

## Molecular Orbital Calculations on Bis-Acetylacetonate Copper(II)

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A modified Wolfsberg-Helmholz molecular orbital calculation has been carried out for Bis-Acetylacetonate Copper(II) with particular attention paid to the symmetry of the resulting ground state as a function of input parameters. Using only oxygen basis orbitals, a  $\sigma$  orbital contains the unpaired spin, while inclusion of the carbon pi system produces a  $\pi$  orbital ground state. These results were independent of VSIE's and choice of oxygen basis orbitals. The  $\pi$  ground state is considered to result from deficiencies in the model rather than justification for Ferguson's<sup>1</sup> ordering of the levels. The results were not considered sufficiently reliable to postulate band assignments. The character of the molecular orbitals is compared with ESR data, and the choice of realistic oxygen basis orbitals is discussed.

The question of the electronic structure of the bis-acetylacetonate of copper(II),  $\text{Cu}(\text{AA})_2$ , has aroused considerable controversy.<sup>1-3</sup> Initially, Ferguson<sup>1</sup> proposed a pi ground state, based on polarized crystal spectra. This assignment was highly unorthodox, since it reversed the positions of the most and least stable energy levels as predicted by simple crystal field theory. This conclusion was questioned by Piper and Belford,<sup>2</sup> who showed that the crystal structure was such as not to allow unambiguous determination of the polarizations for the crystal bands, and that a lack of knowledge of the effectiveness of perturbing vibrations in causing transitions precluded any basis for convincing assignments of the bands from the available spectra. They did present some evidence,<sup>2</sup> such as the effect of polar adducts on the solution spectrum, that indicated that the conventional sigma ground state was more probable.

Recently, Dijkgraaf<sup>4</sup> attempted to interpret the  $\text{Cu}(\text{AA})_2$  crystal spectrum in terms of Davydov splitting assuming the conventional energy level diagram

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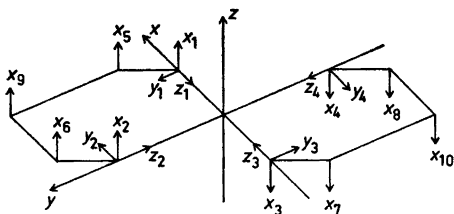


Fig. 1. The coordinate system for copper acetylacetonate.

for square-planar complexes.<sup>5</sup> However, this novel approach has since been demonstrated<sup>6,7</sup> to be both experimentally and theoretically unfounded.

Maki and McGarvey<sup>8</sup> studied the electron spin resonance, ESR, spectrum of this complex in a  $\text{Pd}(\text{AA})_2$  lattice. Their results were concluded to be in agreement with crystal field predictions.

Of the various studies of this complex, only Ferguson's<sup>1</sup> conclusions produced inconsistencies with crystal field theory. His contention<sup>1</sup> that a  $\pi$  antibonding level was least stable (contained the unpaired spin), while the usual ground state  $\sigma$  orbital was most stable was rationalized by the argument that since only one orbital on the ligand oxygens is fixed by the nuclear framework, (the CO bond), it would be possible that the other hybrid orbitals are such as to avoid an orbital which would be directed towards the metal, resulting in a very stable  $\sigma$  orbital. No theoretical justifications for these arguments were offered.<sup>1</sup>

In this work, we present a molecular orbital calculation of the Wolfsberg-Helmholz type,<sup>9</sup> as modified by Ballhausen and Gray<sup>10</sup> with the prime interest in investigating the effects of various parameters on the resulting energy level scheme. Previous MO calculations on this complex have employed Hückel theory<sup>11</sup> where only copper  $d$  orbitals were used. Crystal field calculations have also been done.<sup>12</sup>

In order to maintain maximum flexibility, the MO's are considered for the whole molecule. Previous calculations<sup>13-15</sup> have preferred to use ligand MO's obtained from a separate calculation.

#### THE MOLECULAR ORBITALS

The coordinate system for the complex is shown in Fig. 1. The proper symmetry orbitals are constructed for the ligand and metal under  $D_{2h}$  symmetry, and are listed as sigma,  $\sigma$ , pi ( $\pi$ ), or inplane pi, ( $\pi'$ ), in Table 1. A problem immediately arises as to the choice of basis orbitals for the  $\sigma$  and  $\pi'$  orbitals on oxygen. There is no prior knowledge on hybridization available. In particular, the basis orbitals for oxygen-metal bonding are determined in part by the hybridization of the oxygen orbital in the CO bond.

However, Peters<sup>16</sup> has analyzed the SCF functions of formaldehyde,  $\text{H}_2\text{CO}$ , a model for the CO bond, in terms of localized orbitals. His conclusions were that the atomic orbitals on oxygen do not hybridize significantly, such that the oxygen orbital in the CO bond is primarily  $2p$ , with perhaps an upper limit of 10 %  $2s$  character, while the two lone pairs are primarily  $2p$  and  $2s$  orbitals.

Table 1. Symmetry orbitals for Cu(AcAc)<sub>2</sub>.

$D_{2h}; \Gamma_i$	Metal	Ligand		
		Sigma $\sigma$	Pi $\pi$	In-plane pi $\pi'$
$a_{1g}$	$3d_{z^2}, 4s$	$\frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$	—	—
»	$3d_{xy}$	—	—	$\frac{1}{2}(y_1 + y_2 + y_3 + y_4)$
$b_{1g}$	$3d_{x^2-y^2}$	$\frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$	—	—
»	—	—	—	$\frac{1}{2}(y_1 - y_2 + y_3 - y_4)$
$b_{2g}$	$\sqrt{\frac{1}{2}}(3d_{xz} - 3d_{yz})$	—	$\begin{cases} \frac{1}{2}(x_5 - x_6 + x_7 - x_8) \\ \frac{1}{2}(x_1 - x_2 + x_3 - x_4) \end{cases}$	—
$b_{3g}$	$\sqrt{\frac{1}{2}}(3d_{xz} + 3d_{yz})$	—	$\begin{cases} \sqrt{\frac{1}{2}}(x_9 + x_{10}) \\ \frac{1}{2}(x_5 + x_6 + x_7 + x_8) \\ \frac{1}{2}(x_1 + x_2 + x_3 + x_4) \end{cases}$	—
$a_{1u}$	—	—	$\begin{cases} \frac{1}{2}(x_5 - x_6 - x_7 + x_8) \\ \frac{1}{2}(x_1 - x_2 - x_3 + x_4) \end{cases}$	—
$b_{1u}$	$4p_z$	—	$\begin{cases} \sqrt{\frac{1}{2}}(x_9 - x_{10}) \\ \frac{1}{2}(x_5 + x_6 - x_7 - x_8) \\ \frac{1}{2}(x_1 + x_2 - x_3 - x_4) \end{cases}$	—
$b_{2u}$	$\sqrt{\frac{1}{2}}(4p_x + 4p_y)$	$\frac{1}{2}(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4)$	—	$\frac{1}{2}(y_1 + y_2 - y_3 - y_4)$
$b_{3u}$	$\sqrt{\frac{1}{2}}(4p_x - 4p_y)$	$\frac{1}{2}(\sigma_1 - \sigma_2 - \sigma_3 + \sigma_4)$	—	$\frac{1}{2}(-y_1 + y_2 + y_3 - y_4)$

In accordance with Peters' results,<sup>16</sup> the oxygen orbitals will remain unhybridized, though the effect of adding 10 %  $2s$  character to the CO bond will be assessed. The choice of unhybridized oxygen orbitals is supported by previous MO calculations,<sup>17</sup> where it was concluded that a choice of hybridization was arbitrary at best, and even the optimum choice did not yield as reasonable results as the unhybridized orbitals. It is considered of interest here to also include one calculation with the basis orbitals used to interpret the ESR data,<sup>8</sup> where  $\sigma = sp^2$ , and  $\pi$  and  $\pi'$  are pure  $2p$  orbitals, and the carbon pi system is neglected. In all, four different oxygen basis orbitals will be considered; I— $2p$  on O in the CO bond, no hybridization, including O  $2s$ ; II—same as I, only  $2s$  on O are neglected; III—CO bond contains 10 %

 Table 2. Four sets of oxygen basis orbitals.<sup>a</sup>

Orbital	Case I	Case II	Case III	Case IV
$\pi$	$2p_x(\pi)$	$2p_x(\pi)$	$2p_x(\pi)$	$2p_x(\pi)$
$\varphi_a$	$\sqrt{\frac{1}{2}}[2p_y + 2p_z](\sigma, \pi')$	$\sqrt{\frac{1}{2}}[2p_y + 2p_z](\sigma, \pi')$	$\sqrt{\frac{1}{2}}[2p_y + 2p_z](\sigma, \pi')$	$2p_y(\pi')$
$\varphi_b$	$2s(\sigma)$	—	$\sqrt{\frac{18}{20}}2s - \sqrt{\frac{1}{20}}[2p_y - 2p_z](\sigma, \pi')$	$\sqrt{\frac{1}{3}}2s + \sqrt{\frac{2}{3}}2p_z(\sigma)$

<sup>a</sup> The orbital type, *i.e.*  $\sigma$ ,  $\pi$ , or  $\pi'$ , is indicated in parentheses.

2s character; IV—the Maki-McGarvey basis orbitals.<sup>8</sup> These four sets of basis orbitals are given in Table 2, and the resulting group overlap integrals in Table 3, based on the distances Cu—O = 1.92 Å, O—C = 1.28 Å, and C—C = 1.39 Å.<sup>18</sup> The carbon basis orbital is always taken as a 2p pi-type orbital. It should be pointed out that the calculated overlaps in Table 3 reflect the fact that some of the oxygen basis orbitals possess not pure  $\sigma$  or  $\pi'$  bonding characteristics, such that the conventional overlaps must be multiplied by the proper orbital coefficient in Table 2. The Synek<sup>19</sup> radial functions available for copper and the Clementi *et al.*<sup>20</sup> oxygen and carbon orbitals are used.

Table 3. Group overlaps for the four basis orbitals.<sup>a</sup>

		Case I	Case II	Case III	Case IV
$a_{1g}:\sigma$	$G(4s, \varphi_a)$	0.2340	0.2340	0.2340	0
$a_{1g}:\sigma$	$G(4s, \varphi_b)$	0.5348	—	0.5814	0.5784
$a_{1g}:\sigma$	$G(3d, \varphi_a)$	-0.0607	-0.607	-0.607	0
$a_{1g}:\sigma$	$G(3d, \varphi_b)$	-0.0918	0	-0.1063	-0.1232
$a_{1g}:\pi'$	$G(3d, \varphi_a)$	0.0892	0.0892	0.0892	0.1262
$a_{1g}:\pi'$	$G(3d, \varphi_b)$	0	0	-0.0282	0
$a_{1g}:\sigma$	$G(3d, \varphi_a)$	0.1052	0.1052	0.1052	0.2135
$b_{1g}:\sigma$	$G(3d, \varphi_b)$	0.1590	0	0.1842	0
$b_{2g}:\pi$	$G(3d, \pi)$	0.0892	0.0892	0.0892	0.0892
$b_{3g}:\pi$	$G(3d, \pi)$	0.0892	0.0892	0.0892	0.0892
$b_{1u}:\pi$	$G(4p, \pi)$	0.3318	0.3318	0.3318	0.3318
$b_{2u}:\sigma, \pi'$	$G(4p, \varphi_a)$	0.2659	0.2659	0.2023	0.2348
$b_{2u}:\sigma, \pi'$	$G(4p, \varphi_b)$	0.5160	0	0.3080	0.2347
$b_{3u}:\sigma, \pi'$	$G(4p, \varphi_a)$	0.2659	0.2659	0.2023	0.2348
$b_{3u}:\sigma, \pi'$	$G(4p, \varphi_b)$	0.5160	0	0.3080	0.2347

<sup>a</sup> Group overlaps not involving the copper orbitals are as follows: ( $b_{2g,3g,1u}:\pi$ )  $G(2p_O, 2p_C) = 0.2865$ ; ( $b_{3g,1u}:\pi$ )  $G(2p_C, 2p_C) = 0.5273$ , where the subscripts O and C refer to oxygen and carbon.

The valence state ionization energies, VSIE's, for copper are determined as illustrated elsewhere.<sup>10</sup> The ligand VSIE's are obtained from the tabulations of Pilcher and Skinner<sup>21</sup> for both carbon and oxygen. For the hybridization states for which no values are available in the literature, an estimate was made by drawing a smooth curve through VSIE's for tabulated hybridizations versus percent 2s character, and taking the appropriate points from this plot. Calculations are performed using both the isolated or "free ion" and "hydride ion" VSIE's. The latter were considered to be more realistic and reliable, but recently it has been contended that this choice has no justification.<sup>17</sup> Therefore both sets of values are employed and are given in Table 4.

The secular equations are solved in a self consistent manner, until input configuration and charge matched the output values.<sup>10</sup> Each case listed in Table 2 was calculated twice, once including and once neglecting the carbon pi system. In calculations involving only the oxygens, 33 electrons are placed in the lowest orbitals,<sup>8</sup> and upon inclusion of the carbons, this number is 37. For case II, where the oxygen 2s orbital is neglected, the number of electrons is decreased by 8.

Table 4. Coulomb integrals and self-consistent charges and configurations.<sup>a</sup>

Orbital	Case I		Case III		Case IV		
	FI	HI	FI	HI	FI	HI	
Only oxygen basis orbitals	$\varphi_a(O)$	-143.6	-101.7	-143.6	-101.7	-143.6	-101.7
	$\varphi_b(O)$	-143.6	-101.7	-269.0	-230.0	-208.0	-177.3
	$\pi(O)$	-143.6	-101.7	-143.6	-101.7	-143.6	-101.7
	$\pi(C)$	-90.5	-79.3	-90.5	-79.3	-90.5	-79.3
	3d	-162.2	-132.7	-164.6	-133.4	-152.8	-126.6
	4s	-113.4	-94.7	-114.5	-94.7	-106.6	-89.7
Carbon pi sys.-term included	4p	-70.1	-53.9	-71.3	-53.8	-64.8	-49.3
		$s^{.44}p^{.40}d^{9.55}$	$s^{.45}p^{.40}d^{9.77}$	$s^{.47}p^{.39}d^{9.56}$	$s^{.47}p^{.43}d^{9.72}$	$s^{.51}p^{.38}d^{9.57}$	$s^{.50}p^{.43}d^{9.77}$
		$q = 0.63$	$q = 0.38$	$q = 0.64$	$q = 0.38$	$q = 0.54$	$q = 0.30$
	3d	-139.2	-125.4	-138.2	-124.0	-134.3	-120.6
	4s	-101.0	-91.0	-100.1	-90.0	-96.7	-86.7
	4p	-61.8	-51.6	-60.8	-50.6	-57.7	-47.3
		$s^{.36}p^{.24}d^{9.85}$	$s^{.42}p^{.34}d^{9.87}$	$s^{.38}p^{.24}d^{9.85}$	$s^{.43}p^{.35}d^{9.87}$	$s^{.45}p^{.27}d^{9.82}$	$s^{.48}p^{.39}d^{9.85}$
		$q = 0.55$	$q = 0.37$	$q = 0.53$	$q = 0.35$	$q = 0.46$	$q = 0.28$

<sup>a</sup> Coulomb integrals are given in  $(10^3) \text{ cm}^{-1}$ . FI and HI denote the "free ion" and "hydride ion" ionization potentials for the ligand atoms.

## RESULTS

The resulting energy levels for Cases I, III, and IV are listed in Table 5, using only the oxygen orbitals, and in Table 6 when the whole chelate is considered. Placing 33 electrons into the lowest orbitals in Table 5 gives a

Table 5. Calculated orbital energies using only oxygen orbitals basis.<sup>a</sup>

Orbital	Free ion VSIE's			Orbital	Hydride ion VSIE's				
	I	III	IV		I	III	IV		
5a <sub>1g</sub>	68.9	114.6	a <sub>1g</sub>	61.4	5a <sub>1g</sub>	57.0	94.3	a <sub>1g</sub>	51.6
3b <sub>2,3u</sub>	36.3	-37.3	b <sub>1u</sub>	-39.9	3b <sub>2,3u</sub>	27.8	-27.9	b <sub>1u</sub>	-30.0
2b <sub>1u</sub>	-42.9	-43.5	b <sub>2,3u</sub>	-40.2	2b <sub>1u</sub>	-32.6	-32.5	b <sub>2,3u</sub>	-30.4
3b <sub>1g</sub>	-126.6	-124.5	b <sub>2g</sub>	-123.5	3b <sub>1g</sub>	-93.8	-92.4	b <sub>1g</sub>	-93.1
2b <sub>2,3g</sub>	-135.1	-135.5	a <sub>1g</sub>	-126.3	2b <sub>2,3g</sub>	-97.6	-97.6	b <sub>2,3g</sub>	-97.1
4a <sub>1g</sub>	-139.0	-137.9	b <sub>2,3g</sub>	-132.9	1a <sub>1u</sub>	-101.7	-101.7	b <sub>1g</sub>	-101.7
1a <sub>1u</sub>	-143.6	-143.6	a <sub>1u</sub>	-143.6	4a <sub>1g</sub>	-102.2	-101.9	a <sub>1u</sub>	-101.7
2b <sub>2,3u</sub>	-145.5	-145.1	b <sub>1g</sub>	-143.6	2b <sub>2,3u</sub>	-103.5	-103.1	a <sub>1g</sub>	-102.2
1b <sub>1u</sub>	-147.6	-147.9	b <sub>2,3u</sub>	-145.0	1b <sub>1u</sub>	-105.5	-105.5	b <sub>2,3u</sub>	-103.1
2b <sub>1g</sub>	-160.7	-159.1	b <sub>1u</sub>	-146.5	2b <sub>1g</sub>	-125.9	-123.2	b <sub>1u</sub>	-104.4
3a <sub>1g</sub>	-160.8	-162.4	a <sub>1g</sub>	-149.9	3a <sub>1g</sub>	-131.2	-131.8	a <sub>1g</sub>	-123.5
1b <sub>2,3g</sub>	-168.3	-164.6	b <sub>2,3g</sub>	-161.1	1b <sub>2,3g</sub>	-134.9	-135.7	b <sub>2,3g</sub>	-128.5
2a <sub>1g</sub>	-169.5	-172.0	a <sub>1g</sub>	-165.3	2a <sub>1g</sub>	-135.3	-136.4	a <sub>1g</sub>	-130.6
1b <sub>2,3u</sub>	-276.0	-269.0	b <sub>2,3u</sub>	-208.2	1b <sub>2,3u</sub>	-236.8	-230.0	b <sub>2,3u</sub>	-177.3
1b <sub>1g</sub>	-280.4	-275.5	b <sub>1g</sub>	-220.5	1b <sub>1g</sub>	-239.6	-234.5	b <sub>1g</sub>	-186.6
1a <sub>1g</sub>	-285.2	-281.0	a <sub>1g</sub>	-226.0	1a <sub>1g</sub>	-234.5	-238.9	a <sub>11</sub>	-190.7

<sup>a</sup> Energies in  $(10^3) \text{ cm}^{-1}$ . The case IV levels are relabelled due to the ordering differing from I and III.

Table 6. Calculated orbital energies, including carbon pi system.<sup>a</sup>

Orbital	Free ion VSIE's			Orbital	Hydride ion VSIE's			
	I	III	IV		I	III	IV	
4b <sub>1g</sub>	63.5	63.4	63.1	5a <sub>1g</sub>	55.1	90.5	b <sub>1u</sub> <sup>b</sup>	53.8
5a <sub>1g</sub>	62.4	103.1	56.7	4b <sub>1u</sub>	54.1	54.1	a <sub>1g</sub>	50.4
4b <sub>3g</sub>	48.3	48.3	48.3	4b <sub>3g</sub>	41.6	41.5	b <sub>3g</sub>	41.6
3b <sub>2,3u</sub>	32.1	-32.0	-45.9	3b <sub>2,3u</sub>	26.6	-26.4	b <sub>2,3u</sub>	-29.4
3b <sub>1u</sub>	-45.5	-44.9	-42.9	3b <sub>1u</sub>	-38.1	-37.4	b <sub>1u</sub>	-35.4
3b <sub>2g</sub>	-61.0	-61.0	-61.0	3b <sub>2g</sub>	-50.7	-50.7	b <sub>2g</sub>	-50.6
2a <sub>1u</sub>	-62.8	-62.8	-62.8	2a <sub>1u</sub>	-52.4	-52.4	a <sub>1u</sub>	-52.4
3b <sub>3g</sub>	-111.0	-110.9	-110.7	3b <sub>3g</sub>	-90.9	-90.9	b <sub>3g</sub>	-90.5
2b <sub>1u</sub>	-114.7	-114.6	-110.9	3b <sub>1g</sub>	-92.6	-91.0	a <sub>1g</sub>	-92.0
3b <sub>1g</sub>	-116.0	-111.9	-114.4	2b <sub>1u</sub>	-95.9	-95.8	b <sub>1u</sub>	-95.1
4a <sub>1g</sub>	-128.9	-127.0	-118.3	4a <sub>1g</sub>	-101.2	-99.7	b <sub>1g</sub>	-98.8
2b <sub>2g</sub>	-132.9	-132.2	-129.3	2b <sub>2,3u</sub>	-103.2	-102.8	b <sub>1g</sub>	-101.7
2b <sub>3g</sub>	-134.0	-133.4	-130.6	2b <sub>3g</sub>	-108.9	-108.8	b <sub>2,3u</sub>	-102.5
3a <sub>1g</sub>	-138.0	-136.6	-132.2	1a <sub>1u</sub>	-112.7	-112.7	b <sub>2g</sub>	-107.9
2b <sub>2,3u</sub>	-144.8	-144.4	-143.9	2b <sub>3g</sub>	-113.5	-113.4	a <sub>1u</sub>	-112.7
1a <sub>1u</sub>	-151.5	-151.5	-143.9	1b <sub>1u</sub>	-116.6	-116.5	b <sub>3g</sub>	-112.8
2b <sub>1g</sub>	-151.5	-151.6	-151.5	2b <sub>1g</sub>	-120.9	-117.7	b <sub>1u</sub>	-116.2
1b <sub>1u</sub>	-153.0	-152.9	-152.6	3a <sub>1g</sub>	-124.5	-122.9	a <sub>1g</sub>	-118.6
2a <sub>1g</sub>	-155.8	-155.8	-155.1	2a <sub>1g</sub>	-128.9	-127.9	b <sub>2g</sub>	-124.6
1b <sub>3g</sub>	-156.9	-156.7	-155.7	1b <sub>3g</sub>	-128.9	-127.9	b <sub>3g</sub>	-124.8
1b <sub>3g</sub>	-157.0	-156.8	-155.9	1b <sub>2g</sub>	-128.9	-128.3	a <sub>1g</sub>	-126.3
1b <sub>2,3u</sub>	-276.3	-269.1	-208.8	1b <sub>2,3u</sub>	-236.9	-230.1	b <sub>2,3u</sub>	-177.3
1b <sub>1g</sub>	-278.3	-272.2	-215.8	1b <sub>1g</sub>	-238.9	-233.4	b <sub>1g</sub>	-185.4
1a <sub>1g</sub>	-281.2	-275.4	-220.9	1a <sub>1g</sub>	-242.2	-237.0	a <sub>1g</sub>	-190.3

<sup>a</sup> Energies in (10<sup>8</sup>) cm<sup>-1</sup>.<sup>b</sup> Case IV energy levels are relabelled due to level scheme differing from I and III.

3b<sub>1g</sub> ground state orbital in all four cases. With the inclusion of the carbons, the proper allocation of the 37 electrons yields a 3b<sub>3g</sub> MO with the unpaired spin in each case. The self-consistent VSIE's, configurations, and charges, *q*, on the copper are recorded in Table 4. The energy levels for Case II are not listed as they are very close to Case I.

## DISCUSSION

The most striking feature of these calculations is the fact that neglect of the carbon pi system results in a b<sub>1g</sub>(σ) ground state orbitals, as predicted by crystal field theory, while the inclusions of the carbons produces a b<sub>3g</sub>(π) orbital with the unpaired electron. These results hold true throughout all permutations of free ion and hydride ion VSIE's, inclusion and neglect of the carbon pi system, and all four cases of oxygen basis orbitals. This seems to indicate, at least within the Wolfsberg-Helmholz framework, that a π ground state is possible for this molecule.

An attempt to assign the observed bands in Cu(AA)<sub>2</sub> on the basis of these calculations is deemed very questionable on a number of grounds, (*vide infra*).

The observed " $d-d$ " transitions are at 14 500, 15 6000, 18 000 and perhaps at 26 000  $\text{cm}^{-1}$ ,<sup>1,2</sup> plus some charge transfer bands at higher energies.<sup>4,11,16</sup> Inspection of the energy levels in Tables 5 and 6 reveals that for the calculations for the whole chelate, the ground state  $3b_{3g}$  and the next lower  $3b_{1g}(\sigma)$  levels are only some 200 to 4000  $\text{cm}^{-1}$  apart, depending on the oxygen basis orbitals. Thus if one makes the unlikely assumption that the  $3b_{3g} \leftarrow 3b_{1g}$  has not been observed in the low energy side of the spectrum, then the three  $d-d$  bands of 14 500, 15 600 and 18 000  $\text{cm}^{-1}$  might be assigned to  $3b_{3g} \leftarrow 4a_{1g}$ ,  $3b_{3g} \leftarrow 2b_{2g}$ , and  $3b_{3g} \leftarrow 2b_{3g}$ , in that order, with  $3b_{3g} \leftarrow 3a_{1g}$  perhaps attributable to the 26 000  $\text{cm}^{-1}$  shoulder, and the charge transfer bands originating from a transition such as  $2a_{1u} \leftarrow 3b_{3g}$ . The numerical agreement is best for Case I, and worst for Case IV, but still not sufficient to make any assignment convincing. Also, numerical agreement based on this above assignment is always better for the use of free ion rather than hydride ion ligand VSIE's. For the latter VSIE's the energy levels tend to be crowded even more closely together. Until the band polarizations are definitely established,<sup>2,3</sup> these assignments can only be considered guesses. Inspection of the eigenvectors shows some additional deficiencies, and casts further doubt on the reliability of the energy level ordering.

For the calculations neglecting the carbons, a more conventional level ordering is obtained, with a  $3b_{1g}$  ground state orbital. However, there exists no better basis for assignments here, particularly in view of the fact that it is indicated that there will be significant interaction between metal and complete ligand orbitals. It is significant that even in this situation the  $3b_{3g}(\pi)$  level is just below the  $\sigma$  ground state orbital.

The molecular orbital energies including the whole chelate, do indicate that part of Ferguson's hypothesis can be rationalized, that of a  $\pi$  ground state. However, the  $b_{1g}$  level is always closest to the ground state orbital, sometimes by as little as 800  $\text{cm}^{-1}$ , such that the remaining unorthodox aspect of his<sup>1</sup> energy level diagram, that of having the antibonding  $b_{1g}$  level most stable, can not be justified within this MO scheme. Case II, where the oxygen  $2s$  orbitals are neglected represents the most favorable possible situation for producing a stable  $b_{1g}(\sigma)$  orbital, and even here  $b_{1g}$  is directly below the  $\pi$  orbital containing the single spin. Thus Ferguson's band assignments<sup>1</sup> are considered to be inconsistent with the present calculations. These conclusions are unaffected by choice of parameters.

The Maki-McGarvey<sup>8</sup> oxygen basis orbitals produced an energy level scheme not seriously inconsistent with that predicted by crystal field theory, (see Table 5) while the inclusion of the carbon  $\pi$  system yielded the  $b_{3g}(\pi)$  ground state orbital, as with the other oxygen orbitals. The choice of these basis orbitals is most inappropriate, aside from the fact that the SCF results<sup>16</sup> indicate no substantial oxygen hybridization, since they<sup>8</sup> imply that the oxygen orbital in the CO bond have  $s^2p$  hybridization. Such an oxygen orbital would have directional properties almost orthogonal to those required by the geometry of the chelate. The effect of this unrealistic choice of basis orbitals<sup>8</sup> on the ESR parameters has not been estimated.

One disturbing feature of all the calculations is revealed in the eigenvectors. Many of the antibonding orbitals involving the copper  $d$  functions tend to be

more ligand than metal orbitals, as opposed to the primarily metal character expected for them. The free ion VSIE's uniformly produced antibonding orbitals with greater metal character than the hydride ion VSIE's, indicating that the former values might be more realistic of the two in this case, as was also implied by the energy level spacings. Similarly, the antibonding MO's for the calculations with the carbon pi system tended to have more metal character than those resulting from use of only the oxygen orbitals.

As the ESR analysis produced numerical estimates to the covalencies for some of the orbitals,<sup>8</sup> it is of interest to compare these estimates to those derived from this MO calculation. In Table 7 we compare the ESR results with those obtained for Case I, judged the most reasonable here, and Case IV, which used the basis orbitals employed in the ESR work.<sup>8</sup> On the basis of numerical agreement, the comparison seems to favor the Case IV orbitals, though the difference between Case I and IV is not significant. The calculated values generally indicate a greater covalency, though the values for the  $b_{1g}(\sigma)$

Table 7. Per cent metal character in antibonding orbitals.

Orbital	ESR results <sup>a</sup>	Molecular orbital calculations			
		Case IV		Case I	
		Ox + C <sup>a</sup>	Ox <sup>b</sup>	Ox + C	Ox
$b_{1g}(\sigma)$	~81	86.8	79.8	70.7	23.9
$a_{1g}(\pi')$	~85	62.9	38.1	55.0	51.9
$b_{2g}(\pi)$	{ ~99	79.7	{ 33.6	72.9	{ 21.7
$b_{3g}(\pi)$		8.6		6.1	

<sup>a</sup> Ox + C indicates use of both oxygen and carbon pi orbitals.

<sup>b</sup> Ox indicates use of only oxygen orbitals.

and  $a_{1g}(\pi')$  orbitals can be considered consistent with the ESR data,<sup>8</sup> as long as the free ion VSIE's are used. However, for the  $b_{2g}$ ,  $b_{3g}(\pi)$  orbitals, where the ESR data predict an ionic bond, the calculation imposes significant covalency for the  $b_{2g}$  orbital, and primarily ligand character for the  $b_{3g}$  orbital. The source of this major discrepancy can not be readily isolated, though it seems to reflect on a deficiency in the MO scheme, particularly with respect to the  $b_{3g}$  bond. It has been noted<sup>17</sup> that strong  $\pi$ -bonding is an automatic consequence of the assumptions inherent in the Wolfsberg-Helmholz type calculations, and this effect could be blamed for the extraordinarily destabilized  $b_{3g}(\pi)$  orbital and resulting  $\pi$  ground state, and thus the  $b_{3g}$  eigenvector would not be expected to be particularly realistic. To blame *all* the discrepancies on this cause might be an unnecessary oversimplification. The unrealistic choice of oxygen orbitals used in the ESR interpretation,<sup>8</sup> their overlap integrals, which differed significantly from those used here, and the necessity



of their<sup>8</sup> assuming band assignments in order to obtain the covalency parameters may all contribute to this apparent inconsistency between the two analyses. A similar recent ESR analysis on copper(II) diethyldithiocarbamate<sup>22</sup> produced the results that the  $\pi'$  bond is completely ionic, while the  $\pi$  bond is appreciably covalent, the opposite to that concluded for  $\text{Cu}(\text{AA})_2$ .<sup>8</sup> The inability of this type of MO theory in giving satisfactory interpretations of spectra is not without some precedent.<sup>23</sup>

Another aspect of this analysis to be noted concerns the relative energies of the antibonding  $b_{2g}$  and  $b_{3g}$  orbitals which contain electrons. When the carbons are neglected, these two levels become degenerate under  $D_{2h}$  symmetry. Ferguson's<sup>1</sup> crystal spectrum led him to conclude that  $b_{3g}$  was above  $b_{2g}$ . Piper and Belford used Ferguson's ordering for these two levels as one of their arguments for contending that his analysis<sup>1</sup> is incorrect, by claiming that the  $b_{2g}$   $b_{3g}$  degeneracy is lifted due to the O—Cu—O angle being slightly greater than  $90^\circ$ . Since the overlap between the metal  $d$  orbital and  $b_{2g}$  orbital would thus be slightly greater than for the  $b_{3g}$  orbital, they argued<sup>2</sup> that the antibonding  $b_{2g}$  orbital must be above the  $b_{3g}$  orbital.

This argument<sup>2</sup> would suffice *if* we were certain that the carbon pi orbitals played no part in determining the energies of the Cu—O bonds. However, as soon as complete chelate MO's are allowed to interact with the metal orbitals, this line of reasoning becomes invalid when applied alone. From symmetry considerations, it is clear that the copper  $b_{2g}$  orbital can only bond with a ligand pi orbital containing an *odd* number of nodes in the molecular plane, while the  $b_{3g}$   $d$  orbital can only bond to a ligand orbital with an *even* number of nodes in the ligand plane. The energies of two MO's containing different number of nodes will differ, and therefore there is no simple method for determining whether  $b_{2g}$  or  $b_{3g}$  is higher without knowledge of the ligand molecular orbitals. In this analysis, it is clear that for all cases considered,  $b_{3g}$  lies above  $b_{2g}$ , contrary to the simple overlap argument. Though these calculations were performed assuming a  $90^\circ$  O—Cu—O angle, one test calculations based on overlaps computed for the true angle of  $93.5^\circ$  revealed that this effect was insignificant in relation to the other consideration in determining the positions of the  $b_{2g}$  and  $b_{3g}$  antibonding orbitals.

#### SUMMARY

*a.* The present MO calculations indicate that a  $b_{3g}(\pi)$  ground state orbital is a theoretical possibility within the W—H framework if the whole chelate pi system is taken into consideration. Upon neglect of the carbons, the more conventional  $b_{1g}(\sigma)$  orbital contains the lone spin, though the ordering of the remaining levels offers no consolation. However, since it is known<sup>17</sup> that such MO schemes tend to overemphasize  $\pi$  bonding, and since the next lower level is always the  $b_{1g}$ , these calculations do not seem to form sufficient basis for claiming a serious deviation from simple crystal field predictions, and perhaps indicate rather deficiencies inherent in the calculation scheme.

*b.* Even after assuming the  $b_{3g}$  ground state orbital is real, Ferguson's<sup>1</sup> ordering of the energy levels in this complex can not be rationalized within this MO framework, even under the most favorable circumstances.

c. Assignment of the bands is attempted for calculations involving the complete pi system, but is considered very speculative, at best. The results predict an unlikely "*d-d*" transition around 4000 cm<sup>-1</sup>. The energy level spacing indicate that the free ion VSIE's are more realistic than the hydride ion VSIE's in these calculations.

d. The most reasonable basis orbitals for oxygen are concluded to be Case I, where the CO bond contains a 2*p* orbital on the oxygen, and the three remaining orbitals are unhybridized. The least realistic hybridization scheme is considered to be that used previously in the ESR interpretations.<sup>8</sup>

e. Several of the eigenvectors for the antibonding orbitals involving copper *d* functions tended to be more ligand than metal, contrary to the primarily metal character expected. This discrepancy might also be attributed to the over-importance of pi bonding in the calculation scheme.<sup>17</sup> Free ion VSIE's produced more reasonable results than the hydride ion VSIE's. Agreement between the covalencies as obtained from the ESR measurements<sup>8</sup> and from these calculations is fair for the *b*<sub>1g</sub>(σ) and *a*<sub>1g</sub>(π') bonds, but very poor for the π bonds.

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