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Electronic Spectra of Pseudotetrahedral Bis(bidentate)copper(II) Complexes: Spectral Assignment and Effect of Ligand Asymmetry[§]

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Abstract

The electronic spectra (d–d transitions) of the following pseudotetrahedral complexes, $Cu(L{-}L)_2^{2+}$, L–L = 2,2′-dipyridylamine (HDPA); 3,3′-dimethyl-2,2′-dipyridylamine (HMPA); 2-pyridyl-2′-pyrimidylamine (HPPA); 2-pyridyl-2′-thiazolylamine (HPTA) were interpreted by the Angular Overlap Model (AOM) in D_2 symmetry for symmetrically bonded ligands and C_2 for asymmetrically bonded ligands. AOM expressions were found in which the bite angle (α), the dihedral angle (2ω) and the ligand pitch angle (ψ) were retained as variables. Such an approach permitted the use of experimental α, 2ω and ψ values in the spectral fit procedure so that the extracted AOM parameters were free from geometry contributions. Neglect of the real ψ values produces a large distortion as to the real π-bonding picture in the studied complexes. The geometry-free AOM parameters were further substantiated by using them in calculating the non-coincidence between the molecular symmetry axes and the g-tensor axes, as well as the charge transfer transitions. Contributions to transition energies by s–d and p–d mixing in D_2 symmetry were found to be negligible.

Introduction

The pseudotetrahedral copper(II) complexes with 2,2′-dipyridylamine and its derivatives have been studied thus far with the purpose of finding spectra–structure correlations [1, 2]. Among the large number of such compounds [1], the structures of the complexes $Cu(L{-}L)_2^{2+}$, where L–L = 2,2′-dipyridylamine, HDPA [3a], 2,2′-dipyridylamide, DPA [3b], 3,3′-dimethyl-2,2′-dipyridylamide, MPA [4] and 2-pyridyl-2′-pyrimidylamine, HPPA [2], have been used to calibrate the dependence absorption peak positions *vs.* dihedral angles (the angle contended between the NCuN-planes of the two chelate rings) [2]. Table I lists the relevant literature data on the transition energies, the dihedral angles (2ω), the bite angles (α) and the pitch angles (ψ) of the four complexes; it also gives the transition energies for two other related pseudotetrahedral chromophores $Cu(N{-}N)_2$, for which X-ray determined structures are lacking.

The X-ray diffraction data reveal [3, 4] that the coordinated ligands in these complexes are strongly non-linear and the ligand pitch angle ψ (the angle between the LML-plane and the pyridine plane, where L indicates the donor atoms of the ligand) characterizing this non-linearity takes different non-zero values for each complex (see Table I). Therefore, the π-interactions M–L are anisotropic and the AOM (adopting different e_π values) seems to be more appropriate to describe this situation as opposed to the Crystal Field Theory. The latter was used recently [1, 2, 6] with the aim of explaining the spectral behaviour and the g-factor values for these complexes. The neglect of the ligand structure, as implicitly assumed in the CF treatment, or use of a limited set of structure-defining angles (α and 2ω in [1, 2]) could produce misleading results (*vide infra*) and for this reason such calculations should be viewed with caution.

We intend to take α, 2ω and ψ explicitly into account in the AOM energy expressions; if these angles are taken from X-ray diffraction studies, or varied until a good fit with the electronic spectra is obtained, it may be expected that the geometrical contributions to the extracted AOM spectral parameters would be eliminated and these parameters would reflect the electronic structure of the complexes [7]. This is perhaps the only way to obtain geometry-free AOM parameters that can be compared among themselves or transferred to other complexes.

Theoretical

Treatment in D_2 Symmetry

The orientation of the coordinate axes as required by group theory stipulates that the Z axis bisects the chelate angle α [8] (see Fig. 1). This is however not the only possible choice (see [9]) and the X and Y

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TABLE I. Transition Energies and Structural Angles of the Copper(II) Dipyridylamine Complexes.

Complex	α (°)	2ω (°)	ψ[g] (°)	r(Cu–N)[h] (Å)	Band positions (polarization) (KK)			
Cu(HDPA)$_2^{2+}$	95.6[a]	55.6[a]	22.5 43.0	1.94(1)[a] 1.99(1)[a]	7.5[d]	10.4(z)[e]		13.5(y)[e] 15.7(x)[e]
Cu(MPA)$_2$[i]	93.27[b]	57.4[b]	10.2 11.2	1.945(2)[b] 1.963(2)[b]	8.7[c]		12.5[f]	16.4[c]
Cu(HPPA)$_2^{2+}$	93.42[c]	53.8[c]	7.3 8.7	1.971(1)[c] 1.980(1)[c]	7.5[d]		10.4[d]	15.7[d]
Cu(DPA)$_2$[l]	93.63[n]	58.8[n]	4.3 5.8	1.952(2)[n] 1.955(2)[n]	~5[n]	9.9[d]	m	~15.6[d]
Cu(HPTA)$_2^{2+}$	j	j	j	j	7.6[d]		10.3[d]	16.0[d]
Cu(PTA)$_2$[l]	j	j	j	j	8.7[d]		13.0[k]	16.9[d]

[a] Ref. [3a]. [b] Ref. [4]. [c] Ref. [2], reflectance spectra. [d] Ref. [1], reflectance spectra. [e] Ref. [5], single-crystal spectra, the notations in parenthesis x, y, z refer to coordinate axis orientation as shown in Fig. 1. However in Ref. [5] $x \rightarrow z, y \rightarrow x, z \rightarrow y$. [f] Ref. [2], solution spectrum in CH_2Cl_2. [g] Atomic coordinates given in [3, 4] have been used in this work to calculate ψ values. [h] The two r(Cu–N) values correspond to the two Cu–N bonds of a bidentate ligand. [i] L–L loses a proton on coordination. [j] The structures of these complexes have not been determined. [k] Near-IR solution spectrum from Ref. [1], solvent = acetonitrile. [l] PTA and DPA stand for the deprotonated forms of the parent ligands HPTA and HDPA, respectively. [m] No peak is observed but there is broad absorption with an ill-defined maximum at about 13 kK [1]. [n] Ref. [3b].

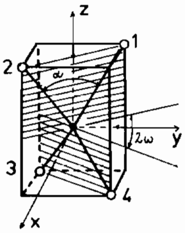

Fig. 1. Orientation of the coordinate axes in symmetrically coordinated bis-bidentate complexes. The sets (1, 2) and (3, 4) enumerate the bonding atoms of the two bidentate ligands respectively.

axes may be interchanged [10]. Our choice (Fig. 1) produces a simpler relation between the ligand's polar coordinates and the angles α and 2ω, and this is the reason for using it here.

Standard techniques described by Schäffer *et al.* [11, 12] were used to find the matrix elements of the AOM operator in the d–AO basis and D_2 symmetry in terms of the AOM parameters $e_{\lambda\omega}$ (for their definition see [11, 12]). The summations in the standard F matrices were performed in such a way so as to obtain expressions in which the angles α, 2ω and ψ were retained as variables. The results are collected in Appendix 1 (A.1.1.–A.1.6). As limiting cases these expressions reproduce the d-orbital energies in D_{2h} ($2\omega = 0°$, $\psi = 0$) and T_d ($2\omega = 90°$, $\alpha = 109.47°$, $\psi = 0°$).

Treatment in C_2 Symmetry

In the case of an asymmetric bidentate ligand M(L′–L″)$_2$, where L′ ≠ L″ or L′ = L″ but r(M–L″) ≠ r(M–L′) or/and $\psi' \neq \psi''$ (see Fig. 2a–c), for each value of the dihedral angle $2\omega \neq 90°$ two molecular structures are possible.

These structures are given in Figs. 2b and 2c. They can be best viewed in the limit of planar geometry ($2\omega = 0°$ and $2\omega = 180°$) when Fig. 2b produces a *trans*-L′,L″ or rhomboidal (C_{2h}) structure and Fig. 2c a *cis*-L′,L″ or trapezoidal (C_{2v}) structure. Experimental data show [13–15] that the rhombic structure is more frequently realized.

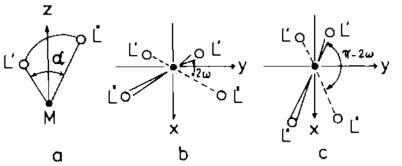

Fig. 2. Orientation of the coordinate axes and possible structures of asymmetrically coordinated bis-bidentate complexes. In Fig. 2a the z axis bisects the bite angle. Figs. 2b and 2c are drawn viewed down the z axis.

The structure variations with the dihedral angle are illustrated in Fig. 3.

As seen from Fig. 2a the Z-axis is no longer a C_2 axis for a chelate complex with asymmetric bidentate ligands. The same holds for the Y axis. Hence in our choice $C_2 \equiv X$ only, since rotation about X exchanges equivalent M–L′ and M–L″ bonds respectively. In C_2 point group $x^2 - y^2$, z^2, yz transform as A and xz, xy as B irreducible representations.

When passing from D_2 to C_2 symmetry, each term f(α, 2ω, ψ)$e_{\lambda\omega}$ in expressions A.1.1.–A.1.6. has to

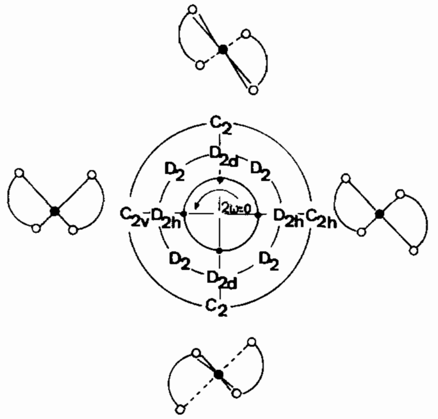

Fig. 3. The symmetries resulting upon rotation about the *z* axis of the two ligands with respect to each other, expressed by the dihedral angle (2ω). Inner rim is for symmetric ligands, outer rim for asymmetric ligands. Four limiting cases with asymmetric ligands are drawn schematically outside the rims.

be replaced by $(^1/_2)[f(\alpha, 2\omega, \psi')e'_{\lambda\omega} + f(\alpha, 2\omega, \psi'')e''_{\lambda\omega}]$, where $e'_{\lambda\omega}$, $e''_{\lambda\omega}$ are the AOM-parameters and ψ' and ψ'' are the ψ angles corresponding to the two non-equivalent M–L′ and M–L″ bonds respectively.

There are non-zero off-diagonal matrix elements which appear for C_2 additionally to D_2*. These off-diagonal elements provide the mixing of the orbitals of equal symmetry in C_2 and are dependent on $e'_{\lambda\omega}$, $e''_{\lambda\omega}$ and the angles α, 2ω, ψ' and ψ''. Consequently, the number of AOM parameters needed in a C_2-treatment of the studied complexes is 6. To reduce this number the parameter ratios $e''_{\lambda\omega}/e'_{\lambda\omega}$ should be written as overlap integral ratios [16, 17]:

$$e''_{\lambda\omega}/e'_{\lambda\omega} = S''^{2}_{\lambda\omega}/S'^{2}_{\lambda\omega} \qquad (1)$$

We shall use eqn. 1 separately for $\lambda\omega = \sigma, \pi c$ and πs in the C_2 treatment and thus reduce the number of AOM parameters to 3.

Results and Discussion

Assignment of the Electronic d–d Spectra

D_2-treatment

As is known from the literature [2–4] the copper–pyridine moiety can be approximated to C_{2v} symmetry. Therefore, it is possible to find an AOM-reference frame in which the σ and π interactions of the metal and ligand orbitals are diagonal and are expressed by the AOM-parameters e_σ, $e_{\pi c}$ and $e_{\pi s}$ ($e_{\pi c}$ and $e_{\pi s}$ refer to directions ‖ and ⊥ to the pyridine ring, respectively) [11, 12]. Furthermore, $e_{\pi s} \neq e_{\pi c}$ since the Cu–N bond does not have cylindrical symmetry and $e_{\pi c} = 0$, because pyridine has no in-plane π-orbitals.

Using expressions A.1.1–A.1.6, written in a form suitable for computer programming, and experimental α and 2ω values (see Table I) we have interpreted the d–d spectra of the complexes under consideration. As the three fitting parameters we used e_σ, $e_{\pi s} \equiv e_\pi(\perp)$ ($e_{\pi c} \equiv e_\pi(\parallel) = 0$) and the ψ angle. The reason to choose ψ as a variable and α, 2ω to be taken from experimental data is seen from Table I: in fact for all the three structure-defining angles, only ψ shows variations of more than several degrees (α = 93–96°, 2ω = 54–59° but ψ = 4–43°).

There are no X-ray data for the complexes Cu-$(\text{HPTA})_2^{+2}$ and Cu(PTA)_2 and for this reason we have adopted α = 94° and 2ω = 56°, mean values of the remaining four complexes for which the structures are known. Such an averaging procedure is justified for complexes differing only as to their remote substituents.

Initially in the treatment to obtain the AOM parameters we worked in the double group D_2' with the spin–orbit coupling constant $\zeta(\text{Cu}^{2+}) = -0.829$ kK [18] or lower. The effect of the spin–orbit coupling on the calculated transition energies, however, was found to be very weak as opposed to planar complexes of Cu(II) [19]. In subsequent treatments it was neglected. The spectral assignments and the best-fit e_σ, $e_{\pi s}$ and ψ parameter values are collected in Tables II and III.

Two possible assignments were obtained for all the complexes under consideration: (I) neglecting ψ (setting ψ = 0°) and (II) taking the ψ-angle as fitting parameter. To save space we give these two assignments only for Cu(HDPA)_2^{2+}. It can be seen from Table III that the neglect of ψ produces negative values of $e_\pi(\perp)$, implying π-back bonding M → L (π-acceptor ligands) whereas if the real ψ values are used the $e_{\pi s}$ values are positive, implying π-donor behaviour of the ligands. As can be seen from the symmetry selection rules in the D_2 group the transitions $b_2 \rightarrow b_3$, $b_1 \rightarrow b_3$ and $a \rightarrow b_3$ are expected to be *z*, *y*- and *x*-polarized respectively, and the comparison with experiment confirms strongly assignment II. It is also seen that obviously the D_2 symmetry is operative in determining the polarization behaviour of the d–d bands and that there is no need to go down to C_2 to explain this behaviour: the selection rules in C_2 predict for $xy \rightarrow yz$ and $xz \rightarrow yz$ both *z* and *y* polarization and in fact one component is missing from the experimental pattern.

The d–d transition energies as a function of the ψ angle are illustrated in Fig. 4.

The comparison of the AOM parameter values obtained in the treatments I and II (see Table III, the data on Cu(HDPA)_2^{2+}) shows that the neglect of ψ produces lower e_σ and $e_{\pi s}$ values, $e_{\pi s}$ even

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*The expressions are lengthy but they can easily be obtained from the $F_{\lambda\omega}$ matrices [11, 12] by performing the necessary summations.

TABLE II. Calculated d–d Transition Energies. For I and II Alternatives, see Text.

Transitions	Calculated transition energies[a]							
	$Cu(HDPA)_2^{2+}$			$Cu(MPA)_2$	$Cu(HPPA)_2^{2+}$	$Cu(DPA)_2$	$Cu(PTA)_2$	$Cu(HPTA)_2^{2+}$
	I[d]	II	exp. polarizations[c]	II	II	II	II	II
$a(x^2-y^2)^e \rightarrow b_3(yz)$	7.4(7.5)	7.7(7.5)	b	11.4(12.5)	9.5(10.4)	9.9(9.9)	9.6(8.9)	7.7(7.6)
$b_2(xz) \rightarrow b_3(yz)$	13.6(13.5)	9.6(10.4)	z	8.8(8.7)	7.5(7.5)	7.3(~5)	8.3(8.9)	9.7(10.3)
$b_1(xy) \rightarrow b_3(yz)$	10.3(10.4)	13.3(13.5)	y	12.6(12.5)	11.0(10.4)	12.1(f)	13.0(13.0)	13.8(f)
$a(z^2)^e \rightarrow b_3(yz)$	15.6(15.7)	15.3(15.7)	x	16.7(16.4)	15.7(15.7)	16.9(~15.6)	16.6(16.9)	15.4(16.0)

[a] For comparison the experimental values are given in parentheses (see Table I). [b] The polarization of this band was not reported in ref. [5]. [c] Experimental polarizations taken from ref. [5]. [d] A non-zero value for $e_\pi(\parallel) = 1.4$ kK was obtained in this case. [e] The z^2 and x^2-y^2 orbitals were heavily mixed via the AOM operator. The Table lists the orbital with the higher LCAO coefficient. [f] No peak is observed but there is broad absorption with an ill-defined maximum at about 13 kK [1].

TABLE III. Calculated AOM-Parameters (kK) and ψ-Angle Values (°).

AOM-Parameters and ψ[a]	$Cu(HDPA)_2^{2+}$		$Cu(MPA)_2$	$Cu(HPPA)_2^{2+}$	$Cu(DPA)_2$	$Cu(PTA)_2$	$Cu(HPTA)_2^{2+}$
	I	II	II	II	II	II	II
e_σ	5.90	7.50	7.30	6.50	7.50	7.40	7.60
$e_{\pi s}$	−3.6	3.5	3.0	3.5	4.0	3.9	3.7
ψ[b]	0	37	10	5	7	16	38
		$\begin{bmatrix}22.5\\43\end{bmatrix}$[c]	$\begin{bmatrix}10.2\\11.2\end{bmatrix}$	$\begin{bmatrix}7.3\\8.7\end{bmatrix}$	$\begin{bmatrix}4.3\\5.8\end{bmatrix}$	d	d

[a] The error in e_σ is ±0.05 kK, that in $e_{\pi s}$ is ±0.2 kK and ψ values are accurate ±2°. [b] For comparison the experimental values of ψ are listed in parentheses below the calculated ones. [c] The two ψ-values differ considerably. The mean value was used in D_2 but the two different values were employed in the C_2 treatment. [d] Structural parameters for these complexes are unknown; $\alpha = 94°$ and $2\omega = 56°$ were employed during the calculations (see text) and e_σ, $e_{\pi s}$ and ψ were extracted from the spectral fitting procedure.

becoming negative in I. In other words the negative $e_{\pi s}$ value and the implicit π-acceptor behaviour of the ligand are artifacts which disappear in the correct treatment, including the ψ value.

As expected for structurally similar ligands the e_σ values in Table III lie in a narrow range (7.3–7.6 kK). The e_σ value for the ligand HPPA is an exception lying about 1 kK lower than this range. This exception however can be explained in terms of the negative inductive effect generated by the second nitrogen atom in the pyrimidine ring decreasing the σ-donor ability of the ligand. The protolysis equilibrium constants for pyridine (pK = 5.21 [20]) and pyrimidine (pK = 0.65 [20]) support this claim.

The e_σ parameters for other nitrogen-donor ligands are 7.0–7.8 kK [16, 21] for ligand without π-MO's and about 9 kK for the π-donor dpm* [22]. The e_σ values from Table III are similar to those of π-lacking ligands, and lower than the e_σ values of the dpm complexes for which the high e_σ value is due to deprotonation at the donor nitrogen atom in the pyrol ligand enhancing the sigma donor capacities of the ligand.

The influence of the $e_{\pi s}/e_\sigma$ ratio on the transition energies is illustrated in Fig. 5, from which it can be seen that $b_1 \rightarrow b_3$ is the only transition which is almost independent of this ratio. The highest d–d transition $a \rightarrow b_3$ rises in energy with decreasing $e_{\pi s}/e_\sigma$ values, *i.e.* with decreasing π-donor and increasing σ-donor ability of the ligand. The ΔE *vs.* $e_{\pi s}/e_\sigma$ dependence for the two $a \rightarrow b_3$ transitions is non-linear, due to the large mixing between $A(z^2)$ and $A(x^2-y^2)$.

It can be seen from Table IV that the ψ values for the deprotonated complexes $Cu(DPA)_2$ and $Cu(PTA)_2$ are lower than those for the parent undeprotonated species. This can be easily explained if one takes into account that the inclusion of the imine nitrogen (in $Cu(DPA)_2$ and $Cu(PTA)_2$) in the aromat-

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*dpm = 3,3′,5,5′ tetramethyldipyrromethene. The e_σ value was obtained neglecting ψ. Provided ψ is accounted for, the e_σ value is expected to rise further.

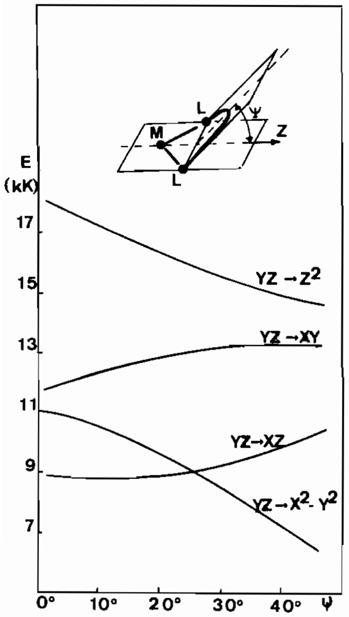

Fig. 4. d–d transition energies (in kK) calculated as a function of the ligand pitch angle (ψ). The curves are plotted with $2\omega = 55.6°$, $\alpha = 95.6°$, $e_\sigma = 7.5$ kK, $e_{\pi s} = 3.5$ kK chosen as an example.

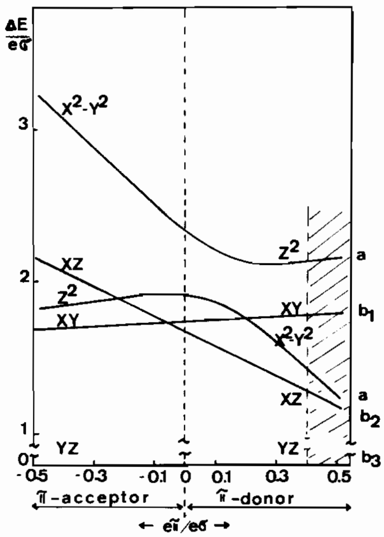

Fig. 5. d–d transition energies (in e_σ units) calculated as a function of the $e_{\pi s}/e_\sigma$-ratio. The curves are plotted for $2\omega = 56°$, $\alpha = 94°$, $\psi = 23.5°$, mean values for the complexes under consideration. The leading term of d-AO is only given. D_2 symmetry group notation is shown on the left hand side. Ground state is hole in $d_{yz}(b_3)$. Shaded area depicts the region of $e_{\pi s}/e_\sigma$ ratios for the studied complexes.

ic system makes the ligand more rigid and hence larger ψ values are less probable.

C_2-treatment

Using the experimental values for ψ' and ψ'' (as well as those for α and 2ω) we have interpreted the d–d spectra in the C_2 group. The AOM-parameter ratios $e''_{\pi s}/e'_{\pi s}$ and e''_σ/e'_σ were found from the approximate formula 1 and the $e'_{\pi c}$, $e''_{\pi c}$ in compliance with the real geometry were set equal to zero. The two-atomic overlap integrals in eqn. 1 were calculated with Slater-type orbitals [23] and the experimental metal–ligand distances (Table I). The results show that the lowering of symmetry $D_2 \rightarrow C_2$ cannot alter the band assignments made within the D_2 group. The d–d transition energies in $Cu(HDPA)_2^{2+}$ are shifted by no more than 0.6 kK and are negligible for the other complexes. The calculated AOM values are given in Table IV.

TABLE IV. AOM-Parameter Values for the Asymmetric Copper(II) Dipyridylamine Complexes in a C_2-treatment.

Parameter	$Cu(HDPA)_2^{2+}$	$Cu(MPA)_2$	$Cu(HPPA)_2^{2+}$
r' (Å)	1.99(1)	1.963(2)	1.980(1)
r'' (Å)	1.94(1)	1.945(2)	1.971(1)
e'_σ (kK)	6.5	7.1	6.6
e''_σ (kK)	8.3	7.5	6.8
$e'_{\pi s}$ (kK)	3.4	2.8	3.4
$e''_{\pi s}$ (kK)	4.3	3.0	3.5

It can be seen from Table IV that the $e_{\pi s}$ differences are small, with the possible exception of $e_{\pi s} = 4.3$ kK for $Cu(HDPA)_2^{2+}$. There is a net correlation between the e_σ values for the separate complexes with the M–L distance. Such a correlation within the same complex is trivial; it arises from the way the $e''_{\lambda\omega}/e'_{\lambda\omega}$ ratio was determined using the M–L bond distances.

By comparing Tables III and IV it can be seen that the geometry idealization (*i.e.* neglecting non-zero ψ values and using D_2 instead of C_2 symmetry) affects considerably the AOM parameters. Since both ψ and C_2 symmetry are taken explicitly into account here the AOM parameters thus obtained contain no geometry contributions.

The lowering of symmetry $D_2 \rightarrow C_2$ produces considerable mixing of z^2 and $x^2 - y^2$ with yz in the ground state term of $Cu(HDPA)_2^{2+}$:

$$0.991(yz) - 0.130(x^2 - y^2) + 0.030(z^2) \qquad (2)$$

The LCAO coefficients however are much lower for the remaining two complexes:

$$Cu(MPA)_2: 0.999(yz) - 0.019(x^2 - y^2) + 0.007(z^2)$$

$$Cu(HPPA)_2^{2+}: 0.999(yz) - 0.014(x^2 - y^2) + 0.006(z^2) \qquad (3)$$

Charge Transfer Transitions

Unlike the complex ions ($Cu(HDPA)_2^{2+}$ and $Cu(HPPA)_2^{2+}$) which change the Cu coordination number from 4 to 6 upon dissolution, the neutral

$Cu(MPA)_2$ and $Cu(PTA)_2$ retain their geometry and the d–d bands are shifted only slightly [1]. Hence, the crystal and solution spectra of the ions may differ, while the neutral complexes are expected to have similar spectra in both phases. We cannot use the CT solution spectra of the complex ions together with the AOM parameters extracted from crystal spectral analysis of the d–d bands, but we may attempt to do so for the neutral complexes. To check the reliability of the AOM parameters obtained from the d–d spectral analysis, we have tried to interpret the charge transfer (CT) bands of the neutral $Cu(MPA)_2$ and $Cu(PTA)_2$ complexes. We have calculated the CT-transition energies by a modification of the Jϕrgensen method [24] in which we use the AOM spectral parameters obtained from the d–d spectral analysis [25]. The expressions for the CT-transition energies of d^9 M in D_2 ligand field and the parametrization scheme are given elsewhere [26].

The Racah-parameter B for Cu(II) and the spin-pairing parameter D were calculated with the charge (+2) and electronic configuration (d^9, $q = 9$) of M using the formulae of Jϕrgensen [24]. The parameter $E - A$, the difference between the increase in core-attraction E when going from q to $q + 1$ and the average interelectronic repulsion energy, is dependent only on the nature of M and for the first transition metal series from the spectra of dithiocarbamate complexes was found to be 2.7 kK [25]. This value was used in our CT calculations without further improvement. The only unknown quantities in these calculation $W_1 = E(z^2) - E_\pi(\mathrm{L})$ and $W_2 = E_{\pi^*}(\mathrm{L}) - E(yz)$ are dependent both on the nature of M and that of L. For this reason W_1 and W_2 were left as variational parameters, so as to fit best the five CT-band positions in $Cu(MPA)_2$ and were used without change for $Cu(PTA)_2$. The results obtained are listed in Table V.

TABLE V. Experimental [1] and Calculated[a] Energies and Assignments of the CT-Transitions in $Cu(MPA)_2$ and $Cu(PTA)_2$.

Assignment	$Cu(MPA)_2$	$Cu(PTA)_2$		
	exp.[b] (calc.)	exp.		calc.
		c	d	
$\pi \rightarrow d_{yz}$	24.7(23.5)	23.0	23.0	(23.7)
$d_{xz} \rightarrow \pi^*$	26.0(26.0)			(25.3)
$d_{x^2-y^2} \rightarrow \pi^*$	28.6(28.4)	26.5	25.8	(26.6)
$d_{xy} \rightarrow \pi^*$	29.9(29.8)	27.6	26.8	(28.7)
$d_{z^2} \rightarrow \pi^*$	(33.7)	32.8	32.0	(33.6)
$d_{yz} \rightarrow \pi^*$	33.3(33.9)			(33.7)
L → L [1]	(–)			(–)

[a] $W_1 = 31.4$ kK, $W_2 = 17.6$ kK. [b] Solution spectrum in dichloromethane (dielectric constant $\epsilon = 8.9$). [c] Solution spectrum in methanol ($\epsilon = 32.6$). [d] Solution spectrum in acetonitrile ($\epsilon = 36.2$).

It is shown in Table V that on going from $Cu(MPA)_2$ to $Cu(PTA)_2$ the CT-transition energies are shifted to lower values. If the parameters W_1 and W_2 for $Cu(MPA)_2$ and $Cu(PTA)_2$ were equal, this behaviour is easily understood by comparing the shifts that occur with the d-orbital energy differences in these two complexes. However, a possible source for this low-frequency shift may be the lower energy of the structures $Cu^+{-}N^-$ and $Cu^-{-}N^+$ (corresponding to the excited state of the M → L and L → M CT-transitions, respectively) in the solvent with the higher dielectric constant (see text under Table V). Indeed, the comparison between the CT-transition energies in $Cu(PTA)_2$ in methanol ($\epsilon = 32$) and in acetonitrile ($\epsilon = 36.2$) shows that, even for the same complex $Cu(PTA)_2$, the rise in dielectric constant is accompanied by lowering the CT-transition energies (compare the experimental data from Table V). The d-orbital orderings of $Cu(PTA)_2$ in these two solvents are nearly the same [1], so that the solvent effect is the only one left. This supports the mechanism of ionic structures being involved in the excited states.

Mutual Orientation of the Main g-Factor and Molecular Axes

As mentioned above the lowering of the symmetry ($D_2 \rightarrow C_2$), due to asymmetry in coordination, produces mixing of the z^2 and $x^2 - y^2$ orbitals with the ground state orbital (yz). Such a mixing results in a reorientation of the g-ellipse in the yz-plane [27] with respect to the y, z axes leaving unchanged the g_x component. That is why we are concerned only with the y,z-plane g-factors.

The ground state wave function in a general form (see eqns. (2, 3)) is:

$$\varphi = c_1'(yz) + c_2'(x^2 - y^2) + c_3'(z^2) \tag{4}$$

Using the expressions given elsewhere [27] and transforming the d-set from [27] into our basis, after some algebra we obtain the following formula giving the angle η^0 between the (y, z) and $(g_{y'}, g_{z'})$-axis:

$$\eta^0 = (1/2)\tan^{-1}\left[\frac{2c_1c_2 - Wc_2}{c_1^2 - c_2^2 - Wc_1}\right] \tag{5}$$

where

$$W = 2\sqrt{3}c\,\frac{1 + E(xy)/E(xz)}{1 - E(xy)/E(xz)} \tag{6}$$

and

$$c_1 = -(1/2)c_2' - (\sqrt{3}/2)c_3'$$

$$c_2 = c_1'$$

$$c_3 = (\sqrt{3}/2)c_2' - (1/2)c_3' \tag{7}$$

c_1', c_2' and c_3' are the coefficients in eqn. (4). We used the expressions (4)–(7) and the mixing coefficients in eqns. (2, 3) in this work to calculate the angles η^0; 36°, 10° and 9° were obtained for Cu(HDPA)$_2^{2+}$, Cu(MPA)$_2$ and Cu(HPPA)$_2^{2+}$, respectively.

This angle was experimentally determined only for Cu(HDPA)$_2^{2+}$, $\eta^\circ = 40^\circ$ [5]. Compared with 36° calculated with an orbital reduction factor (k) unity the agreement is good. This is an indirect substantiation of the parameter values used in the calculation as well as the effect of orbital mixing on the g-values. The agreement may be 'improved' by varying k below unity [27].

Effect of s–d and p–d Interactions on the d–d Transition Energies

In D_2 symmetry, z^2, $x^2 - y^2$ and s transform as A and yz, xz and xy as well as p_x, p_y, p_z are B_3, B_2 and B_1 respectively. Consequently, s–d and p–d interactions are possible from symmetry considerations and these interactions may affect the d–d transition energies and change the assignment (see [28], for example).

On the other hand for a ligand located on the z axis of the M-centered coordinate system (C_{2v}) the resulting s–d and p–d interactions are fully described by the parameters h defined as follows [28]:

$$\text{d–s: } (z^2|A^z|s) = h_{\text{sd}}$$

$$\text{d–p: } (z^2|A^z|p_z) = h_{\text{pd}\sigma}$$

$$(yz|A^z|p_y) = h_{\text{pd}\pi\text{s}}$$

$$(xz|A^z|p_x) = h_{\text{pd}\pi\text{c}} \qquad (8)$$

where A^z is the C_{2v} AOM operator defined with respect to the M–L$_z$ axis. The right hand side indices of h stand for the orbital notations (s–d, p–d) and the type of overlap (σ, πs, πc) with the ligands MO. We have used the polar coordinates of the ligand donor atoms from Fig. 1 and a procedure (second order perturbation) described elsewhere [28] to find expressions for the corrections $\Delta E''$ to the d–AO energies in D$_2$; the results are listed in Appendix 2 (eqns. A.2.1–A.2.6). It follows from eqns. A.1.1–A.1.6 and A.2.1–A.2.6 that the number of parameters required for the full (s–p–d) description of the d–d transition energies in D_2 has arisen to 6. Unfortunately, such a number of parameters can hardly be found from the available experimental data for *one* complex; however, e_{sd} and e_{pd} may be considered as transferable [29] and the experimental α and 2ω data may be used to make the problem tractable (see also [30] for further discussion of the transferability of AOM parameters).

Inserting $\alpha \sim 94^\circ$ and $2\omega \sim 56^\circ$ from Table I and $e_{\text{sd}} \sim 1.4$ kK [29] (see also [30]), $e_{\text{pd}} \sim 0.7$ kK [30] and neglecting $e_{\text{pd}\pi\text{s, c}}$ as non-essential [29] we get $\Delta E''$ values −0.87 kK and −1.53 kK for z^2 and $x^2 - y^2$ and −0.76 kK for xz, yz and xy respectively. Hence, with the exception of $x^2 - y^2$, all d-AO's are shifted parallel. The $x^2 - y^2$ orbital is pushed down by about 0.7 kK with respect to the remaining d-AO's. This amount however is redistributed by the large AOM off-diagonal element between the two transitions $z^2 \rightarrow yz$ and $x^2 - y^2 \rightarrow yz$ and thus it is further reduced per single transition.

As a whole it may be concluded that both s–d and p–d interactions are not essential in the AOM assignment of the spectra for the studied complexes and we may work in a d-only AOM treatment.

Concluding Remarks

(i) The results obtained show that the inclusion of both the dihedral angle and the bite angle, characterizing the Cu(L–L)$_2$ geometry in D_2 symmetry, into the interpretation of the electronic spectra of such complexes is essential. However, the variations of these angles is small for the four complexes considred here and taken separately they cannot explain the observed spectral differences. More important is the fact that the coordinated ligands are strongly non-linear, which together with the large non-zero values of the ψ-angle has a dominant effect on the d-orbital energies and (through the d-orbital mixing) on the g-values.

(ii) The asymmetry of the coordinated ligands and the accompanying lowering of the symmetry of the chromophore ($D_2 \rightarrow C_2$) affect only slightly the transition energies. This, however, produces mixing of the z^2 and $x^2 - y^2$ orbitals with the ground state orbital (hole in yz) which is essential in understanding the non-coincidence of the main g-tensor axes with the molecular axes for Cu(HDPA)$_2^{2+}$, and possibly also for the other two complexes.

(iii) Crystal field theory was found to be unable to yield all the d–d bands. This is attributed specifically to the non-linearity of the ligands, ignored by the crystal field theory (structureless ligands) and accounted for in AOM by the AOM parameter values, as predicted theoretically by Schäffer [12].

(iv) s–d and p–d interactions were found to be ineffective in scrambling the d–d transitions. All the transitions are shifted parallel, with the possible exception of the x^2–$y^2 \rightarrow yz$ and to a lesser extent (by configuration interaction) $z^2 \rightarrow yz$. Such interactions may be ignored in the spectral assignments for the pseudotetrahedral copper(II) complexes considered here.

(v) Finally, the AOM parameters obtained here are free from geometry contributions and as such are thought to be transferable to other similar Cu(II) complexes.

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Appendix 1

Matrix Elements of the AOM Operator of d-AO's in D_2 Symmetry

By applying consistently the AOM formalism [11, 12] and summing over the donor atom coordinates we have obtained the following matrix elements of the AOM operator (A) for the d-AO basis and D_2 symmetry, where α, 2ω and ψ referring to the geometry of the complex as a whole have been retained as variables:

$$\begin{aligned}(x^2-y^2|A(D_2)|x^2-y^2) = {}& 3\sin^4(\alpha/2)\cos^2(2\omega)e_\sigma + 4[\sin(2\omega)\sin(\alpha/2)\cos(\psi) + {}^1\!/_2\cos(2\omega)\sin(\alpha)\sin(\psi)]^2 e_{\pi s}\\ & + 4[\sin(2\omega)\sin(\alpha/2)\sin(\psi) - {}^1\!/_2\cos(2\omega)\sin(\alpha)\cos(\psi)]^2 e_{\pi c}\end{aligned} \tag{A.1.1}$$

$$(z^2|A(D_2)|z^2) = (3\cos^2(\alpha/2) - 1)^2 e_\sigma + 3\sin^2(\alpha)\sin^2(\psi)e_{\pi s} + 3\sin^2(\alpha)\cos^2(\psi)e_{\pi c} \tag{A.1.2}$$

$$\begin{aligned}(xy|A(D_2)|xy) = {}& 3\sin^4(\alpha/2)\sin^2(2\omega)e_\sigma + 4[\cos(2\omega)\sin(\alpha/2)\cos(\psi) - {}^1\!/_2\sin(2\omega)\sin(\alpha)\sin(\psi)]^2 e_{\pi s}\\ & + 4[\cos(2\omega)\sin(\alpha/2)\sin(\psi) + {}^1\!/_2\sin(2\omega)\sin(\alpha)\cos(\psi)]^2 e_{\pi c}\end{aligned} \tag{A.1.3}$$

$$\begin{aligned}(xz|A(D_2)|xz) = {}& 3\sin^2(\omega)\sin^2(\alpha)e_\sigma + 4[\cos(\omega)\cos(\alpha/2)\cos(\psi) + \sin(\omega)\cos(\alpha)\sin(\psi)]^2 e_{\pi s}\\ & + 4[\cos(\omega)\cos(\alpha/2)\sin(\psi) + \sin(\omega)\cos(\alpha)\cos(\psi)]^2 e_{\pi c}\end{aligned} \tag{A.1.4}$$

$$\begin{aligned}(yz|A(D_2)|yz) = {}& 3\cos^2(\omega)\sin^2(\alpha)e_\sigma + 4[\sin(\omega)\cos(\alpha/2)\cos(\psi) + \cos(\omega)\cos(\alpha)\sin(\psi)]^2 e_{\pi s}\\ & + 4[\sin(\omega)\cos(\alpha/2)\sin(\psi) - \cos(\omega)\cos(\alpha)\cos(\psi)]^2 e_{\pi c}\end{aligned} \tag{A.1.5}$$

$$\begin{aligned}(z^2|A(D_2)|x^2-y^2) = {}& -\sqrt{3}\cos(2\omega)\sin^2(\alpha/2)(3\cos^2(\alpha/2) - 1)e_\sigma + 2\sqrt{3}\sin(\alpha)\sin(\psi)[\sin(2\omega)\sin(\alpha/2)\cos(\psi)\\ & + {}^1\!/_2\cos(2\omega)\sin(\alpha)\sin(\psi)]e_{\pi s} - 2\sqrt{3}\sin(\alpha)\cos(\psi)[\sin(2\omega)\sin(\alpha/2)\sin(\psi)\\ & - {}^1\!/_2\cos(2\omega)\sin(\alpha)\cos(\psi)]e_{\pi c}\end{aligned} \tag{A.1.6}$$

Appendix 2

Corrections $\Delta E''$ to the d-AO Energies in D_2 Due to s–d and p–d Interactions ($\psi = 0$)

The following corrections should be added to the d-orbital energies in D_2 symmetry so as to account for the s–d and p–d mixing:

$$\Delta E''(z^2) = -e_{\mathrm{sd}}(1 + 3\cos(\alpha))^2 \tag{A.2.1}$$

$$\Delta E''(x^2 - y^2) = -12 e_{\mathrm{sd}} \sin^4(\alpha/2)\cos^2(2\omega) \tag{A.2.2}$$

$$\Delta E''(xy) = -(\sqrt{3} e_{\mathrm{pd}\sigma}{}^{1/2} - 2 e_{\mathrm{pd}\pi\mathrm{c}}{}^{1/2})^2 \sin^2(\alpha)\sin^2(\alpha/2)\sin^2(2\omega) \tag{A.2.3}$$

$$\Delta E''(yz) = \Delta E''(xz) = -(\sqrt{3}\sin(\alpha)\sin(\alpha/2) e_{\mathrm{pd}\sigma}{}^{1/2} + 2\cos(\alpha)\cos(\alpha/2) e_{\mathrm{pd}\pi\mathrm{c}}{}^{1/2} - 2\cos(\alpha/2) e_{\mathrm{pd}\pi\mathrm{s}}{}^{1/2})^2 \sin^2(2\omega) \tag{A.2.4}$$

In eqns. (A.2.1)–(A.2.4) we have used the notations [28]:

$$e_{\mathrm{sd}} = (h_{\mathrm{sd}}{}^2)/(\Delta E_{\mathrm{sd}}) \tag{A.2.5}$$

$$e_{\mathrm{pd}\lambda\omega} = (h_{\mathrm{pd}\lambda\omega}{}^2)/(\Delta E_{\mathrm{pd}}), \quad (\lambda = \sigma, \pi \text{ and } \omega = \mathrm{c, s}) \tag{A.2.6}$$

where ΔE_{sd} and ΔE_{pd} are the s–d and p–d energy differences, respectively.