The coordination of π-conjugated bidentate ligands

A. Ceulemans*, L.G. Vanquickenborne

Chemistry Department, University of Leuven, Leuven, B-3030, Belgium

Abstract - Double bonding in chelated metal complexes gives rise to specific electronic effects on the metal d-orbitals. It is shown how these interactions can be incorporated in a ligand field model. Special emphasis is placed on the symmetry characteristics of the resulting hamiltonian. Specific predictions of this model with regard to the trigonal splitting in chiral trischelates and to the orthorhombic field in planar bischelates are confronted with the most recent experimental data.

INTRODUCTION

Coordination of a bidentate ligand can be viewed as a ring closure reaction, leading to the formation of a "heterocyclic" compound. If the bidentate ligand is unsaturated, cyclic delocalization of the ligand π-orbitals is possible through the intermediary of the d-orbitals on the metal. Already in 1961 Orgel has offered a description of these interactions, using symmetry based molecular orbital type arguments (ref. 1). For a proper discussion of the metal valence structure, it is useful to reformulate these results in a ligand field model, which incorporates the interactions due to ligand π-conjugation in an effective hamiltonian over the d-orbitals. In a previous publication (ref. 2) such a model was developed, starting from the conventional Angular Overlap Model (AOM). The method allows to treat any type of bridging ligand in any coordination geometry. In the present paper we will briefly review this model in the light of recent contributions by Schäffer and Yamatera (ref. 3), and by Atanasov, Schönherr and Schmidtke (ref. 4). Furthermore a critical discussion of available spectrosopic and magnetic evidence on double bonding in chelated metal complexes will be presented.

THE MODEL

In conventional ligand field theory, the field of both saturated and unsaturated bridging ligands is taken to be the additive result of two independent localized interactions, involving the metal and the ligator atoms at both ends of the bridge. If the chelate is a planar π-system, different e_π parameters for in-plane ($\pi\|$) and out-of-plane ($\pi\perp$) interactions are usually allowed for (non-linear ligation), but this does not violate the basic postulate of ligator additivity (refs 5,6). In such a scheme, the primary role of the bridge seems to be a purely geometrical one : the strain of the molecular link between two ligators causes deviations from orthoaxiality and even introduces bent M-L bonds. Attempts have been made to relate the circular dichroism of chiral chelates to such geometrical effects (ref. 7). However, as we have argued elsewhere (ref. 2), this restricted view of the role of the bidentate bridge cannot be maintained in the case of a π-conjugated bidentate : indeed in this case the conjugation gives rise to a *through bridge* electronic coupling between the frontier $p\perp$ orbitals on the ligator atoms. The corresponding ligand field cannot be expressed by the AOM method, unless one is willing to abandon the picture of two independent ligator atoms.

To illustrate how additivity breaks down, we start by considering a ML_2 unit, consisting of a d-metal in the origin and two separate ligands on x and y axis. As far as the out-of-plane π interactions of these ligands are concerned, the ligand on the x-axis will contribute to the energy of d_{xz} by an amount of $e_{\pi\perp}$, and similarly for the ligand on the y-axis and d_{yz}. The total AOM matrix for a (d_{xz}, d_{yz}) basis is the sum of these two diatomic interactions

$$\begin{pmatrix} e_{\pi\perp} & 0 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & e_{\pi\perp} \end{pmatrix} = \begin{matrix} xz \\ yz \end{matrix} \begin{pmatrix} \overset{xz}{e_{\pi\perp}} & \overset{yz}{0} \\ 0 & e_{\pi\perp} \end{pmatrix} \qquad (1)$$

Clearly the total energy matrix in eq. 1 preserves the degeneracy of d_{xz} and d_{yz}, and thus must have a pseudo-tetragonal symmetry. The actual symmetry of the unit is C_{2v} though. In this symmetry the ligator p_z orbitals form a_2 and b_2 combinations. Following Orgel (ref. 1) we will label these resp. as χ and ψ. In the χ combination the p_z orbitals are *out−of−phase*, while in the ψ combination they are *in−phase*.

X−type   ψ−type
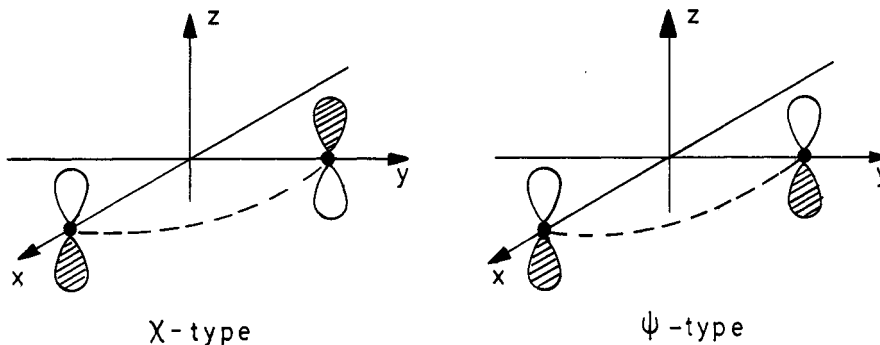
The perturbation matrices which describe the interactions of these SALC's with the (d_{xz}, d_{yz}) basis can easily be derived. Thereby two new parameters are required : e_ψ and e_χ. The total interaction matrix becomes :

$$e_\psi \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix} + e_\chi \begin{pmatrix} 1/2 & -1/2 \\ -1/2 & 1/2 \end{pmatrix} = \begin{pmatrix} 1/2(e_\psi + e_\chi) & 1/2(e_\psi - e_\chi) \\ 1/2(e_\psi - e_\chi) & 1/2(e_\psi + e_\chi) \end{pmatrix} \qquad (2)$$

In this equation the e_ψ and e_χ parameters are defined in such a way that the traces of the corresponding matrices add up to *two*, which is the number of ligators. This convention was used in refs. 3 and 4, and has the advantage that, upon a gradual diminution of the phase-coupling, the e_ψ and e_χ parameters converge to the $e_{\pi\perp}$ parameter of the conventional model. In our previous treatment (ref. 2) we defined the ψ and χ matrices as $\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$ and $\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$ respectively, so that the individual traces were equal to the number of ligators. This definition has the advantage that - in cases of strong phase-coupling - the corresponding parameter values usually fall within the normal range of $e_{\pi\perp}$ parameters for unidentate non-linear ligators. Of course the two conventions only differ by a factor of two. To avoid further confusion, we propose that the symbols e_ψ and e_χ should always be used for parameters that obey the conventions in eq. 2. In order to analyse the results in eq. 2 it is convenient to perform a symmetry partitioning of the total interaction matrix, as shown in eq. 3.

$$\begin{pmatrix} 1/2(e_\psi + e_\chi) & 1/2(e_\psi - e_\chi) \\ 1/2(e_\psi - e_\chi) & 1/2(e_\psi + e_\chi) \end{pmatrix} = 1/2(e_\psi + e_\chi) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + 1/2(e_\psi - e_\chi) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad (3)$$

Here the term in $e_\psi + e_\chi$ has tetragonal symmetry, since it does not lift the degeneracy of d_{xz} and d_{yz}. It therefore corresponds to the conventional cellular term, obtained by summing the two diatomic interactions. On the other hand, the traceless term in $e_\psi - e_\chi$ induces a characteristic orthorhombic splitting of the degeneracy. The corresponding D_{2h} symmetry may be identified as the holohedrized form of the actual C_{2v} point group, and is aligned along the bisector of the bite angle.

The cellular approach remains valid, as long as the D_{2h} term is close to zero, i.e. if $e_\psi = e_\chi$. This will only be realized if inter-ligator interactions are weak, so that the ψ and χ ligand combinations have similar orbital energies. *In a conjugated chain such an approximation cannot be maintained.* Indeed in such a case the two SALC's become part of delocalized MO's that extend over the whole chain. Usually there will be a substantial energy difference between ψ and χ type MO's, giving rise to different values

for e_ψ and e_χ. In fact, if we limit our attention to the frontier HOMO and LUMO of the ligand chain, they will often be found to exhibit alternate phases of the outer orbitals. Hence if π-donor interactions are of the ψ type, π-acceptor interactions will usually be of the χ type, or vice versa. The corresponding e_ψ and e_χ parameters thus will have different signs. As eq. 3 shows, such a synergism of donor and acceptor interactions will lead to a pronounced D_{2h} term. In our previous publication (ref. 2) we have coined the term *phase—coupled* ligators. This term indicates that the main role of the conjugated bridge is to impose definite phase relationships between the ligator orbitals in the frontier MO's.

Simple Hückel theory often allows an unequivocal prediction of the sign of the D_{2h} component, even if it is not clear whether donor or acceptor interactions are predominant. As an example α-diimine ligands, such as 2,2'-bipyridyl (bipy), are predicted to have a negative D_{2h} splitting, while β-disubstituted ligands, such as the acetylacetonate anion (acac⁻), should have a positive D_{2h} splitting (ref. 2).

bipy : $\ell_\psi - \ell_\chi < 0$ acac: $\ell_\psi - \ell_\chi > 0$
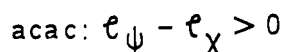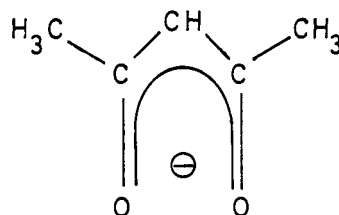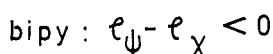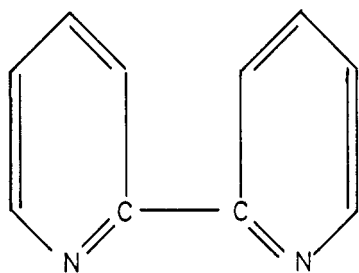
A change from α to β type ligands thus is predicted to have a dramatic effect on the phase-coupling term. For this reason, a systematic comparison of experimental results for both types of ligands seems to offer the most reliable strategy towards a convincing experimental demonstration of the phase-coupling effect.

THE TRIGONAL FIELD IN TRISCHELATED COMPLEXES

As a first example we apply the phase-coupling model to a regular hexacoordinated complex, consisting of three bidentate ligands (refs. 2,8,9). The individual out-of-plane ($\pi_\perp$) interaction matrices can easily be obtained from eq. 3 by applying the standard AOM techniques.
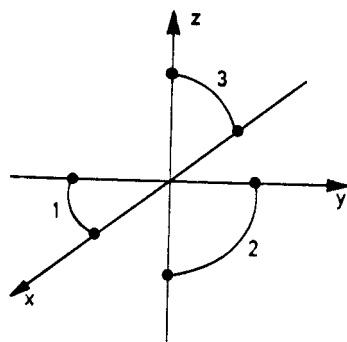
$$V_1 = \tfrac{1}{2}(e_\psi + e_\chi)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}^{xz\ yz} + \tfrac{1}{2}(e_\psi - e_\chi)\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}^{xz\ yz}$$

$$V_2 = \tfrac{1}{2}(e_\psi + e_\chi)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}^{xy\ xz} + \tfrac{1}{2}(e_\psi - e_\chi)\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}^{xy\ xz}$$

$$V_1 = \tfrac{1}{2}(e_\psi + e_\chi)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}^{xy\ yz} + \tfrac{1}{2}(e_\psi - e_\chi)\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}^{xy\ yz} \quad (4)$$

The total sum of these interactions in the t_{2g} orbital basis may be partitioned in an octahedral and a trigonal term, as shown in eq. 5.

$$V_1 + V_2 + V_3 = (e_\psi + e_\chi)\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}^{xy\ xz\ yz} + \tfrac{1}{2}(e_\psi - e_\chi)\begin{pmatrix} 0 & -1 & -1 \\ -1 & 0 & -1 \\ -1 & -1 & 0 \end{pmatrix}^{xy\ xz\ yz} \quad (5)$$

Here the first term in $e_\psi + e_\chi$ represents the octahedral field, which provides a global energy shift of the t_{2g} shell. A similar term can be obtained by a conventional non-linear ligator model. On the other hand the second term in $e_\psi - e_\chi$ only arises in the case of a phase-coupling effect. It is the resultant of the local D_{2h} fields of the three bidentates. The sum of these three fields has trigonal symmetry and gives rise to a splitting of the t_{2g} shell in subshells of e and a_1 symmetry. The corresponding energy difference is given in eq. 6.
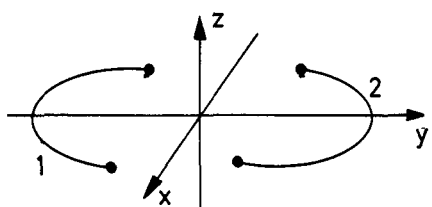
$$\epsilon(e) - \epsilon(a_1) = \tfrac{3}{2}(e_\psi - e_\chi) \tag{6}$$

When confronting this phase-coupling result with experiment, it must be kept in mind that minor geometric distortions from orthoaxiality also contribute to the observed trigonal splitting. In this respect the $Cr(acac)_3$ compound presents a favorable example, since its first coordination sphere of oxygen atoms is nearly octahedrally arranged (ref. 4). In fact only about 10 % of the observed trigonal splitting of the t_{2g} orbitals in $Cr(acac)_3$ can be attributed to geometric effects. The other 90 % thus must be due to phase-coupling through the conjugated $acac^-$ bridge. Estimates for the trigonal field parameter, $e_\psi - e_\chi$, in eq. 5 range from +1400 cm^{-1} to +2000 cm^{-1}. The positive sign of this parameter has been confirmed by polarized absorption spectra of $Cr(acac)_3$, doped in a lattice of $Al(acac)_3$ (ref. 4), and is in agreement with the Hückel results.

For the $Cr(bipy)_3^{3+}$ complex, an opposite trigonal splitting is expected. Spectroscopic confirmation is less straightforward in this case, since there is a sizeable trigonal geometric distortion which seems to counteract the phase-coupling effect (ref. 10).

THE ORTHORHOMBIC FIELD IN PLANAR BISCHELATED COMPLEXES

Electronic structure characterization in square planar bischelated complexes has been remarkably successful, especially through the use of single crystal EPR measurements on low spin Co^{2+} compounds (ref. 11). In line with earlier conventions the $M(LL)_2$ bischelated compound will be placed in the xy coordinate plane, with the y axis along the bisector of the two bridges. The $\pi\perp$ interaction matrices are obtained by rotating the matrix in eq. 2 over 45° about the z axis.

$$V_1 = V_2 = \begin{array}{c} \\ xz \\ yz \end{array}\!\!\begin{array}{cc} xz & yz \\ \begin{pmatrix} e_\chi & 0 \\ 0 & e_\psi \end{pmatrix} \end{array} \tag{7}$$

As before the total matrix may be expressed as a sum of two terms of different symmetry. These terms are easily recognized as a tetragonal and an orthorhombic term. The corresponding parameters are seen to be twice as large as in the monochelated complex of eq. 3.

$$V_1 + V_2 = (e_\psi + e_\chi)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + (e_\psi - e_\chi)\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \tag{8}$$

The orthorhombic term in $e_\psi - e_\chi$ is due to the phase-coupling effect and gives rise to a splitting of d_{xz} and d_{yz}. Its sign determines the resulting orbital ordering. Hence for β-disubstituted bidentates, one expects the $d_{yz} > d_{xz}$ ordering, corresponding to a positive $e_\psi - e_\chi$ parameter. This is indeed confirmed by the measurement of the g-factor anisotropy in several quadridentate Co^{2+} Schiff Base complexes, containing two β-disubstituted conjugated bridges (refs. 11,12). A case in point is the Co(salen) complex (salen = N,N'-ethylenebissalicylaldimine), depicted below.

$$H_2C - CH_2$$
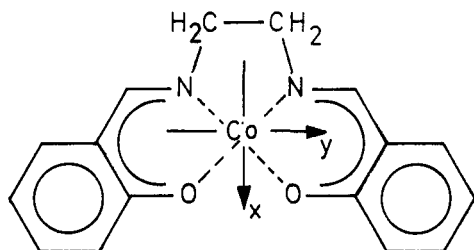
Co (salen)

$$d_{yz} > d_{xz}$$

As we have pointed out, these results should be compared with measurements on similar compounds, in which there has been a phase change of the bidentate π-conjugation. Recently we have been able to perform such measurements, using the $C_{10}H_{20}N_8$ macrocyclic ligand, which contains two α-diimine unsaturated bridges (ref. 13). In the $Co(C_{10}H_{20}N_8)Cl_2$ compound, diluted in the diamagnetic $Ni(C_{10}H_{20}N_8)Cl_2$ lattice, one indeed observes a reversal of the g-factor anisotropy, as compared to Co(salen). This reversal clearly points to a sign change of the orthorhombic splitting, now with $d_{xz} >$ d_{yz}.
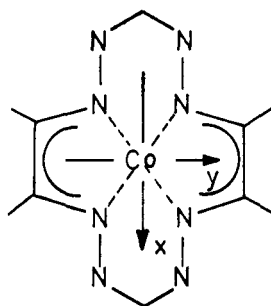
$$Co \, C_{10}H_{20}N_8 \, Cl_2$$

$$d_{xz} > d_{yz}$$

CONCLUSION

Electronic coupling between the ligator orbitals via a conjugated bridge gives rise to a specific symmetry lowering of the ligand field. Usually the sign and orientation of the low symmetry component can be determined from Hückel theory. This opens a new way to modulate spectral and magnetic properties of transition-metal complexes by changing the nature of the conjugated bridges.

REFERENCES

1. L.E. Orgel, *J. Chem. Soc.*, 3683 (1961).
2. A. Ceulemans, M. Dendooven, and L.G. Vanquickenborne, *Inorg. Chem.*, *24*, 1153 (1985).
3. H. Yamatera and C.E. Schäffer, *Abstract presented at the XXIV Int. Conf. Coord. Chem.*, Athens, August 1986, Chimika Chronika (New Series), Special Issue, August 1986, p. 125.
4. M.A. Atanasov, T. Schönherr, and H.-H. Schmidtke, *Theor. Chim. Acta (Berlin)*, *77*, 59 (1987).
5. C.E. Schäffer, *Struct. Bonding (Berlin)*, *5*, 68 (1968).
6. C.K. Jørgensen : "Modern Aspects of Ligand Field Theory"; North-Holland publishing Co. : Amsterdam, 1971; ch. 17.
7. C.E. Schäffer, *Proc. Roy. Soc. (London)*, *A297*, 96 (1967).
8. A. Ceulemans, N. Bongaerts, and L.G. Vanquickenborne, *Inorg. Chem.*, *26*, 1566 (1987).
9. A. Ceulemans, N. Bongaerts, and L.G. Vanquickenborne, in : "Photochemistry and Photophysics of Coordination Compounds", H. Yersin and A. Vogler (Eds.); Springer-Verlag : Berlin, 1987; p. 31.

10. A. Hauser, M. Mäder, W.T. Robinson, R. Murugesan, and J. Ferguson, *Inorg. Chem.*, *26*, 1331 (1987).

11. C. Daul, C.W. Schläpfer, and A. von Zelewsky, *Struct. Bonding (Berlin)*, *36*, 129 (1979).

12. A. Ceulemans, M. Dendooven, and L.G. Vanquickenborne, *Inorg. Chem.*, *24*, 1159 (1985).

13. A. Ceulemans, R. Debuyst, F. Dejehet, G.S.D. King, M. Vanhecke, and L.G. Vanquickenborne, *submitted for publication*.