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SIX-COORDINATE COPPER COMPLEXES WITH $g_{\parallel} < g_{\perp}$ IN THE SOLID STATE

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CONTENTS

A. INTRODUCTION

Six-coordinate copper complexes cannot be rigorously octahedral according to the Jahn—Teller theorem [1], the highest symmetry compatible with this theorem being tetragonal [2—5]. Tetragonal distortion can be either elongation or compression of the octahedra. In principle ESR spectra provide a powerful tool for the assignment of stereochemistry in that opposite molecular *g* patterns for the two distortions are expected [6,7], $g_{\parallel} > g_{\perp}$ for elongation and $g_{\parallel} < g_{\perp}$ for compression. However, this pattern can be unambiguously recognized only from experiments on magnetically dilute complexes, since in the case of undiluted complexes exchange interactions [8,9] result in a crystal average of the ESR spectra and the molecular *g* values are not generally obtained. The crystal *g* values may have a pattern opposite to that of the molecular *g* values, thus possibly leading to erroneous conclusions, depending on the relative orientation of the chromophores. In particular it is often found that elongated chromophores are coupled in the lattice in an antiferrodistortive fashion in a way which simulates a compressed octahedron. It is worth mentioning that when dynamic Jahn—Teller effects are operative, X-ray structures can reveal compressed chromophores which are actually given by a time and/or space average of elongated octahedra. This point has not always been fully understood, and many conflicting reports have appeared in the literature. It is our aim to review the theoretical aspects of the molecular g values of isolated chromophores and their relationship to the crystallographic g values under exchange narrowing conditions between coupled chromophores. Some six-coordinate compounds with $g_\parallel < g_\perp$ in the solid state are also reviewed, grouped according to whether they are tetragonally compressed or antiferrodistortively coupled elongated chromophores, with particular interest in those complexes experiencing dynamic Jahn—Teller distortion.

B. MOLECULAR g AND A VALUES

The ESR spectra of hexacoordinate copper(II) complexes are often quasi axial [6,10,11] with small lower symmetry components superimposed which determine some splitting of the $g_\perp$ values. Although the actual symmetry of the complex may be very low, so that the principal directions of the A and g tensors cannot be predicted a priori but must be experimentally determined, the present theoretical analysis is restricted to orthorhombic D_{2h} symmetry for the sake of simplicity. In this case the linear combinations of the five real d orbitals spanning the irreducible representations of the group are

$|a_g(1)\rangle = \cos\alpha\,|x^2 - y^2\rangle + \sin\alpha\,|z^2\rangle$
$|a_g(2)\rangle = \sin\alpha\,|x^2 - y^2\rangle - \cos\alpha\,|z^2\rangle$
$|b_{1g}\rangle = |xy\rangle$
$|b_{2g}\rangle = |xz\rangle$
$|b_{3g}\rangle = |yz\rangle$

The g and A values which can be calculated by standard perturbation techniques [7] are as shown in Table 1. In the limit of $\alpha = 0°$ or $\alpha = 90°$ the above expressions reduce to D_{4h} symmetry, with the unpaired electron in the $d_{x^2-y^2}$ orbital or in the d_{z^2} orbital respectively.

It is well known that in the limit of axial symmetry it is quite easy to obtain structural information from the g and A values [6,7,10,12] since for an elongated octahedron $g_\parallel > g_\perp$; $|A_\perp| < |A_\parallel| \simeq 120—200 \times 10^{-4}$ cm^{-1} while for a compressed octahedron $g_\perp > g_\parallel \cong 2.0023$; $|A_\parallel| > |A_\perp|$. Often the perpendicular component of A for elongated octahedra is so small that it is not experimentally detected. Low symmetry components may alter this pattern a little, as shown by the expressions of Table 1. It is worth mentioning, however, that one cannot expect very large variations from the values of axial symmetry. For example the g_z value in the case of a compressed octahedron will rarely exceed 2.05 unless the ligand field strength is very low, as in CuF_6 chromophores.

A sample calculation setting $k_z = 1$, $\zeta_z = 830$ cm^{-1}, $\Delta_{xy} = 12{,}000$ cm^{-1} shows that in order to have $g_z = 2.05$, α must be ca. 73°, which is a very large admixture of $d(z^2)$ and $d(x^2 - y^2)$. In ligand field terms α is given by

$$\alpha = \tfrac{1}{2}\cot^{-1}\frac{2\langle x^2 - y^2|\hat{V}|z^2\rangle}{\langle x^2 - y^2|\hat{V}|x^2 - y^2\rangle - \langle z^2|\hat{V}|z^2\rangle} \qquad (1)$$

TABLE 1

The expressions for the principal values of g and A tensors in D_{2h} symmetry[a]

$$g_{xx} = \frac{2(\cos\alpha + \sqrt{3}\sin\alpha)^2 k_x^2\zeta_x}{\Delta_{yz}} + 2.0023$$

$$A_{xx} = P\Big[-\kappa + \tfrac{2}{7}(\cos 2\alpha - \sqrt{3}\sin 2\alpha) + \frac{2\sqrt{3}}{7}\sin 2\alpha\,\frac{k_x^2\zeta_x}{\Delta_{xy}}$$
$$-\tfrac{3}{7}\Big(\cos 2\alpha - \sqrt{\tfrac{3}{3}}\sin 2\alpha\Big)\frac{k_x^2\zeta_x}{\Delta_{xz}} + 2\,\frac{k_x^2\zeta_x}{\Delta_{xz}}(\cos\alpha + \sqrt{3}\sin\alpha)^2\Big]$$

$$g_{yy} = 2(\cos\alpha - \sqrt{3}\sin\alpha)\,\frac{k_y^2\zeta_y}{\Delta_{xz}} + 2.0023$$

$$A_{yy} = P\Big[-\kappa + \tfrac{2}{7}(\cos 2\alpha + \sqrt{3}\sin 2\alpha) - \frac{2\sqrt{3}}{7}(\sin 2\alpha)\,\frac{k_y^2\zeta_y}{\Delta_{xy}}$$
$$-\tfrac{3}{7}\Big(\cos 2\alpha + \sqrt{\tfrac{3}{3}}\sin 2\alpha\Big)\frac{k_y^2\zeta_y}{\Delta_{yz}} + 2\,\frac{k_y^2\zeta_y}{\Delta_{xz}}(\cos\alpha - \sqrt{3}\sin\alpha)^2\Big]$$

$$g_{zz} = \frac{8\cos^2\alpha\, k_z^2}{\Delta_{xy}}\zeta_z + 2.0023$$

$$A_{zz} = P\Big[-\kappa - \tfrac{4}{7}\cos 2\alpha + \tfrac{3}{7}\Big(\cos 2\alpha + \frac{\sqrt{3}}{3}\sin 2\alpha\Big)\frac{k_z^2\zeta_z}{\Delta_{yz}}$$
$$+\frac{3}{7}\,\frac{k_z^2\zeta_z}{\Delta_{xz}}\Big(\cos 2\alpha - \frac{\sqrt{3}}{3}\sin 2\alpha\Big) + 8\cos^2\alpha\,\frac{k_z^2\zeta_z}{\Delta_{xy}}\Big]$$

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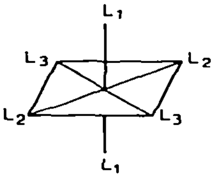
[a] α is defined in the text; ζ is the spin-orbit coupling constant; k_i the orbital reduction factor; the Δ_i's are the energy separations between the ground and the indicated orbital; $P = 2\, g_N \mu_N \mu_B\, (1/r)^3$ where μ_B is the Bohr magneton, μ_N is the nuclear magneton, g_N is the nuclear g factor, and r is the distance between the electron and the nucleus. κ accounts for the contribution which brings the contact interaction into the value for the hyperfine splitting.

where $\hat{V}$ is the appropriate ligand field operator. Using octahedral coordinates for the donor atoms and setting $e\sigma_1 = 4000$ cm^{-1}, $e\sigma_2 = 3000$ cm^{-1}, $e\sigma_3 = 2000$ cm^{-1} for ligands labelled as in the scheme below give $\alpha = 81°$ and $g_z = 2.01$



which is quite far from the limit of 2.05. The anisotropy associated with the e_λ values is pretty large, since the Dq values of ligands 1, 2 and 3 would be 1200, 900 and 600 cm^{-1} respectively [13,14], (neglecting π-bonding).

C. FERRO- AND ANTIFERRODISTORTIVE ORDER

In order to use the expressions of Table 1 for obtaining structural information it is necessary to have the experimental molecular g and A values. These data are available whenever the ESR spectra are recorded in dilute media, i.e. with the paramagnetic species diluted into a diamagnetic host. When the pure paramagnetic sample is investigated magnetic exchange interactions are in general operative among different ions in the crystal, and if the difference in the resonance field of a pair of ions is smaller than the exchange interaction, only one line is observed which is exchange narrowed [8,9]. The latter is in general the case for copper(II) complexes [6] so the ESR spectra of pure undiluted complexes yield only crystal g values which may be used to give structural information only with much caution (Fig. 1). Only if the structure is known can one attempt to calculate the molecular g values, assuming that the principal g directions can be fixed with some confidence [15,16].

It is apparent therefore that the crystal g values can be closer to or further from the molecular g values depending on the relative orientations of the octahedra in the lattice. If there is no symmetry restraint in the crystal, as is often the case, the octahedra can be in every relative orientation, determined by lattice forces and/or cooperative interactions among them. However, two interesting limiting cases deserve some attention. For the sake of simplicity we

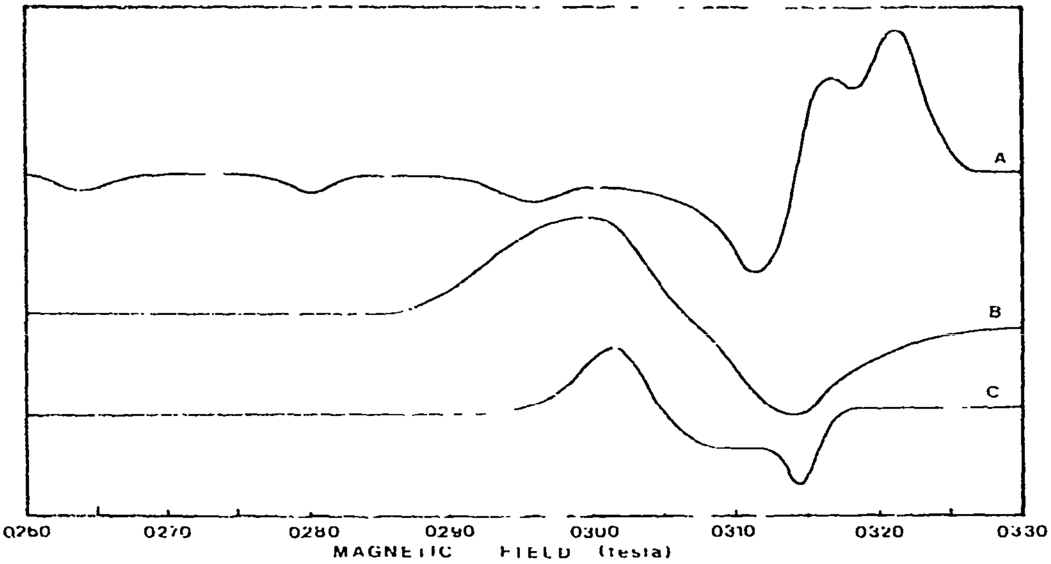


Fig. 1. Polycrystalline powder ESR spectra of Cuen$_3^{2+}$ cations (A) doped into Znen$_3$(NO$_3$)$_2$; (B) undiluted dichloride; (C) undiluted sulfate. The g values measured on single crystals are $g_1 = 2.248$, $g_2 = g_3 = 2.082$; $g_1 = 2.16$, $g_2 = 2.12$, $g_3 = 2.07$; and $g_1 = 2.159$, $g_2 = 2.134$, $g_3 = 2.053$ respectively.

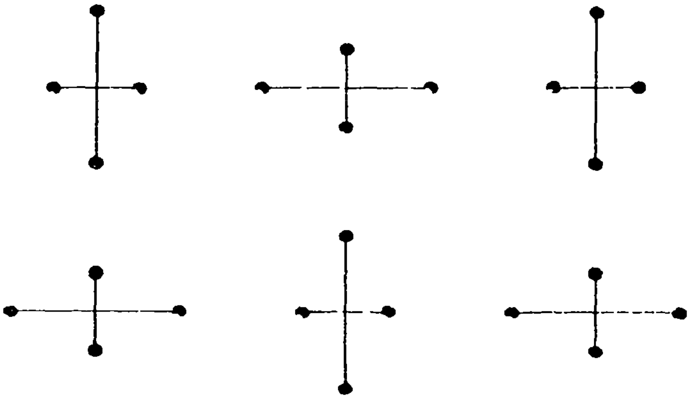


Fig. 2. Antiferrodistortive arrangement of tetragonally distorted six-coordinated chromophores. The other two bonds are orthogonal to the plane.

take into consideration axially elongated or compressed octahedra, the extension to absolute lack of symmetry being rather obvious. The most favourable orientation is that in which all the principal axes (of either elongation or compression) of the octahedra are parallel to each other, so that all the sites are equivalent in every orientation of the crystal in the static magnetic field. The exchange interactions result in a washing out of the hyperfine structure, but the g values are not altered, so that in this case the crystal g values coincide with the molecular g values and they can be meaningfully compared to the calculated values. This situation is often referred to as ferrodistortive order [17] of distorted octahedra. The ferro- prefix has its origin in the similarity of this order to that observed in ferromagnetic materials. In the latter case all the spins are oriented parallel to each other, while in the former the distortion axes are oriented parallel to each other. It is worth mentioning that ferrodistortive order does not imply ferromagnetic exchange among the distorted octahedra, and this point will become clearer later.

The other interesting limiting case is that in which in one plane, long and short axes alternate according to the scheme shown in Fig. 2. Perpendicular to this plane a short (or a long) axis is found in the case of elongated (or compressed) octahedra respectively. This order is called antiferrodistortive order [17]. In this case only one molecular g value is obtained, which is that perpendicular to the plane and is the molecular $g_\perp$ component for both elongated and compressed octahedra. In the plane the molecular $g_\parallel$ and $g_\perp$ values are averaged by the exchange interaction and the crystal g value cannot be taken as molecular g value.

A possible deviation from the antiferrodistortive limiting case occurs when the long axis of the magnetically inequivalent molecules form an angle $2\gamma \neq 90°$ (see Fig. 3). By standard techniques it is easy to show that the principal crystal g values in the plane are related to the molecular values through the

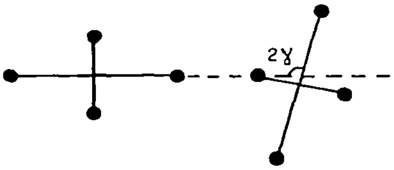


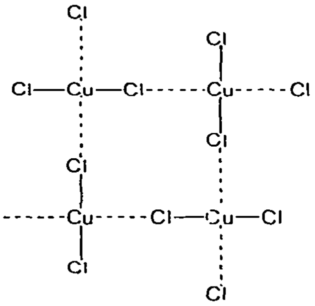
Fig. 3. A perturbation of the antiferrodistortive order with the angles between long axes ≠ 90°. The third bond direction is orthogonal to the plane.

following relations [15]

$$
\begin{aligned}
g_1^2 &= g_\parallel^2 \cos^2\gamma + g_\perp^2 \sin^2\gamma \\
g_2^2 &= g_\parallel^2 \sin^2\gamma + g_\perp^2 \cos^2\gamma
\end{aligned}
\qquad (2)
$$

From this formula it is apparent that for $2\gamma = 90°$ the spectra will be isotropic in the plane, while for $2\gamma \neq 90°$ anisotropic components will show up. Angles 2γ different from 90° can originate from bond angles different from 90° in the pseudo octahedron or from a twisting of the elongation axis of two octahedra relative to each other. When long and short bonds of the octahedra do not lie exactly in a plane, crystallographic g values do not yield the molecular values directly, since no symmetry results. However, if the atomic distortions are small and the non-planarity of short and long bonds is minimal, then one may refer to the antiferrodistortive model and will find that two principal crystallographic g values almost bisect the angles formed by the copper donor bonds.

A typical example of antiferrodistortive order of elongated octahedra is given by several polymeric tetrachlorocuprates [18]. Complexes of general formula $(\mathrm{Cat})_2\mathrm{CuCl}_4$, where Cat = NH_4^+ [19], RNH_3^+ [20–23], $[\mathrm{Pt(NH)_3}]_4^{2+}$ [24], $[\mathrm{NH_3(CH_2)}_n\mathrm{NH_3}]^{2+}$ [25,26], are formed by essentially square coplanar CuCl_4 moieties linked together according to the scheme shown in Fig. 4. Two chlorine atoms are terminal, while four are bridging. All the terminal bonds are short and are almost parallel to each other, while the bridging chlorine atoms form a two-dimensional layer structure. The four short bonds around each copper atom are about 230 pm long, while the long bonds range between 280 and 320 pm. Notwithstanding these long bond distances, the spectral and magnetic properties are definitely those of elongated octahedra. A detailed study of the ESR spectra of $\mathrm{NH_3(CH_2)_3NH_3CuCl_4}$ has been performed [27]. The crystals are orthorhombic, space group *Pnma* [26], and the orientation of the copper octahedra in the crystal is as shown in Fig. 5. The deviations from the simple picture of antiferrodistortive order described above are rather small, in the sense that the long and short bonds do not lie exactly in a plane. The layer is puckered by canting CuCl_4 units by 1.6° and 9.6° in the a and c directions respectively. The layers are separated by layers of protonated amine cations. The ESR spectra showed that one principal g direction is parallel to b, with $g_b = 2.053$. The principal $g_\perp$ values are isotropic (2.169). These values are



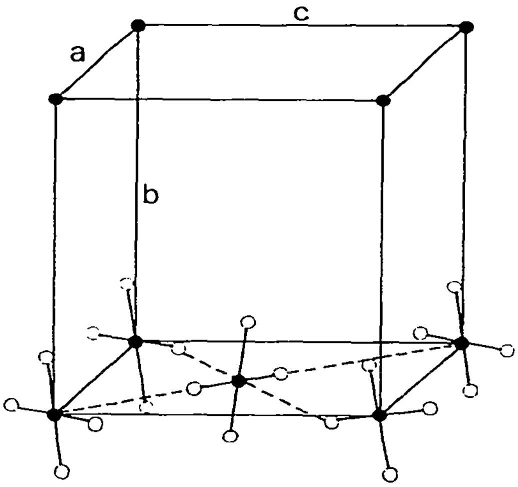


Fig. 4. A scheme of the structure of Cat_2CuCl_4 complexes. Two other Cu—Cl short bonds are orthogonal to the plane.

Fig. 5. Schematic representation of the structure of the $CuCl_6$ chromophore in $(NH_3$-$(CH_2)_3NH_3)CuCl_4$ (ref. 26).

typical of $CuCl_4^{2-}$ moieties [28]. There is considerable evidence of exchange interactions within the layers. The above results have been used to calculate the principal molecular g values by assuming that 2γ of relationship (2) is that formed by the bond directions (90°). Assuming furthermore that $g_b = g_\perp$ of the molecule, $g_\parallel$ is found to be 2.285, a value which compares well to those usually reported for elongated octahedral copper(II) complexes [6].

Another interesting feature of these spectra is that the exchange coupling constant which is operative in the ac plane is known from magnetic susceptibility measurements to be positive [29,30], i.e. the exchange interaction is of the ferromagnetic type, showing that the antiferrodistortive order does not imply antiferromagnetic exchange. There is a further typical example of crystal g values which are far from the molecular values and which if taken erroneously as molecular values might lead to incorrect conclusions about the structure of the complex. $CuSO_4 \cdot 5\ H_2O$ is known to crystallize in the triclinic system, space group $P\bar{1}$, with two independent copper ions in the unit cell [31,32]. Both the copper ions are practically identical and are coordinated by four water molecules and two oxygen atoms of two sulphate groups giving an elongated octahedron. The elongation axes of the two independent octahedra form an angle of ca. 85°. ESR spectra were run [33] at 0.33, 0.81 and 1.18 cm^{-1} and only one line was detected at the two lower frequencies for all the orientations of the crystal in the static magnetic field with axial g values $g_\parallel = 2.09$, $g_\perp = 2.27$. However at the highest frequency two lines were resolved in the single crystal spectra and principal g values were found to be $g_\parallel = 2.37$

TABLE 2

Crystallographic g values for some copper(II) complexes antiferrodistortively coupled

Complex	$g(H_{\parallel}c)$		$g(H_{\perp}c)$		Ref.
K_2CuF_4	2.09		2.28		84
Rb_2CuF_4	2.09		2.28		84
	g_1	g_2		g_3	
Ba_2CuF_6	2.05	2.20		2.36	74, 84
Na_2CuF_6	2.09		2.46		84
$Ba_2Cu(OH)_6$	2.05	2.12		2.23	85
$Sr_2Cu(OH)_6$	2.05	2.11		2.24	85

and $g_\perp$ = 2.08 in accord with the view of elongated octahedra. Apparently increasing the spectrometer frequency makes the exchange interaction smaller than the separation of the resonance fields, so that the lines are no longer exchange narrowed and the individual components are resolved. The exchange coupling constant was estimated to be 0.15 cm^{-1}. Other cases of antiferrodistortive coupling of elongated octahedra have been reported from which the molecular g values have sometimes been tentatively calculated by assuming the main directions of the g^2 tensor. Those for which a compressed octahedral structure has been taken into consideration, even for comparison purposes are reported in Table 2.

D. COOPERATIVE EFFECTS IN CHROMOPHORES EXPERIENCING DYNAMIC JAHN—TELLER DISTORTIONS

Copper(II) ions in solid compounds may sit in sites such that an orbitally degenerate ground state would be required. Such high site symmetry however, is the result of time-averaged distortions; by coupling of electronic states with the vibrations dynamic distortion takes place. This situation has been found to occur only in six-coordinated complexes with T_h or D_3 site symmetry [34,36]. The coupling of the ^2E electronic state with vibrations of E_g species, as referred to O_h symmetry, gives rise to tetragonal distortions along the copper—donor bond. The energy dependence on the coordinates of the doubly degenerate vibration for the isolated molecule in the gas phase is reported in Fig. 6. The energy of the undistorted chromophore, E_0, is the point where the potential surface crosses the vertical axes; three equivalent minima correspond to the three tetragonal distortions along three orthogonal directions. The energy difference between E_0 and the minima of the curve is that gained in the Jahn—Teller distortions. As long as cooperative effects are absent or negligible the three distortions are equally probable and equivalent. When the thermal energy is larger than the saddle between the three minima, dynamic Jahn—Teller distortion takes place. At relatively high temperatures averaged C_3 or higher symmetries may result in the solid state. In this case the mechan-

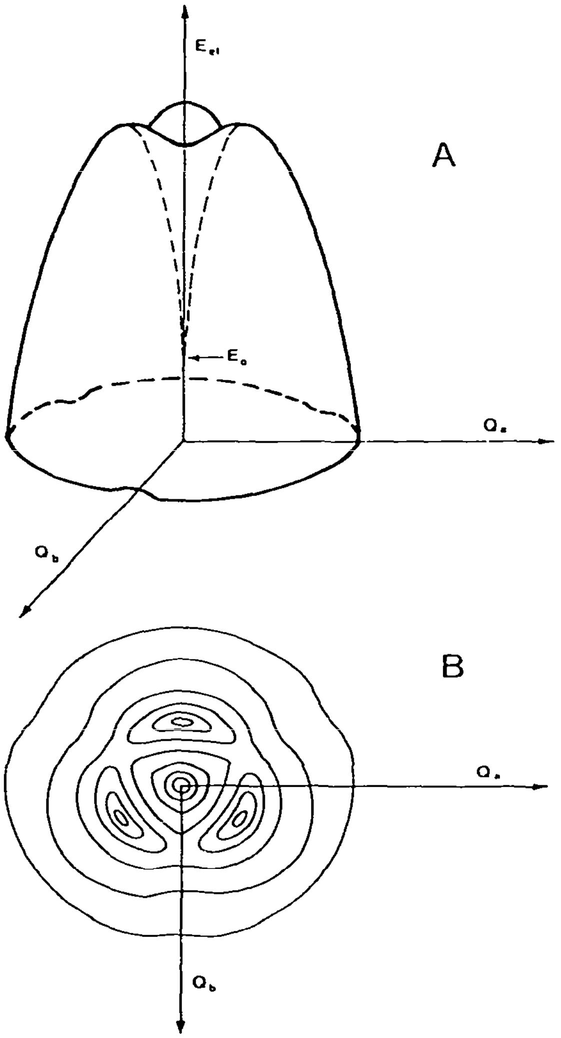


Fig. 6. The potential surface $E(Q_A, Q_B)$ for a ^2E electronic ground state (A) and its contour map (B).

ism of freezing of the Jahn—Teller distortion is strongly dependent on environmental and/or cooperative effects. For example, in undiluted complexes when one chromophore is frozen out into either its elongated or compressed distortion this somehow affects the distortion of the contiguous molecules. The importance and the structural consequences of such solid state effects are not easily generalized nor always detected.

For example Cu(OMPA)$_3^{2+}$ (where OMPA is octamethylpyrophosphoramide) has D_3 symmetry at room temperature [37] as a consequence of dynamic

Jahn—Teller effects; the ESR powder spectra reflect this situation giving an isotropic g value of 2.25 and show evidence of exchange narrowing since no hyperfine splitting is observed [38]. At 90 K, probably as a consequence of a phase transition, the Jahn—Teller distortions are frozen out [36]. Three magnetically non equivalent molecules are detected with a g pattern ($g_z = 2.510$; $g_y = 2.102$; $g_x = 2.080$) typical of elongated tetragonal octahedra. A single crystal study has shown that the three directions of elongation are orthogonal to each other. Hyperfine splitting is clearly detected in correspondence with the g_z direction with $A_z \simeq 95 \times 10^{-4}$ cm^{-1}. Unless further studies are undertaken cooperative effects do not show up.

The case of $Cuen_3SO_4$ in which the copper atom again has D_3 symmetry at room temperature [39] is different from those discussed above. Hydrogen bonding between bound en and the counterion sulfate gives rise to strong interactions within the crystal. At room temperature the D_3 symmetry is the result of a dynamic Jahn—Teller effect; indeed, an early investigation of the electronic spectra [40] had found that the energy of the transitions and their polarizations were not consistent with such a high symmetry. The ESR spectra, averaging over the three distortions, simulate D_3 symmetry [41—43]. At 180 K, however, a phase transition occurs and three ESR signals appear showing that three magnetically non-equivalent sites are formed with a g pattern different from that observed at room temperature. The three sites are equally populated (within experimental error) and are equivalent to each other. The g values are completely anisotropic with $g_1 = 2.159$, $g_2 = 2.134$ and $g_3 = 2.053$. Although g_1 and g_2 are sufficiently close to each other so that one might be tempted to consider them as the split components of $g_\perp$, and $g_\parallel < g_\perp$, suggesting a compressed octahedral distortion, the considerations of Section B rule out the possibility of this interpretation. In particular, attempts to compare the observed g values with the theoretical expectations of Table 1 give $k_z = 3.92$ [44], which is obviously meaningless. On the contrary the g values are consistent with an antiferrodistortive ordering of the chromophores for each magnetically non-equivalent site. No hyperfine splitting is observed and the lines appear to be exchange narrowed. One principal direction of g is found parallel to a bond direction, while the others bisect the M—N bonds in the tetragonal plane.

A single crystal X-ray investigation at 120 K has shown [45] that the unit cell is triclinic with $Z = 2$. The copper complex has a compressed tetragonal geometry although the thermal ellipsoids are particularly large. As a matter of fact the root mean square displacements at 120 K are similar to those of room temperature [39], which were considered large in comparison to those of complexes not experiencing Jahn—Teller effects, e.g. the nickel(II) complex [46].

Such a peculiarity was interpreted to give support to the view of an arrangement of tetragonally elongated octahedra coupled in such a way as to simulate tetragonally compressed octahedra. Such a choice was based on:

(i) The impossibility of accounting for three ESR signals with a single compressed chromophore.

(ii) The similarity of the powder ESR spectra with those of $Cuen_3Cl_2 \cdot$

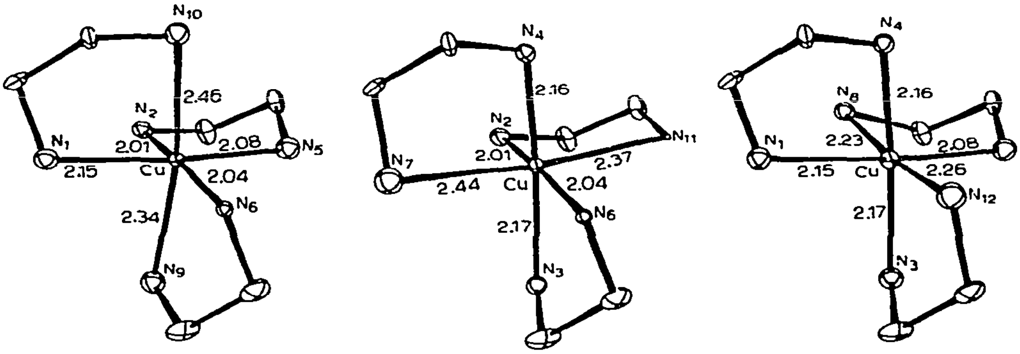


Fig. 7. The three distorted chromophores of Cuen$_3$SO$_4$ obtained through the refinement discussed in the text.

0.75 en which is known by X-ray data [45,47] to be tetragonally elongated.

(iii) The consideration that when copper is doped into the zinc analogue (Znen$_3$(NO$_3$)$_2$) the chromophore is tetragonally elongated. An analysis of the *g* values for the undiluted Cuen$_3$SO$_4$ on the basis of an antiferrodistortive order gives the same *g* pattern for a doped Cuen$_3$(NO$_3$)$_2$ complex.

Attempts were made to account for the diffuse electron density seen in the Fourier synthesis around the nitrogen atoms by assigning them to disordered positions. The refinement was possible only if a population of 2/3 was assigned to the positions which are closer to the copper ion and a population of 1/3 to the further positions. This corresponds to describing three elongated complexes. The three chromophores which result from this analysis are reported in Fig. 7. They are substantially different from each other in contrast with the observation that the three *g* sets obtained from the single crystal spectra are equivalent within experimental error. If three equivalent chromophores are required, then the antiferrodistortive ordering imposed by doubling the nitrogen positions within each chromophore is not quite satisfactory. One may conclude therefore that the elongation axes of the low temperature structure of Cuen$_3$SO$_4$ are actually largely misaligned, and that the simple antiferrodistortive order does not apply and the angular deviations in the distorted octahedra may play a role in determining the X-ray diffraction pattern. On the other hand an arrangement of elongated octahedra which cannot be related in a simple way to antiferrodistortive order was found in the X-ray structure of Cuen$_3$Cl$_2$ · 0.75 en.

The picture of the Cuen$_3$SO$_4$ crystals below 180 K as obtained by the ESR and X-ray data is that of an assembly of domains, related by the trigonal axis of the room temperature cell. Within each domain elongated octahedral chromophores are present arranged in such a way that the elongation axes are largely misaligned. The number of domains must be large.

Another interesting case of Jahn—Teller distorted complexes which can give rise to different complicated behaviour is that of the hexanitrocuprates(II) of general formula $M^I_2M^{II}Cu(NO_2)_6$ [48,49]. Several X-ray reports at variable temperatures are now available [50—58]. The high temperature phases are cubic when M^{II} = Pb, with the copper ion having T_h site symmetry as a result of dynamic Jahn—Teller distortion. At low temperatures the situation is somewhat similar to that of $Cuen_3^{2+}$, the ESR spectra [59—61] indicating that the chromophores are coupled in antiferrodistortive order [17,62]. However, owing to strong cooperative effects each domain is very large so that they can be detected through microphotography. As a consequence the population of the three differently oriented domains may be non-equivalent and strain may favour one orientation with respect to the other two [59]. Accordingly, the single crystal ESR spectra display three signals of different intensities but no copper hyperfine is ever resolved. Sometimes even a single signal can be detected [63]. This means that a single domain is formed which can be suitable for X-ray studies. Such studies have shown that the structure of the chromophore is tetragonally compressed with the nitrogen having anomalously large thermal ellipsoids: again, the compressed octahedron may be the result of antiferrodistortive coupling of elongated octahedra. Another interesting point in these structural data is that if the bond distances of the compressed chromophores are compared to those of similar elongated complexes such as $K_2CaCu(NO_2)_6$ [50], the short bond in the compressed complex compares well with one of the short bonds in the elongated complex, while the long bonds of the compressed complex correspond to the average of one short and one long bond of the elongated complex.

The transition from dynamic to static Jahn—Teller distortions occurs through two phase transitions [64—66]: the former leaves dynamic distortions on the plane where the elongation axes of antiferrodistortively coupled ions lie; the latter corresponds to a completely frozen situation and is separated from the former only by a few degrees. The two situations are not different in the X-ray experiment but the dynamic nature of the high temperature factors can be shown quite nicely through anomalous angular dependence of the linewidths in the ESR spectra [62].

Such peculiar behavior of the lead hexanitrocuprates(II) has been attributed to the strong net of covalent Cu—N—O—Pb bonds spread all over the crystal [60]. When Pb is substituted by alkaline earth ions the elongated chromophores are antiferrodistortively ordered at room temperature [17]. It is reasonable to think that at high temperature dynamic Jahn—Teller distortions may occur and indeed this has been found to be the case for $K_2CaCu(NO_2)_6$ at 180°C [50]. A similar ferro- and antiferrodistortive order of elongated octahedra as determined by the counterion is found for the $Cu(pyNO)_6X_2$ complexes where pyNO is pyridine N-oxide and X=ClO_4, BF_4 [67,68]. In both cases the copper has a trigonal site symmetry at room temperature [69]: at low temperature the tetrafluoroborate is ferrodistortively coupled whereas the perchlorate is antiferrodistortively coupled (Table 3).

TABLE 3

Crystallographic g values for the classes of compounds which include at least one complex experiencing dynamic Jahn—Teller distortion with $g_{\parallel} < g_{\perp}$ for the frozen chromophores

Compound	Temp. (K)		g_1		g_2		g_3	Ref.
$Cu(PyNO)_6(BF_4)_2$	298	$2.16\ g_{\parallel}(C_3)$		$2.18\ g_{\perp}(C_3)$				67, 68
	90		2.37		2.08		2.07	
$Cu(PyNO)_6(ClO_4)_2$	298	$2.17\ g_{\parallel}(C_3)$		$2.19\ g_{\perp}(C_3)$				67, 68
	77		2.08		2.22		2.23	
$K_2CaCu(NO_2)_6$			2.23			2.06		17
$Tl_2CaCu(NO_2)_6$			2.25		2.07		2.05	17
$Cs_2CaCu(NO_2)_6$			2.26		2.07		2.06	17
$K_2SrCu(NO_2)_6$			2.25		2.07		2.06	17
$Tl_2SrCu(NO_2)_6$			2.25			2.06		17
$Rb_2SrCu(NO_2)_6$			2.26		2.07		2.05	17
$Cs_2SrCu(NO_2)_6$			2.26		2.07		2.06	17
$K_2BaCu(NO_2)_6$			2.24		2.07		2.05	17
$K_2PbCu(NO_2)_6$	298		2.12			2.12		17, 59, 63
	273		2.06		2.143		2.152	
$Tl_2PbCu(NO_2)_6$	298		2.12			2.12		17
	245		2.06			2.15		
$Rb_2PbCu(NO_2)_6$			2.06			2.15		62
$Cs_2PbCu(NO_2)_6$			2.06			2.15		62
$KZn_{0.9}Cu_{0.1}F_3$	295		2.27			2.27		84
	5		2.46			2.11		
$Cu(en)_3SO_4$	295		2.126			2.11		41—43
	180		2.053		2.134		2.159	
$(Cu, Zn)(en)_3(NO_3)_2$	295	$g_{iso} = 2.139$			$A_{iso} = 56 \cdot 10^{-4}\ cm^{-1}$			42
	70	2.248		2.082	$168 \cdot 10^{-4}$			
$Cu(en)_3Cl_2 \cdot 075$ en	298		2.07		2.12	2.16		45, 47
$Cu(en)_3Cu(CN)_3$	298		2.07		2.14	2.17		45

E. TETRAGONALLY COMPRESSED OCTAHEDRA

There is a number of truly tetragonally compressed octahedra (Table 4) either diluted in the host lattices and as pure solids. The diluted chromophores are of two types: (i) those which undertake the distortion of the host lattice, i.e. the host complex is by itself compressed; (ii) those which occupy lattice defects of crystals which do not have any relationship with the guest complex. In the latter case the structure of the complex is unknown and there is no simple relationship between the type of host lattice and the induced distortion of the resulting copper complex.

The complexes with MX_6 chromophores doped into host complexes whose structures have been solved by X-ray analysis, are those with X = F in

TABLE 4

g values of tetragonally compressed six-coordinated copper(II) complexes

Cu^{2+} in:	g_z	g_x	g_y	A_z	A_x	A_y	Ref.
Diluted single crystal							
$CdWO_4$	2.012	2.302	2.496	92	15	—	75
$ZnWO_4$	2.000	2.434	2.379	77	—	18	75
$MgWO_4$	2.013	2.334	2.385	76	—	18	75
CsCl	2.012	2.217	2.217	151	—	—	86
NH_4Cl (Center I)	2.045	2.254		11	75		86—91
NH_4Cl (Center II)	2.000	2.219		233	67.2		86—91
NH_4Cl (Center III)	2.009	—		118	—		86—91
NH_4Br (Center I)	2.004	2.217	2.217	182	—		92—95
NH_4Br (Center II)	2.029	2.190		170	—		92—95
NH_4Br (Center III)	2.035	2.204		70	—		92—95
ZnF_2	2.061	2.428	2.354	53	18	8	72
Ba_2ZnF_6	1.990	2.360		125			
$(NH_4)_2Zn(NH_3)_2(CrO_4)_2$	2.017	2.230	2.216	147	10	10	96
$Cd(pz)_2Cl_2$ (at 77 K)	2.010	2.210	2.210	130	—	—	97
$Cu(NH_3)_2Ni(CN_4) \cdot 2\ C_6H_6$	2.019	2.232	2.232	90	58		78
(Cu, Zn)-3-pyridine sulfonate	2.030	2.202	2.263	74	55		98
Cu in L-histidine hydrocloride monohydrate	2.013	2.153	2.262	131	31	62.4	99
Cu in diglycine—barium chloride monohydrate	2.021	2.217		143	10		100, 101
Diluted powder spectra							
$Cu(NH_3)_2Cl_2$—NH_4Cl	2.000	2.223		228	65		102
$Cu(NH_3)_2Cl_2$—$Mg(NH_3)_2Cl_2$	2.007	2.224		81	76		102
$Cu(NH_3)_2Br_2$—NH_4Br	2.008	2.178		141	—		102
$Cu(NH_3)_2Br_2$—$Mg(NH_3)_2Br_2$	2.016	2.174		157	—		102
Undiluted single crystal							
		g_1		g_2	g_3		
Diethylenetriamine copper(II) nitrate		2.103		2.118	2.135		
Bis(methoxyacetate)diaquo copper(II)		2.079		2.167	2.348		83
Bis(2,2'-bipyridyl) copper(II) nitrate		2.029		2.170	2.205		103

$Ba_2Zn_{1-x}Cu_xF_6$ and $Zn_{1-y}Cu_yF_2$ with $x = 0.3$ and $y = 0.01$ respectively. The ZnF_2 compound has a compressed octahedral structure [70,71] (Zn—F distances 204 and 201.5 pm) which apparently induced a similar distortion in the doped copper. However the g value is very large [72] and has been tentatively accounted for by a large angular deviation (smaller F—Cu—F angle in the tetragonal plane = 79.8° and small ligand field strength). The barium hexafluorozincate also has a compressed octahedral structure [73] with Zn—F distances of 196 and 205 pm. The copper doped complex shows a $g_\parallel$ value of 1.99 [74] which is quite consistent with expectation since second order terms are expected to decrease the $g_\parallel$ value below the spin only value in the pure Ba_2CuF_6 complex. The ESR spectra are typical of elongated chromophores antiferrodistortively coupled.

Small $g_\parallel$ values are also observed for copper(II) doped into several tungstates of bivalent ions [75]. In this case a CuO_6 compressed chromophore occurs whose degree of relative compression can be deduced from the cell constants.

Finally there are some diluted chromophores formed by four weak ligands in the tetragonal plane and two strong axial ligands. Typical are the CuO_4N_2, $CuCl_4N_2$ and CuN_6 chromophores present in the complexes $(NH_4)_2Zn(NH_3)_2(CrO_4)_2$ [76], Cd(pyrazole)$_2$Cl$_2$ [77] (see Table 4) and $Cd(NH_3)_2\,(Ni(CN)_4) \cdot 2\,C_6H_6$ [78] respectively. The interesting feature of the ESR spectra of the latter complex is that the $g_\parallel$ and $g_\perp$ values are slightly temperature dependent, a characteristic which has also been found for other copper(II) complexes with the unpaired electron in the $d(z^2)$ orbital [74]. The origin of the temperature dependence was attributed to vibronic coupling, an effect which shows up more neatly for a $g_\parallel \simeq 2.00$.

The pure compounds reported as tetragonally compressed have been analyzed by means of X-ray methods [80,81]. All of them are of low symmetry and show spin exchange. Therefore the crystal g values can be related to molecular values only through an arbitrary choice of the main g directions [82,83].

F. CONCLUSIONS

ESR spectra of six-coordinated copper(II) complexes showing $g_\parallel < g_\perp$ can be assigned to a compressed tetragonal distortion if (i) there is evidence that exchange interactions are not operative i.e. the hyperfine coupling constant is resolved and (ii) $g_\parallel$ is close to the spin only value. Values larger than 2.05 should be considered suspiciously unless $g_\perp$ is larger than 2.25. Low symmetry components might in principle relax this condition.

When exchange narrowing is operative in the crystal, assigning a compressed tetragonal distortion on the basis of the ESR spectra is hazardous because antiferrodistortive type of order may be operative. Values of $g_\parallel$ larger than 2.05 ($g_\perp < 2.25$) and g directions bisecting the copper—donor bonds are strong indications of the latter kind of coupling.

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