

quieting,<sup>31</sup> to note that the best-fit interelectron repulsion factors in the clamben complex imply a negative value for Racah's  $B$  parameter. The small Condon-Shortley parameters together with the large reduction in the effective spin-orbit coupling coefficient both reflect a considerable radial expansion of the  $d$  orbitals in these complexes with respect to the free ion. This accords well with the large  $e_{\sigma}$  values observed through the operation of the electroneutrality principle. Thus it appears that the adoption of a low-spin configuration, involving some migration of  $d$  electrons to regions lying between and above the primary metal-ligand bonds, facilitates a closer approach of the ligands—obviously in a synergic fashion. The consequently augmented donation of negative charge from the ligands reduces the effective nuclear charge on the metal and this is reflected in the reduced  $F_2$ ,  $F_4$ , and  $\zeta$  values as the  $d$  electron cloud expands.<sup>32</sup> At the same time, the increased  $\sigma$  donation from the salen and clamben chelates depletes the ligand electron density to the point that their usual (that is, within high-spin complexes) role as  $\pi$  donors is markedly decreased and possibly reversed; both analyses are characterized by small, negative  $e_{\pi\perp}(\text{O})$  parameter values.

Comparison of the  $e_{\sigma}$  and  $e_{\pi\perp}$  values between the two complexes reveals greater  $\sigma$ -donor and  $\pi$ -acceptor roles of the imine ligands than of the salicylidene oxygens. A relatively enhanced electron donation to the metal atom in the clamben system is associated with a greater nephelauxetic effect as evidenced by the smaller value of  $F_2$ . These same trends appear to account for the much reduced ligand-field contribution of the coordination voids in the clamben complex also. Thus we expect that while lower-lying and more strongly bonding metal  $s(p)$ -ligand interactions characterize the clamben system, the "bond orbitals"<sup>3,8</sup> associated with the voids will be more  $s$ -like and less well bound, resulting in a diminished interaction with the  $d_{z^2}$  orbital of the metal. As the values of  $e_{\sigma}(\text{void})$  are determined empirically largely by fitting the spin-forbidden bands at 8300 and 11 000  $\text{cm}^{-1}$  in the salen and clamben complexes, respectively, these spectral features are to be seen as the direct manifestation of the changing character of the "residual" orbitals associated with the coordination voids. This proposal is clearly one that deserves further investigation in future studies.

The large nephelauxetic effect observed in these and other low-spin complexes invites a fresh appraisal of the factors governing the selection of high- and low-spin forms by complexes in general. The established view rests upon the arguments Griffith<sup>28</sup>

applied to octahedral complexes in which the spin state adopted depends upon the relative magnitudes of ligand-field and electron-pairing energies,  $\Delta$  and  $\Pi$ . The pairing energy is presumed to be greater in the low-spin arrangement. This is certainly true if these energies are expressed in units of the interelectron repulsion parameters  $F_2$  and  $F_4$  (or  $B$  and  $C$ , as desired). However, the gross reduction observed in these parameters for low-spin complexes (which we surmise to be a general feature) adds a second layer to the " $\Delta$  vs.  $\Pi$ " concept in that the change in pairing energy expressed in terms of wavenumbers (e.g.) will be much less than as first envisaged and, indeed, could be a decrease in principle. We shall report on this proposition elsewhere.

The ligand-field effects of misdirected valence are pursued in the following two papers.

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Registry No. Co(salen), 14167-18-1; Co(clamben), 36870-52-7.

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- (29) Contributions from metal core electrons do, of course, arise and are manifest in the defining potential of the  $d$  functions but explicitly excluded from the cellular potentials that ultimately contribute only to the globally nonspherical ligand-field potential.
- (30) The association of a positive  $e_{\pi\sigma}$  parameter with misdirected valency in the negative  $xz$  quadrant may be deduced alternatively by examination of the phases of the equivalent potential expressed as a superposition of spherical harmonics (of the local  $Y_1^2$  and  $Y_1^4$ ) for ligand-field sources displaced off-axis in the given frame, followed by rotation.
- (31) Racah's  $B$  parameter is related to the difference between intrinsically positive Slater-Condon-Shortley parameters.
- (32) The large reductions in interelectron repulsion parameters and spin-orbit coupling coefficient both attest a much reduced effective nuclear charge and large nephelauxetic effect. The small orbital reduction (large  $k$  values) in the magnetic moment operators is *not* in conflict with these findings within the modern interpretation of ligand-field theory, as discussed in section 11.7 of ref 3 or in ref 2, for example. Only within the incorrect view of ligand-field theory as a division of molecular-orbital theory, does one expect reductions in Condon-Shortley and spin-orbit coupling parameters to be accompanied by qualitatively similar reductions in Stevens' orbital reduction factor.

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## Ligand Fields from Misdirected Valency. 2. Bent Bonding in Copper(II) Acetylacetonates<sup>†</sup>

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Analyses of the  $d-d$  spectra of  $\text{Cu}(\text{3-methylacac})_2$ ,  $\text{Cu}(\text{acac})_2$ ,  $\text{Cu}(\text{phenoxycarbonyl}(\text{acetate}))_2$ ,  $\text{Cu}(\text{3-phenylacac})_2$ , and  $\text{Cu}(\text{acac})_2(\text{quinoline})$  ( $\text{acac} \equiv \text{acetylacetonate}$ ) have been performed within the cellular ligand-field (CLF) model. A coherent view of the bonding electron distribution within the series has been formed and the ligand-field analyses consistently recognize the contribution of coordination voids as well as misdirected valence between metal and chelate deriving from ligand tilting, ring strain, and the role of the nonbonding oxygen lone pairs.

### 1. Introduction

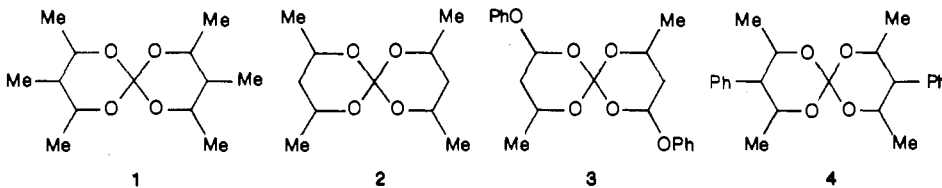
The  $d$  orbital splittings in copper(II) acetylacetonates have been the focus of repeated ligand-field studies and have generated an extensive literature with respect to the use of vibronic selection rules in the assignment of  $d-d$  spectra in planar, centrosymmetric chromophores. A comprehensive review<sup>1</sup> in 1972 by Smith, together with more recent work, has established two main contenders

for the assignments in copper(II) acetylacetonates, which are principally differentiated by their (implicit) inclusion or exclusion of ligand-field contributions<sup>2-4</sup> from the coordination voids above and below the molecular planes. The importance of that con-

<sup>†</sup> No reprints available from this laboratory.

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Table I. Geometrical Parameters and d-d Spectral Transition Energies for Acetylacetonate Complexes of Copper(II)



no.	complex	Cu-O, Å	bite, deg	$\alpha$ , deg	$\angle$ Cu-O-C, deg	transition energies, cm <sup>-1</sup>			
1	Cu(3-Meacac) <sub>2</sub>	1.91	92.5	1.8	127	15 500	15 800	19 200	
2	Cu(acac) <sub>2</sub>	1.92	93.5	~5	~127	14 500	15 600	18 000	
3	Cu((phenoxycarbonyl)acetonate) <sub>2</sub>	1.93	93.0	4.2	126	14 200	15 600	18 100	
4	Cu(3-Phacac) <sub>2</sub>	1.91	91.4	11.4	128	15 400	16 900	19 000	20 600

<sup>a</sup>Tilt angle  $\alpha$  is the angle between the coordination plane CuO<sub>4</sub> and the acac chelate plane.

tribution is now established,<sup>5</sup> and its inclusion has characterized our analyses of the cobalt species in the preceding study<sup>6</sup> as well as the present copper systems.

The assignment of Belford and Hitchman,<sup>7</sup> which still finds favor<sup>8</sup> today, was based upon the use of both vibronic selection rules and a study of the variation with temperature of the d-d spectral band intensities. The energies of the observed transitions were also reproduced within the angular overlap model<sup>9</sup> (AOM) parameterized by  $e_{\sigma}$ ,  $e_{\pi\parallel}$  and  $e_{\pi\perp}$ , referring to metal-ligand interactions characterized with respect to the chelate planes and idealized to overall C<sub>2v</sub> molecular symmetry. Moreover, a recent study<sup>10</sup> of a five-coordinate quinoline adduct of bis(acetylacetonato)copper(II) has been claimed to support the Belford-Hitchman assignments in the planar systems. Nevertheless, experimental polarization ratios obtained from crystals in which the molecular alignments are far from ideal are rather small, and one discerns room for doubt in the nonunique vibronic and uncertain intensity analyses. Further, notwithstanding the reproduction of the band energies by the AOM, the noninclusion of any ligand-field void contribution into the analysis contrasts sharply with widespread evidence<sup>3,5</sup> of the firm depression of the d<sub>z<sup>2</sup></sub> orbital energy by this d-s interaction. Hitchman<sup>11</sup> has recognized the early neglect of this contribution, defending it, however, on the grounds of the effective reproduction of spectral bands without it and explaining it by reference to the proximity at some 3.1 Å of neighboring acetylacetonate carbon atoms above and below the copper atom in the reference molecule. There is no reason to suppose, however, that the void contribution should be significantly diminished by such weak interactions as may or may not result through these long contacts, as demonstrated elsewhere;<sup>5</sup> those distances are not untypical of van der Waals contacts anyway.

The other main assignment, proposed by Hathaway,<sup>12</sup> is, as noted by Smith,<sup>1</sup> in line with those put forward for other planar copper(II) complexes involving oxygen ligands; for example, in the sheet silicate, Egyptian blue,<sup>5,11,13</sup> or in tetrakis(triphenylarsine oxide)copper(II) bis(dichlorocuprate(I)).<sup>14</sup> Hathaway<sup>12</sup> has claimed more reliable vibronic analysis from investigation of the spectrum of the 3-methylacetylacetonate derivative, for here the sole molecule in the unit cell guarantees maximal polarization ratios for analysis. Unfortunately, the lattice is triclinic<sup>15</sup> and polarization studies can be difficult then; this study has been criticized by Belford and Hitchman.<sup>7</sup>

The cellular ligand-field<sup>26</sup> (CLF) analyses presented here begin with the spectrum<sup>16</sup> of the 3-phenylacetylacetonate derivative in

which four transitions are resolved, so providing a more testing and rewarding basis for study. Good reproduction of all transition energies throughout the series of four planar copper(II) acetylacetonates is achieved without neglect of void contributions. The central result of the study, however, is the clear demonstration of an amount of bent bonding between the metal and the acetylacetonate donors that correlates with the degree of nonplanarity in the chelates throughout the series.

## 2. Energy Separation between d<sub>xz</sub> and d<sub>yz</sub> Orbitals in Cu(3-Phacac)<sub>2</sub>

Spectral d-d transition energies and some geometrical details of four closely related acetylacetonate complexes of copper(II) are collected in Table I. Complex 2 was the object of the vibronic analysis by Belford and Hitchman;<sup>7</sup> complex 1 was that studied by Hathaway.<sup>12</sup> For these two molecules, and also<sup>7</sup> for 3, only three spectral bands, at best, are resolved while four distinct transitions are observed<sup>16</sup> for the 3-phenylacac complex, 4. That system provides an important key for the present study.

Each of the four bands in this d<sup>9</sup> complex must arise from orbitally nondegenerate transitions. The minimum energy separation observed is ca. 1500 cm<sup>-1</sup> and so, for any assignment at all, the d<sub>xz</sub> and d<sub>yz</sub> ligand-field orbitals must be split by at least that amount. Splitting of these orbitals arises by virtue of the inexact 4-fold symmetry of the oxygen donor groups and via the agency of any ligand-field potential operating out of the donor atom plane. Spin-orbit coupling may contribute to the magnitude of the splitting but only in conjunction with these primary ligand-field conditions. In terms of the CLF model, the first issue to be resolved, therefore, is whether reasonable values for  $e_{\pi\perp}(\text{O})$ —referring to oxygen  $\pi$  donation normal to the coordination plane—can give rise to an  $xz$ - $yz$  splitting of 1500 cm<sup>-1</sup>, given that the disposition of the donor atoms around the metal is only slightly different from tetragonal.<sup>18</sup> An unequivocally negative result is attested by the following details.

Paying no heed to spectral assignments—and therefore staying free of all earlier proposals—we computed<sup>19</sup> d-orbital energies within the full d<sup>9</sup> basis for  $e_{\sigma}(\text{O})$  in the range 3000–9000 cm<sup>-1</sup>;  $e_{\pi\parallel}(\text{O})$ , 0–2500 cm<sup>-1</sup>;  $e_{\pi\perp}(\text{O})$ , 0–5000 cm<sup>-1</sup>;  $e_{\sigma}(\text{void})$ , 0 to –4000 cm<sup>-1</sup>; with  $\zeta = 0$  or 800 cm<sup>-1</sup>. Within these wide ranges a rough but adequate generalization is evident from the “basic” CLF model. The effect upon the  $xz$ - $yz$  splitting by spin-orbit coupling is very approximately additive and never greater than about 500 cm<sup>-1</sup>. In addition, a further splitting of about 100 cm<sup>-1</sup> for every 1000 cm<sup>-1</sup> increase in  $e_{\pi\perp}(\text{O})$  occurs more or less independently of the remaining parameter values. So, even with the unacceptably high value  $e_{\pi\perp}(\text{O}) \sim 5000$  cm<sup>-1</sup>, the largest splitting calculated is about 1000 cm<sup>-1</sup>. The observed value is reproduced only for  $e_{\pi\perp}(\text{O}) \sim 10000$  cm<sup>-1</sup>.

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**Table II.** Copper(II) Acetylacetonates: "Best-Fit" Parameter Values ( $\text{cm}^{-1}$ ) and Calculated Transition Energies ( $\text{cm}^{-1}$ )

$e_{\sigma}(\text{O})$	6000	5700	6000	5800
$e_{\pi_{\parallel}}(\text{O})^f$	100	100	100	400
$e_{\pi_{\perp}}(\text{O})$	1200	1300	1200	200
$e_{\pi_{\sigma\parallel}}(\text{O})^f$	400	400	400	100
$e_{\pi_{\sigma\perp}}(\text{O})$	0	$\pm 1100$	$\pm 1400$	+400
$e_{\sigma}(\text{void})$	-3600	-3100	-3300	-100 <sup>e</sup>
$\sum^c$	21200	21400	21800	25500
$\zeta^f$	700	700	700	700
	Transition Energies, $A_2^a \rightarrow$			
15295 ( $B_1/B_2$ )	14397 ( $B_1$ ) <sup>b</sup>	15315 ( $B_1$ )	11462 <sup>d</sup> ( $A_1$ )	
15863 ( $B_2/B_1$ )	15518 ( $B_2$ )	17051 ( $B_2$ )	14897 ( $A_1$ )	
18562 ( $A_1$ )	18227 ( $A_1$ )	19217 ( $A_1$ )	15913 ( $B_2/B_1$ )	
19682 ( $A_1$ )	19194 ( $A_1$ )	20779 ( $A_1$ )	16398 ( $B_1/B_2$ )	

<sup>a</sup>Term labels for  $C_{2v}$  symmetry. <sup>b</sup>Energies given for  $\text{Cu}(\text{acac})_2$ ; those for  $\text{Cu}(\text{phenoxycarbonylacetate})_2$  are very similar. <sup>c</sup>The ligand-field trace,  $\sum = \sum^{\text{ligands}}(e_{\sigma} + e_{\pi_{xx}} + e_{\pi_{yy}})$ . <sup>d</sup>Observed<sup>10</sup> bands at 10750, 14300, 16000, and 16400  $\text{cm}^{-1}$ . <sup>e</sup>For the quinoline adduct  $e_{\sigma}(\text{axial}) \equiv e_{\sigma}(\text{void}) + e_{\sigma}(\text{quinoline})$ . <sup>f</sup>Values held fixed, but see text.

Of course, the need for so large a value arises from the coordination geometry being so nearly square, the bite angle (Table I) in this molecule being  $91.4^\circ$ . While there seems no good reason to doubt the crystallographic evidence,<sup>18</sup> the possibility of extreme sensitivity of the  $xz$ - $yz$  splitting to the bite angle was examined. Recalculating the d orbital energies but with a geometry based upon a chelate bite of  $94.5^\circ$  (larger than any observed in the molecules in Table I) only doubles the efficacy of  $e_{\pi_{\perp}}(\text{O})$  to split the  $xz, yz$  pair; that is,  $\zeta = 800 \text{ cm}^{-1}$  and  $e_{\pi_{\perp}}(\text{O}) \sim 5000 \text{ cm}^{-1}$  now yields the observed minimum separation of  $1500 \text{ cm}^{-1}$ . *The splitting of this pair of orbitals thus emerges as the key issue in the present analysis.*

We seek a more effective ligand-field potential that operates perpendicular to the coordination plane. At the phenomenological level we find it in the second coordination shell from the noncoplanarity of chelate and coordination planes. Tilt angles,  $\alpha$ , describing the folding of the acetylacetonate chelates about the  $\text{O}\cdots\text{O}$  vector, are included in Table I; in all cases, the chelates tilt one up and one down, maintaining an inversion center in the complex. A qualitative association of spectral resolution with tilt angle throughout the series of acac complexes is obvious. For **1**, which is nearly planar, there is effectively a resolution into only two spectral maxima; for **4**, the large tilt angle of  $11.4^\circ$  is accompanied by a clear separation into four bands. We pursue this correlation quantitatively within the ligand-field analysis by supposing the  $\text{Cu}-\text{O}$  interactions to involve bent bonds and parameterize the potential with  $e_{\pi_{\sigma\perp}}(\text{O})$  to describe misdirected valency normal to the coordination plane as in Figure 1a of the preceding paper.<sup>6</sup>

### 3. Analyses for the Series of Copper(II) Acetylacetonates

We anticipate the correlation of spectral resolution with chelate tilt angle throughout the series to be associated with a variation in the value of  $e_{\pi_{\sigma\perp}}(\text{O})$ ; we also expect other parameter values to change little. Further, a consistent view that ligand-field parameters reflect electron density in a molecule requires our recognition of the nonbonding lone pairs on the oxygen donors so that the results of the preceding study<sup>6</sup> of cobalt(II) Schiff-base complexes should qualitatively carry over to the present copper(II)

acetylacetonates. We presume that ligand-field contributions from the nonbonding lone pairs in the planes of the acetylacetonate moieties are represented by  $e_{\pi_{\sigma\parallel}} > 0$ . On the other hand we expect significant  $\pi$  donation from the oxygen atoms normal to these planes and hence that  $e_{\pi_{\perp}}(\text{O}) > 0$ . Our starting point for the copper-acac analyses, therefore, is that  $E(xy) > E(xz, yz) > E(x^2 - y^2)$ .

Our discussion centers on the sketch heading Table II, from which we observe how an essentially two-peak spectrum for the near-planar complex **1** resolves into a four-peak spectrum in the most bent molecule, **4**. We presume that the resolution occurs in the obvious manner indicated in the diagram and, therefore, that the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals are nearly degenerate in the planar species, as shown. The splitting of the  $xz, yz$  orbital pair is affected by little other than the  $e_{\pi_{\sigma\perp}}(\text{O})$  parameter; that of the  $z^2, x^2 - y^2$  pair depends upon  $e_{\pi_{\sigma\parallel}}(\text{O})$  also but is reproduced ultimately also by variation in  $e_{\pi_{\sigma\perp}}(\text{O})$  acting in second order. An alternative assignment in which the  $z^2$  orbital is presumed to be nearly degenerate with the  $xz, yz$  pair in **1** is unsustainable if even approximately reasonable values of other CLF  $e$  parameters are also to cause it to become near-degenerate with the  $x^2 - y^2$  orbital in **4**. The parameter values listed in Table II were determined, then, as follows. That for  $e_{\pi_{\sigma\parallel}}(\text{O})$  was fixed at the small, nominally positive value by analogy with the results for the cobalt Schiff-base complexes.<sup>6</sup> A zero value for  $e_{\pi_{\sigma\perp}}(\text{O})$  was presumed for **1** in view of the near-perfect planarity of this molecule. The value of  $400 \text{ cm}^{-1}$  for  $e_{\pi_{\sigma\parallel}}(\text{O})$  represents a numerical maximum if an energy separation for the  $xz, yz$  orbital pair is not to be calculated larger than  $1000 \text{ cm}^{-1}$  and so be resolved experimentally. Finally, optimization of the remaining variables to reproduce the observed transition energies yielded the values in the first column of the table; the spin-orbit coupling parameter,  $\zeta$ , was fixed at  $700 \text{ cm}^{-1}$  throughout these analyses. The splitting of the lower energy band in the spectra of molecules **2** and **3** is about  $1000 \text{ cm}^{-1}$ , and this establishes  $e_{\pi_{\sigma\perp}}(\text{O})$  at ca.  $1100 \text{ cm}^{-1}$ . A fitting process similar to that for **1** yields the values in the second column. Finally, for **4**, when the tilt angle is  $11^\circ$ , the larger spectral splitting now requires  $e_{\pi_{\sigma\perp}}(\text{O}) \sim 1400 \text{ cm}^{-1}$ , yielding the remaining values in

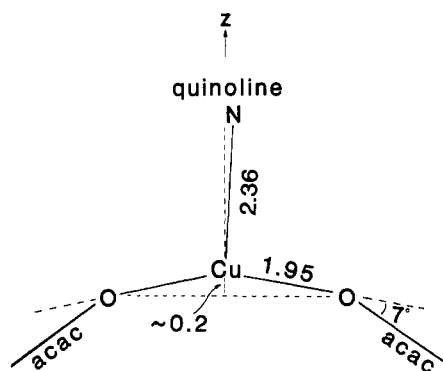


Figure 1. Schematic geometrical details of  $\text{Cu}(\text{acac})_2(\text{quinoline})$ .

Table II. The corresponding calculated transition energies, together with their major speciation (in idealized  $C_{2v}$  symmetry), are also given there. As in several other recent studies, we note the virtual constancy of the ligand-field trace,  $\Sigma$ , throughout this series; the value of this sum is some 5–10% less than that for chlorocopper(II) complexes<sup>20</sup> and insignificantly different from the trace found for a score for copper(II) amine systems.<sup>21,22</sup>

The signs of the  $e_{\pi\sigma\perp}(\text{O})$  parameters in these studies are indeterminate. Positive or negative signs correspond, as described in section 1 of part 1,<sup>6</sup> to the “bend bonds” between oxygens and copper lying two “above” the coordination plane and, for the centrosymmetrically related ligands, two “below”. However, there is no point of reference in these analyses that confers any meaning to “above” and “below”. Both signs of  $e_{\pi\sigma\perp}(\text{O})$  yield identical results. While we expect that the bent bonds “really” do lie in the obvious places with respect to the chelate planes, the orientations of these latter are communicated to the computation only by the  $e_{\pi\sigma\perp}$  parameters themselves. This unavoidable loss of information is simply a consequence of the overall molecular symmetry.

#### 4. A Five-Coordinate Quinoline Adduct

An analysis<sup>10</sup> of the five-coordinate quinoline adduct of copper(II)-acac has been used to support the Belford-Hitchman assignments in the planar species. As the present analyses do not support these early assignments and, in particular, include contributions from the coordination voids, it is appropriate now to see if a similar view of the electron density distribution can reproduce the observed spectrum of the quinoline complex. Essentially three bands are observed although the polarization study<sup>10</sup> establishes a fourth. Our CLF analysis is characterized by the same large number of parameters required for the four-coordinate species above but without some of the simplification afforded by correlations across that series. We expected to find extensive parameter correlation within the analysis of the quinoline complex in consequence, together with a corresponding uncertainty in our conclusions. It transpires that the firmly established assignments afforded by the polarization analysis remove all important ambiguity from the present CLF study.

The coordination geometry<sup>25</sup> is shown schematically in Figure 1. Typically for square-pyramidal complexes, the metal atom lies some 0.2 Å above the chelate donor atom plane. The chelate planes are tilted down from the O-Cu-O planes by 7°, so describing the misdirected valence of a magnitude intermediate with respect to that in the four-coordinate series. The sign of  $e_{\pi\sigma\perp}(\text{O})$  is relevant in this case, for the direction of chelate tilt is defined internally with respect to both the displaced metal atom and the fifth ligand. The other major parameter change to be expected from adduct formation relates to the loss of one of the coordination

voids. The value of  $e_{\sigma}(\text{axial})$  in the present analysis refers to the sum of  $e_{\sigma}(\text{void})$  and  $e_{\sigma}(\text{quinoline})$ . By reference to the similar situation<sup>5</sup> in the structurally analogous pentaamine  $[\text{Cu}(\text{NH}_3)_5]^{2+}$  and in recognition of the moderately long Cu-N bond length (2.36 Å) here, it was anticipated that  $e_{\sigma}(\text{axial})$  would be of small magnitude and indeterminate sign (a priori).

Comprehensive calculations in which  $e_{\sigma}(\text{axial})$ ,  $e_{\sigma}(\text{O})$ ,  $e_{\pi\perp}(\text{O})$ ,  $e_{\pi\parallel}(\text{O})$ , and  $e_{\pi\sigma\perp}(\text{O})$  are varied widely while  $e_{\pi\sigma\parallel}(\text{O})$  is held fixed at 400  $\text{cm}^{-1}$ , as suggested by the analyses of the four-coordinate species, and  $\zeta = 700 \text{ cm}^{-1}$  quickly reveal a central difficulty. Most parameter sets, whether or not they allow reproduction of the observed transition energies, yield the highest-energy band as  ${}^2A_2 \rightarrow {}^2A_1$ , as characterized within the overall  $C_{2v}$  molecular pseudosymmetry, instead of  ${}^2A_2 \rightarrow {}^2B_1$  as determined by Hitchman from his polarization study.<sup>10</sup> This provides the key for our CLF analysis in that the correct level ordering is only reproduced for (modest) positive values of  $e_{\pi\parallel}(\text{O})$ . The essentially unique parameter set given in Table II reproduces observed transition energies well, as shown, and confers substantial  ${}^2A_2 \rightarrow {}^2B_1$  character to the band at ca. 16 400  $\text{cm}^{-1}$ . That mixing between  $\rightarrow B_1$  and  $\rightarrow B_2$  character occurs is to be traced to the imperfect  $C_{2v}$  molecular symmetry, which results especially from the Cu-N vector being displaced from the ideal principal molecular diad, as well as to the effects of spin-orbit coupling.

The sign of  $e_{\pi\sigma\parallel}(\text{O})$  is established in this case and, like that in the cobalt species of part 1,<sup>6</sup> is positive, indicating a dominance of the lone-pair effect over any bent bonding due to ring strain. The adoption of positive  $e_{\pi\sigma\parallel}(\text{O})$  in the analyses of the four-coordinate species is thus supported.

Finally, we note the much smaller value for  $e_{\pi\perp}(\text{O})$  in the quinoline adduct than in the planar acac species (Table II) and presume this reflects a diminished ligand donor role on increasing the coordination number from four to give in accord with the electroneutrality principle. We observe a larger Cu-O bond length in the quinoline adduct (Table I and Figure 1) in agreement with this proposal.  $\pi$  donation is expected to be more sensitive to such changes than  $\sigma$  donation but, as usual, we do not advocate a simple correlation with bond length here as we are comparing donation to  $\text{CuO}_3$  in the planar species with donation to  $\text{CuO}_3\text{N}$  in the adduct.

#### 5. Discussion

The analysis of the d-d spectra of these four-coordinate copper(II) acetylacetonates began with the “conventional” CLF scheme parameterized simply by locally diagonal  $\sigma$  and  $\pi$  variables and was found wanting. Taken together with the “common-sense” chemical view of the expected electron density near the metal atom requiring recognition in ligand-field terms, that finding demonstrates the need for the off-diagonal  $e_{\pi\sigma}$  parameter. Some measure of correlation between the various parameters in these analyses is inevitable with so many variables and so limited a data base, and recognition of this demanded the detailed exposition provided in the preceding section. Nevertheless, it is persuasive to see so consistent a parameterization emerging throughout the series of four- and five-coordinate complexes in which the only major change is in  $e_{\pi\sigma\perp}(\text{O})$ , correlating transparently with the tilt angles.

We presume that the nonzero values of  $e_{\pi\sigma\perp}(\text{O})$  relate only to the “bent bonding” occasioned by the tilting chelate groups. On the other hand, values of  $e_{\pi\sigma\parallel}(\text{O})$  probably reflect contributions from both aspects of misdirected valence illustrated in Figure 1 of part 1.<sup>6</sup> This supposition derives partly from a recognition of the “ring strain” implied by the large Cu-O-C angles in the chelate (ca. 130°) as well as the presence of the nonbonding electron lone pair on each oxygen donor and partly upon the relative magnitudes of  $e_{\pi\sigma\parallel}(\text{O})$  and  $e_{\pi\parallel}(\text{O})$  established by the CLF analysis of the quinoline adduct. Thus any ring strain effect is expected to result in displacement of the Cu-O “ $\sigma$ ” bond toward the inside of the chelate ring and hence to furnish a contribution in the opposite sense to that produced by the lone pair. Equation 5 of part 1<sup>6</sup> describes the  $e_{\pi\sigma}$  parameter as a sum of contributions (over  $\chi$ ) separately, and so in the present complexes we expect to monitor their net contribution and observe some cancellation. However,

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at the same time, their individual contributions to  $e_{\pi\parallel}$ —through eq 3 of part 1—will be both positive (because we consider positive denominators throughout this discussion) and hence additive, numerically as well as algebraically. We believe that the comparable values of  $e_{\pi\sigma\parallel}(\text{O})$  and  $e_{\pi\parallel}(\text{O})$  in the quinoline complex do not merely indicate experimental error or model tolerances but that they actually support the notion of both modes of misdirected valence within the planes of these chelate groups. Whether the same circumstances prevail in the cobalt complexes described in part 1<sup>6</sup> is not clear, partly through the much more difficult analyses there being based primarily upon  $g$  tensors and partly in view of the differing relative contributions to those expected from bent bonding and lone pairs in the more strongly bound systems.

In passing, we may conjecture on the reason why the acetylacetonate chelates tilt in the quinoline adduct. One cannot rule out steric forces, which we suppose play their part in the four-coordinate species. However, by tilting in the sense observed, the chelates may be maximizing overlap with metal orbitals lying in the  $xy$  plane, for that is where the repulsive effect of the electrons in the half-filled  $d_{xy}$  orbital is least. A similar proposal<sup>22</sup> has been made recently within an analysis of the formally tetrahedral  $\text{CuCl}_4^{2-}$  ion in  $\text{Cs}_2\text{CuCl}_4$ .

In summary: the present CLF analyses provide a coherent account of the valence electron distributions in a series of related complexes that lies well with mainstream chemical concepts. At the same time, confusion over the interpretation of the resultant ligand-field properties is hopefully dispelled. Throughout this<sup>6,23</sup> and the previous<sup>5,20,24</sup> series of studies we have proffered the view<sup>2,3,4,17</sup> that all ligand-field phenomena are to be seen as sequential on the underlying bonding, that, in Werner complexes at least, the role of the transition-metal  $d$  orbitals is mainly to react to the electron distribution in the bonding and other higher lying orbitals rather than to be significantly involved in the primary bonding process itself. We see the  $d$  electrons as interacting with the underlying framework of bonds "already" formed. We need not refer *explicitly* to overlap integrals within this formalism—

which, we emphasize, is merely a consequence of nature's endorsement of the basic ligand-field structure—but where such language is deemed useful we must always recognize that the overlap is not that between metal  $d$  orbitals and simple ligand functions. That view neglects the all-important electron redistribution that takes place on molecule formation. Accordingly, guesses about the relative magnitudes of such overlap integrals are wholly unreliable. Our view always has been that ligand-field parameters should be allowed free rein. The contrary view that incorporates interpretation into the approach from the beginning only serves to mix together incompatible model structures.

Inter alia, the features of electron density that seem well attested by the present analyses are (1) that acetylacetonate groups act as  $\sigma$  donors towards the copper and as  $\pi$  donors using the delocalized  $\pi$  orbitals normal to the acac plane, (2) that copper-acac bonding within or close to the acac plane is "nonideal" in the sense that geometrical constraints imposed by the chelate—and possibly crystal packing—cause misalignment of ligand orbitals and metal-oxygen vectors, (3) that such misdirected valence involves bent bonds within the chelate planes and, to a variable extent, normal to those planes, (4) that within the planes, the ligand-field analyses support the idea of a smaller bite angle defined by the bonding electron density than by the chelate donor atoms, (5) that the nonbonding lone pairs on the oxygen donors have a noticeable effect upon the  $d-d$  spectra, and (6) that the ligand-field contributions from the coordination voids throughout the series are important and similar to those established for many other similar coordinationally sparse species.

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## Ligand Fields from Misdirected Valency. 3. Ligand Hybridization in Tetragonal-Octahedral Nickel(II) Thiocyanates<sup>†</sup>

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Ligand-field analyses of the  $d-d$  spectra of seven hexacoordinate nickel(II) complexes, parameterized within the cellular ligand-field model, are presented. Several of these provide a bench mark to help substantiate the primary object of the present study: namely, to show how inclusion of a locally nondiagonal, ligand-field parameter,  $e_{\pi\sigma}$ , obviates the need to consider the thiocyanate ligand as a  $\pi$  donor in *trans*- $\text{Ni}(\text{NH}_3)_4(\text{NCS})_2$  but as a  $\pi$  acceptor in  $\text{Ni}(\text{en})_2(\text{NCS})_2$  ( $\text{en} \equiv$  ethylenediamine). It is argued that the nonzero value of  $e_{\pi\sigma}$  in the latter system monitors the ligand-field effect of the nominal  $sp^2$  nonbonding lone-pair electrons established by bending of the Ni-N-CS angle.

### 1. Introduction

The utility of ligand-field analysis as a chemical discipline surely requires that its conclusions consistently match those from more widely based techniques. It is disquieting to note, therefore, a (repeated<sup>1</sup>) observation<sup>2</sup> that angular overlap model (AOM) parameters appear to define a  $\pi$ -donor role for isothiocyanate ligands in some nickel(II) complexes but  $\pi$ -acidic behavior in others that are closely related. Thus, for  $\text{Ni}(\text{NH}_3)_4(\text{NCS})_2$  in which the *trans* Ni-NCS angles<sup>3</sup> are approximately  $180^\circ$ ,  $e_{\sigma}(\text{NCS})$  and  $e_{\pi}(\text{NCS})$  values have been reported<sup>2</sup> as 3843 and  $125 \text{ cm}^{-1}$ , respectively, while values of 2123 and  $-409 \text{ cm}^{-1}$  are claimed<sup>2</sup>

for  $\text{Ni}(\text{en})_2(\text{NCS})_2$  in which<sup>4</sup> Ni-N-C is  $140^\circ$ . These observations were made in two studies<sup>1,2</sup> that otherwise sought to establish a simple relationship between bond length and  $e_{\sigma}$  values for Ni-N bonds. The association of the smaller  $e_{\sigma}$  value in the second complex with a longer Ni-NCS bond (2.15 vs. 2.07 Å) has obvious qualitative appeal, but no ready explanation of the reversed  $\pi$ -bonding role seems to be at hand. Moreover, on purely phenomenological grounds, it has been proposed<sup>1</sup> that the Ni-NCS bond

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