Calculation of the Molecular-orbital Parameters for Some CuN$_4$ Chromophores

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Molecular-orbital parameters (a_1, b_1, and c_1) have been calculated for the square-coplanar CuN$_4$ chromophore in [Cu(NH$_3$)$_4$][PtCl$_4$], β-phthalocyaninatocopper(II), and tetraphenylporphinatocopper(II) using a more complete model than has been used previously involving metal–ligand and ligand–ligand overlap integrals and charge-transfer states. In order to obtain a reasonable correlation of the magnetic g and A values and the electronic transition energies, it is necessary to use a Cu$^+$ wavefunction to represent the radially expanded Cu^{2+} wavefunction in these complexes. The experimental g and A values are reproduced with reasonable σ- and π-bonding coefficients with σ bonding > out-of-plane π bonding > in-plane π bonding. The σ-bonding coefficients are essentially independent of the π-bonding coefficients but very dependent on the electronic energies involved. In the non-centrosymmetric tetraphenylporphinatocopper(II), d–p mixing is important.

THE large body of magnetic and spectral data on copper(II) chelate complexes collected in the literature [1-3] has prompted an attempt to rationalise the data using a more complete molecular-orbital (m.o.) model than has been used [2,4-6] previously, where ligand effects such as spin–orbit coupling, nuclear moment, and ligand–ligand overlap have been approximated or neglected. Many workers have used either a parametrised crystal-field model with orbital-reduction parameters,[1,7] or a simplified m.o. model.[4-6] The present paper reports the results of performing the more complete m.o. calculations on tetra-amminecopper(II) tetrachloroplatinate(II), β-phthalocyaninatocopper(II) and αβγδ-tetraphenylporphinatocopper(II), for all of which crystallographic [8-10] and e.s.r. data (including metal and ligand hyperfine data) are available.[4-6] These complexes have been treated in an exact D_{4h} symmetry and the relevant m.o. coefficients and electronic energy levels calculated.

THEORY AND CALCULATION OF g AND A VALUES

The relevant molecular orbitals for a square-coplanar four-co-ordinate copper(II) complex in D_{4h} symmetry [2] with a hole in the $d_{x^2-y^2}$ orbital are (1)—(3) using the reference

$$\psi(b_{1g}^*) = a_1 d_{x^2-y^2} - a_2 N_s(s^1 - s^2 + s^3 - s^4) - a_3 N_1(-p_x^1 + p_y^2 + p_x^3 - p_y^4) \quad (1)$$

$$\psi(b_{2g}^*) = b_1 d_{xy} - b_2 N_2(p_y^1 + p_x^2 - p_y^3 - p_x^4) \quad (2)$$

$$\psi(e_g^*) = \begin{Bmatrix} c_1 d_{xz} - c_2 N_3(p_z^1 - p_z^3) \\ c_1 d_{yz} - c_2 N_3(p_z^2 - p_z^4) \end{Bmatrix} \quad (3)$$

axes defined in Figure 1. These are antibonding orbitals with positive overlap between the metal and ligand function and with negative ligand coefficients. The bonding m.o.s may be obtained by changing the signs of the ligand coefficients. The bonding m.o.s used are those corresponding to $\psi(b_{2g})$ and $\psi(e_g)$. The normalisation coefficients (N) allow for ligand–ligand overlap as in (4)—(7).

$$N_s = \tfrac{1}{2}[1 - 2S(s,s)_{cis} + S(s,s)_{trans}]^{-\frac{1}{2}} \quad (4)$$

$$N_1 = \tfrac{1}{2}[1 - S(p_\sigma,p_\sigma)_{cis} - S(p_\pi,p_\pi)_{cis} + S(p_\sigma,p_\sigma)_{trans}]^{-\frac{1}{2}} \quad (5)$$

$$N_2 = \tfrac{1}{2}[1 + S(p_\sigma,p_\sigma)_{cis} + S(p_\pi,p_\pi)_{cis} - S(p_\pi,p_\pi)_{trans}]^{-\frac{1}{2}} \quad (6)$$

$$N_3 = 2^{-\frac{1}{2}}[1 - S(p_\pi,p_\pi)_{trans}]^{-\frac{1}{2}} \quad (7)$$

In order to calculate the g and A values the spin–orbit, magnetic and hyperfine-interaction matrices must be set up. For the spin–orbit interaction an operator of $H_{so} = \zeta_m l \cdot S + \zeta_L \Sigma_i l_i \cdot S$ was used, in which all the terms involving the spin–orbit coupling in the overlap region are ignored in view of the $\langle r^{-3}\rangle$ dependence [11] of the spin–orbit coupling constant ζ. A similar form of operator was used for the hyperfine interaction. However, with the magnetic operator in the form $L + g_eS$, the orbital angular momentum in the bonding region must be taken into account. The simplest way to do this is to write the operator for the central metal explicitly and then refer it to the ligand framework,[7] *i.e.* as in (8).

$$l_z^1 = -\mathrm{i}\left[(x + R)\frac{\delta}{\delta y} - y\frac{\delta}{\delta x}\right] = l_z - \mathrm{i}R\frac{\delta}{\delta y} \quad (8)$$

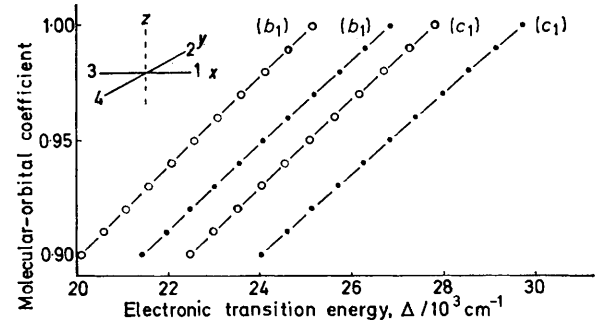

FIGURE 1 Plots for [Cu(pc)] of the calculated molecular-orbital parameters b_1 (left-hand pair of lines) and c_1 (right-hand pair of lines) against the electronic transition energies $\Delta_\parallel$ (xy) and $\Delta_\perp$ (xz, yz) respectively, for $\zeta = 828$ cm^{-1} and $a_1 = 0.854$ (●) and $\zeta = 720$ cm^{-1} and $a_1 = 0.885$ (○). $a_3/a_2 = 1.4$ and Cu^{2+}–N is 1.93 Å

Since there has been some confusion in the literature over the evaluation of integrals involving derivatives of s and p orbitals some analytical expressions for the derivatives of the Slater-type orbitals are given:

$$\frac{\delta}{\delta x}|ns\rangle = -\zeta \cdot 2^{-\frac{1}{2}}\left\{|np_x\rangle - \frac{2(n-1)}{[2n(2n-1)]^{\frac{1}{2}}}|(n-1)p_x\rangle\right\} \quad (9)$$

$$\frac{\delta}{\delta x}|np_x\rangle = \zeta \cdot 5^{-\frac{1}{2}}\Bigg(|nd_{x^2-y^2}\rangle - 3^{-\frac{1}{2}}|nd_{z^2}\rangle + \frac{2(n-2)}{[2n(2n-1)]^{\frac{1}{2}}}[3^{-\frac{1}{2}}|(n-1)d_{z^2} - |(n-1)d_{x^2-y^2}\rangle] + (5/3)^{\frac{1}{2}}\{|ns\rangle - \frac{2(n+1)}{[2n(2n-1)]^{\frac{1}{2}}}|(n-1)s\rangle\}\Bigg) \quad (10)$$

$$\frac{\delta}{\delta y}|np_x\rangle =$$

$$\zeta\,.\,5^{-\frac{1}{2}}\left\{|nd_{xy}\rangle - \frac{2(n-2)}{[2n(2n-1)]^{\frac{1}{2}}}\,|(n-1)d_{xy}\rangle\right\} \quad (11)$$

In Table 1 are given values of the integral $\langle ns|(\delta/\delta x)|np_x\rangle_{R=0}$ for some common ligands; these agree well with the values (positive) given by Misetich and Watson,[11] but not with the negative values of Smith.[12] They were calculated using the Clementi and Roetti,[13] Hartree–Fock–Roothaan wavefunctions, as were all the other radial properties, such as overlap integrals and $\langle r^n\rangle$, used in this paper.

TABLE 1

Values (10^4) of the integral $\langle ns|(\delta/\delta_x)|np_x\rangle_{R=0}$ for some common ligands

C^+	2 723	C	2 936	C^-	3 049
N^+	3 093	N	3 308	N^-	3 405
O^+	3 464	O	3 755	O^-	3 904
Si^+	3 402	Si	3 286	Si^-	3 132
P^+	3 688	P	3 602	P^-	3 496
S^+	3 942	S	3 908	S^-	3 815
		Se	3 214	Se^-	3 210
		F	4 168	F^-	4 305
		Cl	4 165	Cl^-	4 093
		Br	3 214	Br^-	3 175
		I	2 684	I^-	2 866

TABLE 3

E.s.r. and structural data used (A in 10^{-4} cm^{-1}, bond distances in Å)

Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$Cu	$A_{\perp}$Cu	$A_{\parallel}$N	$A_{\perp}$N	Cu–N (eq)	N–N *cis*	Cu–N (ax)	Cu–Pt
[Cu(pc)]	2.160	2.045	218.8	30.1	17.79	15.53	1.83, 1.93	2.58, 2.74	3.38, 3.34	
[Cu(tpp)]	2.190	2.045	201.3	33.0	16.14	14.56	1.98	2.80		
$[Cu(NH_3)_4][PtCl_4]$	2.217	2.051	211.0	28.0	15.50	10.50	2.00	2.83		3.32

The calculation[14] of the g and A values involved first diagonalising the spin–orbit-coupling energy matrix and then making the eigenvectors diagonal with respect to the magnetic and hyperfine interactions respectively, a procedure that was considered more accurate than trying to derive and use analytical expressions. The upper triangles of the Hermitian spin–orbit, hyperfine, and orbital-angular-momentum matrices are given in the Appendix. The spin–orbit coupling constant, ζ, was taken as 828 cm^{-1} for Cu^{2+} and 74 cm^{-1} for N,[15] ζ for Cu^+ (d^{10}) was estimated as 720 cm^{-1} by assuming $\zeta \propto Z_{\text{eff.}}\langle r^{-3}\rangle$, where $Z_{\text{eff.}} \propto \langle r^{-1}\rangle$. $P = g_e\beta_e g_N\beta_N\langle r^{-3}\rangle$ was taken as 356.67×10^{-4} cm^{-1} for $^{63}Cu^+$, 390.27×10^{-4} cm^{-1} for $^{63}Cu^{2+}$, and 3.985×10^{-4} cm^{-1} for ^{14}N from recent literature values of fundamental constants and nuclear moments.[16,17] Table 2 gives more relevant values of $\langle r^{-1}\rangle$ and $\langle r^{-3}\rangle$. The e.s.r.[4-6,18] and structural data[8-10] used in the calculation are the literature values as shown in Table 3.

An iterative procedure was used in which initial estimates of a_1, $\Delta_{\parallel}$, and $\Delta_{\perp}$ were obtained from the experimental g and A values (by using closed-form crystal-field expressions for the g and A values including orbital-reduction parameters). Then, for given values of b_1, c_1, and the hybridisation ratio, g and A values were calculated using the matrix procedures. The values of a_1, $\Delta_{\parallel}$, and $\Delta_{\perp}$ were then adjusted according to the deviations of the calculated g and A values from the observed ones and the matrix procedure repeated; this process usually converged in less than six cycles to give g values to within $\pm 0.000\,2$ and the A values to within $\pm 0.3 \times 10^{-4}$ cm^{-1}. The calculations were able to reproduce the experimental g values exactly and the A^{Cu} values to within 0.3×10^{-4} cm^{-1}. To this level of accuracy the covalence a_1 is accurate to ± 0.001 and the transition energies to ± 100 cm^{-1}. The values of the Fermi contact term[19] (K) are close to those expected from the empirical relation $K = \frac{2}{3}\chi/\langle r^{-3}\rangle = \frac{2}{3}\,[4.89a_1^2 + 1.51(1 - a_1^2)]/\langle r^{-3}\rangle$. The available nitrogen hyperfine-splitting data has not been used to derive the covalency parameters because of the sensitivity of the parameters to the assumptions made about the complex. Table 4 gives the variation in the covalency parameters a_1^2 and the s–p hybridisation as a function of the oxidation state for $[Cu(NH_3)_4][PtCl_4]$. The experimental hyperfine splittings are corrected for dipolar and orbital-angular-momentum effects.[2] An uncertainty arises from the mixing coefficient of the nitrogen 1s orbital in the ground-state wavefunction since this is difficult to estimate.[20,21] Previously, it has been approximated as $S(1s,3d)$ which is an order of magnitude less than $S(2s,3d)$, but can have an effect through the cross-term between the 1s and 2s functions.[22] Since the 2s function is negative at the nucleus and positive in the overlap region, the 1s,3d mixing term is taken as negative. Table 5 gives some overlap integrals and values of $A_s = \frac{8\pi}{3}\,g_e\beta_e g_N\beta_N|\psi(0)_i\psi(0)_j|$ for i, j = 1 or 2.

TABLE 2

Some $\langle r^{-1}\rangle$ and $\langle r^{-3}\rangle$ values

	Cu^+	Cu^{2+}	N
$\langle r^{-1}\rangle a_0^{-1}$	1.398 47	1.470 01	0.957 683
$\langle r^{-3}\rangle a_0^{-3}$	7.553 73	8.264 87	3.099 29

TABLE 4

Variation of the covalency parameters a_1^2 and the sp^n hybridisation

	a_1^2	n
Cu^+–N	0.787 90	4.00
Cu^{2+}–N	0.724 97	4.00
Cu^{2+}–N^-	0.620 75	5.02

TABLE 5

Some s,d overlap integrals and A_s values (10^{-4} cm^{-1})

	Cu^+	Cu^{2+}		A_s
S (1s, 3d)	0.009 00	0.004 59	(1s, 1s)	10 589.4
S (2s, 3d)	0.082 99	0.056 28	(1s, 2s)	2 333.86
			(2s, 2s)	514.371

Other effects[22] such as ligand-core polarisation have been ignored, but may not be negligible. The charge-transfer states were included by expanding the basic 8 × 8 antibonding wavefunction matrix to a 14 × 14 matrix by including the bonding functions $\psi(b_{2g})$ and $\psi(e_g)$ and proceeding in a similar manner to that described above.

These calculations differ in two main ways from those carried out previously. First, an exact matrix-diagonalisation procedure is used rather than approximate first-order expressions; secondly, many of the integrals are calculated exactly, whereas previously they were only roughly calculated, [*e.g.* $\langle s|(\delta/\delta x)|p_x\rangle$, *etc.*].

RESULTS AND DISCUSSION

$[Cu(NH_3)_4][PtCl_4]$.—This complex[8] consists of a square-planar array of ammonias co-ordinated to the copper(II) ion at a distance of 2.00 Å, and two distant axial platinum ions at 3.32 Å. In the calculation the effect of the platinum ions has been ignored, since σ bonding of the platinum to the copper(II) d_{z^2} orbital does not affect the e.s.r. parameters and as the $(3d,5d)$ π- and δ-overlap integrals are one and two orders of magnitude less, respectively, than the in-plane $(2p,\ 3d)$ σ- and π-overlap integrals with the nitrogen ligands, and will only affect the calculation to a small extent. Table 6 lists some of the relevant overlap integrals.[23] The ammonia was assumed to bond as a purely σ-bonding ligand with no π-bonding capability, *i.e.* $b_1 = c_1 = 1.0$, but because of the non-zero overlap integrals the coefficients b_2 and c_2 are not zero although small. Charge-transfer states were ignored and $a_3 = 2a_2$, *i.e.* approximate sp^4 hybridisation was assumed. Table 7 lists the covalency parameters a_1, the Fermi contact term K, and the electronic transition energies Δ_{xy} and $\Delta_{xz,yz}$ calculated with the listed approximations.

TABLE 6

Copper(II)-to-ligand (Pt and N) overlap integrals ($\times 10^5$)

	Pt⁺ (ref. 23)			N	
	σ	π	δ	σ	π
Cu^+	1 167	504	63	8 380	5 826
Cu^{2+}	681	250	27	6 781	3 933

TABLE 8

The Cu–N overlap integrals ($\times 10^5$) for [Cu(pc)] for Cu–N bond lengths of (*a*) 1.83 and (*b*) 1.93 Å

	(*a*)						(*b*)					
	N (eq)			N (ax)			N (eq)			N (ax)		
	s	σ	π	s	σ	π	s	σ	π	s	σ	π
Cu^+	10 419	9 526	7 810	794	1 435	434	9 137	8 870	6 579	897	1 526	479
Cu^{2+}	7 417	8 166	5 500	366	796	223	6 322	7 348	4 519	399	854	243

Using a Cu^{2+} wavefunction (ζ 828 cm^{-1}) and calculating the g and A values excluding all the ligand functions (equivalent to a crystal-field model) yields electronic energy levels (23 200—24 500 cm^{-1}) much higher than the observed[1,24] values (*ca.* 18 000—20 000 cm^{-1}). Inclusion of the ligand function lowers the electronic energies significantly, but still leaves them 2 500 cm^{-1} above the observed values. Substantially increasing the nitrogen hybridisation ratio causes only a trivial lowering of the calculated electronic energies. A reduction of the spin-orbit coupling constant ζ to 800 cm^{-1}, to allow for the lowering of the charge on the Cu^{2+} ion due to covalency, resulted in lower energies, but only by 500 cm^{-1}. [Previous workers have assumed that the variation of ζ with charge is negligible, based on the experimental spin-orbit coupling constants for Cu^{2+} (d^9), Cu^+ (d^9s^1), and Cu (d^9s^2),[2,12,25] whereas we have based the charge variation on our estimated value of ζ for Cu^+ (d^{10}).] The inclusion of in-plane and out-of-plane π bonding of *ca.* 6% would yield transition energies close to the experimental values, but this level of π bonding seems excessive for NH_3 especially when we have ignored the effect of charge-transfer states which would yield higher values again. In order to reproduce the experimental electronic energies it is necessary to assume that the radial Cu^{2+} wavefunction is expanded[26] by the crystal-field potential and to use the free-ion Cu^+ wavefunction to represent the radially expanded Cu^{2+} wavefunctions of the complex without implying that the charge on the copper is +1. This procedure gives transition energies in good agreement with the observed data [Table 7(*ii*)].

TABLE 7

a_1, K, $\Delta_\parallel$ and $\Delta_\perp$ parameters for $[Cu(NH_3)_4][PtCl_4]$

Assumptions	a_1	K	$\Delta_\parallel$ (10³ cm⁻¹)	$\Delta_\perp$ (10³ cm⁻¹)
(*i*) Cu^{2+} wavefunction				
(*a*) Complete neglect of ligands	0.881	0.335	23.2	24.4
(*b*) Inclusion of ligands	0.886	0.351	20.2	20.9
(*c*) $a_3 = 3a_2(sp^9)$	0.886	0.352	20.0	20.7
(*ii*) Cu^+ wavefunction				
(*a*) Complete neglect of ligands	0.910	0.356	21.6	22.7
(*b*) Inclusion of ligands	0.921	0.379	17.9	18.6
(*c*) $a_3 = 3a_2(sp^9)$	0.922	0.380	17.8	18.5

Phthalocyaninatocopper(II), [Cu(pc)].—The CuN_4 chromophore in [Cu(pc)] is strictly square-coplanar and two independent structure determinations report two Cu–N bond lengths, 1.83 (ref. 27) and 1.93 Å (ref. 9) respectively, consistent with the axial e.s.r. spectrum (Table 3).

While the presence of two nitrogen atoms in the axial direction (3.35[9] and 3.38 Å[27]) suggests an elongated octahedral stereochemistry, the magnitudes of the overlap integrals for nitrogen ligands at this distance are an order of magnitude smaller than the equatorial overlap integrals (Table 8) and the complex may reasonably be considered as four-square-coplanar. In view of the problem associated with the calculations for $[Cu(NH_3)_4]$-$[PtCl_4]$, the calculations for [Cu(pc)] were carried out with both Cu^+ and Cu^{2+} wavefunctions, sp^2 hybridisation was assumed ($a_3 = 1.4a_2$) together with in-plane and out-of-plane π bonding, and low-energy charge-transfer states. The assumption of sp^2 hybridisation may only be approximately true (*cf.* pyrrole[28] has approximate $sp^{1.7}$) but any increase in s-orbital participation in the hybrid only increases the electronic energies slightly (500 cm^{-1} for $sp^{1.5}$ hybridisation).

For this complex the absence of a satisfactory assignment of the d—d spectra and charge-transfer spectra[4,5] makes it impossible to define the π-bonding coefficients

b_1 and c_1. Consequently, these have been systematically varied between 1.00 and 0.90 (implying $<19\%$ π bonding) and the electronic energies required to reproduce the experimental g and A values calculated. For comparative purposes the calculation was performed using the two reported values for the Cu–N bond length since the value of 1.83 Å was used earlier, but as the only effect was to reduce the transition energies by 1 000 cm^{-1} and to increase the covalency parameter a_1 by *ca.* 0.004 the results are not reported in detail. Plots of b_1 and c_1 against the transition energies (for Cu–N 1.93 Å) are given in Figure 1 (Cu$^+$ and Cu^{2+} wavefunctions plus complete neglect of ligand wavefunctions), Figure 2 (Cu^{2+} wavefunctions plus inclusion of ligand wavefunctions), and Figure 3 (Cu$^+$ wavefunctions plus inclusion of ligand wavefunctions).

From Figures 1—3 it is of interest that within any given set of assumptions the covalency parameter a_1 is remarkably constant regardless of the different assumptions made from an ionic model (0.85) to the value of 0.90 in the m.o. model when the ligand wavefunctions are included. The difficulty of explaining the very large *d–d* transition energies invoked in previous calculations on the magnetic data [3,29] on [Cu(pc)] is also avoided by the inclusion of the relevant ligand wavefunctions, which reduce the values of $\Delta_{\parallel}$ and $\Delta_{\perp}$ to $<20\,000$ cm^{-1} for a square-coplanar CuN$_4$ chromophore.[1,29,30] The range of values of b_1 and c_1 implies the presence of some π bonding with the out-of-plane always greater than the in-plane π bonding, but *both* are significantly less than the in-plane σ bonding as chemical intuition would predict. This avoids the earlier suggestion [3,4] that the out-of-plane π bonding was actually greater than the in-plane σ bonding (Table 9). Unfortunately, without precise values for the energies of the electronic transition, it is not possible to predict the most probable values of b_1 and c_1 between 0.9 and 1.0. The inclusion of charge-transfer states at 45 000 cm^{-1} without any π bonding raises the electronic energies by <500 cm^{-1}, but may raise them by up to 2 000 cm^{-1} in the presence of π bonding. Irrespective of the assumption made using this model, and for reasonable values of c_1 and b_1, there is always an appreciable separation of $\Delta_{\perp}$ and $\Delta_{\parallel}$ with $\Delta_{\parallel}$ having higher energy, which in itself suggests the presence of strong out-of-plane π bonding in [Cu(pc)].

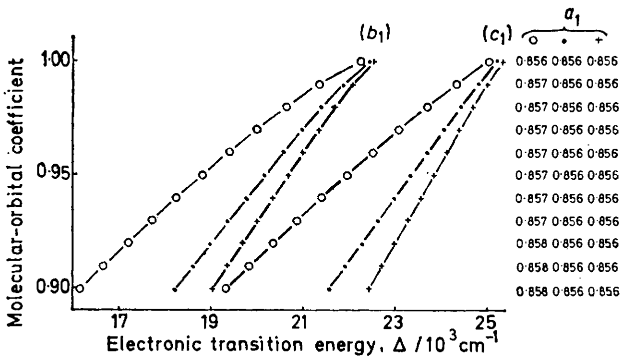

FIGURE 2 Plots for [Cu(pc)] of the calculated m.o. parameters b_1 and c_1 against the electronic transition energies $\Delta_{\parallel}$ (*xy*) and $\Delta_{\perp}$ (*xz*, *yz*) respectively, using a Cu^{2+} wavefunction ($\zeta = 828$ cm^{-1}), and including ligand wavefunctions: (○) excluding charge-transfer states; (●) and (+) including charge-transfer states at 60 000 and 45 000 cm^{-1}. $a_3/a_2 = 1.4$. Other details as in Figure 1

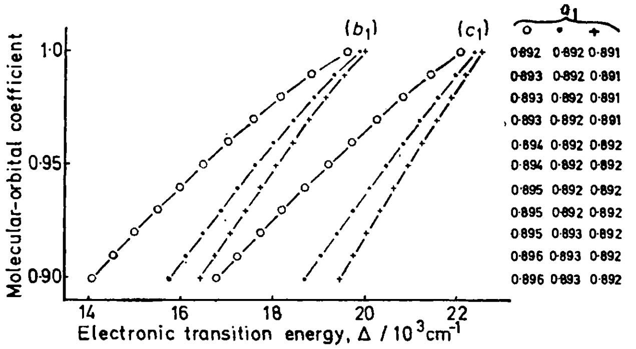

FIGURE 3 Plots for [Cu(pc)] of the calculated m.o. parameters b_1 and c_1 against the electronic transition energies $\Delta_{\parallel}$ (*xy*) and $\Delta_{\perp}$ (*xz*, *yz*) respectively, using a Cu$^+$ wavefunction ($\zeta = 720$ cm^{-1}) and including ligand wavefunctions. $a_3/a_4 = 1.4$. Details as in Figure 2

TABLE 9

Calculated molecular-orbital parameters for [Cu(pc)] using comparable assumptions and the indicated data sources

	Present data	Ref. 5
a_1^2	0.740	0.741 *
$b_1^2 = 1.0$	$\Delta_1 = 24\,200$ cm^{-1}	$\Delta_1 = 30\,000$ cm^{-1}
$\Delta_1 = 17\,000$ cm^{-1}	$c_1^2 = 0.88$	$c_1^2 = 0.60$

* In ref. 5 the value of a_1^2 was incorrectly calculated from the nitrogen hyperfine splitting without allowing for the field dependence of the splitting in Gauss.

Tetraphenylporphinatocopper(II), [Cu(tpp)].—The CuN$_4$ chromophore in this complex [10] is not strictly square-coplanar but has a slight tetrahedral distortion (towards D_{2d} symmetry) but since this distortion is small (1.2°) it is ignored together with the weak axial interaction present. The relevant overlap integrals are shown in Table 10. The calculations for [Cu(tpp)] were carried out in the same way as for [Cu(pc)] and the data recorded as plots of the m.o. coefficients b_1 and c_1 against transition energies in Figures 4 (Cu$^+$ and Cu^{2+} wave-

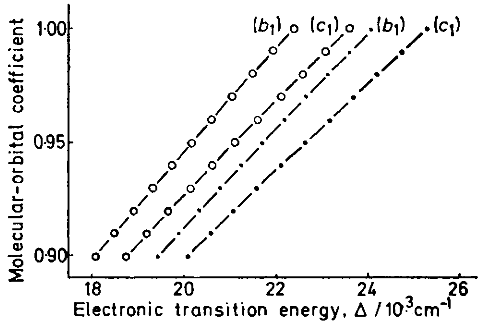

FIGURE 4 Plots for [Cu(tpp)] of the calculated m.o. parameters b_1 and c_1 against the electronic transition energies $\Delta_{\parallel}$ (*xy*) and $\Delta_{\perp}$ (*xz*, *yz*) respectively, for $\zeta = 828$ cm^{-1} and $a_1 = 0.859$ (●) and 720 cm^{-1} and $a_1 = 0.866$ (○). $a_3/a_2 = 1.4$, Cu^{2+}–N 1.98 Å

function plus neglect of ligand functions), 5 (Cu^{2+} wavefunction plus ligand wavefunction), and 6 (Cu^+ wavefunction plus ligand wavefunctions) for different effects of charge-transfer bands. The data used were those given in Table 3 and the results are similar to those obtained for [Cu(pc)] except that the predicted values for $\Delta_{\parallel}$ and $\Delta_{\perp}$ are rather closer in energy than those obtained for [Cu(pc)]. This arises due to the slight difference in the g and A values listed in Table 3, such that for a common value for b_1 and c_1 there is actually a cross-over point of the $\Delta_{\parallel}$ and $\Delta_{\perp}$ values for b_1, $c_1 = 0.97$. In Table 11 the parameters derived from the literature data are compared with those derived from the present model using similar assumptions. As with [Cu(pc)] the present model predicts lower energies than those predicted in the earlier literature,[6,30] but comparable to those predicted[30] for the CuN_4 chromophore from a plot of $g_{\parallel}$ against the angular distortion from a square-coplanar to a tetrahedral stereochemistry. Energies of 16 500 and 19 500 cm^{-1} were obtained, which compare favourably with the ranges available in Figures 3—6, but when these energies are used to calculate the m.o. coefficients using a model which excludes ligand wavefunctions the results display more out-of-plane π bonding than σ bonding (Table 11). In general the electronic transition energies predicted for [Cu(tpp)] are slightly lower in energy than for [Cu(pc)] which may be a reflection of the longer Cu–N bond length present in [Cu(tpp)] (Table 3).

TABLE 10

Overlap integrals ($\times 10^5$) for [Cu(tpp)]

	s	σ	π
Cu^+–N	8 533	8 521	6 033
Cu^{2+}–N	5 820	6 942	4 092

TABLE 11

Calculated molecular-orbital parameters for [Cu(tpp)] using comparable assumptions and the indicated data source

	Present work	Ref. 6	Ref. 31
a_1^2	0.706	0.789[a]	0.783[b]
$b_1^2 = 1.0$	$\Delta_{\parallel} = 20\ 500\ cm^{-1}$	$\Delta_{\parallel} = 26\ 300\ cm^{-1}$	$\Delta_{\parallel} = 19\ 500\ cm^{-1}$
$c_1^2 = 0.846$	$\Delta_{\perp} = 16\ 200\ cm^{-1}$	$\Delta_{\perp} = 24\ 500\ cm^{-1}$	$\Delta_{\perp} = 16\ 500\ cm^{-1}$

[a] In ref. 5 the value of a_1^2 was incorrectly calculated from the nitrogen hyperfine splitting, using a dipolar correction of the wrong sign. [b] $b_1 = 0.967$ and $c_1 = 0.835$.

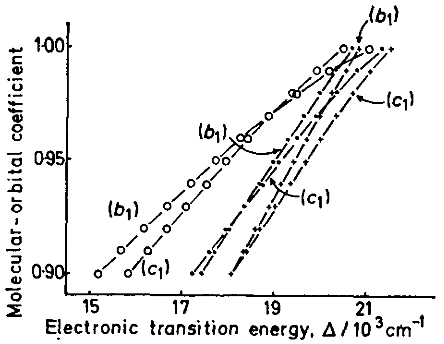

FIGURE 5 Plots for [Cu(tpp)] of the calculated m.o. parameters b_1 and c_1 against the electronic transition energies $\Delta_{\parallel}$ (xy) and $\Delta_{\perp}$ (xz, yz) respectively using a Cu^{2+} wavefunction, $\zeta = 828$ cm^{-1}, $a_3/a_2 = 1.4$, Cu–N 1.98 Å, and including ligand wavefunctions: (○) excluding charge-transfer states (a_1 0.841); (●) and (+) including charge-transfer states at 60 000 and 45 000 cm^{-1} respectively (both a_1 0.842)

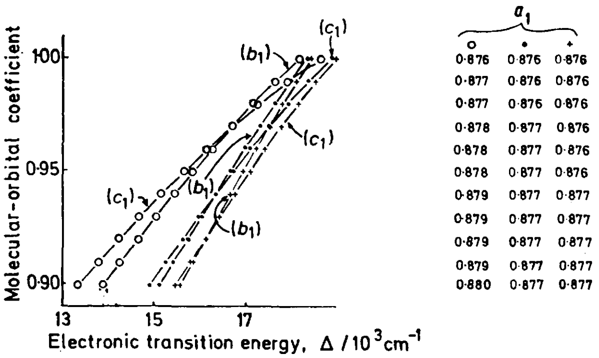

FIGURE 6 Plots for [Cu(tpp)] of the calculated m.o. parameters b_1 and c_1 against the electronic transition energies $\Delta_{\parallel}$ (xy) and $\Delta_{\perp}$ (xz, yz) respectively, using a Cu^+ wavefunction and including ligand wavefunctions. Details as in Figure 5

For [Cu(tpp)] the covalency parameter a_1^2 is 10% lower than the value calculated for [Cu(pc)] and $[Cu(NH_3)_4][PtCl_4]$ and which is not accounted for by the different Cu–N bond lengths present. Since [Cu(tpp)] lacks an inversion centre {compared to [Cu(pc)] and $[Cu(NH_3)_4][PtCl_4]$}, $4p$ mixing into the $3d$ orbital is possible, which would decrease $|A_{\parallel}|$ and increase $|A_{\perp}|$ for a $d_{x^2-y^2}$ ground state, as well as increasing the value of a_1^2 relative to that deduced neglecting the p-orbital mixing. The new covalency parameter $a_1'^2$ is related to the old covalency parameter by the approximate first-order equation $\alpha_1'^2 \simeq 5/(12\alpha^2 - 7)a_1^2$, where α^2 is the percentage of d–p orbital mixing $|\alpha d_{x^2-y^2} - (1 - \alpha^2)^{\frac{1}{2}}p_z\rangle|$. Thus a 10% increase in a_1^2 only requires *ca.* 4% p-orbital mixing to account for the changes and will concomitantly result in a 10% increase in the electronic transitions. An attempt to confirm these conclusions by carrying out the above type of calculation in D_{2d} symmetry is in progress.

APPENDIX

State number	1	2	3	4
State (anti-bonding)	$^2B_{1g}+\frac{1}{2}$	$^2B_{1g}-\frac{1}{2}$	$^2B_{2g}+\frac{1}{2}$	$^2B_{2g}-\frac{1}{2}$
State number	5	6	7	8
State(anti-bonding)	$^2E_g+\frac{1}{2}(xz)$	$^2E_g-\frac{1}{2}(xz)$	$^2E_g+\frac{1}{2}(yz)$	$^2E_g-\frac{1}{2}(yz)$

(*a*) Non-zero elements of the upper triangle of the spin-orbit coupling matrix. Multiply each element by $\zeta_M \cdot \nu_L = \zeta_L/\zeta_M$.

$(1,\ 3) = -i(a_1b_1 - 2a_3b_2N_1N_2\nu_L)$; $(1,\ 6) = \frac{1}{2}(a_1c_1 - 2a_3c_2N_1N_3\nu_L)$; $(1,\ 8) = i(1,\ 6)$; $(2,\ 4) = -(1,\ 3)$; $(2,\ 5) = -(1,\ 6)$; $(2,\ 7) = (1,\ 8)$; $(3,\ 6) = -\frac{i}{2}(b_1c_1 + 2b_2c_2N_2N_3\nu_L)$;

$(3, 8) = \mathrm{i}(3, 6)$; $(4, 5) = (3, 6)$; $(4, 7) = -(3, 8)$; $(5, 7) = -\frac{\mathrm{i}}{2}c_1^2$; $(6, 8) = -(5, 7)$

(*b*) Non-zero elements of the upper triangle of the orbital-angular-momentum matrices

(*i*) x

$(1, 7) = i(a_1c_1 - 2\cdot3^{\frac{1}{2}}a_2c_1N_5\langle s|d\rangle - 2\cdot3^{\frac{1}{2}}a_3c_1N_1\langle p_\sigma]d_\sigma\rangle - 2a_1c_2N_3\langle p_\pi|d_\pi\rangle + 2a_2c_2N_5N_3\{R[\langle s^2|(\delta/\delta z)|pz^2\rangle - 2\langle s^1|(\delta/\delta z)|p_z^2\rangle + \langle s^2|(\delta/\delta z)|p_z^4\rangle] - \langle s|p\rangle_{trans} + 2^{\frac{1}{2}}\langle s|p\rangle_{cis}\})$; $(2, 8) = (1, 7)$; $(3, 5) = -\mathrm{i}[b_1c_1 - 2b_1c_2N_3\langle p_\pi|d_\pi\rangle - 4b_2c_1N_2\langle p_\pi|d_\pi\rangle + (b_2c_2N_3/2N_2)]$; $(4, 6) = (3, 5)$

(*ii*) y

$(1, 5) = (1, 7)_x$; $(2, 6) = (2, 8)_x$; $(3, 7) = -(3, 5)_x$; $(4, 8) = -(4, 6)_x$

(*iii*) z

$(1, 3) = -2\mathrm{i}[a_1b_1 - 2\cdot3^{\frac{1}{2}}a_2b_1N_5\langle s|d\rangle - 2\cdot3^{\frac{1}{2}}a_3b_1N_1\text{-}\langle p_\sigma|d_\sigma\rangle - 4a_1b_2N_2\langle p_\pi|s_\pi\rangle - (a_3b_2N_2/2N_1) + 2a_2b_2N_5N_2\text{-}\{R[\langle s^1|(\delta/\delta y)|p_y^1\rangle - 2\langle S^1|(\delta/\delta x)|p_x^2\rangle + \langle S^1|(\delta/\delta y)|p_y^3\rangle]; -\langle s|p\rangle_{trans} + 2^{\frac{1}{2}}\langle s|p\rangle_{cis}\}]$; $(2, 4) = (1, 3)$; $(5, 7) = \text{-}\mathrm{i}\,[c_1^2 - 4c_1c_2N_3\langle p_\pi|d_\pi\rangle - 4Rc_2N_3^2\langle p_y^2|(\delta/\delta y)|p_z^1\rangle]$; $(6, 8) = (5, 7)$

(*c*) Non-zero elements of the upper triangle of the hyperfine-interaction matrices. Multiply each element by $P_{\mathrm{M}}\cdot\pi_{\mathrm{L}} = P_{\mathrm{L}}/P_{\mathrm{M}}$

(*i*) x

$(1, 2) = \left(\frac{a_1^2}{7} + \frac{2}{5}a_3^2N_1^2\Pi_{\mathrm{L}}\right)$; $(1, 5) = 3\left(\frac{a_1c_1}{14} - \frac{a_3c_2}{5}N_1N_3\Pi_{\mathrm{L}}\right)$; $(1, 7) = \mathrm{i}(a_1c_1 - 2a_3c_2N_1N_3\Pi_{\mathrm{L}})$; $(2, 6) = -(1, 5)$; $(2, 8) = (1, 7)$; $(3, 4) = \left(\frac{b_1^2}{7} + \frac{2}{5}b_2^2N_2^2\Pi_{\mathrm{L}}\right)$; $(3, 5) = -\mathrm{i}(b_1c_1 + 2b_2c_2N_2N_3\Pi_{\mathrm{L}})$; $(3, 7) = 3\left(\frac{b_1c_1}{14} + \frac{b_2c_2}{5}N_2N_3\Pi_{\mathrm{L}}\right)$; $(4, 6) = (3, 5)$; $(4, 8) = -(3, 7)$; $(5, 6) = \left(\frac{c_1^2}{7} - \frac{2}{5}c_2^2N_3\text{-}\Pi_{\mathrm{L}}\right)$; $(5, 8) = -\frac{3\mathrm{i}c_1^2}{14}$; $(6, 7) = -(5, 8)$; $(7, 8) = -2\left(\frac{c_1^2}{7} + \frac{c_2^2}{5}N_3^2\Pi_{\mathrm{L}}\right)$

(*ii*) y

$(1, 2) = -\mathrm{i}(1, 2)_x$; $(1, 5) = (1, 7)_x$; $(1, 7) = -(1, 5)_x$; $(2, 6) = (2, 8)_x$; $(2, 8) = (2, 6)_x$; $(3, 4) = -\mathrm{i}(3, 4)_x$; $(3, 5) = (3, 7)_x$; $(3, 7) = -(3, 5)_x$; $(4, 6) = (4, 8)_x$; $(4, 8) = -(4, 6)_x$; $(5, 6) = 2\mathrm{i}\left(\frac{c_1^2}{7} + \frac{c_2^2}{5}N_3^2\Pi_{\mathrm{L}}\right)$; $(5, 8) = \mathrm{i}(5, 8)_x$; $(7, 8) = -\mathrm{i}\left(\frac{c_1^2}{7} - \frac{2}{5}c_2^2N_5^2\Pi_{\mathrm{L}}\right)$

(*iii*) z

$(1, 1) = -2(1, 2)_x$; $(1, 3) = -2\mathrm{i}(a_1b_1 - 2a_3b_2N_1N_2\Pi_{\mathrm{L}})$; $(1, 6) = (1, 5)_x$; $(1, 8) = \mathrm{i}(1, 5)_x$; $(2, 2) = 2(1, 2)_x$; $(2, 4) = (1, 3)$; $(2, 5) = (1, 5)_x$; $(2, 7) = -\mathrm{i}(1, 5)_x$; $(3, 3) = -2\text{-}(3, 4)_x$; $(3, 6) = -\mathrm{i}(3, 7)_x$; $(3, 8) = (3, 7)_x$; $(4, 4) = 2(3, 4)_x$; $(4, 5) = \mathrm{i}(3, 7)_x$; $(4, 7) = (3, 7)_x$; $(5, 5) = \left(\frac{c_1^2}{7} + \frac{4}{5}c_2^2N_3^2\Pi_{\mathrm{L}}\right)$; $(5, 7) = -\mathrm{i}c_1^2$; $(6, 6) = -(5, 5)$; $(6, 8) = (5, 7)$; $(7, 7) = (5, 5)$; $(8, 8) = (6, 6)$

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