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Single-Crystal Electronic and Electron Spin Resonance Spectra of Three Tris-Chelate Copper(II) Complexes

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The single-crystal polarized electronic and esr spectra of monoprotonated 1,8-bis(dimethylamino)naphthalenetris(hexafluoroacetylacetonato)copper(II), tris(2,2′-bipyridyl)copper(II) perchlorate, and tris(1,10-phenanthroline)copper(II) perchlorate are reported. The single-crystal g factors of $Cu(bipy)_3(ClO_4)_2$ are shown to correlate with the tetragonal elongated copper–nitrogen directions rather than with the approximate trigonal D_3 axis. The in-plane g factors correlate with a d_{xy} rather than a $d_{x^2-y^2}$ ground state for the copper(II) ion in this CuN_6 chromophore. The measurement of the polarized single-crystal electronic spectra of the two complexes with monoclinic cyrstals showed clear evidence for misalignment of the extinction and g factor directions in the *ac* planes. The reasons for this are discussed and the electronic spectra assigned (by associating a given spectrum with the nearest g factor) in an effective symmetry of D_2 and yield a one-electron orbital sequence: $d_{xy} > d_{z^2} > d_{x^2-y^2} \approx d_{xz} \approx d_{yz}$. The implication of these results with respect to the operation of the dynamic Jahn–Teller distortion in tris-chelate copper(II) complexes is discussed.

The electronic properties of tris-chelate transition metal complexes have received a great deal of attention in the literature.[1] In general these properties have been interpreted in D_3 symmetry with minor perturbations to lower symmetry crystal fields. In the case of tris-chelate copper(II) complexes with three equivalent ligands, X-ray structure determinations[2,3] have indicated the presence of regular CuN_6 or CuO_6 chromophores which are not obviously reconciled with the lack of spherical symmetry[4] associated with the d^9 configuration of the copper(II) ion. The electronic properties[5-12] of these complexes have been interpreted in terms of a dynamic Jahn-Teller[13] distortion of the local molecular chromophores operating in a high-symmetry crystal lattice. The precise form of this distortion has never been made clear[7] in the case of tris-chelate copper(II) complexes involving three equivalent ligands, except that it is likely to be of a form that is a subgroup of the D_3 point group, namely, C_2 (or ultimately C_1). It was recognized that the most likely form of the distortion consistent with C_2 symmetry was the elongated tetragonal distortion[6,7] of two trans pairs of ligands (Figure 1B) to produce the most common type of static stereochemistry of the copper(II) ion, namely, elongated rhombic or tetragonal octahedral. However, little mention was ever made[14] of the equally possible type of distortion consistent with a C_2 symmetry, that of cis-distorted octahedral for which two possible forms occur depending on whether the cis ligands involved belong to the same or different chelate ligands (Figure 1C(i) and C(ii), respectively). In tris-chelate copper(II) complexes with *nonequivalent ligands* the tetragonally distorted form is recognizable in the molecular structure[15] of (2,2′-bipyridyl)bis(hexafluoroacetylacetonato)copper(II) and the cis-distorted form[16] in bis(2,2′-bipyridyl)(nitrito)copper(II) nitrate (Figure 1C(i)). The electronic properties[14,17] of both of these forms have been described in detail and shown to correlate closely with the cartesian axes shown in Figure 1B and 1C(ii), respectively. What was not recognized at that time was that these cartesian axes do not correspond with the cartesian axes of a tris-chelate copper(II) complex involving strict D_3 symmetry (Figure 1A) but involve a rotation of the z and y axes about the x axis (C_2 axis) by 45°. This arises as it is impossible to impose a C_2 type distortion on a trigonal complex along its principal z axis, which will remove the degeneracy of the d^9 electron configuration of the copper(II) ion in this stereochemistry. It then becomes relevant to ask whether this rotation of axes will occur in statically distorted copper(II) complexes where *three equivalent chelate ligands* are involved. Recently the crystal structures of three complexes of the copper(II) ion involving three equivalent chelate ligands have been determined[18-20] and are shown in Figure 2. In all three complexes an elongated rhombic (or approximately tetragonal) octahedral CuL_6 chromophore is present and in each case the elongation is along two Cu–L bonds trans to each other. As the local molecular axes of $Cu(bipy)_3(ClO_4)_2$ are aligned parallel (space group $P\bar{1}$) and are only misaligned slightly in $\{C_{14}H_{19}N_2\}\{Cu(hfacac)_3\}$ and $Cu(phen)_3(ClO_4)_2$ (space groups $P2/n$ and $C2/c$, respectively), the single-crystal electronic properties of all three complexes have been examined (as described previously[4,21,22]) and are now reported.

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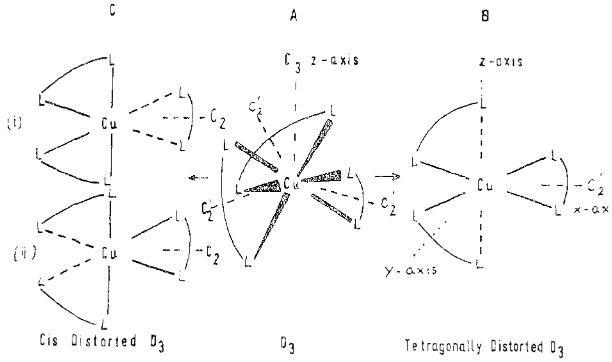

Figure 1. Molecular structures of tris-chelate copper(II) complexes: A, regular trigonal (D_3); B, cis-distorted D_3 (C_2); C, tetragonally distorted D_3 (C_2).

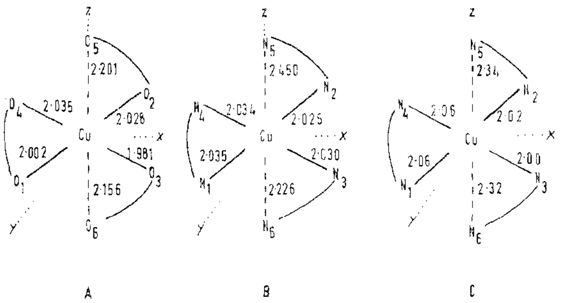

Figure 2. Molecular structures: A, monoprotonated 1,8-bis(dimethylamino)naphthalene tris(hexafluoroacetylacetonato)copper(II); B, tris(2,2′-bipyridyl)copper(II) diperchlorate; C, tris(1,10-phenanthroline)copper(II) diperchlorate (hereafter referred to as $\{C_{14}H_{19}N_2\}\{Cu(hfacac)_3\}$, $Cu(bipy)_3(ClO_4)_2$, and $Cu(phen)_3(ClO_4)_2$, respectively).

Experimental Section

Preparation. Crystals of $\{C_{14}H_{19}N_2\}\{Cu(hfacac)_3\}$ were initially provided by Professor M. R. Truter (University College, London) and then prepared as reported in the literature.[23] Crystals of $Cu(bipy)_3(ClO_4)_2$ and $Cu(phen)_3(ClO_4)_2$ were prepared[19,20] by the literature methods. All crystals were satisfactorily characterized by microanalysis (University College, Cork) and by X-ray crystallographic techniques.[22]

Results

Esr Spectra. The single-crystal esr spectra of all three complexes yielded three crystal *g* factors (Table I) with the spectra of $Cu(bipy)_3(ClO_4)_2$ and $Cu(phen)_3(ClO_4)_2$ yielding some evidence for copper nuclear hyperfine structure on the highest *g* factors only. In the case of $Cu(bipy)_3(ClO_4)_2$ the crystal *g* factors are equivalent to the local molecular *g* factors as the local CuN_6 chromophores of the two molecules in the triclinic unit cell[19] (space group $P\bar{1}$) are aligned parallel. The direction angles of the *g* factors and some relevant molecular directions in the CuN_6 chromophore of $Cu(bipy)_3(ClO_4)_2$ are listed in Table II. The *g* factors are clearly axial with $g_3 > (g_2 + g_1)/2$ consistent with either a $d_{x^2-y^2}$ or a d_{xy} ground state for the copper(II) ion. The direction of g_3 correlated reasonably well (10°) with the direction of the elongated Cu-N(5) and Cu-N(6) bond (taking into account the small angular distortions present due to the presence of chelate ligands) and *not* with the direction of the C_3 principal axis of the regular trigonal chromophore of D_3 symmetry (Figure 1A). The directions of the in-plane *g* factors are shown in Figure 3; they lie neither exactly along the copper-nitrogen directions nor exactly along their bisectors but are nearer to the latter (10 ± 5°) consistent with a predominantly d_{xy} ground state[4] (see electronic spectra). This is the first time that such a ground state has been so clearly demonstrated for a statically distorted tris-chelate copper(II) complex involving three equivalent chelate ligands and is consistent with the d_{xy} ground state found in $Cu(hfacac)_2\,bipy$[14] and in $Cu(hfacac)_2(py)_2$[24] in which nonequivalent ligands are present.

Table I. Single-Crystal *g* Factors of $\{C_{14}H_{19}N_2\}Cu(hfacac)_3$, $Cu(bipy)_3(ClO_4)_2$, and $Cu(phen)_3(ClO_4)_2$

	g_1	g_2	g_3
$\{C_{14}H_{19}N_2\}Cu(hfacac)_3$	2.1231	2.1623	2.3032
$Cu(bipy)_3(ClO_4)_2$	2.0521	2.0797	2.2495
$Cu(phen)_3(ClO_4)_2$	2.0754	2.0847	2.2414

Table II. Direction Angles (deg) of *g* Factors and Some Local Molecular Directions for $Cu(bipy)_3(ClO_4)_2$[a]

	a	*b′*	*c′*
g_1	23	83	68
g_2	−69	52	46
g_3	−82	−39	52
Cu-N(1)	81	50	41
Cu-N(2)	−78	−65	−28
Cu-N(3)	19	−71	−88
Cu-N(4)	−22	70	83
Cu-N(5)	87	43	−47
Cu-N(6)	−88	−38	52
Cu-C_2 (bisector of N(1)-Cu-N(3)	35	76	58
Cu-C_2' (bisector of N(1)-Cu-N(4)	−60	50	55
⊥ to CuN(1)N(3) plane	77	44	−49

[a] *c′* is perpendicular to *a* in the *ac* plane and *b′* is perpendicular *ac′*.

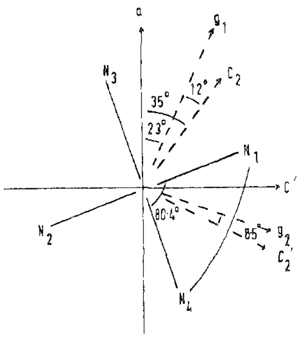

Figure 3. Orientation of the in-plane copper-nitrogen ligand directions and *g* factors in $Cu(bipy)_3(ClO_4)_2$.

In $\{C_{14}H_{19}N_2\}\{Cu(hfacac)_3\}$ and $Cu(phen)_3(ClO_4)_2$ the crystal *g* factors are not equivalent to the local molecular *g* factors as molecular misalignment is present.[18,20] In the former the four molecules in the unit cell give rise to two different orientations. The *z* axes of the two magnetically inequivalent pairs of molecules are misaligned when viewed down the *c* axis (2α = 19° 24′) but are mutually parallel and orientated at 3° to the *a* axis when viewed down the *b* axis. The *x* and *y* axes are also misaligned (2α = 21° 12′). In $Cu(phen)_3(ClO_4)_2$ the *z* molecular axes of symmetry-related pairs are virtually aligned (2α < 6°) but the *x* and *y* axes are misaligned (2α = 24°). In both complexes the misalignments present rule out the use of the direction angles of the crystal *g* factors to distinguish between the presence of a d_{xy} or $d_{x^2-y^2}$ electronic ground state for the copper(II) ion. Even if a d_{xy} ground state is assumed, it is then difficult to define the precise directions of the local molecular *x* and *y* axes in view of the angular distortions of the Cu-N bonds

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due to the effect of the chelate rings present and the absence of any strict symmetry at the copper(II) ions. If the x axis in $Cu(phen)_3(ClO_4)_2$ is *assumed to bisect* the N(1)-Cu-N(4) angle, then the local molecular g factors can be resolved as $g_z = 2.2414, g_y = 2.090$, and $g_x = 2.075$ and agree reasonably well with the molecular g factors for $Cu(bipy)_3(ClO_4)_2$. There is one significant difference between the in-plane g factors of these three complexes: in $\{C_{14}H_{19}N_2\}\{hfacac)_3Cu\}$ and $Cu(phen)_3(ClO_4)_2$ the lowest g factor (g_1) bisects the internal N(1)-Cu-N(4) chelate ligand angle (as in $Cu(hfacac)_2bipy$[14]) whereas in $Cu(bipy)_3(ClO_4)_2$ it is the intermediate g factor (g_2) which bisects this angle. The reason for this is not understood but may be due to the greater angular distortions[19] present in the CuN_6 chromophore of $Cu(bipy)_3(ClO_4)_2$ associated with the marked difference in the out-of-plane copper–nitrogen bond lengths compared with those in $Cu(phen)_3(ClO_4)_2$.[20]

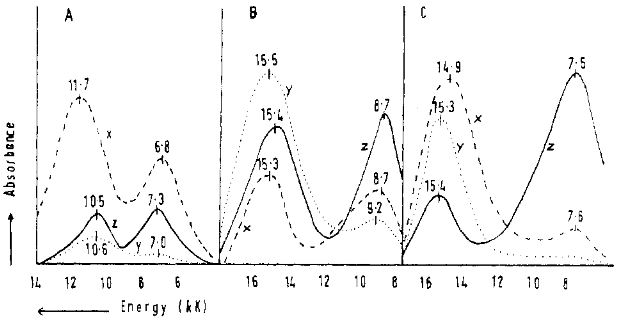

Figure 4. Room-temperature polarized single-crystal electronic spectra: A, $\{C_{14}H_{19}N_2\}\{Cu(hfacac)_3\}$; B, $Cu(bipy)_3(ClO_4)_2$; C, $Cu(phen)_3(ClO_4)_2$.

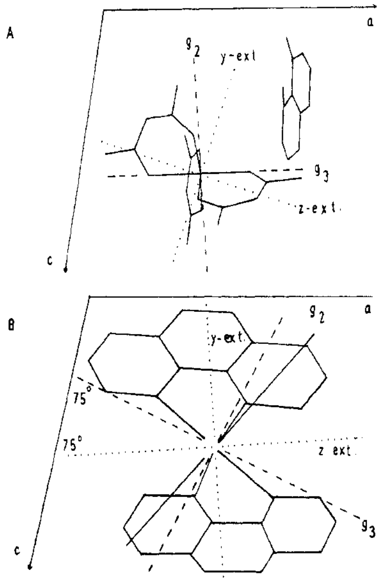

Figure 5. Projection down the b axes of the monoclinic unit cells of (A) $\{C_{14}H_{19}N_2\}\{Cu(hfacac)_3\}$ and (B) $Cu(phen)_3(ClO_4)_2$ showing the relative orientations of the g factors and the extinction directions of the electronic spectra in the ac planes.

Electronic Spectra. The spectra of all three complexes were measured in developed faces of the crystals or in faces obtained by cutting the crystals in the appropriate directions and are shown in Figure 4. Each spectrum was measured parallel to an observed extinction direction, which in the monoclinic crystals involved the directions of the b crystallographic axes and two arbitrary directions in the ac planes, which are indicated in the projections of these unit cells shown in Figure 5A and B. In both complexes there exists significant misalignment of the optical extinction directions and the directions of the local molecular g factors which occur in this ac plane, namely, 23° in $\{C_{14}H_{19}N_2\}Cu(hfacac)_3$ and 30° in $Cu(phen)_3(ClO_4)_2$. This effect arises due to the presence of large polarizable groups whose axes are misaligned with respect to the local molecular axes (or their vector components) as reflected in the observed g factor directions.[25,26] In $\{C_{14}H_{19}N_2\}Cu(hfacac)_3$, the polarizable groups are the 1,8-bis(dimethylamino)naphthalene cations and in $Cu(phen)_3(ClO_4)_2$ they are the 1,10-phenanthroline ligands. Such misalignments introduce an uncertainty into the assignment of the electronic spectra which are usually assigned by reference to the numerical magnitude of the g factor measured parallel to the extinction direction of the electronic spectrum.[4] In the present two complexes, as the misalignment is not more than 30°, it is assumed that the electronic spectra may be "associated" with the nearest g factor and are labeled accordingly.

This misalignment of the g factor and extinction directions is readily measured in monoclinic crystals as the misalignment is restricted to the ac plane. This is especially convenient in $\{C_{14}H_{19}N_2\}Cu(hfacac)_3$ where the main face of the crystal is the {010} face.[18] With triclinic crystals no such restrictions apply and even if the electronic spectra are measured parallel to the extinction directions in a given crystal face these directions do not necessarily correspond to the pure spectra. In these triclinic crystals a knowledge of the directions of the g factors may not be of any help if there is an inherent misalignment of the g factors and extinction directions. Consequently in triclinic crystals it is essential to measure the polarized electronic spectra in as many crystal directions as possible (in both natural and cut faces) in an attempt to observe the maximum polarization effect and to then associate these spectra with the nearest g factors. This effect adds a further uncertainty to the labels assigned to the observed spectra and is relevant to the spectra of $Cu(bipy)_3(ClO_4)_2$ (Figure 4B), which involves a triclinic crystal system. For the above two reasons, the polarized single-crystal spectra of the three complexes shown in Figure 4 are not necessarily pure spectra nor absolutely assigned with respect to the g factors. However, notwithstanding these limitations, there are broad similarities in the three spectra which provide some justification for the following attempt to assign the spectra.

All three sets of spectra (Figure 4) show two band maxima separated by 7-9 kK, with both bands showing marked polarization. The sense of this polarization is most similar in $Cu(bipy)_3(ClO_4)_2$ and $Cu(phen)_3(ClO_4)_2$ as might be expected from the close similarity of the chelate ligands present. In both sets of spectra the low-energy bands between 7.6 and 9.2 kK are mainly z polarized and the high-energy bands at 14.9-15.5 kK are x and y polarized (a situation which closely parallels that observed in the spectra[14] of $Cu(hfacac)_2bipy$). The extent of the polarization in the spectra of $\{C_{14}H_{19}N_2\}\{Cu(hfacac)_3\}$ is less marked but this may be associated with the misalignment present. In z and x polarization the intensities of the spectra are approximately equally divided between the two main bands; in y polarization the main intensity lies with the high-energy band.

Assignment of the Electronic Spectra. There is least uncertainty in the electronic spectra of $Cu(phen)_3(ClO_4)_2$ and they will be assigned first assuming that the electronic selection rules are appropriate. In view of the close similarity

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Table III. Assignment of the Electronic Spectra (kK) in D_2 Symmetry with a d_{xy} Ground State and Tetragonality ($T = R_S/R_L$)[a] of Four Tris-Chelate Copper(II) Complexes

Transition	Polarizn	$Cu(phen)_3(ClO_4)_2$	$Cu(bipy)_3(ClO_4)_2$	$\{C_{14}H_{19}N_2\}$-$\{Cu(hfacac)_3\}$	$Cu(hfacac)_2bipy$[14]
$d_{z^2} \rightarrow d_{xy}$	z	7.6	8.7	7.0	9.4
$d_{x^2-y^2} \rightarrow d_{xy}$	z	15.4	15.4	10.5	13.0
$d_{xz} \rightarrow d_{xy}$	x	14.9	15.3	11.7	14.4
$d_{yz} \rightarrow d_{xy}$	y	15.3	15.5	10.6	14.6
Tetragonality (T)		0.878	0.869	0.920	0.860

[a] R_S = mean short in-plane bond length; R_L = mean long out-of-plane bond length.

between the electronic properties of this complex and those of $Cu(bipy)_3(ClO_4)_3$ and the small molecular misalignment present in the former, it is reasonable to assume that the same electronic ground state is appropriate, namely, d_{xy}. The crystallographic site symmetry[20] of the copper(II) ion is C_1 but in view of the marked polarization observed in the electronic spectra a higher effective symmetry must be present and the most reasonable symmetries are C_2 and C_{2v} (with an x principal axis) and D_2. All are consistent with the observation of three g factors and although an effective symmetry of C_2 would be very attractive in describing the distortion from D_3 symmetry, it requires that z- and y-polarized spectra should only differ in relative intensity. This is clearly not the case in any of the spectra of Figure 4. In C_{2v} symmetry there are no electronically allowed bands[4] in x polarization, whereas the observed spectra involve, marginally, the greatest band intensity in this polarization. In D_2 symmetry two bands are electronically allowed in z polarization and one each in x and y polarization, consistent with the observed spectra. The electronic selection rules for a copper(II) ion in D_2 symmetry with a d_{xy} ground state have been given previously[4,14] and result in the assignment shown in Table III. On the basis of the electronic selection rules it is not possible to decide whether the band at 7.6 kK should be assigned as the $d_{z^2} \rightarrow d_{xy}$ or the $d_{x^2-y^2} \rightarrow d_{xy}$ transition, which both appear in z polarization; however as the former reflects the degree of tetragonal distortion present[4,27] and as the tetragonalities[4] (T) of the present complexes are relatively high (Table III), the assignment of the band at 7.6 kK as the $d_{z^2} \rightarrow d_{xy}$ transition is most reasonable, leaving the band at 15.4 kK to be assigned as the $d_{x^2-y^2} \rightarrow d_{xy}$ transition. This yields a tentative one-electron orbital sequence of $d_{xy} > d_{z^2} > d_{xz} > d_{yz} > d_{x^2-y^2}$, an order which is comparable to that previously deduced for the complex[14] $Cu(hfacac)_2bipy$ except for the higher energy of the $d_{x^2-y^2}$ level. The electronic spectra of $Cu(bipy)_3(ClO_4)_2$ may be assigned in an analogous manner to yield the assignment given in Table III. The assignment of the electronic spectra of $\{C_{14}H_{19}N_2\}Cu(hfacac)_3$ is less obvious due to the overriding intensity of the x-polarized spectra in both of the observed bands. An assignment comparable to that given above (see Table III) is only possible if the relatively intense band at 6.8 kK in x polarization is ignored. This is only justified if an intensity-borrowing mechanism from a low-energy charge-transfer band is operating which results in spectra in one polarization dominating the other two. Such a mechanism has been invoked to account for this type of intensity distribution in the spectra of bis(benzoylacetonato)copper(II)[28] and bis(3-methylacetonato)copper(II).[29] There is a marked similarity between the relative intensities and polarization of the electronic spectra of these three complexes (taking into account the different band energies involved due to the different stereochemistries present and an interchange of the x- and y-axis labels) which could arise from a comparable intensity-borrowing mechanism associated with the presence of an in-plane short-bonded acetylacetonate chelate ligand. Without this mechanism it is very difficult to see how the appearance of two bands of comparable intensity in both x and z polarization can be accounted for by any electronic selection rules. For this reason the data of Table III are included as a very tentative assignment of the electronic spectra of $\{C_{14}H_{19}N_2\}\{Cu(hfacac)_3\}$ but yield a one-electron orbital sequence comparable to that more definitely established for the other two complexes.

A referee has pointed out that these three complexes may well be subject to fluxional behavior involving a dynamic or pseudodynamic[24] Jahn–Teller effect. As all three complexes involve *three* equivalent chelate ligands, this is most likely to result in the equal population of the three equivalent potential wells which are misaligned by approximately 90° with respect to each other and would yield an isotropic esr spectrum due to exchange coupling[4] of the three nonequivalent sites. This situation is unlikely to give rise to the observed polarization of the electronic spectra and the clear rhombic crystal g factors. A more likely fluxional behavior is the pseudo-Jahn–Teller type distortion postulated for $Cu(hfacac)_2(py)_2$,[24] where clear rhombic g factors were observed (which varied slightly with temperature), and yet the electronic spectra showed no polarization or even change of intensity with orientation. As the polarized single-crystal spectra of $Cu(bipy)_3(ClO_4)_2$ and $Cu(phen)_3(ClO_4)_2$ show clear polarization (Figure 4B and C), fluxional behavior is unlikely to be present in these complexes, but as the spectra of $\{C_{14}H_{19}N_2\}\{Cu(hfacac)_3\}$ only show a change of intensity with orientation, fluxional behavior is possible in this complex. This possibility is supported by the observation[24] in a polycrystalline sample of $\{C_{14}H_{19}N_2\}Cu$-$Zn(hfacac)_3$ of an isotropic esr spectrum at room temperature but an anisotropic one at the temperature of liquid nitrogen; however, it must await a detailed single-crystal examination of $\{C_{14}H_{19}N_2\}Cu$-$Zn(hfacac)_3$ and a determination of the crystal structure of $\{C_{14}H_{19}N_2\}Zn(hfacac)_3$ for further clarification.

Discussion

The correlation of the stereochemistries and electronic properties of the above three tris-chelate copper(II) complexes leaves little doubt that in these chromophores with three equivalent ligands the usual elongated rhombic octahedral distortion is present with the elongation axes the dominant symmetry axes of the CuX_6 chromophores and not the threefold axes of the parent tris-chelate copper(II) complex of D_3 symmetry. Consequently the one-electron orbital sequence associated with an elongated rhombic octahedral stereochemistry with a d_{xy} ground state is appropriate,

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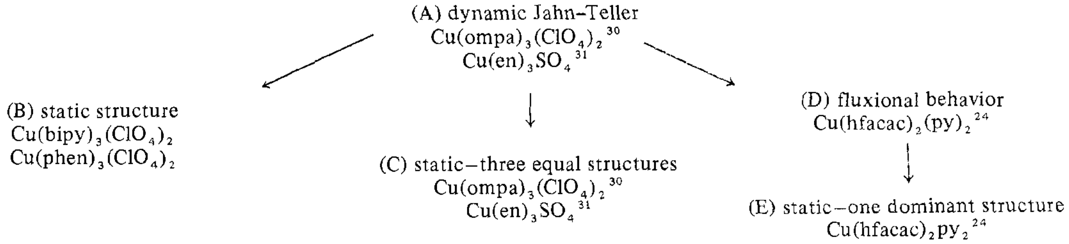
Chart I. Structural Possibilities for the Tris-Chelate Copper(II) Complexes



namely, $d_{xy} > d_{z^2} > d_{x^2-y^2} \approx d_{xz} \approx d_{yz}$, and within this sequence the effect of the different chelate ligands will only change the energies of the one-electron orbitals in a minor way. The in-plane chelate, N(1)-N(4), may effect the energies of the d_{xz} and d_{yz} orbitals and the out-of-plane chelate ligands N(2)-N(5) and N(3)-N(6) may limit the extent of the axial elongation possible[1] (restricted tetragonal distortion) and reduce the separation of the d_{z^2} and d_{xy} levels.

These results question the earlier suggestion that the $Cu(bipy)_3^{2+}$, $Cu(phen)_3^{2+}$, and $Cu(en)_3^{2+}$ cations will always involve a D_3 symmetry and undergo a dynamic Jahn-Teller distortion. The latter will only arise when these cations are present in high-symmetry crystal lattices, such as trigonal or hexagonal, in which the copper(II) ion may occupy a special position of D_3 symmetry. When these cations are present in lower symmetry crystals, such as monoclinic and triclinic, where the copper(II) ion does not occupy a special position, the more usual[4] static elongated rhombic octahedral stereochemistry will be present and no genuine dynamic Jahn-Teller effect will operate. The most likely structure will represent one of the three equally possible dynamic Jahn-Teller states as in $Cu(bipy)_3(ClO_4)_2$ and $Cu(phen)_3(ClO_4)_2$. A less likely possibility is that a mixture of all three possible structures may be observed in equal distribution as for $Cu(ompa)_3(ClO_4)_2$[30] and $Cu(en)_3SO_4$[31] or in unequal distribution as in $Cu\text{-}Zn(hfacac)_2(py)_2$.[24] These various possibilities are summarized in Chart I.

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Registry No. $Cu(phen)_3(ClO_4)_2$, 36502-34-8; $Cu(bipy)_3(ClO_4)_2$, 14375-99-6; $(C_{14}H_{19}N_2)Cu(hfacac)_3$, 31117-62-1.

(30) R. C. Koch, J. H. Venable, Jr., and M. D. Joesten, *J. Chem. Phys.*, 59, 6312 (1973).

(31) B. J. Hathaway and P. C. Power, unpublished results.

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Copper Halide Adducts of Copper Schiff Base Complexes. Structure and Magnetic Properties

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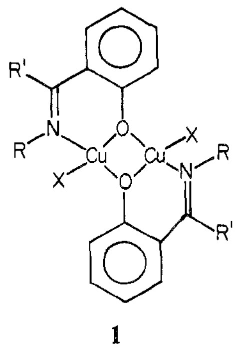
The complete crystal and molecular structures of four complexes, dichlorobis(*N*-methylsalicylaldimino)dicopper(II), dichlorobis(*N*-ethylsalicylaldimino)dicopper(II), dibromobis(*N*-ethylsalicylaldimino)dicopper(II), and dichloro[*N*,*N'* ethylenebis(2-hydroxyacetophenimino)copper(II)]copper(II) have been determined by X-ray diffraction analyses. The magnetic moments of the complexes are dependent on temperature but not pressure, indicating the absence of any significant volume changes, in agreement with the X-ray data. The magnetic properties are found to be more a function of structure than of the electronic properties of the ligands. In each case, increased distortion of the copper environment from planar is accompanied by reduced antiferromagnetic interaction between the pairs of copper atoms. Replacement of chlorine atoms attached directly to the interacting copper atoms has no significant effect on the magnetic properties in dichlorobis(*N*-ethylsalicylaldimino)dicopper(II). Using these results and the magnetic properties, the copper environments may now be deduced in a series of analogous binuclear copper complexes.

Introduction

Binuclear complexes, **1**, exhibit an antiferromagnetic coupling, $|J|$, between the copper atoms and fall phenomenologically into two general groups according to the nitrogen substituent R. When R is bulky or methyl, $|J|$ is much less than for R = *n*-alkyl, and distortion from planar toward tetrahedral copper, as indicated by the electronic spectra, is slightly greater than for R = *n*-alkyl.[2a] These data suggest that dis-



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[2] (a) C. M. Harris and E. Sinn, *J. Inorg. Nucl. Chem.*, 30, 2723 (1968); (b) E. Sinn and W. T. Robinson, *J. Chem. Soc., Chem. Commun.*, 359 (1972).