

Unusual Ligand Field Effects in Square-Planar Cobalt(II) Complexes of Quadridentate Schiff Bases

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Divalent cobalt forms with Schiff base ligands a variety of stable complexes that have great potential interest as synthetic oxygen carriers. Especially, square-planar compounds of the CoN_2O_2 and $\text{CoN}_2\text{N}'_2$ type have been subject to extensive magnetic and spectroscopic studies. In the opening section, these studies are briefly reviewed and a general group-theoretical treatment of the g tensor in low-spin d^7 complexes is presented. In those cases where the empirical d -orbital order and the ground-state eigenvector could be determined, two unusual features are observed: (i) The symmetry of the ligand field is definitely lower than the expected tetragonal holohedron symmetry. The resulting anisotropy is characteristic of unsaturated bidentate ligands and is known as the Orgel effect. (ii) The d_{z^2} orbital is almost nonbonding, due to a pronounced $4s-3d_{z^2}$ orbital mixing. Both features are beyond the scope of conventional ligand field parameterization schemes. The present paper is concerned with the application of a more refined Hamiltonian, which incorporates the effect of $s-d$ mixing and of Orgel anisotropy, at the level of a ligand field formalism. As a result one obtains new expressions for the d -orbital energies, which can be used to investigate structural changes of the coordination sphere. This refined model is able to explain why weak axial coordination of a fifth ligand induces a dramatic destabilization of the d_{z^2} orbital. These conclusions have a direct bearing on the oxygen-binding problem. Another interesting result is the extreme magnitude of the Orgel effect in $\text{N}_2\text{N}'_2$ quadridentates, which has now for the first time been identified.

Introduction

Divalent cobalt forms with tetradentate Schiff bases a variety of stable complexes that have a potential interest as model systems for oxygen-binding biomolecules.^{1,2} In some favorable cases a detailed empirical characterization of the d -orbital energies has been achieved. As indicated by Daul et al.¹ these conclusions are essentially consistent with the results of extended molecular orbital calculations. In contrast, a popular and widespread ligand field model such as the angular-overlap model (AOM) is considerably less successful in explaining the observed electronic structure. The deficiencies of the additive point ligand model can only be remedied if one is willing to amend the basic postulates of the model. We have recently described when and how this can be done within the framework of a local ligand field model.^{3,4} It is the purpose of the present work to confront the observed anomalies in Co(II) Schiff base complexes with this extended model description. Possible implications for our understanding of the functional behavior of this class of compounds will also be discussed.

I. Electronic Structure of Square-Planar Compounds

This section will be devoted to a terse discussion of the empirical d -orbital ordering in square-planar Schiff base Co(II) complexes of the CoN_2O_2 and $\text{CoN}_2\text{N}'_2$ type. An excellent review of the relevant experimental results has recently been published.¹ Daul, Schlöpfer, and von Zelewsky also presented¹ a simplified ground-state model that offers a straightforward interpretation of the EPR data. The present analysis is mainly concerned with a more thoroughgoing discussion of the symmetry aspects of this ground-state model.

The molecular point group⁵ is nearly C_{2v} , with the twofold axis in the x direction of the conventional Cartesian frame (see Figure 1). Previous studies on d^8 and d^9 square-planar compounds invariably point to the presence of a strong equatorial field, which causes a splitting of the five d orbitals into a single highly antibonding orbital, in case d_{xy} , and a cluster of four closely spaced nonbonding or weakly interacting orbitals.^{3,6,7} In a low-spin Co(II) system, the cluster set will contain seven electrons. Depending on which orbital is singly occupied, four different doublet ground states are conceivable. Hence, contrary to the d^8 or d^9 case, the

Table I. Doublet States Resulting from the $(d_{z^2}, d_{x^2-y^2}, d_{xz}, d_{yz})^7$ Configuration^a

state	energy vs. $ ^2A_2 yz\rangle$
$ ^2A_2 yz\alpha\rangle = (xz)^2(z^2)^2(x^2-y^2)^2(yz\alpha) $	
$ ^2A_2 yz\beta\rangle = (xz)^2(z^2)^2(x^2-y^2)^2(yz\beta) $	
$ ^2A_1 z^2\alpha\rangle = (xz)^2(z^2\alpha)(x^2-y^2)^2(yz)^2 $	$E(yz) - E(z^2) - 5B$
$ ^2A_1 z^2\beta\rangle = (xz)^2(z^2\beta)(x^2-y^2)^2(yz)^2 $	
$ ^2A_1 x^2-y^2\alpha\rangle = (xz)^2(z^2)^2(x^2-y^2\alpha)(yz)^2 $	$E(yz) - E(x^2-y^2) + 15B$
$ ^2A_1 x^2-y^2\beta\rangle = (xz)^2(z^2)^2(x^2-y^2\beta)(yz)^2 $	
$ ^2B_1 xz\alpha\rangle = (xz\alpha)(z^2)^2(x^2-y^2)^2(yz)^2 $	$E(yz) - E(xz)$
$ ^2B_1 xz\beta\rangle = (xz\beta)(z^2)^2(x^2-y^2)^2(yz)^2 $	

^a Energy differences with respect to the $|^2A_2 yz\rangle$ level are expressed as functions of d -orbital energies and Racah's interelectronic repulsion parameter B . In the character table of $C_{2v}(x)$ a B_1 state is symmetric with respect to σ_{xz} ($=\sigma_1$) and antisymmetric with respect to σ_{xy} ($=\sigma_2$) (conventions as in ref 1 and 7).

orbital nature of the Co(II) ground state constitutes a real problem.

A. Ground State Eigenvector. First, consider the cluster eigenorbitals that the single unpaired electron might occupy. In $C_{2v}(x)$, d_{xz} and d_{yz} follow unique symmetry representations and therefore diagonalize the LF Hamiltonian; d_{z^2} and $d_{x^2-y^2}$ are totally symmetric and might be mixed by the low-symmetry features of the ligand field. Since the complex is almost orthoaxial, orbital mixing is unlikely to be a major effect and the four cluster eigenorbitals essentially correspond to d_{z^2} , $d_{x^2-y^2}$, d_{xz} , and d_{yz} . The matching doublet states and relative energy expressions are listed in Table I. In view of the large interelectronic repulsion energy the $|^2A_1 x^2-y^2\rangle$ state can safely be disregarded as a possible ground state. Since the remaining three doublet states are interconnected via off-diagonal spin-orbit coupling matrix elements, the actual ground state will have a composite nature and at least involves three components.¹ The main purpose of magnetic measurements has been to estimate the directional cosines of the ground-state eigenvector in the functional space of the three doublets $|^2A_1 z^2\rangle$, $|^2B_1 xz\rangle$, and $|^2A_2 yz\rangle$. A precise description of this space requires the use of the double group $C_{2v}^*(x)$. This group contains only one two-valued representation, E' . Hence, all doublet states transform as E' , while all quartet states give rise to two E' representations. The components of E' are defined but for unitary equivalence, and fixed partners must be chosen by imposing a

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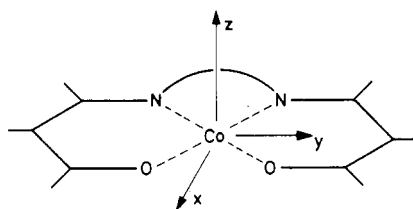


Figure 1. Conventional Cartesian coordinate system for square-planar complexes of Co(II) with quadridentate Schiff base ligands. The molecular point group is $C_{2v}(x)$, with symmetry elements $C_2(x)$, σ_{xz} , and σ_{xy} . In complexes of the $\text{CoN}_2\text{N}'_2$ type, oxygen ligands are replaced by imino groups.

Table II. Standard Symmetry Behavior of the Canonical Kramers Doublets in $C_{2v}(x)$ (Coordinate Axes as in Figure 1)^a

	$C_2(x)$	σ_{xz}	σ_{xy}
$ E' + 1/2\rangle$	$-i E' - 1/2\rangle$	$ E' - 1/2\rangle$	$-i E' + 1/2\rangle$
$ E' - 1/2\rangle$	$-i E' + 1/2\rangle$	$- E' + 1/2\rangle$	$i E' - 1/2\rangle$
$\Gamma^{E'}(C_2(x)) = \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$	$\Gamma^{E'}(\sigma_{xz}) = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\Gamma^{E'}(\sigma_{xy}) = \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}$	
$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$	$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	

^a Also shown are the corresponding representational matrices $\Gamma^{E'}$ for an ordered-row vector ($|E' + 1/2\rangle$, $|E' - 1/2\rangle$) and the Pauli spin matrices σ .

standard set of representational matrices. It is convenient to choose canonical basis functions, ($|E' + 1/2\rangle$, $|E' - 1/2\rangle$), in such a way that their symmetry behavior precisely corresponds to the symmetry behavior of the usual spin functions ($|\alpha\rangle$, $|\beta\rangle$), which are quantized along the z axis. The required representational matrices can easily be found if one realizes that electron spins have even parity under spatial inversion (see ref 8, page 174). As a consequence, a reflection and a twofold rotation normal to the reflection plane transform spin functions in an identical way. The planes of symmetry σ_{xz} and σ_{xy} can thus be replaced by respectively $C_2(y)$ and $C_2(z)$. As a result, the three nontrivial symmetry elements of $C_{2v}(x)$ are mapped on three equivalent C_2 rotations around the three Cartesian directions.

The appropriate representational matrices then immediately follow from the general expressions of angular momentum theory (see e.g. ref 9, Chapter 13):

$$\Gamma^{E'}(C_2(x)) = -i\sigma_x \quad (1a)$$

$$\Gamma^{E'}(\sigma_{xz}) = \Gamma^{E'}(C_2(y)) = -i\sigma_y \quad (1b)$$

$$\Gamma^{E'}(\sigma_{xy}) = \Gamma^{E'}(C_2(z)) = -i\sigma_z \quad (1c)$$

In eq 1 σ_x , σ_y , and σ_z represent the well-known Pauli spin matrices. Explicit formulas are given in Table II.

Clearly, in the quantization scheme proposed here Kramers components are not eigenfunctions of the principal twofold axis, $C_2(x)$, but they are symmetry adapted to the horizontal plane of symmetry σ_{xy} . This reflection element transforms the $|E' + 1/2\rangle$ and $|E' - 1/2\rangle$ partners in a different way and therefore acts as a splitting field.⁸ Symmetry-adapted components for an arbitrary ground-state eigenvector are easily obtained by first projecting eigenfunctions of σ_{xy} and next adjusting their phases so as to meet the prescribed symmetry behavior under the remaining symmetry elements. Introducing the three complex numbers c_1 , c_2 , and c_3 to denote eigenvector coefficients, one obtains

$$|E' + 1/2\rangle = c_1|A_2 yz\beta\rangle + c_2|A_1 z^2\alpha\rangle + c_3|B_1 xz\beta\rangle \quad (2a)$$

$$|E' - 1/2\rangle = c_1|A_2 yz\alpha\rangle + c_2|A_1 z^2\beta\rangle - c_3|B_1 xz\alpha\rangle \quad (2b)$$

where $|E' - 1/2\rangle$ has been obtained by applying the σ_{xz} operation

to the $|E' + 1/2\rangle$ function (as indicated in Table II).

This equation can further be specified by applying the time reversal operator θ . Its action on spin functions can be represented by σ_y , while its action on spatial functions and constants simply corresponds to complex conjugation, symbolized by the conjugating operator K_0 . At this point a phase factor convention has to be introduced since time reversal—being a shift operator—does not specify an absolute phase. Following the convention of Abragam and Bleaney,⁹ we define θ as in eq 3. Now one can require that

$$\theta = i\sigma_y K_0 \quad (3)$$

the conjugational properties of the E' Kramers doublet be strictly isomorphous to the properties of the (α, β) spin basis, thus implying that the effect of θ on the E' components is equivalent to the effect of $i\sigma_y$ on the electron spin functions:

$$\theta|\alpha\rangle = -|\beta\rangle; \quad \theta|E' + 1/2\rangle = -|E' - 1/2\rangle \quad (4a)$$

$$\theta|\beta\rangle = |\alpha\rangle; \quad \theta|E' - 1/2\rangle = |E' + 1/2\rangle \quad (4b)$$

These conditions allow determination of the effect of complex conjugation on the c_i coefficients in eq 2. Combining eq 2–4, one can restate the ground-state eigenvectors with the use of three real parameters a , b , and c .

$$|E' + 1/2\rangle = ia|A_2 yz\beta\rangle + b|A_1 z^2\alpha\rangle + c|B_1 xz\beta\rangle \quad (5a)$$

$$|E' - 1/2\rangle = ia|A_2 yz\alpha\rangle + b|A_1 z^2\beta\rangle - c|B_1 xz\alpha\rangle \quad (5b)$$

Finally, in order to predict the relative signs of the parameters a , b , and c in eq 5, spin-orbit coupling (soc) interactions have to be taken into account explicitly. In the absence of an external magnetic field, the ground-state energy is given by

$$\langle E' \pm 1/2 | \mathcal{H}^0 + \mathcal{H}_{\text{soc}} | E' \pm 1/2 \rangle = a^2 \langle A_2 | \mathcal{H}^0 | A_2 \rangle + b^2 \langle A_1 | \mathcal{H}^0 | A_1 \rangle + c^2 \langle B_1 | \mathcal{H}^0 | B_1 \rangle + \zeta(3^{1/2}ab + ac + 3^{1/2}bc) \quad (6)$$

where \mathcal{H}^0 incorporates ligand field and d-d repulsion terms and ζ is the one-electron soc parameter ($\zeta > 0$). Energy expressions for the \mathcal{H}^0 matrix elements can be found in Table I. In view of the variational principle the signs of a , b , and c must be chosen in such a way as to minimize the ground-state energy. Clearly, only the cross terms in ζ will influence this choice. Ideally, one would require $ac < 0$, $ab < 0$, and $bc < 0$, but these three conditions cannot be fulfilled simultaneously. So, parameter signs cannot be fixed a priori. However, in any two-state approximation (i.e., if one parameter is relatively unimportant), the sign of the product of the two dominant parameters will be negative.

In conclusion, the symmetry behavior of the fictitious component labels $+1/2$ and $-1/2$ of the Kramers doublet precisely correspond to respectively the α and β z -axis-quantized spin components. Upon this symmetry equivalence rests the spin Hamiltonian formalism,^{8,9} which is discussed in the next paragraph.

B. Magnetic g Factors. Several expressions for the g tensor of the Zeeman splitting in low-spin Co(II) complexes are available in the literature,^{1,10–12} but so far little attention has been paid to the signs of the tensor components. As indicated in the previous paragraph a correct application of the splitting field procedure leads to a fixed equivalence between the Kramers doublet components and the (α, β) spin functions. From there on, the g tensor is uniquely defined. In view of the C_{2v} symmetry, the principal components will be directed along the Cartesian axes, defined in Figure 1. They can be expressed as functions of a , b , and c as follows:

$$\begin{aligned} g_x &= 2.0023(a^2 + b^2 - c^2) - 4(3^{1/2})ab \\ g_y &= 2.0023(-a^2 + b^2 + c^2) - 4(3^{1/2})bc \\ g_z &= 2.0023(-a^2 + b^2 - c^2) + 4ac \end{aligned} \quad (7)$$

In contrast to previously published expressions,¹ the g tensor in eq 7 is fully consistent with the sign criterion proposed by

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Table III. Magnetic g Factors and Lowest Excited Doublet States^a in CoN₂O₂ and CoN₂N'₂ Schiff Base Complexes (EPR Data^b from Ref 1, 16, and 17 and Spectral Data^c from Ref 1, 14, and 18)

chromophore	ligand ^d	g_x	g_y	g_z	$ ^2A_1 z^2\rangle$	$ ^2B_1 xz\rangle$	$ ^2A_1 x^2 - y^2\rangle$
CoN ₂ O ₂	a ₂ en ^e	3.90	1.69	1.78	[0.100]	0.400 (103)	0.800 (16)
	salen	3.81	1.66	1.74	[0.115]	0.390 (65)	0.830 (16)
	acacen	3.26	1.88	2.00	[0.180]	0.394 (71)	0.840 (13)
	acacpn	3.16	1.90	2.01	[0.205]	0.397 (96)	0.850 (20)
CoN ₂ N' ₂	ambpn	2.70	1.98	2.07	0.625 (22)	1.105 (73)	
	amben	2.66	1.98	2.01			
	ambchxn				0.575 (20)	1.087 (74)	

^a Excited-state energies are given in μm^{-1} . ^b Values in square brackets were estimated from the g factors by a two-state interaction model. ^c Other energies refer to absorption spectra in CHCl₃ or related solvents. Extinction coefficients in $\text{L M}^{-1} \text{cm}^{-1}$ are also indicated. ^d Ligand abbreviations are as in ref 1. ^e Polycrystalline sample. g tensor orientation is assumed to be the same as in the other CoN₂O₂ complexes.

Pryce.¹³ This means that in the limit of axial symmetry the two g_{\perp} components should have equal sign and magnitude. This is verified in eq 8 for three cases of axial C_{4v} symmetry.

$$C_{4v}(x):c = 0 \quad g_{\perp} = g_x = g_y \quad (8a)$$

$$C_{4v}(y):a = 0 \quad g_{\perp} = g_x = g_z \quad (8b)$$

$$C_{4v}(z):a = c \quad g_{\perp} = g_x = g_y \quad (8c)$$

This more consistent definition of the g tensor should lead to a reconsideration of the Co(II) hyperfine and quadrupole tensors.

Returning to eq 7, each component is seen to contain three squared terms, which stem from the spin contributions to the magnetic moment, and one cross term, containing the orbital angular momentum contribution. The latter term must be attenuated by the so-called orbital reduction factors, which in principle should reflect the anisotropy of the C_{2v} point group.¹⁴ In any two-state limit, i.e. if one of the parameters (a , b , c) approaches zero, the largest spin and orbital contributions are found in one and the same g component (eq 7). Moreover, in view of the sign inequalities, derived from eq 6, both moments will have parallel orientations, yielding one large g component. This merely arises as a direct consequence of the addition of spin and orbital moments under spin-orbit coupling. Indeed in a more than half-filled shell ground state, soc interactions tend to align resultant spin and orbital angular momenta.¹⁵

Single-crystal EPR measurements on several square-planar Co(II) Schiff base complexes always reveal a similar pattern of g factor anisotropy.¹ Table III offers a selection of data from the literature.^{1,16-18} The principal component of the g tensor is g_x , while g_y and g_z are both small and nearly degenerate, but with a slight preponderance of g_z over g_y . In absolute amplitude: $|g_x| \gg |g_z| > |g_y|$. Clearly such anisotropy is characteristic of the (a , b) two-state system, with the unpaired electron in d_{yz} and d_{z^2} . Under soc interactions these orbitals combine into magnetic orbitals, carrying angular momentum along the x axis. In such a two-state approximation g_y and g_z are strictly degenerate. Also, since only absolute g values are known, the g tensor expressions (with $c = 0$) do not allow one to distinguish between a and b parameters. As an example, in the (a , b) two-state limit the g values for Co(salen) can equally well be approximated, from $a = 0.96$, $b = -0.27$ or $a = 0.27$, $b = -0.96$. As indicated by von Zelewsky et al.,¹ these shortcomings of the two-state approximation can be overcome by considering admixture of the third doublet state, $|^2B_1 xz\rangle$, with eigenvector coefficient c . Since $|g_x| > |g_y|$, the secondary anisotropy in the ground state is closer to the (a , c) two-state system than to the (b , c) two-state system, which means that a marks the dominant eigenvector component. As

a result, in square-planar compounds the unpaired electron mainly resides in d_{yz} , but the $|^2A_1 z^2\rangle$ state is extremely close to the ground state.

By performing full-scale LF calculations involving all states of the d^7 manifold, we have carefully investigated the validity of the three-state model. While it is true that the actual ground state consists of a considerable number of quartet and doublet components, the above conclusions never appear to be altered, since the lowest doublet states by far remain the determining factors. One of the reasons is that S^2 commutes with the Zeeman operator¹⁵ so that no doublet-quartet cross terms occur in the g tensor expressions. Only if quartet states are very near to the ground state can g_y and g_z be inverted. Also, the effect of d_{xz} - $d_{x^2-y^2}$ orbital mixing, due to small angular distortions of square-planar geometry,¹¹ appears to be negligible.

Single-crystal EPR spectra thus provide an unequivocal assignment of the principal ground-state components. These conclusions are also confirmed by a detailed analysis of the hyperfine interaction, as discussed in ref 1 and 16. Provided reasonable estimates of the spin-orbit constant ζ and the orbital reduction factor(s) are made, the energy separation of the two lowest doublet states can be evaluated. Table III includes a crude estimate of the $|^2A_1 z^2\rangle$ excited-state energy, based on a simple two-state model with a typical $\zeta = 0.04 \mu\text{m}^{-1}$ value and an orbital reduction factor equal to 1. As can be seen from the table the energy gap in CoN₂O₂ chromophores is very small indeed. A larger gap is anticipated in CoN₂N'₂ complexes.^{17,18} We will return to this point in the next paragraph.

Even if more detailed fitting procedures are involved, higher excited states cannot be calculated accurately from EPR data. This is due to the inherent uncertainty of the nephelauxetic approximation but also to the fact that large changes of the energies of remote states produce only minor changes in the ground-state eigenvector. Hence, the position of $|^2A_1 d_{z^2}\rangle$ in CoN₂N'₂ complexes and the position of the other two cluster levels must be inferred from absorption spectra.

C. Electronic Spectra. Electronic spectra of Co(II) square-planar N₂O₂ complexes^{1,14,19} show two band systems in the low-energy region: a structured absorption at approximately $0.4 \mu\text{m}^{-1}$ ($\epsilon \approx 70 \text{ L M}^{-1} \text{cm}^{-1}$) and a weak peak at $0.8 \mu\text{m}^{-1}$ ($\epsilon \approx 15-20 \text{ L M}^{-1} \text{cm}^{-1}$). Detailed peak positions for several different N₂O₂ ligands are listed in Table III. Apparently all these ligands exert nearly identical ligand fields, since they all produce approximately the same spectrum, irrespective of the nature of their substituents.

Extinction coefficients are typical of spin-allowed d-d transitions. Moreover, since absorption spectra of analogous Ni(II) compounds are completely transparent² in the spectral region below $1.6 \mu\text{m}^{-1}$, the CoN₂O₂ bands must in all probability be attributed to the remaining intracluster transitions: viz. $|^2A_2 yz\rangle \rightarrow |^2B_1 xz\rangle$ and $|^2A_2 yz\rangle \rightarrow |^2A_1 x^2 - y^2\rangle$. Following Hitchman¹⁴ it is reasonable to assign the stronger absorption at $0.4 \mu\text{m}^{-1}$ to the C_{2v} -allowed $^2A_1 \rightarrow ^2B_1$ transition and to interpret the weaker band at $\sim 0.8 \mu\text{m}^{-1}$ as a dipole-forbidden, vibronically allowed $^2A_2 \rightarrow ^2A_1$ transition.²⁰

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The low-energy spectrum of the $\text{CoN}_2\text{N}'_2$ chromophore also displays two band systems, but at different energies.¹⁸ The stronger absorption ($\epsilon \approx 75$) has shifted to shorter wavelength ($\bar{\nu} \approx 1.1 \mu\text{m}^{-1}$), and a weaker transition ($\epsilon \approx 20$) is found at about $0.6 \mu\text{m}^{-1}$. In view of the preceding assignment of the CoN_2O_2 -type complexes, earlier tentative assignments¹⁸ of $\text{CoN}_2\text{N}'_2$ spectra need revision. Since both types of chromophore have the same molecular symmetry and the same ground state, it is only logical to use identical assignment criteria.¹⁴ Hence, we attribute the stronger absorption band at $1.1 \mu\text{m}^{-1}$ to a ${}^2A_2 \rightarrow {}^2B_1$ transition and the low-energy band to ${}^2A_2 \rightarrow {}^2A_1$. Especially, the assignment of the $1.1\text{-}\mu\text{m}^{-1}$ band seems compulsory, in view of its peculiar band shape, which is extremely similar to the corresponding absorption in the CoN_2O_2 chromophore. On the other hand, the totally symmetric state at $0.6 \mu\text{m}^{-1}$ could have the unpaired electron in $d_{x^2-y^2}$ or d_{z^2} . The $d_{x^2-y^2}$ alternative is improbable though, since it would mean that on going from CoN_2O_2 to $\text{CoN}_2\text{N}'_2$ the $|{}^2A_1 x^2-y^2\rangle$ state and the $|{}^2B_1 xz\rangle$ state would shift in opposite directions. A more convincing argument in favor of a $|{}^2A_1 z^2\rangle$ state at $0.6 \mu\text{m}^{-1}$ comes from the EPR results. As indicated in the previous paragraph—and in Table III— g factors are less anisotropic in $\text{CoN}_2\text{N}'_2$ than in CoN_2O_2 . Hence, the $|{}^2A_1 z^2\rangle$ is expected at higher energies. Indeed, elaborate model calculations with $|{}^2A_1 z^2\rangle$ at $0.5 \mu\text{m}^{-1}$ and $|{}^2B_1 xz\rangle$ at $1.1 \mu\text{m}^{-1}$ yield satisfactory estimates of the empirical g value. The ${}^2A_2 \rightarrow |{}^2A_1 x^2-y^2\rangle$ transition is expected well above $1.1 \mu\text{m}^{-1}$, but its exact position could not be located, since it is probably hidden under more intense absorption bands.

In both chromophores, transitions from cluster orbitals to d_{xy} are masked by intense charge-transfer or intraligand bands at energies higher than $1.6 \mu\text{m}^{-1}$. However the d_{xy} orbital can approximately be located by comparison with the d - d spectra of similar Ni(II) complexes. Usually these complexes exhibit one broad and structureless spectral feature² at about $1.8 \mu\text{m}^{-1}$ that corresponds to a spin-allowed transition from the set (d_{z^2} , $d_{x^2-y^2}$, d_{xz} , d_{yz}) to d_{xy} . Also in square-planar Cu(acacen) two absorption peaks at 1.64 and $1.84 \mu\text{m}^{-1}$ have been assigned^{14,21} to $d_{z^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{xy}$ transitions. If similar energy gaps are adopted for the spin-allowed transitions to d_{xy} in Co(II) complexes, several spin-forbidden transitions are predicted in the IR region. These could very well account for the observed minor details of the absorption spectra and the additional peaks that appear in circular dichroism spectra.¹⁸

II. Empirical vs. Theoretical Ligand Field

When suitable values²² are adopted for the Racah parameters, $B = 0.07 \mu\text{m}^{-1}$ and $C = 0.3 \mu\text{m}^{-1}$, the state energies in Table III can be reduced to orbital energies, either by using the approximate energy expressions of Table I or by comparing the observed energies with the results of more elaborate LF calculations, including the effect of spin-orbit coupling ($\zeta = 0.04 \mu\text{m}^{-1}$) and configuration interaction. Semiquantitative orbital energy orderings for average CoN_2O_2 and $\text{CoN}_2\text{N}'_2$ chromophores are displayed in Figure 2. Especially, the position of $d_{x^2-y^2}$ is subject to large uncertainties since a major fraction of the $|{}^2A_2 yz\rangle \rightarrow |{}^2A_1 x^2-y^2\rangle$ transition energy is due to a change in interelectronic repulsion.

If we compare the empirical ligand field with the predictions of a simple AOM treatment for a ML_4 moiety containing four average (nonlinearly ligating) π -donor ligands, several striking features can be observed (cf. Figure 2).

A. Position of d_{z^2} . Apparently d_{z^2} is situated amidst the π -interacting d orbitals at much lower energy than could be anticipated from its σ -antibonding role in the AOM formalism. This is by now a well-established feature of the electronic structure of square-planar compounds and has been observed in a large variety of Ni(II), Cu(II), Pd(II), and Pt(II) complexes.^{3,6,7} The phenomenon is generally attributed to considerable $(n+1)s$ - nd

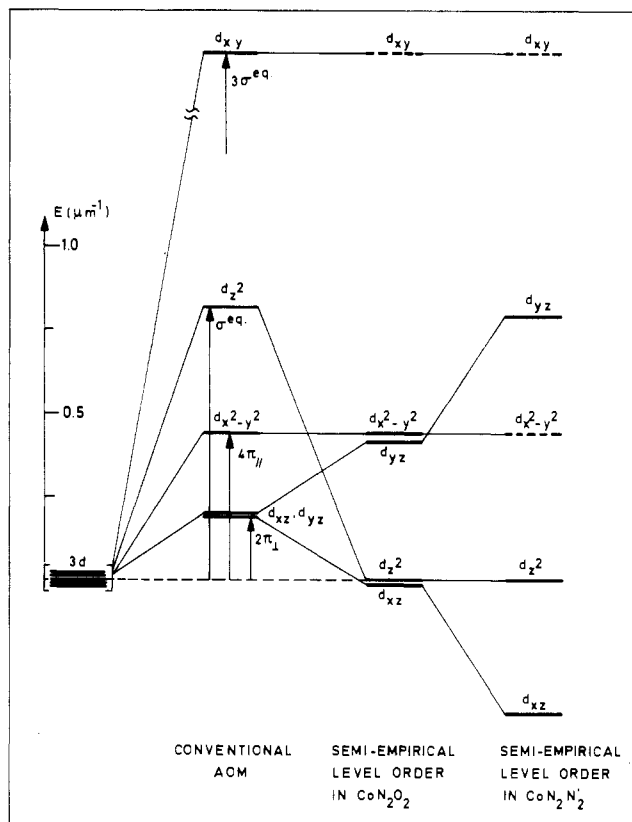


Figure 2. Semiempirical orbital energy diagram in square-planar CoN_2O_2 and $\text{CoN}_2\text{N}'_2$ chelate complexes, as compared to conventional AOM. σ^{eq} symbolizes the average σ parameter of an equatorial ligand; π_{\parallel} and π_{\perp} refer to respectively in-plane and out-of-plane π interactions. Dashed lines denote orbital levels, which cannot be determined accurately.

orbital mixing that stabilizes d_{z^2} as compared to the d -only limit. In the case of square-planar Co(II) porphyrin complexes, which are characterized by a $|{}^2A_1 z^2\rangle$ ground state, direct evidence of considerable $4s$ character in the d_{z^2} orbital is provided by the high value of the isotropic Fermi contact term in the hyperfine coupling.¹¹ The orbital mixing has also been confirmed by recent ab initio calculations.²³

Using a second-order perturbation formalism³ the energy of d_{z^2} is given by

$$\langle d_{z^2} | \mathcal{V} | d_{z^2} \rangle = \langle d_{z^2} | \mathcal{V}^{\text{AOM}} | d_{z^2} \rangle - \sum_{L, L'} D_{11}^L D_{11}^{L'} (e^L)^{1/2} (e^{L'})^{1/2} \quad (9)$$

The first term in eq 9 refers to the usual first-order AOM expression, D_{11}^L is the first element of the AOM rotation matrix, viz. $1/2(3 \cos^2 \theta_L - 1)$, and e^L , $e^{L'}$ are second-order sd mixing parameters. There is ample spectroscopic evidence that the depression of d_{z^2} in symmetrical ML_4 square-planar complexes amounts approximately to σ^L , leaving a virtually nonbonding (d_{z^2} , s) hybrid at zero orbital energy.^{3,6,7,24} Using this experimental observation as a scaling factor for the magnitude of the mixing effect,³ one obtains from eq 9 in a ML_4 complex

$$4e^L = \sigma^L \quad (10)$$

By application of these results to the case of a CoN_2O_2 complex, the position of d_{z^2} is given by

$$\langle d_{z^2} | \mathcal{V} | d_{z^2} \rangle = 1/4(\sigma^N + \sigma^O) - 1/2(\sigma^N \sigma^O)^{1/2} \quad (11)$$

For small differences between σ^N and σ^O , the deviation between

(20) Linear dichroism would of course provide unequivocal assignments, but so far no single-crystal absorption data are available.

(21) Olson, C. D.; Basu, G.; Belford, R. L. *J. Coord. Chem.* **1971**, *1*, 176.

(22) To be compared with free-ion values: $B = 1058 \text{ cm}^{-1}$, $C = 4366 \text{ cm}^{-1}$; $\zeta = 533 \text{ cm}^{-1}$ (ref 8, Appendix A 6.1).

(23) Daul, C.; Weber, J. *Helv. Chim. Acta* **1982**, *65*, 2486.

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geometric and arithmetic mean in eq 11 is negligible and d_{z^2} is almost nonbonding. As a result the d_{xz} - d_{xy} energy gap equals $3\sigma^{\text{eq}}$. From a comparative study of analogous Cu(II) complexes, Hitchman^{14,26} infers a d_{xz} - d_{xy} distance of approximately $2.3 \mu\text{m}^{-1}$. Average equatorial σ parameters in Schiff base Co(II) square-planar complexes can therefore be expected to range from 0.7 to $0.8 \mu\text{m}^{-1}$. These results are comparable to previously reported σ values for strong σ -donor ligands in square-planar Ni(II) complexes.²⁵ Remark that neglect of the mixing phenomenon produces anomalously large σ parameters²⁶ since in the d-only model the d_{xz} - d_{xy} energy gap equals 2σ ; d-only σ values are thus overestimated by a factor of the order of 1.5.

B. Nondegeneracy of d_{xz} and d_{yz} . Clearly, the empirical LF potential contains an orthorhombic component that corresponds to a sizeable splitting of the d_{xz} and d_{yz} orbital energies.¹⁶ However, the AOM potential has at least tetragonal symmetry and thus dramatically fails to account for the observed nondegeneracy of d_{xz} and d_{yz} . The underlying causes of this phenomenon can be understood in the context of a general molecular orbital model and had been recognized by Orgel some 20 years ago.²⁷ As we have shown in a previous paper,⁴ the phase coupling between the $p\pi_{\perp}$ orbitals on the ligator atoms in conjugated bidentate ligands produces a specific breakdown of the AOM additivity postulate and is at the basis of the observed symmetry lowering. Knowing causes and effects, we have implemented a ligand field formalism⁴ of the Orgel effect. It can be readily applied to the ligator system in Figure 1, which—for the present purpose—will be viewed as a sum of two electronically isolated NO or NN' bidentates. Furthermore, it will be assumed that the main π_{\perp} interactions in these anionic ligands stem from the highest occupied bidentate MO, which has in-phase-coupled $p\pi_{\perp}$ orbitals on the ligator atoms.¹ By the Orgel terminology, the ligand subunits are characterized as ψ -type π -donor systems. Since in the present example the bidentate ligands are asymmetrical, Orgel's terminology can no longer be replaced by equivalent symmetry labels. Instead, the distinction between ψ - and χ -type interactions for unsymmetrical bidentates is uniquely based on the relative phases of the outer $p\pi_{\perp}$ orbitals in the highest occupied MO. The d_{xz} and d_{yz} orbitals turn out to be eigenfunctions of this extended LF Hamiltonian, obeying the following energy expressions:

$$\begin{aligned} \langle xz | \mathcal{V} | xz \rangle &= \pi_{\perp}^{\text{O}} + \pi_{\perp}^{\text{N}} - 2(\pi_{\perp}^{\text{N}} \pi_{\perp}^{\text{O}})^{1/2} \\ \langle yz | \mathcal{V} | yz \rangle &= \pi_{\perp}^{\text{O}} + \pi_{\perp}^{\text{N}} + 2(\pi_{\perp}^{\text{N}} \pi_{\perp}^{\text{O}})^{1/2} \end{aligned} \quad (12)$$

Equation 12 applies to a CoN_2O_2 chromophore, but mutatis mutandis holds also for a $\text{CoN}_2\text{N}'_2$ chromophore (equally consisting of two asymmetrical bidentates). For small differences between π_{\perp}^{O} and π_{\perp}^{N} , d_{xz} is lowered to the nonbonding level while d_{yz} is strongly antibonding. The orthorhombic splitting between d_{xz} and d_{yz} roughly corresponds to $4\pi_{\perp}^{\text{eq}}$, with π_{\perp}^{eq} denoting the π_{\perp} strength of an average equatorial ligand.

Upon comparison of eq 12 with the results displayed in Figure 2, several aspects are noteworthy. First of all, the sign of the orthorhombic splitting $E(d_{yz}) > E(d_{xz})$ is correctly predicted in both chromophores.⁴ Second, in the case of CoN_2O_2 , d_{xz} and d_{z^2} are virtually degenerate, which is in perfect agreement with the nonbonding character of either orbital. As has recently been shown by MS-X α calculations²³ on Co(acacen), both orbitals are indeed almost purely metallic while d_{yz} is considerably interacting with the ligand $p\pi_{\perp}$ orbitals. Finally, in the $\text{CoN}_2\text{N}'_2$ complexes, the orthorhombic splitting between d_{xz} and d_{yz} reaches an extreme value of ca. $1.1 \mu\text{m}^{-1}$ (see also section IC).

As can be seen from Figure 2 the effect is partially due to a stabilization of d_{xz} below the nonbonding level. The appropriate orbital mechanism involves a π -acceptor interaction²⁸ between d_{xz}

Table IV. Orbital Energy Expressions for Co(II) Schiff Base Square-Planar Complexes in the Conventional AOM and in the Amended Version (Taking into Account sd Mixing and the Orgel Effect)^a

	model		CoN ₂ O ₂
	conventional	extended	
$E(d_{xy})$	3σ	3σ	$B = 0.07, C = 0.3$
$E(d_{z^2})$	σ	0	$\xi = 0.04$
$E(d_{x^2-y^2})$	$4\pi_{\parallel}$	$4\pi_{\parallel}$	$\sigma = 0.70-0.80$
$E(d_{yz})$	$2\pi_{\perp}$	$4\pi_{\perp}$	$\pi_{\parallel} = 0.11$
$E(d_{xz})$	$2\pi_{\perp}$	0	$\pi_{\perp} = 0.10$

^a Also given is a summary of LF parameters (in μm^{-1}) for CoN_2O_2 complexes. The σ and π values are averages of N and O atoms.

and the lowest unoccupied π^* ligand orbital, which is of the χ type. This cooperative role⁴ of π -donor and π -acceptor interactions in generating pronounced symmetry lowerings is a truly remarkable characteristic of the Orgel effect.

C. In-Plane π Interactions. Although the position of $d_{x^2-y^2}$ is somewhat uncertain due to the dominant contribution of interelectronic repulsion in the relevant transition, it cannot be denied that this orbital is in-plane π antibonding to a considerable extent. According to the additive point ligand model for nonlinear ligators, one has

$$\langle x^2 - y^2 | \mathcal{V} | x^2 - y^2 \rangle = 2\pi_{\parallel}^{\text{O}} + 2\pi_{\parallel}^{\text{N}} \quad (13)$$

For CoN_2O_2 -type complexes, average π_{\parallel} (eq 13) and π_{\perp} (eq 12) parameters are found to be of comparable magnitude (see Table IV). Apparently in the present case, the neglect of in-plane π interactions, which is often advocated in the application of the AOM to nonlinear ligators,^{2,29} is not justified.

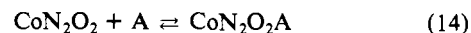
III. Discussion

Square-planar Co(II) complexes of Schiff base ligands rank among the very few low-symmetry complexes, for which a detailed characterization of the empirical ligand field has been achieved. In this respect they are privileged examples to put LF theory to test. Whereas the observed orbital splitting always will fit in with a global Hamiltonian of low-enough symmetry, local ligand field models, especially the AOM, clearly fail to explain the experimental findings, to the point that one might seriously question the validity of these models as parametrization schemes for unsymmetrical complexes.³⁰

Apparently, there are two ways out of this situation. Either one must abandon the usage of simple models altogether and recur to ab initio calculations or one might try to amend the model in order to incorporate the observed anomalies. Usually the latter alternative is refutable since it endows the extended formalism with a great deal of ad hoc character. However, in the present case, the model deficiencies can easily be understood with the aid of simple MO theory and are seen to act in a very specific and restricted way.^{3,4}

Corresponding adjustments of the model can therefore easily be introduced. A summary of the newly derived LF parameters is presented in Table IV. This approach has the advantage that it reestablishes a simple link between the structure of the coordination mantle and the d-orbital energies. It can thus be utilized to describe electronic changes that accompany structural changes in the course of chemical reactions.

For the Co(II) complexes under study, the principal chemical reaction seems to be formation of a five-coordinated square pyramid through the uptake of a fifth monodentate ligand such as water or pyridine:



Quite interestingly, the adduct has an increased dioxygen affinity.³¹

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(28) Notice that the intense CT absorptions in the visible spectra of Co(II) Schiff base complexes are most likely due to metal d \rightarrow ligand π^* transitions.¹⁴ From CoN_2O_2 to $\text{CoN}_2\text{N}'_2$ chromophores these bands are considerably red-shifted.¹⁸ This seems to be in line with the increased importance of π -acceptor interactions in $\text{CoN}_2\text{N}'_2$ complexes.

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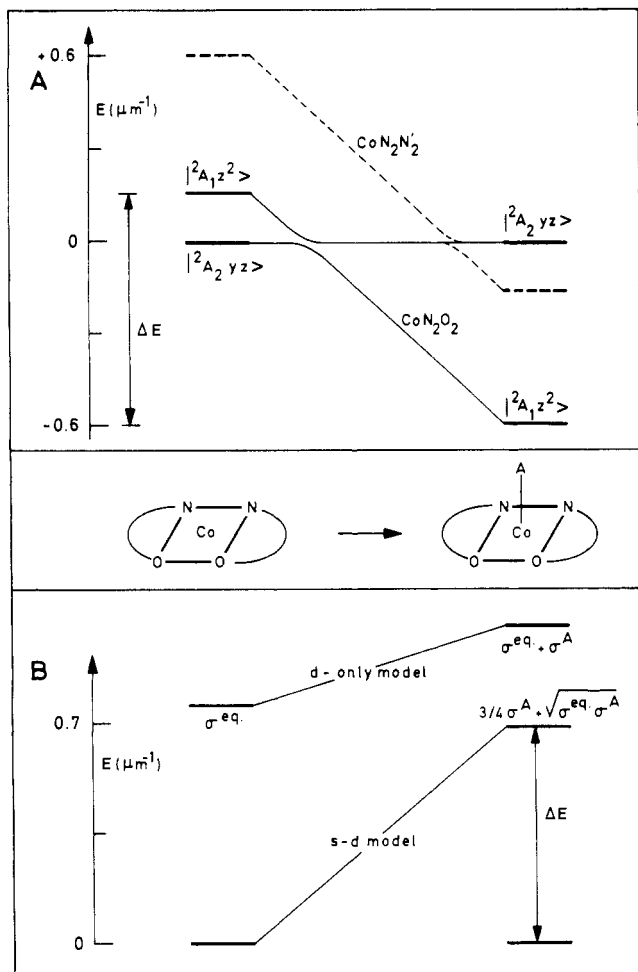


Figure 3. Upper part (A): state correlation diagram of the lowest doublet states for the adduct formation of CoN_2O_2 Schiff base complexes. The dashed line reflects the $|^2A_1 z^2\rangle$ level in the $\text{CoN}_2\text{N}'_2$ analogues. Since this level starts off at about $0.6 \mu\text{m}^{-1}$, compared to $0.15 \mu\text{m}^{-1}$ for CoN_2O_2 , the crossover point will move to the right and the driving force for the reaction will decrease. ΔE denotes the total stabilization of the $|^2A_1 z^2\rangle$ state, relative to the $|^2A_2 yz\rangle$ state. If it is assumed that axial coordination causes only minor changes of the d_{yz} level, ΔE approximately corresponds to the energy change of the d_{z^2} orbital. In the d-only model this energy change equals σ^A . In the extended model, including s-d mixing, ΔE is given by eq 16. Lower part (B): comparison of both results ($\sigma^A = 0.3 \mu\text{m}^{-1}$, $\sigma^{\text{eq}} = 0.75 \mu\text{m}^{-1}$). Clearly only the extended model explains how weak axial ligation can cause substantial ΔE values.

Several aspects of the association reaction in eq 14 will now be discussed in relationship to the extended LF expressions.

As can be anticipated from LF theory, axial approach of a nucleophile mainly affects the d_{z^2} orbital. The energy of d_{z^2} is substantially raised. At the state level this results in a crossover¹ of the $|^2A_2 yz\rangle$ and $|^2A_1 z^2\rangle$ states. While the $|^2A_2 yz\rangle \rightarrow |^2A_1 z^2\rangle$ transition in CoN_2O_2 square-planar complexes occurs at about $0.15 \mu\text{m}^{-1}$ (see Table III), in pyridine adducts the inverse transition is reported^{1,26} at about $0.6 \mu\text{m}^{-1}$. The corresponding state correlation diagram is shown in Figure 3A, assuming that the $|^2A_2 yz\rangle$ state, with d_{z^2} doubly occupied, is largely unaffected by axial perturbations. The total energy change of $|^2A_1 z^2\rangle$ relative to the $|^2A_2 yz\rangle$ state, indicated as ΔE on Figure 3, therefore corresponds to the destabilization of the d_{z^2} level upon adduct formation. In the d-only model ΔE equals the σ^A parameter. Apparently this model is unable to explain how weak axial coordination (σ^A is small) can induce the large observed ΔE values of ca. $0.7\text{--}0.8 \mu\text{m}^{-1}$.

In the extended model s-d mixing will play an important role in the adduct formation, since the energy of the d_{z^2} level is directly affected. Following eq 9, the corrected d_{z^2} energy in a five-co-

ordinate $\text{CoN}_2\text{O}_2\text{A}$ complex is given by

$$\langle d_{z^2} | \mathcal{V} | d_{z^2} \rangle = \frac{1}{4}(\sigma^N + \sigma^O) + \frac{3}{4}\sigma^A - \frac{1}{2}(\sigma^N\sigma^O)^{1/2} + \frac{1}{2}(\sigma^O\sigma^A)^{1/2} + \frac{1}{2}(\sigma^N\sigma^A)^{1/2} \quad (15)$$

The energy change, ΔE , upon adduct formation is obtained by subtracting the energy of d_{z^2} in CoN_2O_2 , given in eq 11.

$$\Delta E = \frac{3}{4}\sigma^A + \frac{1}{2}(\sigma^O\sigma^A)^{1/2} + \frac{1}{2}(\sigma^N\sigma^A)^{1/2} \quad (16)$$

Orbital energy changes with and without s-d mixing are compared in Figure 3B, assuming $\sigma^O \approx \sigma^N \approx \sigma^{\text{eq}}$. Clearly, the incorporation of the s-d mixing effect explains how loosely bound axial ligands can produce substantial destabilization of d_{z^2} . As an example a tentative σ^A value of $0.3 \mu\text{m}^{-1}$, combined with an average σ^{eq} value of $0.75 \mu\text{m}^{-1}$ (Table IV), yields upon substitution in eq 16 a ΔE shift of $0.7 \mu\text{m}^{-1}$.

The simplified diagrams of Figure 3 illustrate two essential features of adduct formation. First of all, the lowering of $|^2A_1 z^2\rangle$ below the crossover point provides the driving force for axial ligand association. Clearly in $\text{CoN}_2\text{N}'_2$ chromophores a similar ΔE drop produces only a very small if any driving force since at the left-hand side of the diagram $|^2A_1 z^2\rangle$ starts off at much higher energy, indicated by the dotted line in Figure 3A. Hence, the relative inertness of $\text{N}_2\text{N}'_2$ -type square-planar compounds toward adduct formation is predicted on the basis of a directly observable spectroscopic gap in the starting material. Several $\text{CoN}_2\text{N}'_2$ chelate compounds indeed show the same electronic spectra in donor and nondonor solvents, which proves that they are not susceptible to nucleophilic attack.³² In other cases the association reaction is observed, but the equilibrium constant is considerably less than for the analogous CoN_2O_2 complexes.³³

A second interesting aspect of adduct formation involves the commonly observed³⁴ increase of in-plane bond distances of about 0.05 \AA . According to Hitchman²⁶ structural changes of this order of magnitude lead to a 10% loss of in-plane LF strength. This is an important effect since it stabilizes the d_{xy} orbital so that high-spin quartet states can approach the adduct ground state. The decrease of the doublet-quartet separation is observable via unusual temperature dependence of the magnetic susceptibility and in some cases even may cause a ground-state spin equilibrium or a permanent spin flip.^{35,36} On the other hand, the slight pyramidalization of the basal plane, which is also concomitant with adduct formation, does not seem to have appreciable influence on the doublet-quartet separation.²⁶

A d-only model is unable to explain how an axial perturbation would bring about the observed structural deformations of the basal plane. Indeed, in conventional AOM d_{z^2} is in-plane σ antibonding, so that a state crossover of the type shown in Figure 3A, which removes one electron from d_{z^2} , would be expected to strengthen equatorial bonds, as opposed to the experimental trends.

In contrast, in the extended model, the observed equatorial bond elongation appears as a natural consequence of s-d mixing. As can be seen from Figure 3B, in the square-planar geometry the difference between both orbital models is at its maximum, while it is far less pronounced in $\text{CoN}_2\text{O}_2\text{A}$. This implies a decrease of s character in the a_1 hybrid upon adduct formation, as a result of which the a_1 orbital acquires a significant degree of in-plane antibonding character and destabilizes the equatorial plane. Hence d-s mixing provides an efficient orbital path for transfer of antibonding character from axial to equatorial sites. At the state level this is reflected in the observed approach of doublet and quartet states.

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In retrospect, perhaps the most striking characteristic of the delicate orbital balance in Co(II) square-planar compounds is the dramatic effect of weak axial perturbations on the energy of $|^2A_1 z^2\rangle$. Clearly, the amplifying factor in this process must be attributed to d-s orbital mixing. It is not surprising that the creation of a singly occupied fairly destabilized antibonding orbital level

leads to facile oxidative-addition reactions.

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Electronic Spectra of the Quadruply Bonded Group 6⁺ Metal Dimers of 2-Methyl-6-oxypyridine

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The spectra of the quadruply bonded dimers $M_2(mhp)_4$ ($M = Cr, Mo$) have been recorded for THF solutions, for KBr pellets at 5 K, and for single crystals at 5 K. For $M = Mo$, a vibrational progression is observed on the $\delta \rightarrow \delta^*$ transition in the solution and KBr pellet spectrum based on the metal-metal stretching frequency in the excited electronic state. The mean frequency of the vibration is decreased from 380 cm^{-1} in the solid to 344 (11) cm^{-1} in solution, suggesting weak axial coordination by the solvent. The mass spectrum of $Mo_2(mhp)_4$ prepared from $Mo_2(O_2CCH_3)_4$ indicated that the compound is not pure but contains on average 18% $Mo_2(mhp)_3(O_2CCH_3)$. This material was found to account for several of the vibrational bands observed in the spectrum of the impure crystals of $Mo_2(mhp)_4$. The pure compound can be obtained from the reaction of $(NH_4)_4Mo_2Cl_8 \cdot NH_4Cl$ with $Na(mhp)$ in methanol. The chromium complex displays weak vibrational structure, with a mean spacing of 305 (13) cm^{-1} in the KBr pellet and 310 (12) cm^{-1} in the crystal. In the crystal spectra, the lowest energy transition is assigned as $\delta \rightarrow \delta^*$. The vibrational structure was assigned to a metal-ligand stretching vibration in the excited electronic state. No progression based on the Cr-Cr stretch was observed.

Introduction

Structural and spectroscopic investigations of the quadruply bonded dimers of the group 6 metals indicate that these dimers can be classified into four broad categories depending on the types of ligands bound to the M_2 unit. The similarity of the metal-metal bond lengths and electronic spectra of compounds within each class suggests that the bonding within each is similar and thus is a function of the ligand system used. The first and most widely studied class of group 6 dimers are those in which the dimetal unit is bridged by four carboxylates. A wide variety of alkane- and arenecarboxylates have been used as ligands. In the case of molybdenum, typical and metal-metal bond lengths are 2.09 Å.² These compounds are usually bright yellow. The reported 0-0 transitions for the first observed electronic transition ($\delta \rightarrow \delta^*$) range from 20 500 to 22 080 cm^{-1} .³⁻⁶ The analogous carboxylates of chromium also appear to form a similar class. Surprisingly, the metal-metal distances in these dimers are longer than in the dimolybdenum compounds. Typical values for the chromium-chromium distance are 2.29-2.4 Å.² Unlike the molybdenum dimers, the color of the chromium dimers depends on the carboxylic acid used as the ligand. There has only been one study of the spectra of these compounds, and the assignments were not definitive.⁷ Recently, the tungsten analogues have been prepared.⁸

The second class involves compounds of the type $[M_2X_8]^{4-}$ where X is a univalent anion. Examples of such ligands are halides, pseudohalides, and alkyl ions. For the molybdenum compounds, the Mo-Mo bond distances range from 2.134 to 2.150 Å.² This distance is somewhat dependent on the counterion used. These compounds tend to be red, with the $\delta \rightarrow \delta^*$ transition typically appearing at 19 000 cm^{-1} .⁹ The only chromium compound in this class is $[Cr_2(CH_3)_8]^{4-}$. For this dimer, the Cr-Cr distance was determined to be 1.980 Å.¹⁰ The absorbance maximum on the $\delta \rightarrow \delta^*$ transition of an Et_2O solution of the lithium salt was reported to be at 22 000 cm^{-1} ($\epsilon \cong 700 M^{-1} cm^{-1}$). The tungsten dimers are also known, but they are extremely

reactive and not readily amenable to study.¹¹⁻¹³

The third class of dimers is of the form $M_2X_4L_4$ where X is a halide and L is a neutral ligand such as a sulfide or phosphine. Compounds of this type are known for molybdenum and tungsten but not for chromium. For molybdenum the Mo-Mo bond lengths span the range 2.130 Å for $Mo_2Cl_4(P(CH_3)_3)_4$ ¹⁴ to 2.144 Å for $Mo_2Cl_4(S(C_2H_5)_2)_4$.¹⁵ These compounds are usually blue or green with an intense absorption at $\sim 17 000 cm^{-1}$. We are currently investigating the spectra of the compounds of this class.

The last class of dimers involves anionic aromatic ligands in which an atom in the ring is directly bonded to the metal. Examples of such ligands are 2-methyl-6-oxypyridine (mhp) and 2,6-dimethoxyphenyl (DMP). These ligands stabilize dimers of all the group 6 metals, and these dimers have the shortest metal-metal bonds observed. In this paper, we present solution, low-temperature solid-state, and single-crystal spectra of the compounds $Mo_2(mhp)_4$ and $Cr_2(mhp)_4$. Our aims in studying these spectra were twofold. First, we wished to determine how these spectra are related to those of other quadruply bonded

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* The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.