ethylenediamine Cu^{II} ion in aqueous solution have charge transfer bands at 235 and 228 nm, respectively. The charge transfer band of $[Cu(H_2O)_6]^{2+}$, on the other hand, is located at 190 nm. Therefore, the charge transfer band of the Cu-aminoacid complexes with maximum at 230 nm can arise from electronic transitions from the amino and carboxylate groups[12] to the partly filled d-orbital of copper. The participation of the carboxylate group is possible through the electrons localized mainly in orbitals of the π system; and through transitions from a lone pair centered on the oxygen atom directly bonded to the metal.

The shoulder at 190 nm in the charge transfer band of Cu-aminoacid complexes can be due to a charge transfer excitation $H_2O \rightarrow Cu^{II}$, to a transition from the oxygen lone pair to copper, or to both at the same time. Substitution of ammonia for water molecules in these complexes leaves unaltered the band at 230 nm, while a shoulder appears at 200 nm, which is in favour of the last posibility. The circular dichroism curve of the $n \rightarrow \pi$ transition is not visible. It is probably masked by the charge transfer band of higher energy.

(8) W. Gaffield and W.G. Galetto, *Tetrahedron*, *27*, 915 (1971).
(9) G. Barth, W. Voelter, E. Bunnenberg, and C. Djerassi, *Chem. Commun.*, 355 (1969)
(10) R.D. Anand and M.K. Hargreaves, *Chem. Commun.*, 421 (1967).
(11) S. Y. Nagakura, *J. Chem. Phys.*, *23*, 1441 (1955).
(12) A.B.P. Lever, *Inorganic Electronic Spectroscopy*, *Elsevier Publ. Co.*, 1968 pag. 360.
(13) K.M. Wellman, W. Mungall, T.C. Mecca, and C.R. Hare, *J. Am. Chem. Soc.*, *89*, 3647 (1967).

In order to account for the optical activity of the charge transfer bands of Cu-aminoacid complexes, Wellman's ideas[13] were followed to work out a molecular scheme considering conformations k or k′ for each geometrical isomer.

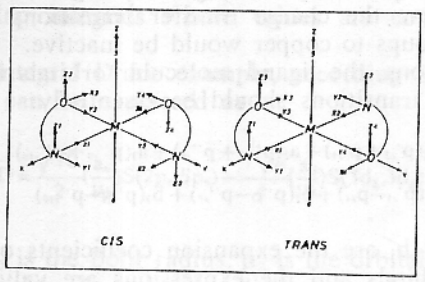

Figure 3. Coordinate systems and labelling of Cis and Trans complexes. Water molecules at positions 5 and 6 have been omitted.

From the point of view symmetry, both geometrical isomers belong to the point group C_2. Figure 3 shows the idealized geometry of these species. Molecular orbitals were defined with conventions stated in Figure 3. In the forthcoming expressions in this work, n_3 and n_4 are unshared electron pairs of the oxygen atoms directly bonded to the metal; p''_{zi} are p_z orbitals of the oxygen atoms bonded to the metal, which are rotated by an angle ρ with respect to the z axis of the local coordinate system. The angle originates in the conformation of the chelated ring; it has been measured in a clockwise sense, looking from the metal towards the oxygen atom, and corresponds to a rotation of the p_r orbital in the plane perpendicular to the respective internuclear metal-oxygen axis. Assuming sp^2 hybridization for the carboxylate group atoms and designating the conformations according to Wellman,[13] it can be shown that the conformation k′ requires ρ to take values from $7/4\pi$ to 2π, because of the spatial arrangement of the R and carbonyl groups with respect to the molecular plane.[14,15] The conformation k, on the contrary, requires ρ to take values from 0 to $1/4\pi$, (Figure 4). As can

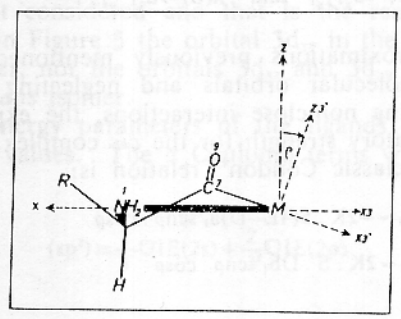

Figure 4. Chelated ring in k′ conformation (left ring of fig. 3). The oxygen atom 3 is eclipsed by the central atom. The y axis points towards the observer.

(14) K.M. Wellman, T.G. Mecca, W. Mungall, and C.R. Hare, *Chem. Eng. News*, *45*, 48 (1967).
(15) F.S. Richardson, D.D. Shillady, and A. Waidrop, *Inorg. Chim. Acta.*, *5*, 279 (1971).

be seen, in both cases the effect of conformation on the π system of the carboxylate group is a torsion of the copper chelated oxygen bond. In this model the nitrogen-copper bond is not distorted.

The experimental evidence already presented gives reason to think that the low energy component of the charge transfer band which is optically active, is due to electronic transitions from molecular orbitals localized mainly in the carboxylate groups, which could correspond to the occupied π levels of higher energy. In this scheme the charge transfer transitions from the amino groups to copper would be inactive. With this assumptions, the ligand molecular orbitals involved in these transitions should be essentially:

$$\pi(A) \sim a_1(p'_{x3}+p'_{x4})+a_2(p''_{x7}+p''_{x8})+a_3(p''_{x9}+p''_{x10})$$

$$\pi(B) \sim b_1(p'_{x3}-p_{x4})+b_2(p''_{x7}-p''_{x8})+b_3(p''_{x9}-p''_{x10})$$

where a_j and b_j are the expansion coefficients of the molecular orbitals and the expressions are valid for both geometrical isomers.

The higher energy component of the charge transfer band may originate in electronic transitions from molecular orbitals localized mainly in the carboxylate groups, where the unshared electron pairs of the oxygen atoms have a higher participation. They would be essentially:

$$n(A) \sim \frac{1}{\sqrt{2}}(n_3+n_4)$$

$$n(B) \sim \frac{1}{\sqrt{2}}(n_3-n_4)$$

This assignation is consistent with CNDO II calculations on formic acid.[16] They indicate that unshared electron pairs of the oxygen atoms bonded to hydrogen correspond to molecular orbitals of lower energy than that of occupied molecular orbitals.

Using the crystal field[17] or the HMO method (see Appendix II), it turns out that the molecular orbital localized mainly in the metal is that having a higher participation (trans complex), or exclusive participation (*cis* complex) of the $d_{x^2-y^2}$ orbital.

In each geometrical isomer the optical activity of the lower energy component of the charge band must be the sum of contributions of two possible transitions, which correspond approximately to:

$$\pi(A) \rightarrow d_{x^2-y^2} \quad \text{and} \quad \pi(B) \rightarrow d_{x^2-y^2}$$

Using the approximations previously mentioned to describe the molecular orbitals and neglecting the terms representing non-close interactions, the expressions of the rotatory strength for the *cis* complex, according to the classic Condon[19] relation is:

$$R_{\pi(A)\rightarrow d} \sim -2K \,.\, S(4E-D)a_1^2 \text{sen}\rho \,.\, \cos\rho$$

$$R_{\pi(B)\rightarrow d} \sim 2K \,.\, S \,.\, Db_1^2 \text{sen}\rho \,.\, \cos\rho$$

where K is $-e^2h/4\pi m_e c$; S is the $S(2p_\pi, 3d_\pi)$ oxygen-metal overlap integral; and the terms D and E are the electronic moment integrals, which are given in the appendix.

Assuming that the energies of these transitions are very similar, a_1 and b_1 equal a. The total rotatory strength of the π→d component of the *cis* complex will be given approximately by:

$$R_{\pi\rightarrow d} \sim -4K \,.\, S(2E-D)a^2 \text{sen}\rho \,.\, \cos\rho \qquad (1)$$

Analogously, for the *trans* complex it is found that:

$$R_{\pi(A)\rightarrow d} \sim -8K \,.\, S \,.\, E(a_1)^2 \text{sen}\rho \,.\, \cos\rho$$

$$R_{\pi(B)\rightarrow d} \sim 4K \,.\, S \,.\, D(b_1)^2 \text{sen}\rho \,.\, \cos\rho$$

the total rotatory strength being the same as that for the *cis* complex.

The optical activity of the component of higher energy of the charge transfer band must be the sum of contributions from two transitions of very similar energy, which can be designated approximately as: $n(A)\rightarrow d_{x^2-y^2}$ and $n(B)\rightarrow d_{x^2-y^2}$. Assuming that n_3 and n_4 are sp^2 hybrids, which is the approximation that better reflects the actual geometry,[20,21] these functions can be described in terms of the local coordinates as:

$$n_3 = \frac{1}{\sqrt{3}}(s_3)+c_{x3}(p_{x3})+c_{y3}(p_{y3})+c_{z3}(p_{z3})$$

$$n_4 = \frac{1}{\sqrt{3}}(s_4)+c_{x4}(p_{x4})+c_{y4}(p_{y4})+c_{z4}(p_{z4})$$

According to symmetry equivalencies in the *cis* complex: $c_{x3}=c_{y4}$; $c_{y3}=c_{x4}$ and $c_{z3}=_{z4}$. In both conformations k and k', the sp^2 hybrids describing the lone pairs deviate from the reference system xy plane. In this way: $c_{z3}=c_{z4}\neq 0$. Therefore, the rotatory strengths of the n→d transitions of the *cis* complex turn out to be:

$$R_{n(A)\rightarrow d} \sim -[\frac{1}{\sqrt{3}}A+c_{y3}B+c_{x3}(4E-D)]c_{z3} \,.\, K \,.\, S$$

$$R_{n(B)\rightarrow d} \sim [\frac{1}{\sqrt{3}}A+c_{y3}B+c_{x3}D]c_{z3} \,.\, K \,.\, S$$

In a similar way for the *trans* complex it is found that:

$$R_{n(A)\rightarrow d} \sim -4K \,.\, S \,.\, E \,.\, c_{x3} \,.\, c_{z3}$$

$$R_{n(B)\rightarrow d} \sim 2K \,.\, S \,.\, D \,.\, c_{x3} \,.\, c_{z3}$$

In these expressions A and B are electric moment integrals, whose details appear in the appendix; the remaining terms have already been defined.

The total rotatory strength associated to the n→d component in both geometrical isomers must correspond approximately to:

$$R_{n\rightarrow d} \sim -2K \,.\, S(2E-D)c_{x3} \,.\, c_{z3}$$

(16) C. Trindle and O. Sinanoglu, *J. Am. Chem. Soc.*, *91*, 853 (1969).
(17) R. Krishnamurthy and W.B. Schaap, *J. Chem. Ed.*, *46*, 799 (1969).
(18) C.J. Ballhausen and H.B. Gray, *Molecular Orbital Theory.*, W. A. Benjamin Inc. 1965.
(19) E.U. Condon, *Rev. Mod. Phys.*, *9*, 432 (1937).
(20) R.D. Gillard, R. Mason, N.C. Payne, and G.B. Robertson, *J. Chem. Soc. (A)*, 1864 (1969).
(21) C.M. Weeks, A. Coopper, and D.A. Norton, *Acta Cryst.*, *B25*, 443 (1969).

Moreover, accepting that: $c_{z3}=-\text{sen}\rho/\sqrt{2}$ and $c_{x3}=\cos\rho/\sqrt{2}$ this expression becomes:

$$R_{n\rightarrow d} \sim K \cdot S(2E-D)\text{sen}\rho \cdot \cos\rho \qquad (2)$$

As can be seen, the expressions (1) and (2) predict that, for a particular conformation of the chelated ring, the $\pi\rightarrow d$ and $n\rightarrow d$ components of the charge transfer band must exhibit Cotton effects of opposite sign.

Evaluation of the D and E integrals shows that (2E–D) is positive. As the product $\text{sen}\rho \cdot \cos\rho$ must be negative for the conformation k', which is sterically prefered in aqueous solution, the preceding treatment leads to conclusions agreeing with experimental evidence, that is to say: the $\pi\rightarrow d$ transition has a negative Cotton effect, while the $n\rightarrow d$ transition has a positive one.

Appendix I

Transition moment integrals

The electric moment integrals for the *cis* complex according to the original coordinate system (Figure 3) are:

$$A=\langle s_3|\bar{y}d_{x^2-y^2}\rangle=-\langle s_4|\bar{x}d_{x^2-y^2}\rangle$$

$$B=\langle p_{y3}|\bar{y}d_{x^2-y^2}\rangle=-\langle p_{x4}|\bar{x}d_{x^2-y^2}\rangle$$

$$D=\langle p_{x3}|\bar{x}d_{x^2-y^2}\rangle=-\langle p_{y4}|\bar{y}d_{x^2-y^2}\rangle$$

$$E=-\langle p_{z3}|\bar{z}d_{x^2-y^2}\rangle=-\langle p_{z4}|\bar{z}d_{x^2-y^2}\rangle$$

For the trans complex:

$$A=\langle s_3|\bar{y}d_{x^2-y^2}\rangle=-\langle s_4|\bar{y}d_{x^2-y^2}\rangle$$

$$B=\langle p_{y3}|\bar{y}d_{x^2-y^2}\rangle=-\langle p_{y4}|\bar{y}d_{x^2-y^2}\rangle$$

$$D=\langle p_{x3}|\bar{x}d_{x^2-y^2}\rangle=-\langle p_{x4}|\bar{x}d_{x^2-y^2}\rangle$$

$$E=-\langle p_{z3}|\bar{z}d_{x^2-y^2}\rangle=-\langle p_{z4}|\bar{z}d_{x^2-y^2}\rangle$$

Transforming the coordinate system in atom 3 into a left-handed coordinate system, x_a, y_a, z_a, and the reference coordinate system (of the central atom) into a right-handed coordinate system, x_b, y_b, z_b by means of the relations:

$$x_a=r_a\text{sen}\theta_a\cos\varphi=z3 \qquad x_b=r_b\text{sen}\theta_b\cos\varphi=z$$

$$y_a=r_a\text{sen}\theta_a\text{sen}\varphi=-x3 \qquad y_b=r_b\text{sen}\theta_b\text{sen}\varphi=x$$

$$z_a=r_a\cos\theta_a=y3 \qquad z_b=r_b\cos\theta_b=-y$$

the integrals D and E can be written as:

$$D=\langle -p_{ya}|\bar{y}_b d_{y_b^2-z_b^2}\rangle=\langle p_{ya}|\bar{y}_b d_{z_b^2-y_b^2}\rangle$$

and

$$E=-\langle p_{xa}|\bar{x}_b d_{y_b^2-z_b^2}\rangle=\langle p_{xa}|\bar{x}_b d_{z_b^2-y_b^2}\rangle$$

Therefore, these integrals, expressed in terms of bipolar coordinates, become:

$$D=N_aN_b\int R_a(\text{sen}\theta_a)R_b(r_b\text{sen}\theta_b)(\cos^2\theta_b-\text{sen}^2\theta_b\text{sen}^2\varphi)(\text{sen}^2\varphi)d\tau$$

$$E=N_aN_b\int R_a(\text{sen}\theta_a)R_b(r_b\text{sen}\theta_b)(\cos^2\theta_b-\text{sen}^2\theta_b\text{sen}^2\varphi)(\cos^2\varphi)d\tau$$

where a and b refer to oxygen and metal orbitals respectively; N_a and N_b are normalization constants and R_a and R_b are radial functions. The evaluation of these integrals can be achieved directly by transformation to elliptical coordinates, following a method similar to that reported by Mulliken for the evaluation of bicentric overlap integrals;[22] or else by conversion to overlap integrals whose values are computed in tables.

The integral D for example, according to the last method can be expressed as:

$$D=\frac{\sqrt{70}}{2}\left(\frac{a_o}{\mu_b}\right)S(2p_\pi,5p_\pi)-\frac{7\sqrt{6}}{4}\left(\frac{a_o}{\mu_a}\right)S(3d_\delta,3d_\delta)$$

where a_o is the Bohr radius, μ_a is the orbital exponent of the oxygen 2p radial function and μ_b is the orbital exponent of the metal 3d radial function.

In the same way it is found that:

$$2E-D=\frac{\sqrt{70}}{2}\left(\frac{a_o}{\mu_b}\right)S(2p_\pi,5p_\pi)-\frac{3\sqrt{6}}{4}\left(\frac{a_o}{\mu_a}\right)S(3d_\delta,3d_\delta)$$

Appendix II

A summary of the Huckel calculations performed on the ideal species *cis*-Ni(amac)$_2$(H_2O)$_2$ to obtain the energy levels sequence of the metal orbitals is given. The qualitative nature of the interpretation of spectral features made in this work justifies the extension of results to the case of the copper(II) complexes.

The calculations were performed by iteration on the configuration and charge of the central atom. They include the atoms directly bonded to the metal and the system of the carboxylate group. The final configuration and charge were applied without iteration to a Huckel calculation for the species *trans*-Ni(amac)$_2$(H_2O)$_2$. Both the *cis* and *trans* complexes were worked under C_2 symmetry.

On the sake of simplicity the matrix elements were determined assuming that the carbonyl group lies in the xy plane of the reference system. Interactions of the lone pairs n_3 and n_4 with the metal orbitals were not considered and that is the reason not to include in Figure 5 the orbital $3d_{xy}$ in the case of the *cis* isomer, nor the orbitals $3d_{xz}$ and $3d_{xy}$ in the case of the *trans* isomer.

The energy parameters of the ligands were taken as fixed values. The σ Coulomb terms were calculated as:

$$(sp^2)=\frac{1}{3}OIE(2s)+\frac{2}{3}OIE(2p)$$

$$(sp^3)=\frac{1}{4}OIE(2s)+\frac{3}{4}OIE(2p)$$

an the π Coulomb terms were given the value of the 2p Orbital ionization Energy.[18] The ligand and metal-

(22) R.S. Mulliken, C.A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, *17*, 1248 (1949).

ligand exchange integrals were obtained by means of the Wolfsberg and Helmholz expression.[23]

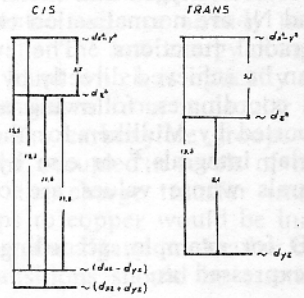

Figure 5. Appendix II. Molecular orbitals scheme of d orbitals sequence. (Figures in kK)

The overlap integrals were computed making use of the radial functions given in references 22, 24, 25 and 26; the internuclear distances of the complex Diaquobis(L-serinato) nickel(II)[27] and overlap integral tables.[22,28,29] The integral $S(2p_\pi, 4p_\pi)$ was calculated from its master formula. The metal-ligand exchange integrals were recalculated in each iteration following the variation of the metal Coulomb integrals. The empirical constant F of the Wolfsberg and Helmholz approximation was given a value of 0.8 in all cases, which is rather low, due to the exclusion of the energy in the non-diagonal terms of the secular matrix.

The Coulomb integrals of the metal were determined in each iteration by means of VSIE functions for different configurations, as shown in reference.[18]

The charge and configuration data corresponding to the last iteration are:

	Charge	Configuration
Input	+0.2078	$3d^{8.5640}\ 4s^{0.5551}\ 4p^{0.6711}$
Output	+0.2073	$3d^{8.5663}\ 4s^{0.5551}\ 4p^{0.6733}$

Figure 5 shows the resulting splitting of the d orbitals.

Application of the input charge and configuration of the last iteration to calculations of the *trans*-complex led to acceptable results:

charge: +0.2378

configuration: $3d^{8.5345}\ 4s^{0.5514}\ 4p^{0.6763}$

The d orbitals splitting of the trans complex also appears in Figure 5.

Acknowledgment. We are grateful to Dr. C. A. Bunton and Dr. F. T. Fox of the Department of Chemistry of the University of California, Santa Barbara, for help in the experimental part of this work. Finantial support of C.O.N.I.C.Y.T. and "Comisión Central de Investigación" of the University of Chile are greatly acknowledged.

(23) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, *20*, 837 (1952).
(24) J.W. Richardson, W.C. Nieuwpoort, R.R. Powell, and W.F. Edgell, *J. Chem. Phys.*, *36*, 1057 (1962).
(25) C.J. Ballhausen and H.B. Gray, *Inorg. Chem.*, *1*, 111 (1962).
(26) M. Zerner and M. Gouterman, *Theoret. Chim. Acta (Berl.)*, *4*, 44 (1966).
(27) Van der D. Helm and B.M. Hossain, *Acta Cryst.*, *B25*, 457 (1969).
(28) H.H. Jaffé and G.O. Doak, *J. Chem. Phys.*, *21*, 196 (1953).
(29) H.H. Jaffé, *J. Chem. Phys.*, *21*, 258 (1953).