The Single-crystal Electronic and Electron Spin Resonance Spectra of Bis-(*N*-n-propylsalicylaldiminato)copper(II)

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The polarised single-crystal electronic and e.s.r. spectra of bis-(*N*-n-propylsalicylaldiminato)copper(II) have been recorded. The correlation of the single-crystal *g*-values and the crystallographic data suggests an approximate $d_{x^2-y^2}$ ground state for the CuO_2N_2 chromophore. The electronic spectra have been assigned in D_{2h} effective symmetry and yield a tentative partial one-electron orbital sequence $d_{x^2-y^2} > d_{xz} > d_{yz} > d_{z^2}$ with the position of the d_{xy} orbital uncertain, but probably near to the d_{xz} and d_{yz} orbitals. The combined spin–orbit and orbital reduction parameters have been evaluated and suggest significant out-of-the-plane π-bonding and possibly some in-plane π-bonding. The results are compared with the published data on Cu(*N*-methylsalicylaldimine)$_2$ (the electronic spectra of which are reassigned with a $d_{x^2-y^2}$ ground state) and with the less certain data on Cu[(±)-*NN*-diethyl-α-alanine]$_2$.

THERE have probably been more papers published on the interpretation of the polarised single-crystal spectra of bis(chelate)copper(II) complexes[1,2] than for any other type of ligand. When the ligand involves purely σ-bonding donor atoms, such as nitrogen in ethylenediamine,[3] the in-plane optical and *g*-tensor axes coincide

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with the copper–ligand directions. When the donor atoms have a π-bonding potential, such as the oxygen in acetylacetone, the in-plane optical and g-tensor axes coincide with the bisectors of the copper–ligand directions.[1,4] However when the ligand atoms are mixed, such as oxygen and nitrogen in the salicylaldimines, and still have a π-bonding potential, then the positions of the optical and g-tensor axes are not so certain.[1,5] The polarised single-crystal electronic spectra of bis(salicylaldiminato)copper(II) {Cu(salim)$_2$},[6] bis-(*N*-methylsalicylaldiminato)copper(II) {Cu(*N*-Mesalim)$_2$},[6] and bis-(*N*-n-propylsalicylaldiminato)copper(II) {Cu(*N*-n-prsalim)$_2$}[7] have been reported. The crystal structures[8,9] of the first two are not ideal for single-crystal measurements and the spectra of the latter complex[7] were recorded and interpreted without a knowledge of the crystal structure. These assignments of the electronic spectra have all assumed a d_{xy} ground state. Recent papers[5,10] on the e.s.r. of the copper(II) ion diluted in various nickel(II) and palladium(II) *N*-substituted salicylaldimine complexes as host lattices have classified the different types of square-coplanar copper(II) chromophore CuO_4, CuN_4, and CuO_2N_4 (involving chelate ligands) according to the local molecular symmetry present. Class I complexes have C_s or C_{2h} approximate symmetry which allow mixing of the $d_{x^2-y^2}$, the d_{xy}, and the d_{z^2} orbitals and the directions of the copper–ligand bonds, the g tensors, and the polarisation directions do not necessarily coincide. Such misalignment has been claimed for the copper(II) ion diluted[11] in Ni(*N*-Mesalim)$_2$, but has not been demonstrated for a magnetically nondilute copper(II) complex. In the diluted Cu(*N*-Mesalim)$_2$ the $g_\perp$ axes are close to the copper–ligand directions ($<15°$), as they are also in Cu(en)$_2$X$_2$ systems.[3] Under these conditions the g-values can be interpreted[10] to a good approximation in D_{2h} symmetry appropriate to Class IIa complexes. Class II complexes have D_{2h} or C_{2v} approximate symmetry and have the principal g directions along the axes defined by symmetry. If the x- and y-axes lie along the copper–ligand directions (Class IIa; $d_{x^2-y^2}$ ground state) only the mixing of the $d_{x^2-y^2}$ and d_{z^2} orbitals can occur by symmetry as in Cu(en)$_2$X$_2$ systems. When the x- and y-axes lie between the copper–ligand directions (Class IIb; d_{xy} ground state) no mixing into the ground state can occur by symmetry, as in Cu(3-Meacac)$_2$[4] and Cu(salim)$_2$.[5] In both Class IIa and IIb complexes the $g_\perp$ anisotropy will be small; in Class IIb it is a function of the separation of the $d_{xz} \longrightarrow d_{xy}$ and $d_{yz} \longrightarrow d_{xy}$ transitions; in Class IIa complexes it is a function of the mixing in of the d_{z^2} orbital into the ground state.

The crystal structure of Cu(*N*-n-propylsalim)$_2$ has recently been reported[12] and with only one molecule in the unit cell is ideal for the measurement of the single-crystal electronic properties.[2] In view of the uncertainties in the published data on this complex the electronic properties have been re-examined in the hope of finding a clear example of Class I behaviour for an undiluted copper(II) complex. These data are now reported and the original data on Cu(*N*-Mesalim)$_2$ re-evaluated and compared with the partial data reported for Cu[($\pm$)-*NN*-diethyl-α-alanine]$_2$ {Cu(Et$_2$-α-Al)$_2$}.

EXPERIMENTAL

Preparation.—Cu(*N*-n-prsalim)$_2$,[7] Cu(*N*-Mesalim)$_2$,[6] and Cu(Et$_2$-α-Al)$_2$[13] were prepared as previously reported; single crystals of these complexes were prepared by slow evaporation of solutions in acetone, chloroform, and dichloroethane, respectively.

Physical Methods.—The electronic and e.s.r. spectra were measured as previously described.[2,14] The crystal morphology was determined by the *X*-ray precession technique.[15] Difficulty was experienced in obtaining the morphology[13] of the crystals of Cu(Et$_2$-α-Al)$_2$.

Crystallographic Data.—Cu(*N*-n-prsalim)$_2$ is triclinic[12] (space-group $P\bar{1}$) with $a = 7.46$, $b = 9.46$, $c = 6.70$ Å, $\alpha = 96°$, $\beta = 85°$, $\gamma = 75° 40'$, and $Z = 1$. The copper(II) ion is situated on a crystallographic centre of symmetry which requires the CuO$_2$N$_2$ chromophore to be planar. The molecule [Figure 1(a)] is not strictly square coplanar as the O(1)–Cu–N(1) angle is 93°. The co-ordination is made up by *trans*-oxygen atoms at 1·86 Å and *trans*-nitrogen atoms at 1·99 Å; the nearest axial approaches are by benzene carbon atoms from neighbouring molecules at 3·15 Å. Cu(*N*-n-prsalim)$_2$ crystallises as dark brown needles elongated along the crystallographic c-axis with the [010], [100], and [001] faces well developed (Figure 1(b)]. The [101] and [110] faces were also developed.

Cu(n-Mesalim)$_2$ is orthorhombic[9] (space-group *Ibam*) with $a = 24.71$; $b = 9.25$; $c = 6.66$ Å, and $Z = 4$. The CuO$_2$N$_2$ chromophore is planar and centrosymmetric, Cu–O = 1·901 Å and Cu–N = 1·989 Å. The four molecules in the unit cell are misaligned about the z-axis with $2\alpha = 70°$. Crystals were obtained as thin needles elongated along the b-axis with the [100] face most pronounced. Cu(Et$_2$-α-Al)$_2$ is triclinic[13] (space-group $P\bar{1}$) with $a = 9.684$, $b = 7.495$, $c = 8.101$ Å, $\alpha = 100.57°$, $\beta = 106.85°$ $\gamma = 124.01°$, and $Z = 1$. The CuO$_2$N$_2$ chromophore is planar and centrosymmetric; the molecular structure is shown in Figure 2(a). Co-ordination along the axial directions is prevented by the conformation of the two ethyl groups and the next-nearest neighbours are carbon atoms at 3·12 Å off the z-axis. Cu(Et$_2$-α-Al)$_2$ crystallises as very small dark

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[4] See, *e.g.*, (*a*) J. Ferguson, *J. Chem. Phys.*, 1961, **34**, 1609; (*b*) R. L. Belford and J. W. Carmichael, *J. Chem. Phys.*, 1967, **46**, 4515; (*c*) B. J. Hathaway, D. E. Billing, and R. J. Dudley, *J. Chem. Soc.* (*A*), 1970, 1420.

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red diamond plates with the crystal morphology of Figure 2(b) (but see above).

As the experimental data for these three complexes are not reported or interpreted in the same detail, they will each be reported and discussed separately.

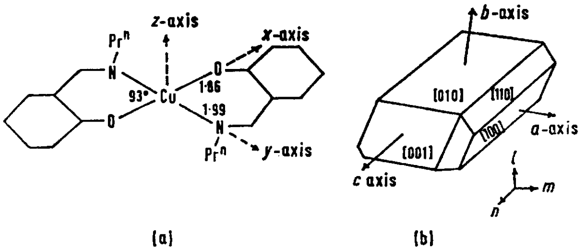

FIGURE 1 Cu(N-n-prsalim)$_2$: (a) molecular structure; and (b) crystal morphology

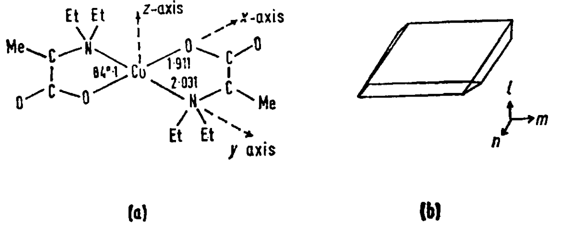

FIGURE 2 Cu(Et$_2$-α-Al)$_2$: (a) molecular structure; and (b) crystal morphology (see text)

RESULTS AND DISCUSSION

Cu(N-n-prsalim)$_2$.—*E.s.r. spectra.* The single-crystal e.s.r. spectra yielded three crysyal g-values which are given in Table 1 along with their direction cosines relative to the [010] face. As there is only one molecule in the unit cell[12] the crystal g-values correspond to the molecular g-values.

TABLE 1

Cu(N-n-prsalim)$_2$: direction cosines of A, single-crystal g-values and B, copper–ligand directions

A	g_3 (2·2254)	g_2 (2·0648)	g_1 (2·0425)
l	0·40219	0·53940	−0·73979
m	−0·69431	0·70640	0·13759
n	0·59681	0·45831	0·65861
B	Cu(1)–ON	Cu–N	Cu–O
l	0·39595	0·42326	−0·83586
m	−0·72968	0·68378	−0·03503
n	0·55747	0·59437	0·54781

$l \equiv$ Perpendicular to ac, $m \equiv$ perpendicular to c in ac, $n \equiv c$.

Electronic spectra. The electronic reflectance spectrum of Cu(N-n-prsalim)$_2$ consists of a single broad flat-topped band at 15·2—16·7 kK, which is only just resolved from the tail of a much more intense band at higher energy which is probably charge transfer in origin.

The polarised single-crystal spectra were determined in all the developed crystal faces. All spectra were recorded parallel to the extinction directions which were found to be consistent with the g-value directions. The x-, y-, and z-polarised spectra (Figure 3) were obtained by analysis of the crystal spectra in the [010], [001], and [100] faces. The x-polarised spectrum contains a single band maximum at 14·8 kK, the y-polarised spectrum a single band maximum at 16·4 kK, and the z-polarised spectrum which was extremely weak showed evidence of two bands, one at *ca.* 15·0 kK, the other at 19·5 kK. Both the x- and y-polarised spectra had indications of shoulders at 19·0—20·0 kK on the intense high-energy band. No evidence for a second high-energy band at 22·0 kK (as previously reported[7]) was found.

E.s.r. Spectra.—The three molecular g-values obtained for Cu(N-n-prsalim)$_2$ (Table 1) are comparable with those previously reported[7] ($g_3 = 2{\cdot}225$, $g_2 = 2{\cdot}064$, and $g_1 = 2{\cdot}038$). If the direction cosines of the molecular g-values are compared with the direction cosines of the ligand directions (Table 1) it can be seen that there is a good correlation between the direction of the highest g-value and the perpendicular to the co-ordination plane as would be expected for an elongated copper(II) stereochemistry. The correlation between the directions of the two lower g-values and the in-plane ligand directions, however, is not as close. It is found that g_1 makes an angle of 13° with the Cu–O direction and g_2 an angle of 10° with the Cu–N direction, the 3° discrepancy being caused by the 93° internal angle of the N-n-prsalim ligand [Figure 1(a)] and the position of g_1 inside this angle. This apparent rotation of the g-values by 10°, to positions intermediate to either the bond directions or the bisectors of the bond angles, can be explained either as experimental error, since even g_3 deviates by 3° from the perpendicular (Table 1), or as a true rotation as has been predicted[10] for these types of complex (Class I behaviour). If it was experimental error causing the apparent rotation then the correlation of g-value directions with in-plane ligand directions would indicate a $d_{x^2-y^2}$ ground state and not a d_{xy} ground state as has usually been assumed for this type of complex.[4,5] If the rotation was a true rotation and not experimental error then it is not easy to define the directions of the x- and y-axes and Cu(N-n-propylsalim)$_2$ must be considered as a Class I type complex (see ref. 5), but as the misalignment is less than *ca.* 15°, to a reasonable approximation it may be considered[10] as a Class IIa type complex

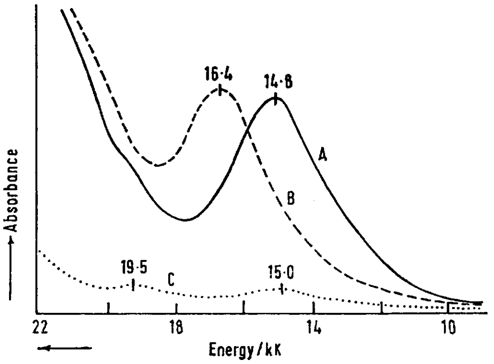

FIGURE 3 The polarised single-crystal electronic spectra of Cu(N-n-propylsalim)$_2$; A, x-polarised; B, y-polarised; C, z-polarised

(symmetry C_{2h}) with the x- and y-axes along the copper–ligand directions and a $d_{x^2-y^2}$ ground state (as above) (but see ref. 16).

Effective Symmetry.—The crystallographic site symmetry [12] of Cu(N-n-prsalim)$_2$ is C_i. As this point-group symmetry would allow no polarisation to occur in the electronic spectra, it is inconsistent with the observed spectra (Figure 3) and suggests that the 'effective' ligand-field symmetry is higher. Because of the crystallographically imposed centre of symmetry and the rhombic g-values observed the effective symmetry is restricted to either D_{2h} or C_{2h}. In D_{2h} symmetry x, y, and z all transform as different representations, therefore markedly different spectra would be expected in the three polarisations (*cf.* Figure 3), but in C_{2h} x and y transform as the same representation and therefore the spectra in these two polarisations should only differ in intensity which does not appear to be the case with the present complex. However, if the rotation of the g-values is real (see e.s.r. spectra) then the symmetry of the molecule must strictly be treated as C_{2h} symmetry with the position of the x- and y-axes not defined; nevertheless as the rotational discrepancy is small (10°) an effective symmetry of D_{2h} is most appropriate. For this reason the assignment of the electronic spectra will be restricted to an effective symmetry of D_{2h} with a $d_{x^2-y^2}$ ground state.

Assignment of the Electronic Spectra.—The vibronic selection rules for a copper(II) ion in D_{2h} symmetry with a $d_{x^2-y^2}$ ground state have been given.[2,17] The b_{1u} out-of-plane bending mode of vibration, in this point-group, has been found to be responsible for the bulk of intensity in the spectra of the Cu(NH$_3$)$_4$X$_2$ [18] and Cu(en)$_2$X$_2$ [3] complexes. Thus the $d_{xz} \longrightarrow d_{x^2-y^2}$, $d_{yz} \longrightarrow d_{x^2-y^2}$, and $d_{z^2} \longrightarrow d_{x^2-y^2}$ transitions would be expected to be observed in x-, y-, and z-polarisations respectively. The $d_{xy} \longrightarrow d_{x^2-y^2}$ transition would only be observed if other modes of vibration were active. The band at 14·8 kK in the x-polarised spectrum is therefore assigned as the $d_{xz} \longrightarrow d_{x^2-y^2}$ transition and the 16·4 kK band in the y-polarised spectrum as the $d_{yz} \longrightarrow d_{x^2-y^2}$ transition. The z-polarised spectrum is very weak with bands at *ca.* 15·0 and 19·5 kK, either of which may be assigned as the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition. It has been suggested,[2,19,20] after a study of CuO$_{6-4}$ chromophores, that there is a correlation between the energy of the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition and the axial bond length; the longer the bond the higher the energy of this transition. Thus it has been suggested that the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition should be the highest-energy transition in square-planar copper(II) complexes, this being shown to be the case [19] in Egyptian Blue (CaCuSi$_4$O$_{10}$) where the highest energy band at 18·8 kK was assigned to this transition, and also [4a] in Cu(3-Meacac)$_2$, where the transition was placed at 19·2 kK. The molecular structure of Cu(N-n-prsalim)$_2$ is approximately square planar [Figure 1(a)] and this suggests that of the two bands in z-polarisation, the band at 19·5 kK should be assigned to the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition. The band at *ca.* 15·0 kK in z-polarisation is then assigned as the $d_{xz} \longrightarrow d_{x^2-y^2}$ and $d_{yz} \longrightarrow d_{x^2-y^2}$ transitions occurring with weak vibronic intensity *via* the b_{2u} and b_{3u} modes of vibration as the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition is strictly forbidden in this polarisation owing to the absence of an a_u mode of vibration [4] in a square-planar system with a $d_{x^2-y^2}$ ground state. This partial activity of the b_{2u} and b_{3u} modes of vibration could explain the appearance of a shoulder at *ca.* 19·0—20·0 kK in the x- and y-polarised spectra as vibronic intensity of the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition. This assignment would yield the partial one-electron orbital sequence: $d_{x^2-y^2} > d_{xz} > d_{yz} > d_{z^2}$, with the position of d_{xy} uncertain, but probably close to d_{xz} and d_{yz} (Table 2).

TABLE 2

The electronic energy levels (kK) and combined spin–orbit and orbital reduction factors for Cu(N-n-prsalim)$_2$, Cu(N-Mesalim)$_2$, and Cu(Et$_2$-α-Al), in D$_{2h}$ symmetry with a $d_{x^2-y^2}$ ground state

	Cu(N-n-prsalim)$_2$	Cu(N-Mesalim)$_2$	Cu(Et$_2$-α-Al)$_2$
$d_{z^2} \longrightarrow d_{x^2-{}^2y}$	19·5	20·7	20·7
$d_{xy} \longrightarrow d_{x^2-y^2}$	14·0—17·0 *	14·0—17·0 *	17·0—21·0 *
$d_{xz} \longrightarrow d_{x^2-y^2}$	14·8	15·2	17·4
$d_{yz} \longrightarrow d_{x^2-y^2}$	16·4	17·0	20·8
$r_{\parallel}$	0·69—0·76 †	0·67—0·74 †	0·71—0·79 †
$r_{\perp}$	0·71	0·71	0·71

* Not observed experimentally. † The above range of values being assumed for the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition.

Orbital Reduction Parameters.—By combining the molecular g-values (Table 1) with the electronic energy levels (Table 2) in the appropriate g-value expressions the combined spin–orbit and orbital reduction parameters,[2] r, can be obtained, with the approximation $r_x \approx r_y = r_{\perp}$. The values obtained are in Table 2, and are comparable with, but slightly lower than, the r-values found for other axial complexes of the copper(II) ion. If these r-values are related to the appropriate molecular orbital coefficients [2] they suggest that as $r_{\perp}$ is relatively low there is significant out-of-plane π-bonding, and depending on the value taken for $r_{\parallel}$, there is either no in-plane π-bonding ($r_{\parallel} = 0·76$) or there is significant in-plane π-bonding ($r_{\parallel} = 0·69$). This situation is comparable with that found for other planar bis(chelate)copper(II) complexes involving potentially π-bonding ligands [2,4] in which only out-of-plane π-bonding is present.

Correlation of the Electronic and Structural Data.—Both the oxygen and nitrogen atoms of the ligands in Cu(N-n-prsalim)$_2$ have clear out-of-the-plane π-bonding

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[20] D. E. Billing, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc.* (*A*), 1970, 1877; R. J. Dudley, B. J. Hathaway, and P. G. Hodgson, *J. Chem. Soc.* (*A*), 1971, 3355.

potential, but only the oxygen atom has in-plane π-bonding potential. This difference is reflected in the copper–ligand bond lengths [Figure 1(a)]; the copper–nitrogen bond length of 1·99 Å is comparable with that observed in other copper(II) complexes involving potentially π-bonding nitrogen ligands, namely 1·99 Å in Cu(α-pic)$_2$-(ClCH$_2$CO$_2$)$_2$[21] and 1·998 Å in Cu(hfacac)$_2$(bipy)[22] [where (α-pic) = α-picoline, (hfacac) = hexafluoroacetylacetone, and (bipy) = 2,2′-bipyridyl] but in which the *r*-values indicated *no* π-bonding of the nitrogen ligands. This suggests that the significant amount of out-of-plane π-bonding present is most probably associated with the oxygen ligand only. If the presence of π-bonding is reflected in the shortening of the copper–oxygen bond, the extremely short Cu–O bond length of 1·86 Å [the shortest observed in any Cu–O bond,[2] even that in Cu(3-Meacac)$_2$,[23] is 1·91 Å] supports the suggestion of significant π-bonding to the oxygen ligand. This preferential π-bonding to the oxygen ligand is reflected in the destabilisation of the d_{xz} orbital relative to that of the d_{yz} orbital and hence the lower energy of the $d_{xz} \longrightarrow d_{x^2-y^2}$ transition although π-bonding to the nitrogen is not ruled out.

It is unfortunate that the electronic spectra do not allow the energy of the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition to be evaluated as this leaves some uncertainty over the presence of in-plane π-bonding of the oxygen ligand. This oxygen atom has a lone pair of electrons (probably in an sp^2 hybridised orbital) which lies in the *xy*-plane and although this is orientated at *ca.* 120° to the Cu–O bond direction, the very short copper–oxygen bond length and the internal O–Cu–N bond angle[12] of 93° could both increase the possibility of some in-plane π-bonding to the d_{xy} orbital. Both these arguments suggest that the d_{xy} transition should have an energy in the lower range of that quoted in Table 1; the lower this energy the lower the value of $r_{\parallel}$ and the greater the extent of in-plane π-bonding. If the energy of the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition were as high as 16—17·0 kK this would place the d_{xy} orbital below the d_{xz} and d_{yz} orbitals, a result which would conflict with past experience,[2] unless appreciable π-bonding occurred to both the d_{xz} and d_{yz} orbitals.

Cu(*N*-Mesalim)$_2$.—The difference in the Cu–O and Cu–N bond lengths as in Cu(*N*-n-prsalim)$_2$ is also observed in Cu(*N*-Mesalim)$_2$;[9] Cu–O = 1·901 Å and Cu–N = 1·989 Å. The single-crystal *g*-values of Cu(*N*-Mesalim)$_2$ have been measured and are $g_a = 2{\cdot}0521$, $g_b = 2{\cdot}2119$, and $g_c = 2{\cdot}0511$. The polarised single-crystal electronic spectra are shown in Figure 4 and are better resolved than the data obtained previously.[6] As the four molecules in the unit cells are misaligned (2α = 70°) these crystal properties do not equate directly with the local molecular properties. Owing to this misalignment it is not possible to determine unambiguously the electronic axes in the complex, namely d_{xy} with the in-plane axes between the ligands or $d_{x^2-y^2}$ with the axes along the bonds [as in Cu(*N*-n-prsalim)$_2$]. The former ground state was assumed, reasonably, in the original assignment[6] of the electronic spectra in D_{2h} symmetry and yielded the one-electron orbital sequence $d_{xy} > d_{x^2-y^2} \approx d_{z^2} > d_{xz} \approx d_{yz}$. This choice of axes also yields only a small rhombic component in the in-plane local molecular *g*-values ($g_x = 2{\cdot}0511$, $g_y = 2{\cdot}0521$, and $g_z = 2{\cdot}2119$). The alternative ground state of $d_{x^2-y^2}$ is suggested by the similarity in stereochemistry of Cu(*N*-Mesalim)$_2$[9] and Cu(*N*-n-prsalim)$_2$[12] particularly the anisotropy in the in-plane bond lengths compared with their virtual equivalence in Cu(salim)$_2$[8] [Cu–O = 1·91 Å and Cu–N = 1·90 Å] and for which the electronic properties are consistent with a d_{xy} ground state as in Cu(3-Meacac)$_2$.[4c] In addition the single-crystal *g*-values for Cu(*N*-Mesalim)$_2$ diluted[10] in Ni(*N*-Mesalim)$_2$ ($g_x = 2{\cdot}0386$, $g_y = 2{\cdot}0561$, and $g_z = 2{\cdot}2157$) also support a $d_{x^2-y^2}$ ground state as the in-plane *g*-values correspond with the bond directions, rather than their bisectors. If a $d_{x^2-y^2}$ ground state is assumed, the local molecular *g*-values[2] are $g_x = 2{\cdot}0500$, $g_y = 2{\cdot}0530$, and $g_z = 2{\cdot}2119$. The misalignment of the local molecular axes being taken into account, the spectra of Figures 3 and 4 are comparable and that of Cu(*N*-Mesalim)$_2$ can be assigned in an analogous way to that of Cu(*N*-n-prsalim)$_2$, yielding the assignment and corresponding *r*-values listed in Table 2. The similarity of the two sets of data strongly supports the equivalent assignments of these two complexes and substantiates the alternative assignment of Cu(*N*-Mesalim)$_2$ with a $d_{x^2-y^2}$ ground state.

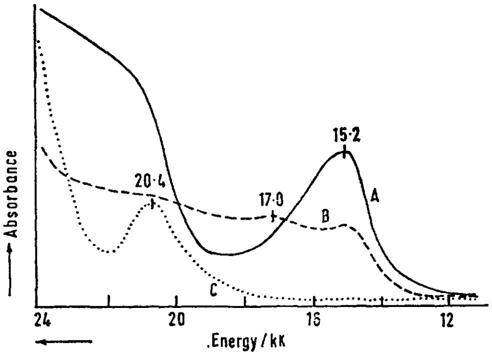

FIGURE 4 The polarised single-crystal electronic spectra of Cu(*N*-Mesalim)$_2$; A, parallel to *b*-axis; B, parallel to *a*-axis; *C*, parallel to *c*-axis

There is no reason for assigning the electronic spectrum of Cu(salim)$_2$ other than with a d_{xy} ground state.[5] The polarised single-crystal spectra of this complex have been reproduced, but the gross misalignment present rules out any definite assignment.

Cu(Et$_2$-α-Al)$_2$.—The single-crystal *g*-values along with their direction cosines using the axes defined in Figure

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2(b) are given in Table 3. Owing to the uncertainty in determining the crystal morphology[14] of this complex it is not possible to assign a definite ground state but the comparability of its molecular structure and that of Cu(*N*-n-propylsalim)$_2$ suggests that it is reasonable to assume a $d_{x^2-y^2}$ ground state, but in view of this the data for this complex are not as reliable as that for Cu(*N*-n-propylsalim)$_2$. The polarised single-crystal spectra (Figure 5) could only be measured in the main face of the crystal. The 0° spectrum is mainly *z*-polarised and tilting failed to improve the spectrum. The 90° spectrum is mainly *y*- and *x*-polarised and tilting in the *xy*-plane enhanced the intensity of the band at 17·3 kK relative to that at 20·8 kK suggesting that the latter is mainly *y*-polarised and the former *x*-polarised. The clear rhombic *g*-values of Table 3 and the similarity of the spectra of Cu(Et$_2$-α-Al)$_2$ and Cu(*N*-n-prsalim)$_2$ suggest the assignment of the former in D_{2h} symmetry with a $d_{x^2-y^2}$ ground state, as in Table 2. There is then a clear similarity in the assignment of the spectra of all three complexes and in the *r*-values present. In all three complexes the energy of the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition is *ca.* 20·0 kK reflecting the high tetragonal distortion present in these coplanar complexes. The low values of $r_{\perp}$ suggests comparable out-of-plane π-bonding and although the range of values quoted for $r_{\parallel}$ does not rule out in-plane π-bonding this is least likely for Cu(Et$_2$-α-Al)$_2$. The comparability of the out-of-plane π-bonding in these three complexes is of interest as it can only arise from the oxygen ligand in Cu(Et$_2$-α-Al)$_2$ as the nitrogen ligand is a tertiary nitrogen atom and can only be involved in σ-bonding to the copper(II) ion. The relatively long Cu–N of 2·03 Å could reflect this absence of π-bonding and is consistent with the high energy of the $d_{xz} \longrightarrow d_{x^2-y^2}$ transition at 20·8 kK. This transition is significantly higher (*ca.* 4·0 kK) than the corresponding transition in Cu(*N*-n-prsalim)$_2$ and Cu(*N*-Mesalim)$_2$ and supports at least the partial involvement of these salim nitrogens in out-of-plane π-bonding. The high energy of the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition is also consistent with the high energy of this transition in the effectively square-coplanar CuN$_4$ chromophore in Na$_4$Cu(NH$_3$)$_4${Cu(S$_2$O$_3$)$_2$}$_2$,H$_2$O[24] which involves in-plane σ-bonding ligands only. If there is any inconsistency it is in the Cu–N bond length of 2·03 Å in Cu(Et$_2$-α-Al)$_2$; this is a relatively long copper–nitrogen bond. For a σ-bonding nitrogen in a square planar stereochemistry a value of 1·98 Å, as found in bis-(1-aminocyclopentanecarboxylato)copper(II)[25] would be expected. Here also a planar stereochemistry is present which is reflected in the high energy of the reflectance spectrum (maximum 19·6 kK; shoulder 17·0 kK); values which are closely comparable with the spectra of Cu(Et$_2$-α-Al)$_2$ (Figure 5). A comparable bond length of 2·03 Å has been observed in {Cu$_2$(OH)$_2$(tmen)$_2$}Br$_2$[26] [where (tmen) = tetramethylethylenediamine] but as this complex is dinuclear the comparison may not be valid. The difference in energy of the $d_{xz} \longrightarrow d_{x^2-y^2}$ and $d_{yz} \longrightarrow d_{x^2-y^2}$ transitions in Cu(Et$_2$-α-Al)$_2$ of 3·4 kK also reflects the significant out-of-plane π-bonding of the oxygen ligand to the copper(II) ion as reflected in the short Cu–O bond length of 1·91 Å although some of this difference may arise from a difference in a purely σ-bonding effect of the non-equivalent ligands present.

TABLE 3

Cu(Et$_2$-α-Al)$_2$: direction cosines of the single-crystal *g*-values

	g_3 (2·1967)	g_2 (2·0507)	g_1 (2·0390)
l	0·1653	−0·8715	0·4616
m	0·8163	0·3836	0·4320
n	0·5536	−0·3054	−0·7748

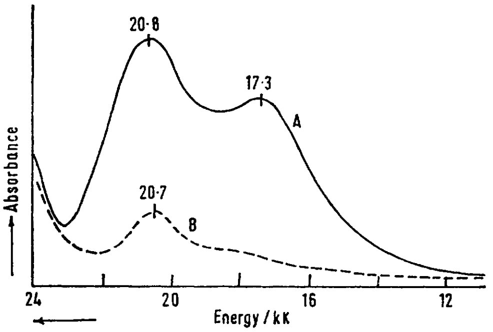

FIGURE 5 The polarised single-crystal electronic spectra of Cu(Et$_2$-α-Al)$_2$; A, 90°; B, 0°

Conclusion.—The results for these rhombic coplanar CuO$_2$N$_2$ chromophores indicate that the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition is at highest energy *ca.* 20·0 kK, consistent with the high tetragonal distortion present. The effect of strong out-of-plane π-bonding to the oxygen ligand is to lower the energy of the $d_{xz} \longrightarrow d_{x^2-y^2}$ transition relative to that of the $d_{yz} \longrightarrow d_{x^2-y^2}$ transition, this difference is *ca.* 4·0 kK when the nitrogen ligand is purely σ bonding but is *ca.* 2·0 kK when the nitrogen is involved in weak π bonding. In the latter case the energies of the $d_{yz} \longrightarrow d_{x^2-y^2}$ and $d_{xy} \longrightarrow d_{x^2-y^2}$ transitions coincide but in the former the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition is *ca.* 2·0 kK lower in energy than the $d_{yz} \longrightarrow d_{x^2-y^2}$ transition.

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