$CpMo(CO)_3H$ (**P-6**) and the β-dicarbonyl sodium salts). The former followed weak acid–weak base behavior and the latter behaved essentially as an acid-exchange resin.

"Effective K_{ea}" Calculations. The numbers for eq 5 were supplied in the following manner. The concentrations of soluble species, $[B^-]$ and [BH], were calculated directly from IR absorbances using Beer's law and the above-determined extinction coefficients. The effective concentration of Ⓟ-A^-, {Ⓟ-A^-}, was assumed to be equal to that of BH, in accordance with eq 4. {Ⓟ-AH} was then determined from the difference between $\{Ⓟ\text{-AH}\}_{\text{initial}}$ and {Ⓟ-A^-}. For example, K_{eq} for experiment 1 of Table III would be calculated as follows:

$$K_{eq} = \frac{[BH]\{P\text{-}A^-\}}{[B^-]\{P\text{-}AH\}} = \frac{(0.011)(0.011)}{(0.008)(0.058 - 0.011)} = 0.32$$

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Anomalous Spin Hamiltonian Parameters of Pseudotetrahedral Copper(II) Complexes. ESR Spectra of Copper(II)-Doped Dichlorobis(triphenylphosphine oxide)zinc(II)

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Abstract: The X-band (9 GHz) ESR spectra of the copper(II)-doped pseudotetrahedral complex dichlorobis(triphenylphosphine oxide)zinc(II) have been recorded on single crystal at 4.2 K. They are interpreted by using the spin Hamiltonian parameters $g_1 = 2.46$, $g_2 = 2.08$, $g_3 = 2.08$, $A_1 = 40 \times 10^{-4}$ cm^{-1}, $A_2 = 25 \times 10^{-4}$ cm^{-1}, $A_3 = 20 \times 10^{-4}$ cm^{-1}. The superhyperfine interaction of the unpaired electron with two equivalent chlorine atoms is also observed. The Q-band (35 GHz) ESR spectra have been recorded at 77 K, yielding $g_1 = 2.43$, $g_2 = 2.09$, and $g_3 = 2.08$. The difference in the g_1 values of the pure and the copper-doped zinc complex is related to structural differences between the copper and zinc lattices. A model including the spin–orbit coupling interaction of the unpaired electron with the ligands is proposed which rationalizes the spin Hamiltonian parameters of $CuCl_4$ and CuX_2Cl_2 pseudotetrahedral chromophores. The anomalously low $A_{\parallel}$ values seen in the ESR spectra of some sulfur-containing copper proteins are related to the covalency of the copper(II)–sulfur bonds.

Pseudotetrahedral copper(II) complexes are far less numerous than the square-planar ones. However they are attracting a large interest since tetrahedral copper(II) chromophores are known to be present in some metalloenzymes and metalloproteins.[1]

The ESR spectra are a powerful tool for the diagnosis of the coordination geometry of copper(II),[2] and as such they have been widely used also for tetrahedral complexes.[3] However their interpretation[4] still is controversial, and not all their features are fully understood.

The main differences seen in the ESR spectra of tetrahedral complexes as compared to the square-planar ones are as follows: (i) both $g_{\parallel}$ and $g_{\perp}$ are larger in tetrahedral complexes; (ii) $A_{\parallel}$ tends to be smaller in the tetrahedral chromophores, while less safe conclusions can be drawn for $A_{\perp}$. An elegant demonstration of this trend has been provided by Bertini et al.,[5] who reported the ESR spectra of copper(II)-doped Zinc(II) and nickel(II) salicylaldiminates, following the variation of the spin Hamiltonian parameters on passing from the tetrahedral to the square-planar chromophores present in the two lattices.

Recently also Marks and Ibers[6] shortly reviewed the main factors influencing the g and A values in four-coordinate copper(II) complexes.[7-10]

The above trends in the values of g are qualitatively well understood, in the sense that the g values must increase on passing from the square-planar to the tetrahedral structures since the energy separation of the electronic levels decreases. The same effect is expected to cause also a decrease of the $A_{\parallel}$ value, so that nothing mysterious seems to be operative, at least at the qualitative level. As a matter of fact there is a large class of tetrahedral copper(II) complexes whose $A_{\parallel}$ values can be reasonably well reproduced with usual formulas. Matters are different in the case of Cs_2CuCl_4, for which $A_{\parallel}$ as small as 25×10^{-4} cm^{-1} has been reported.[11-13] Sharnoff[12] studied thoroughly the system and suggested that the observed g and A values beared the contribution due to the admixture of the metal 4p orbitals in the ground level,[14] allowed by lack of an inversion center on the molecule. In order to reproduce the experimental values, however, he had to include a contribution as high as 13% of the 4p orbitals in the ground level.

Against this interpretation stands the fact that the mixing coefficient seems to be large and that no such large contribution is required in the interpretation of the ESR parameters of other tetrahedral[15] or trigonal-bipyramidal[16] copper(II) complexes, which also lack a center of symmetry.

With the aim to obtain new experimental data on complexes as similar as possible to $CuCl_4^{2-}$, we have now recorded the ESR spectra of copper(II)-doped $Zn(Ph_3PO)_2Cl_2$ (Ph_3PO = triphenylphosphine oxide). The analysis of these new data allowed us to suggest an alternative mechanism for the decrease of the $A_{\parallel}$ values observed in these complexes, which may be relevant to the interpretation of the ESR spectra of metalloenzymes and metalloproteins.

Experimental Section

$Zn(Ph_3PO)_2Cl_2$ and $Cu(Ph_3PO)_2Cl_2$ were prepared as previously reported.[17] Single crystals of both the pure copper and the copper-doped

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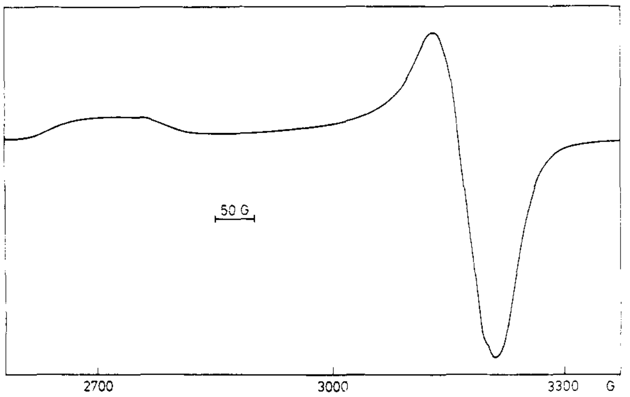

Figure 1. X-Band polycrystalline powder ESR spectrum of copper(II)-doped $Zn(Ph_3PO)_2Cl_2$ recorded at 4.2 K.

zinc complexes were obtained by slow evaporation of dichloromethane–*n*-butylic ether solutions and were characterized by using Weissenberg techniques. X-Band (9 GHz) and Q-band (35 GHz) ESR spectra were recorded with a Varian E-9 spectrometer. Low-temperature spectra were recorded with Oxford Instrument ESR 9 and ESR 35 continuous-flow cryostats.

Results

Both the copper and the zinc lattices are orthorhombic, of space group *Fdd*2, with the metal ion sitting on a C_2 axis, parallel to the *c* crystal axis.[18-20] The polycrystalline powder ESR spectrum of the copper-doped zinc complex is shown in Figure 1. It was recorded at 4.2 K, since no signal could be detected from room temperature to liquid-nitrogen temperature.

This result is not unusual for tetrahedral d^9 complexes, for which the proximity of excited levels to the ground level determines fast spin–lattice relaxation time.[21-22] The spectra of Figure 1 are rather disappointing in the sense that they do not show any resolved hyperfine splitting. The situation is different for the single-crystal spectra. Some indicative spectra recorded with the static magnetic field in the (001) plane are shown in Figure 2. Up to 17 transitions could be resolved for each of the two magnetically nonequivalent sites. They can be attributed to the combined effect of the hyperfine interaction of the unpaired electron with the copper nucleus (^{63}Cu and ^{65}Cu, both with $I = {}^3/_2$ and similar magnetogyric ratios) and with two equivalent chlorine atoms (^{35}Cl and ^{37}Cl, both with $I = {}^3/_2$ and similar magnetogyric ratios). The angular dependence of the $\mathbf{g}^2$ tensor of the two molecules in the (001) plane is shown in Figure 3. The principal *g* values in this rotation are found to be $g_1 = 2.46$, $g_2 = 2.08$, g_1 making an angle of ±16° with the *a* axis. The metal hyperfine splitting has within error the same axes as the **g** tensor, with $A_1 = 40 \times 10^{-4}\ cm^{-1}$, $A_2 = 25 \times 10^{-4}\ cm^{-1}$. The chlorine hyperfine splitting showed a minimum value when the static magnetic field makes an angle of ~30° with the *a* axis. In this orientation an upper limit of $A_{Cl} = 7 \times 10^{-4}\ cm^{-1}$ can be evaluated. The maximum splitting in this rotation corresponds to $A_{Cl} = 17 \times 10^{-4}\ cm^{-1}$, and it is found when the static magnetic field makes an angle of ~30° with the *b* axis.

The spectrum recorded with the static magnetic field parallel to *c* yielded $g_3 = 2.08$ and upper limits for $A_3 = 20 \times 10^{-4}\ cm^{-1}$ and $A_{Cl} = 8 \times 10^{-4}\ cm^{-1}$.

The X-band spectra of the pure copper compound were reported previously.[23] They yielded $g_1 = 2.38$, $g_2 = 2.09$, and $g_3 = 2.07$.

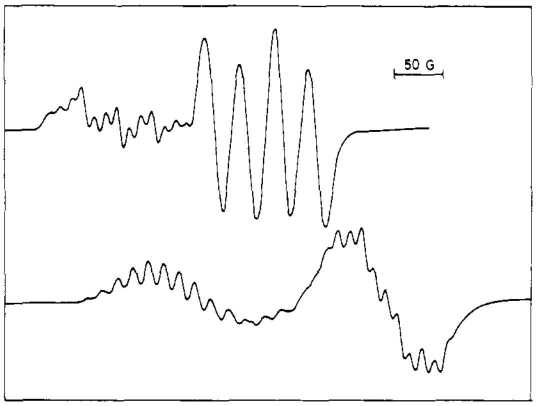

Figure 2. Single-crystal spectra of copper(II)-doped $Zn(Ph_3PO)_2Cl_2$ recorded at 4.2 K with the static magnetic field at 20° (upper) and 70° (lower) from the *b* crystal axis in the (001) plane.

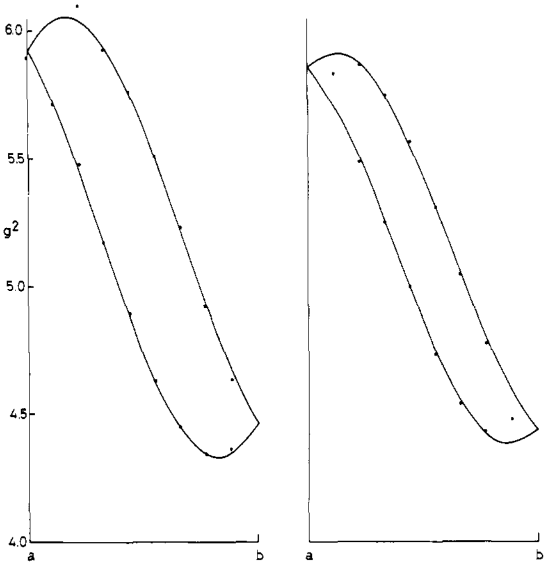

Figure 3. Angular dependence of the $\mathbf{g}^2$ tensor in the (001) plane for copper(II)-doped $Zn(Ph_3PO)_2Cl_2$ (left) and $Cu(Ph_3PO)_2Cl_2$ (right). The curve corresponds to the least-squares fit of the experimental points.

The spectra showed evidence of exchange narrowing effects, so that only one signal was recorded for every crystal orientation.

At Q-band frequency in general two bands are resolved in the (001) plane. The bandwidths are of the order of 200 G. The angular dependence of the g^2 values in this plane is shown in Figure 3. The curve through the experimental points was calculated to give the least-squares error to the points which are neatly separated.[24] In some orientations the difference in resonance fields is small and only one signal is resolved, due to the exchange effects. In this case the bands are sharper. The principal *g* values obtained in this analysis are $g_1 = 2.43$, $g_2 = 2.09$, and $g_3 = 2.08$. g_3 is found parallel to *c*, and g_1 is making an angle of ±11° with the *a* axis. The collapse of the signals of the two magnetically nonequivalent sites in some crystal orientations allows us to estimate that the intermolecular exchange coupling constant is of the order of 0.03 cm^{-1}.

Discussion

The resolved chlorine hyperfine splitting in the present complex is similar to that found in $Cu(phen)_2Cl_2$,[15] suggesting that the unpaired electron delocalization on the two complexes is also similar. If the assumption is made that the largest metal–chlorine interaction is parallel to the bond direction, the observed large splitting when the static magnetic field makes an angle of ~30° with the *b* axis in the (001) plane can be used to assign the **g** tensor to one of the two magnetically nonequivalent molecules present

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in the orthorhombic cell. As a matter of fact at this angular setting the Cu–Cl direction of one molecule is making an angle of 35° with the static magnetic field, while the other is making an angle of 66°.

The copper(II) ion is in slightly different environments in its own and in the zinc lattice. The atomic coordinates of the latter are not available, but they must be close to those of $Co(Ph_3PO)_2Cl_2$.[19,25] The most sensitive parameter in the ESR spectra is the $g_\parallel$ value, which is 2.43 for the pure copper(II) complex and 2.46 for the copper(II)-doped zinc(II) complex, suggesting that the zinc complex is closer to a tetrahedral geometry. A similar effect had been previously noted also for the pure and zinc-doped Cs_2CuCl_4.[12,13] The angular dependence of the g^2 values in the (001) plane does not reveal any large difference in the position of the extremes in both the pure and the zinc-doped complex.

The g values of the pure copper(II) complex can be reproduced by angular overlap calculations[19,26,27] by using the parameters $e_\sigma^{O} = 7600$ cm^{-1}, $e_\pi^{O} = 1100$ cm^{-1}, $e_\sigma^{Cl} = 5500$ cm^{-1}, $e_\pi^{Cl} = 1650$ cm^{-1}, $\zeta = 830$ cm^{-1}, $k_x = 0.88$, $k_y = 0.67$, and $k_z = 0.63$, where k_i is Stevens' orbital reduction factor.[28] The calculated g values are $g_1 = 2.43$, $g_2 = 2.09$, and $g_3 = 2.08$, and the calculated electronic transitions are 5900, 6900, 9900, 10 700 cm^{-1} in good agreement with the experimental values.[23] It must be stressed here that the above procedure requires the diagonalization of the angular overlap–spin–orbit coupling matrix, so that any inconvenience which might occur in a perturbative approach when the spin–orbit coupling constant becomes large compared to the energy separations of the d orbitals is eliminated.

If the same values of the parameters are used, but with the geometrical coordinates seen in the structure of $Co(Ph_3PO)_2Cl_2$, which is less distorted from the tetrahedral symmetry,[19,25] the pattern of levels and of g values is completely reversed ($g_1 = 2.08$, $g_2 = 2.36$, $g_3 = 2.16$) showing that, even in the zinc lattice, the tetrahedron around copper is severely flattened. As a matter of fact the observed g values of the zinc-doped complex can be reproduced by using the e_λ parameters which fit the data of the pure complex and decrease by ~2° the O′–Cu–Cl angle, whose bisector defines the z axis.

Attempts to fit also the copper hyperfine seen in the ZnO_2Cl_2 chromophore were unsuccessful, in every case a larger A_z value being calculated.[29] The only way to obtain the correct values was the way that used very small values for K, the isotropic Fermi interaction constant, and $P = g_e g_N \mu_B \mu_N \langle r^{-3} \rangle$, ~0.23 and 0.015 cm^{-1}, respectively. This result is not unexpected, since the attempts to fit the copper hyperfine of copper(II)-doped Cs_2ZnCl_4 were also unsuccessful. In Table I are shown the spin Hamiltonian parameters for $CuCl_4$ and CuX_2Cl_2 chromophores. $A_\parallel$ has the minimum value for Cs_2CuCl_4, and it increases on replacing two chlorine atoms with two oxygen and two nitrogen atoms, respectively. Also the $g_\parallel$ values are interesting, since the largest value is observed for CuO_2Cl_2 although the energies of the electronic transitions[17] are higher than those observed for Cs_2CuCl_4.[12,30,31] All these considerations show that the simple formulas[32,33] do not hold. Symbols used in (1) are defined in the

$$\Delta g_\parallel = -\frac{8\zeta_d \alpha_1^2 \beta_1^2}{\Delta b_1} \qquad \Delta g_\perp = -\frac{2\zeta_d \alpha_1^2 \gamma_1^2}{\Delta e} \tag{1}$$

$$A_\parallel = P[-K\alpha_1^2 - \tfrac{4}{7}\alpha_1^2 + \Delta g_\parallel + \tfrac{3}{7}\Delta g_\perp]$$

$$A_\perp = P[-K\alpha_1^2 + \tfrac{2}{7}\alpha_1^2 + \tfrac{11}{14}\Delta g_\perp]$$

Appendix. In particular it is difficult to understand why $A_\parallel$ is smaller in $CuCl_4$ as compared to that for CuO_2Cl_2 even if the term due to the metal spin–orbit coupling $P(\Delta g_\parallel + {}^3/_7\Delta g_\perp)$, which opposes the contact and dipolar term $-P\alpha_1^2(K + {}^4/_7)$, must be larger for the oxygen-substituted complex. Also the original explanation by Sharnoff,[12] who introduced the metal 4p contribution, does not seem to be satisfactory, since it fails to explain why in complexes with almost identical geometries the substitution of two chlorine atoms with two oxygen atoms should decrease the 4p admixture, which is determined by the lack of a symmetry center.

Table I. Spin Hamiltonian Parameters for $CuCl_4$ and CuX_2Cl_2 Chromophores

	CuN_2Cl_2[a]	CuO_2Cl_2	$CuCl_4$[b]
$g_\parallel$	2.30	2.43	2.38
$g_\perp$[c]	2.06	2.08	2.09
$A_\parallel$[d]	123	40	25
$A_\perp$[c,d]	9	25	48.5

[a] Reference 8. [b] Reference 6. [c] Average of x and y components. [d] Values ×10^4 in cm^{-1}.

We feel that a unitary explanation of these data is possible, considering that chlorine has a fairly large spin–orbit coupling constant, of the same order of magnitude as the copper(II) constant, and that the metal–chlorine bond must be fairly covalent. This is shown by the chlorine hyperfine data of the CuO_2Cl_2 chromophore which are very similar to those reported for $Cu(phen)_2Cl_2$,[15] and as in that case, they can be interpreted, considering that the unpaired electron is spending 5–10% of its time on each chlorine atom. As a consequence the formulas in (1) are inadequate, and a more complete approach, which includes also the ligand contributions to the spin Hamiltonian parameters, must be used.

For the sake of simplicity we considered a complex of D_{2d} symmetry, the results being easily extended to the lower symmetries of Cs_2CuCl_4 and $Cu(Ph_3PO)_2Cl_2$. The relevant formulas in (2) are given below, while the symbols used are given in the

$$\Delta g_\parallel = -\frac{8\zeta_d}{\Delta b_1}(\alpha_1\beta_1 - \tfrac{1}{2}\alpha_3\beta_2)(\alpha_1\beta_1 - \tfrac{1}{2}\upsilon_L\alpha_3\beta_2) \tag{2}$$

$$\Delta g_\perp = -\frac{2\zeta_d}{\Delta e}(\alpha_1\gamma_1 + \alpha_2\gamma_4 - 2^{-1/2}\alpha_3\gamma_2) \times \left(\alpha_1\gamma_1 + \frac{1}{\sqrt{2}}\upsilon_L\alpha_3\gamma_2 - \upsilon_L\alpha_2\gamma_4\right)$$

$$A_\parallel = P\left[-K\alpha_1^2 - \tfrac{4}{7}\alpha_1^2 + (\alpha_1\beta_1)\left(\alpha_1\beta_1 - \frac{1}{\sqrt{2}}\alpha_3\beta_2\right)^{-1}\Delta g_\parallel + \tfrac{3}{7}(\alpha_1\gamma_1)(\alpha_1\gamma_1 + \alpha_3\gamma_4 - \tfrac{1}{2}\alpha_3\gamma_2)^{-1}\Delta g_\perp\right]$$

$$A_\perp = P\left[-K\alpha_1^2 + \tfrac{2}{7}\alpha_1^2 + \tfrac{11}{14}(\alpha_1\gamma_1) \times \left(\alpha_1\gamma_1 + \alpha_3\gamma_4 - \frac{1}{\sqrt{2}}\alpha_3\gamma_2\right)^{-1}\Delta g_\perp\right]$$

Appendix together with the procedure for obtaining them.

In the limit of $\upsilon_L = \zeta_L/\zeta_{Cu} = 0$ and neglect of the ligand terms, the formulas in (2) reduce to the formulas in (1). Therefore the formulas in (2) have the same limitations as the formulas in (1),

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[33] These formulas are obtained through the perturbative approach, i.e., the spin–orbit coupling constant is assumed to be small compared to the energy separation of the d orbitals. For the present tetrahedral chromophores this assumption may be at fault. A comparison with the exact calculation reported above shows that the g and A values calculated through the formulas in (1) are within 10% from the correct values.

in the sense that they are obtained through a perturbation approach. As shown in ref 33 this approach may give results which are 10% from the exact values. However, since we will not attach too much quantitative meaning to the formulas in (2) but will use them to rationalize a trend of values in this series of complexes, we feel confident to use them. If v_L is included and if α_3 and β_2 have sizable values, i.e., if covalency effects are substantial, then the $g_{\|}$ value is reduced in the case of a ligand having large ζ_L as compared to the case of a ligand having small ζ_L. This may explain why $g_{\|}$ is larger in CuO_2Cl_2 chromophores as compared to that in $CuCl_4$ chromophores, since in the latter, covalency effects associated to copper–chlorine bond must be more pronounced.

In the $A_{\|}$ formula in (2) the term depending on the metal spin–orbit coupling constant does not have the form $P[\Delta g_{\|} + {}^3/_7\Delta g_{\perp}]$ as in eq 1. Since α and β are positive definite, the coefficient of $\Delta g_{\|}$ in (2) is >1 so that the contribution of this term is greater than that expected by using the $\Delta g_{\|}$ as obtained through experiment in eq 1. This effect must be larger for $CuCl_4$ chromophores as compared to that for CuO_2Cl_2 chromophores, explaining why such small $A_{\|}$ values are observed for the former.

The analysis is more complicated for the perpendicular values, since in this case the low-symmetry effects are expected to be more important. Also there are two different contributions of the ligands to both the $g_{\perp}$ and $A_{\perp}$ values, which are of opposite sign and tend to cancel themselves. If it is assumed, however, that the $\alpha_3\gamma_2$ product is the leading one, then the inclusion of the ligand contribution would increase the $g_{\perp}$ value. In the $A_{\perp}$ formula (2) it would give a smaller contribution to the term containing $\Delta g_{\perp}$, thus justifying the large $A_{\perp}$ seen in the $CuCl_4$ chromophore. However, the correction due to $g_{\perp}$ is expected to be smaller than that due to $g_{\|}$.

If the above interpretation is correct, the anomalous ESR spectra of CuX_2Cl_2 complexes (X = Cl, O, N) are essentially due to the covalency of Cu–Cl bonds and to the large spin–orbit coupling of the chlorine atoms. A contribution of the metal 4p orbitals cannot be ruled out, but it cannot be as large as would be required if the ligand contributions would be neglected.

It is interesting to note that these considerations apply also to the copper(II) proteins which have anomalously low $A_{\|}$ values.[34] In fact they are known to contain at least one sulfur atom in the coordination sphere.[35,36] Sulfur is known to yield a fairly covalent bond with copper(II), and its spin–orbit coupling constant is fairly large, close to half that of copper(II).[30,31]

It must be concluded that small $A_{\|}$ values may be found in pseudotetrahedral copper(II) complexes when donor atoms with a large spin–orbit coupling constant and yielding fairly covalent bonds to the metal atom are present in the coordination sphere.

Appendix. Calculations of g and A for a d^1–d^9 Electron Configuration in D_{2d} Symmetry

The calculations are performed following the procedure outlined by McGarvey.[32] The coordinate axes for the metal (M) and the ligands (L) in the complex are shown in Figure 4. The linear combinations of atomic orbitals spanning the irreducible representations of the D_{2d} point group are listed in Table II. Using these functions, we can write the symmetry adapted antibonding molecular orbitals which follow:

$$|a_1\rangle = \delta_1|z^2\rangle + \delta_2\varphi_{xy}(a_1) - \delta_3\varphi_z(a_1) - \delta_4\varphi_s(a_1) \qquad (3)$$

$$|b_1\rangle = \beta_1|x^2 - y^2\rangle - \beta_2\varphi_{xy}(b_1)$$

$$|b_2\rangle = \alpha_1|xy\rangle - \alpha_2\varphi_z(b_2) - \alpha_3\varphi_{xy}(b_2) + \alpha_4\varphi_s(b_2)$$

Table II. Linear Combinations of Metal and Ligand Orbitals Spanning the Irreducible Representations of the D_{2d} Point Group[a]

symmetry label	metal d orbital	ligand orbital[b]
A_1	d_{z^2}	$\varphi_z(a_1) = {}^1/_2(p_z{}^1 - p_z{}^2 + p_z{}^3 - p_z{}^4)$ $\varphi_{xy}(a_1) = (8)^{-1/2}(p_x{}^1 + p_x{}^2 - p_x{}^3 - p_x{}^4 - p_y{}^1 + p_y{}^2 + p_y{}^3 - p_y{}^4)$ $\varphi_s(a_1) = {}^1/_2(s^1 + s^2 + s^3 + s^4)$
B_1	$d_{x^2-y^2}$	$\varphi_{xy}(b_1) = (8)^{-1/2}(p_x{}^1 + p_x{}^2 - p_x{}^3 - p_x{}^4 + p_y{}^1 - p_y{}^2 - p_y{}^3 + p_y{}^4)$
B_2	d_{xy}	$\varphi_z(b_2) = {}^1/_2(p_z{}^1 + p_z{}^2 + p_z{}^3 + p_z{}^4)$ $\varphi_{xy}(b_2) = (8)^{-1/2}(p_x{}^1 - p_x{}^2 - p_x{}^3 + p_x{}^4 - p_y{}^1 - p_y{}^2 + p_y{}^3 + p_y{}^4)$ $\varphi_s(b_2) = {}^1/_2(s^1 - s^2 + s^3 - s^4)$
E	d_{xz}	$\varphi_z(e_1) = {}^1/_2(p_z{}^1 + p_z{}^2 - p_z{}^3 - p_z{}^4)$ $\varphi_x(e_1) = {}^1/_2(p_x{}^1 - p_x{}^2 + p_x{}^3 - p_x{}^4)$ $\varphi_y(e_1) = {}^1/_2(p_y{}^1 + p_y{}^2 + p_y{}^3 + p_y{}^4)$ $\varphi_s(e_1) = {}^1/_2(s^1 - s^2 - s^3 + s^4)$
	d_{yz}	$\varphi_z(e_2) = {}^1/_2(p_z{}^1 - p_z{}^2 - p_z{}^3 + p_z{}^4)$ $\varphi_x(e_2) = {}^1/_2(p_x{}^1 + p_x{}^2 + p_x{}^3 + p_x{}^4)$ $\varphi_y(e_2) = {}^1/_2(p_y{}^1 - p_y{}^2 + p_y{}^3 - p_y{}^4)$ $\varphi_s(e_2) = {}^1/_2(s^1 + s^2 - s^3 - s^4)$

[a] Reference system is defined in Figure 4. [b] Superscript indicates the ligand nucleus on which the orbital is localized. The number refers to Figure 4.

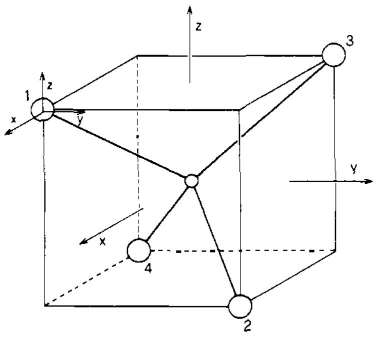

Figure 4. Reference system for ML_4 chromophores.

$$|e_1\rangle = \gamma_1|xz\rangle + \gamma_2\varphi_z(e_1) - \gamma_3\varphi_x(e_1) - \gamma_4\varphi_y(e_1) - \gamma_5\varphi_s(e_1)$$

$$|e_2\rangle = \gamma_1|yz\rangle + \gamma_2\varphi_z(e_2) - \gamma_3\varphi_y(e_2) - \gamma_4\varphi_x(e_2) + \gamma_5\varphi_s(e_2)$$

The signs are chosen to make the orbitals antibonding when the constants take positive values.

The ground state is a mainly metal d_{xy} orbital[12-18] which spans the b_2 irreducible representation of D_{2d}.

Treating the spin–orbit coupling operator as a first-order perturbation on the basis of (3) the $|+\rangle$ and $|-\rangle$ components of the fundamental Kramers doublet in (4) are obtained. The

$$|+\rangle = |b_2+\rangle + a_1|b_1+\rangle + a_2[|e_1-\rangle - i|e_2-\rangle]$$

$$|-\rangle = |b_2-\rangle - a_1|b_1-\rangle + a_2[|e_1+\rangle + i|e_2+\rangle] \qquad (4)$$

symbols + and − on the right hand of (4) refer to the ${}^{+1}/_2$ and ${}^{-1}/_2$ spin components and a_1 and a_2 are

$$a_1 = (i\zeta_d/\Delta b_1)(\alpha_1\beta_1 - {}^1\!/_2 v_L\alpha_3\beta_2)$$

$$a_2 = -(i\zeta_d/\Delta e)({}^1\!/_2\alpha_1\gamma_1 + v_L(8)^{-1/2}\gamma_2\alpha_3 - {}^1\!/_2 v_L\alpha_2\gamma_4) \qquad (5)$$

where $v_L = \zeta_L/\zeta_d$, ζ_L and ζ_d are the one-electron spin–orbit coupling constants for the ligand and metal atom, respectively, and Δb_1 and Δe are the energy separations of the excited $|b_1\rangle$, $|e_1\rangle$ and $|e_2\rangle$ molecular orbitals from the ground state $|b_2\rangle$.

From (4) and (5) the equations in (2) follow. In obtaining them, we had to consider terms containing metal–ligand overlap integrals as well as terms connected to the sp hybridization of the ligand orbitals negligible as compared to the other terms.

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