THE SPECTRA, STEREOCHEMISTRY
AND ELECTRONIC STRUCTURES OF COPPER(II) COMPLEXES

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The relationships between the spectral properties of Cu(II) complexes with different symmetries and the geometries of the molecules are discussed.

1. *Introduction*

The structures of complexes of first-row transition metals are mostly tetrahedral, square-planar or octahedral [1], or distorted modifications of these, whereas the structures of Cu(II) complexes are generally distorted variations of the base-geometries. The spectral and magnetic properties of Co(III), Ni(II), Co(II), Cr(III), etc. complexes are sensitive indicators of changes in the stereochemistry of the molecules [2—6], but in the case of Cu(II) complexes these properties do not give definite information on the structures of the molecules (see *e.g.* [7—10]).

The present paper gives a survey of the spectral, magnetic and *e.s.r.* properties of mononuclear Cu(II) complexes.

2. *Stereochemistry of compounds*

As a result of X-ray, electron- and neutron-diffraction structure investigations, several different geometrical structures can be shown to occur in the stereochemistry of Cu(II) complexes (Table I).

$K_2PbCu(NO_2)_6$ has a regular octahedral structure with six equivalent Cu—N bonds (2.11 Å) [11]. In $Cu(en)_3SO_4$ [12] there are also six equal Cu—N bonds (2.17 Å), but the presence of ethylene bridges lowers the symmetry to trigonal D_3. A flattened tetrahedron (D_{2d}) occurs, for instance, in the Cs_2CuCl_4 molecule [13]. Tetragonally-distorted six-coordination (D_{4h}) is also quite frequent, *e.g.* in $Cu(NH_3)_4(SCN)_2$ there are four shorter (2.08 Å) in-plane bonds (r_p) and two longer (3.00 Å) axial ones (r_a) [14]. Many rhombically-distorted (elongated) octahedral [15], tetragonally-distorted (compressed) [16] and rhombically-distorted (compressed) octahedral compounds [17] are known.

The Cu(II) chelates of aromatic Schiff bases are mainly square-planar, but the same coordination is found in $CaCuSi_4O_{10}$ [18], too. Moreover, Cu(II) complexes

Table I.

Stereochemistry of Cu(II) complexes

Coord. number	Stereochemistry	Symmetry group	Example*
4	square-planar	D_{4h}	$CaCuSi_4O_{10}$
		D_{2h}	$Cu(3-CH_3-acac)_2$
	compressed tetrahedral	D_{2d}	Cs_2CuCl_4
5	trigonal-bipyramidal	D_{3h}	$Cu(NH_3)_2 . Ag(SCN)_3$, $Cr(NH_3)_6 . CuCl_5$
	square-pyramidal	C_{4v}	$Cu(NH_3)_4H_2O . SO_4$
6	octahedral	O_h	$K_2BaCu(NO_2)_6$, $K_2PbCu(NO_2)_6$
	elongated tetragonal	D_{4h}	$Cu(NH_3)_4(SCN)_2$, $Cu(H_2O)_4(COOH)_2$
	compressed tetragonal	D_{4h}	Ba_2CuF_6, K_2CuF_4
	elongated rhombic	D_{2h}	$CsCuCl_3$, $Ba_2Cu(COOH)_6 . 4 H_2O$
	compressed rhombic	D_2	$Cu(dien)_2(NO_3)_2$
	trigonal	D_3	$Cu(en)_3SO_4$, $Cu(dip)_3Cl_2$
	cis-octahedral		$Cu(dip)_2ONO . NO_3$, $Cu(dip)_2I . I$
8	distorted dodecahedral	D_{2d}	$CaCu(CH_3COO)_4 . 6 H_2O$

* Acac: acetylacetone, pdm: propylenediamine, dien: diethylene-triamine, en: ethylenediamine, dip: α, α'-dipyridyl

involving five (trigonal-bipyramidal [19], square-pyramidal [20]) and eight-coordination [21] are also known.

The structure of a complex is influenced or determined by several factors: the JAHN—TELLER effect [22—26], semicoordination [27—32], the variation in tetragonal distortion [24, 33], π-bonding [27, 34, 35], and steric effects [31, 36—41].

3. *Electronic properties of complexes*

The Cu(II) ion has $3d^9$ outer electron configuration; being the total orbital angular moment $L=2$ and the spin multiplicity $r=2$, the spectroscopic ground state is ^2D.

Due to the effects of ligand fields, the ground-state splits (see *e.g.* Fig. 1). In an octahedral (O_h) field the energies of the x^2-y^2 and z^2 orbitals increase, while those of the xy, xz and yz orbitals decrease, the difference in energy being 10 Dq. In the case of a distorted octahedron or other lower symmetries, these levels split further and new energy levels with a maximum number of $(2L+1)$ may arise.

A summary of splitting schemes occurring for different symmetries is given in Figs. 1 and 2; the ground-states can be seen in Table II.

As regards a discussion of the d^9 electronic system on the basis of the ligand field theory, we refer to the literature [7—10, 42, 43].

Table II.

*One electron orbitals playing roles in the longest wavelength transitions
of Cu(II) complexes with various stereochemical arrangements*

$x^2 - y^2$	elongated tetragonal	xy	compressed tetrahedral
	elongated rhombic		square-planar [Cu(acac)$_2$-type]
	square-planar [CaCuSi$_4$O$_{10}$-type]	z^2,	octahedral[a]
	square-pyramidal	$x^2 - y^2$	
z^2	compressed tetragonal	xy, xz,	tetrahedral[b]
	compressed rhombic	yz	
	trigonal-bipyramidal	xz, yz	elongated tetrahedral[c]
	cis-octahedral		

[a, b, c] Orbitally-degenerate states; with the exception of case a, the degeneracy is removed by spin-orbital coupling.
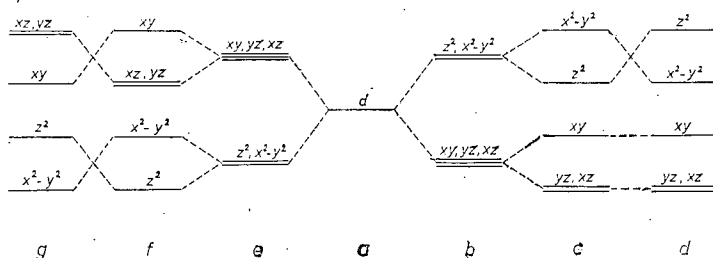

Fig. 1. The splitting of the ground-state of the Cu(II) ion in fields of different symmetries. *a)* free metal ion; *b)* in octahedral (O_h) field; *c)* in elongated tetragonal (D_{4h}) field; *d)* in compressed tetragonal field (D_{4h}); *e)* in tetrahedral (T_d) field; *f)* in compressed tetrahedral (D_{2d}) field; *g)* in elongated tetrahedral (D_{2d}) field.
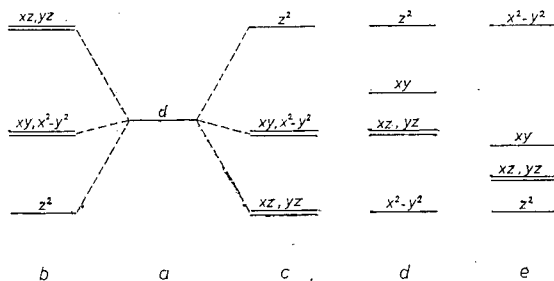

Fig. 2. The splitting of the ground-state of the Cu(II) ion in fields of different symmetries. *a)* free metal ion; *b)* in trigonal (D_3) field; *c)* in trigonal-bipyramidal (D_{3h}) field; *d)* in cis-octahedral (C_{2v}) field; *e)* in square-planar (D_{4h}) field.

4. *Magnetic properties*

When the individual Cu(II) ions in the complex are well separated from each other (~ 5 Å), the effective magnetic moment is in good accordance with the spin-only value (1.73 B.M.) [44]. In practice, the experimental values are somewhat higher; they lie in the range 1.80—2.10 B.M. (Table III) and are practically indepen-

Table III.

Magnetic moments of complexes of different stereochemistry [44]

Compound	Symmetry group	μ_{eff}	Compound	Symmetry group	μ_{eff}
$Cu(NH_3)_4(SCN)_2$	D_{4h}	1.81	$Cu(NH_3)_2 . Ag(SCN)_3$	D_{3h}	1.83
$Cu(NH_3)_4H_2O . SO_4$	C_{4v}	1.87	$Cu(acac)_2$	D_{2h}	1.91
$Cu(dip)_2ONO . NO_3$	C_{2v}	1.89	$Cu(en)_2(BF_4)_2$	D_{2h}	1.88
Cs_2CuCl_4	D_{2d}	1.92	$CaCu(CH_3COO)_4 . 4 H_2O$	D_{2d}	1.94
$K_2CuCl_4 . 2 H_2O$		1.88	$Cu(NH_3)_4(NO_2)_2$	D_{4h}	1.89
$Cu(dip)_2NH_3 . (ClO_4)_2$		1.92			

dent of the stereochemistry. The increase in the moment is a result of the spin-orbit coupling [44]. In simple Cu(II) complexes the electronic ground-state is orbitally nondegenerate, and therefore there is no inherent orbital moment contribution to the magnetic moment of the ground-state. The investigation of magnetic anisotropy offers much more information on stereochemistry [45]. If antiferromagnetic interaction occurs between the Cu(II) ions, then the observed magnetic moment is below the spin-only value [46]; this case, however, is primarily related to multinuclear complexes.
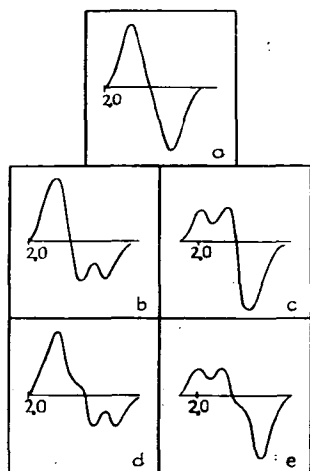
Fig. 3. Schematic structure of the *e.s.r.* spectra of Cu(II) complexes of different symmetries. *a)* isotropic spectrum; *b)* elongated tetragonal, $g > 2.04$; *c)* compressed tetragonal, $g < 2.03$; *d)* elongated rhombic, $g > 2.04$; *e)* compressed rhombic, $g < 2.03$ (derivative curves).

5. *Electron spin resonance spectrum*

Investigation of the *e.s.r.* spectrum [45—50] yields the following informations:

   a) the electronic ground-state of the complex,

   b) the symmetry of the effective ligand field around the central ion,

   c) the orientation of the Cu(II) chromophores in the unit cell.

The spectra can be arranged in three general classes.

   I. Isotropic spectra are observed for compounds with regular octahedral and tetrahedral structures [26, 51—53]; octahedral compounds undergoing JAHN—TELLER distortion; CuL_3X_2-type compounds; and CuL-type compounds with free rotational possibilities (Fig. 3/a).

II. Axial spectra occur [19, 27, 30, 53] when

 a) $g > 2.04$; this is the case for tetragonally-distorted (elongated) octahedral, square-planar, square-pyramidal and trigonal-bipyramidal structures (Fig. 3/b).

 b) $g < 2.03$; in the case of compressed tetragonal, trigonal-bipyramidal, and some compressed rhombic symmetries (Fig. 3/c).

III. Two types of rhombic spectra can be distinguished again [34, 54]:

 a) $g > 2.04$; in the case of elongated rhombic, elongated axial, and distorted square-pyramidal symmetries (Fig. 3/d).

 b) $g < 2.03$; in the case of compressed rhombic, compressed axial, distorted trigonal-bipyramidal and *cis*-octahedral structures (Fig. 3/e).

Table IV illustrates the relations between g values and spectrum types and stereochemistry, for a number of Cu(II) complexes, while the schematic *e.s.r.* spectra for five types mentioned can be seen in Fig. 3.

Table IV.

g values of Cu(II) complexes of different stereochemistry [71]

Spectrum type	Stereochemistry	Example	g values	
Isotropic	octahedral	$K_2PbCu(NO_2)_6$	$g = 2.10$	
	trigonal	$Cu(en)_3SO_4$	$g = 2.13$	
Axial	elongated tetragonal	$Cu(NH_3)_4(SCN)_2$	$g_\perp = 2.056,$	$g_\parallel = 2.237$
	square-planar	$CaCuSi_4O_{10}$	$= 2.054,$	$= 2.326$
	trigonal--bipyramidal	$Cu(NH_3)_2 \cdot Ag(SCN)_3$	$= 2.207,$	$= 2.004$
Rhombic	elongated rhombic	$Cu(dien)_2Br_2 \cdot H_2O$	$g_1 = 2.045,$ $g_3 = 2.213$	$g_2 = 2.097,$
	elongated rhombic	$Ba_2Cu(COOH)_6 \cdot 4 H_2O$	$g_1 = 2.078,$ $g_3 = 2.383$	$g_2 = 2.109,$
	compressed rhombic	$Cu(dien)_2(NO_3)_2$	$g_1 = 2.03,$ $g_3 = 2.16$	$g_2 = 2.13,$
	cis-octahedral	$Cu(dip)_2ONO \cdot NO_3$	$g_1 = 2.029,$ $g_3 = 2.205$	$g_2 = 2.170,$

6. *Spectra*

Four types of transitions have to be taken into account in the spectra of Cu(II) complexes: those below 20 kK: (*i*) $d-d$ transitions; (*ii*) the possible vibrational overtones of the ligand; and those above 20 kK: (*iii*) charge-transfer transitions, (*iv*) intraligand transitions. In the following we deal only with $d-d$ transitions. These transitions are controlled by spin multiplicities (forbidding of intercombinations), and the LAPORTE rule [2, 4, 55, 56]; nevertheless, these selection rules are lifted in these multi-electron systems [2, 55, 56]. The reflection spectra, and especially the polarized single-crystal spectra, give good information on stereochemistry [57, 58]. Similarly to the term-splitting schemes (Figs. 1 and 2), the spectra are also discussed on the basis of one-electron energy levels; *i.e.* the electron-electron interactions are neglected.

I. *Four-coordination*

1. *Compressed tetrahedral structure*

In Cs_2CuCl_4 the Cu—Cl bond-length is 2.22 Å, and the Cl—Cu—Cl angles are 120° and 103° [13, 59]; the molecule is of D_{2d} symmetry. The complex is magnetically anisotropic: $g_1 = 2.083$, $g_2 = 2.103$, $g_3 = 2.384$ [60]. The bonds formed with the strongly polarizable Cl^- ions are predominantly covalent, as proved by the low value of the coupling constant λ [60, 61].

The characteristic maximum appears at 9.50 kK [62] in the fused-salt spectrum, at 7.00 kK [59] in the crystal spectrum, and at 12.40 kK for $CsCd_{1-x}Cu_xCl_3$ compounds. The fused-salt spectrum gives a band lying between the bands of the octahedral and the tetrahedral forms. With increasing temperature this band shifts towards the band of the tetrahedral form [62]. In the spectrum of the $CuCl_4^{2-}$ ion three transitions can be expected (see Fig. 1/f):

$$(z^2)^2(x^2-y^2)^2(xz, yz)^4(xy)^1 \rightarrow (z^2)^2(x^2-y^2)^2(xz, yz)^3(xy)^2, \quad (v_1)$$
$$\rightarrow (z^2)^2(x^2-y^2)^1(xz, yz)^4(xy)^2, \quad (v_2) \qquad (I)$$
$$\rightarrow (z^2)^1(x^2-y^2)^2(xz, yz)^4(xy)^2. \quad (v_3)$$

The bands due to the above transitions appear at 4.28, 7.78 and 8.50 kK. The polarized crystal spectra also give bands between 5 and 9 kK [60]. The reflection spectrum (Fig. 4/1) yields a broad band at around 11.20 kK, which can be divided into two components, at 10.50 and 12.00 kK.

These bands can be assigned to the transitions v_2 and v_3. The data indicate a strong distortion of the molecule. In aqueous solution the experimental band is broadened ($v_{max} = 12.60$ kK). This is very likely due to the presence of $Cu(H_2O)_{6-x}Cl_x$-type species [64]. In pyridine the band shifts even further: ($v_{max} = 14.12$ kK).
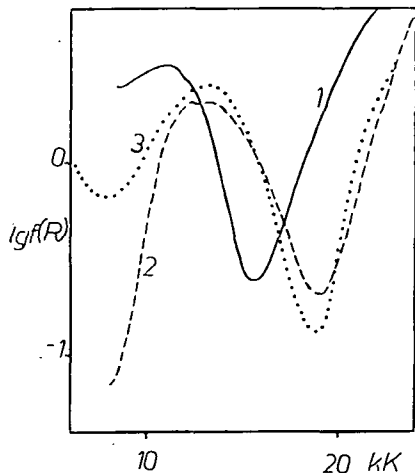
Fig. 4. Reflection spectra. *1:* Cs_2CuCl_4; *2:* $Cu(NH_3)_2 . Ag(SCN)_3$; *3:* $K_2PbCu(NO_2)_6$.

2. *Square-planar arrangement*

In the case of square-planar chelates π-bonds are formed with the xz and yz orbitals of the Cu(II) ion. In these complexes the in-plane bonds are shorter than those in the tetragonally-distorted octahedral molecules. Regular square-planar coordination (D_{4h}) occurs in $CaCuSi_4O_{10}$ [18], where all the Cu—O bond-lengths are roughly the same (1.91 Å).

The band of highest energy in the spectrum is assigned to the transition (see Fig. 2/e):

$$(z^2)^2(xz, yz)^4(xy)^2(x^2-y^2)^1 \rightarrow (z^2)^1(xz, yz)^4(xy)^2(x^2-y^2)^2.$$

The stereochemistry of $Cu(acac)_2$, with ligands capable of π-bonding, is rhombically-distorted square-planar (D_{2h} symmetry) [33, 57]. In the single-crystal spectrum the three bands at 14.50, 15.60 and 18.00 kK are then assigned to the transitions:
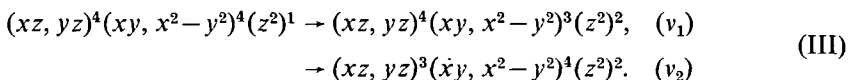
$$(xz, yz)^4(x^2-y^2)^2(z^2)^2(xy)^1 \rightarrow (xz, yz)^4(x^2-y^2)^2(z^2)^1(xy)^2, \quad (\nu_1)$$
$$\rightarrow (xz, yz)^4(x^2-y^2)^1(z^2)^2(xy)^2, \quad (\nu_2) \qquad \text{(II)}$$
$$\rightarrow (xz, yz)^3(x^2-y^2)^2(z^2)^2(xy)^2. \quad (\nu_3)$$
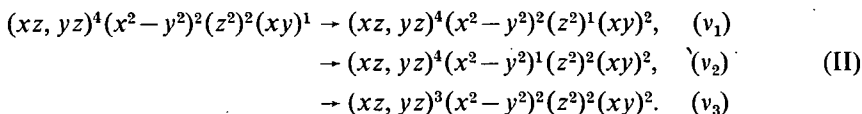
The interpretation of the spectrum becomes possible by the assumption of π-bonding [65]. The band measured in chloroform solution can be divided into three GAUSS bands, at 15.00, 15.20 and 18.80 kK [66]. There is only a slight difference between the spectrum of the crystal and that of the chloroform solution. This fact can be interpreted by the weak intramolecular interaction in the crystalline state [66].

II. Five-coordination

Trigonal-bipyramidal structure

In $Cu(NH_3)_2 \cdot Ag(SCN)_3$ the bond-lengths are: $Cu-N(H)_3 : 2.00$ Å, $Cu-N(CS)$: 1.92 Å [19]. The CuN_2N_3' chromophore has D_{3h} symmetry, and the compound is paramagnetic, with 1.83 B.M. [44]. The e.s.r. spectrum is of axial type, $g_{\parallel} = 2.004$, $g_{\perp} = 2.207$ [20], and the ground orbital is z^2.

According to the term-scheme there are two possible transitions (Fig. 2/c):

$$(xz, yz)^4(xy, x^2-y^2)^4(z^2)^1 \rightarrow (xz, yz)^4(xy, x^2-y^2)^3(z^2)^2, \quad (\nu_1)$$
$$\rightarrow (xz, yz)^3(xy, x^2-y^2)^4(z^2)^2. \quad (\nu_2) \qquad \text{(III)}$$

On the other hand, in the single-crystal spectrum there are three bands [65], at 10.50, 13.30 and 14.60 kK. This fact is interpreted by spin-orbit coupling and by π-bonding, and it is proved by the low values of the coupling constant [67]. NH_3 and NCS^- lie near to each other in the spectrochemical series, and thus the spectrum of the complex is very similar to that of the complex $Cu(NH_3)_5^{2+}$. The reflection spectrum between 10 and 16 kK contains a wide complex band, the three components of which are at 11.20, 13.00 and 14.60 kK. In pyridine the maximum is at 14.60 kK.
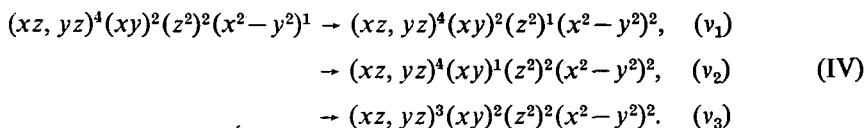

III. Six-coordination

Regular octahedral Cu(II) complexes are hardly known, but several complexes of distorted octahedral structure can be prepared.

1. Octahedral structure

The complex $K_2PbCu(NO_2)$, containing the CuN_6 chromophore, is of octahedral structure [24, 51], but due to the dynamic JAHN—TELLER effect, this is distorted [24, 51]. The e.s.r. spectrum is isotropic, $g = 2.11$, and assuming octahedral geometry (O_h) the ground-state is degenerate (z^2, x^2-y^2). The reflection spectrum

(Fig. 4/3) contains two bands, at 16.50 and 7.00 kK. Due to the JAHN—TELLER effect, the appearance of these bands can be interpreted by distortion of the octahedral symmetry (D_{4h}). Accordingly, the following three transitions have to be taken into account (Fig. 1/c):

$$(xz, yz)^4(xy)^2(z^2)^2(x^2-y^2)^1 \rightarrow (xz, yz)^4(xy)^2(z^2)^1(x^2-y^2)^2, \quad (v_1)$$

$$\rightarrow (xz, yz)^4(xy)^1(z^2)^2(x^2-y^2)^2, \quad (v_2) \qquad \text{(IV)}$$

$$\rightarrow (xz, yz)^3(xy)^2(z^2)^2(x^2-y^2)^2. \quad (v_3)$$

The v_1 band merges into a wide band at around 16.50 kK. In aqueous solution $(v_{max}=13.10 \text{ kK})$ this band indicates the presence of mixed aqua-nitro species. In pyridine the shift appears on a smaller scale $(v_{max}=15.30 \text{ kK})$. The observed change, in comparison with the reflection spectrum, can be interpreted by interaction between the atomic orbitals of copper and the solvent molecules.

2. Tetragonal structure

The complexes $Cu(H_2O)_4(COOH)_2$, $Cu(NH_3)_4(NO_2)_2$, $Cu(NH_3)_4(SCN)_2$, etc. are tetragonally-distorted octahedral ones. $Cu(NH_3)_4(SCN)_2$ is of D_{4h} symmetry and is paramagnetic, with 1.81 B.M. [68]; $g_\perp=2.056$ and $g_\parallel=2.237$; the ground-state is: x^2-y^2 [34]. For this compound the measure of tetragonal distortion $(T=r_p/r_a)$ is $T\sim0.70$.

The low-temperature single-crystal spectrum [34] contains three bands, at 17.90, 15.70 and 14.00 kK; these may be assigned to the transitions (IV). If π-bonding is also formed, then the z^2 and xy orbitals interchange. v_1 is a measure of the tetragonal distortion, and a relationship can be found between v_1 and the in-plane Cu-N bond-lengths. By the use of the spectrum and the e.s.r. data, the spin-orbit reduction factor can be calculated, $k_\parallel=0.74$ and $k_\perp=0.76$. These values indicate the predominant covalent character of the bonds [69]. The broad band appearing at 10—20 kK in the reflection spectrum (Fig. 5/1) can be resolved into three Gaussian curves at 14.00, 16.00 and 17.00 kK. The calculated [70] value of 10 Dq is 12.20 kK. In pyridine, only one, nearly symmetric band is obtained, at 14.50 kK.

Examples of compressed tetragonal symmetry are less known and no polarized single-crystal spectrum for this type is available. Sometimes even the ground-states and the one-electron orbital sequences are controversial in the different references.

Fig. 5. Reflection spectra. 1: $Cu(NH_3)_4(SCN)_2$; 2: $Ba_2Cu(COOH)_6\cdot4 H_2O$; 3: $Cu(dip)_3Br_2$.

3. Rhombic structure

$Ba_2Cu(COOH)_6\cdot4 H_2O$ is of elongated rhombic structure [15] and is paramagnetic, with 1.88 B.M. The e.s.r. spectrum is of rhombic-type [15], $g_1=2.087$, $g_2=2.109$, $g_3=2.383$.
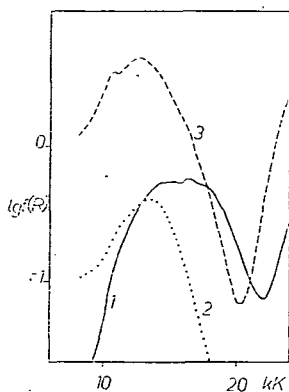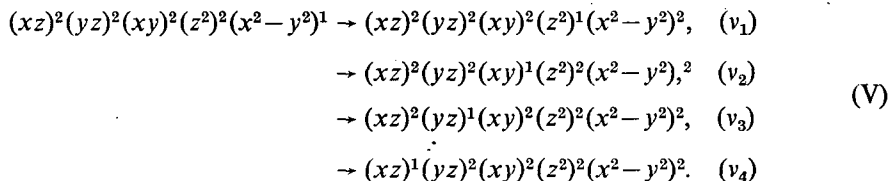
The polarized single-crystal spectrum is similar to those of the tetragonal complexes [34, 69], but spectra polarized in the x and y directions are different. The spectrum can be interpreted by D_{2h} symmetry; the ground-state is x^2-y^2 [71]. Four bands can be distinguished, at 8.40, 10.60, 13.10 and 14.50 kK [71], which can be assigned to the following transitions:

$$(xz)^2(yz)^2(xy)^2(z^2)^2(x^2-y^2)^1 \rightarrow (xz)^2(yz)^2(xy)^2(z^2)^1(x^2-y^2)^2, \quad (v_1)$$

$$\rightarrow (xz)^2(yz)^2(xy)^1(z^2)^2(x^2-y^2),^2 \quad (v_2)$$

$$\rightarrow (xz)^2(yz)^1(xy)^2(z^2)^2(x^2-y^2)^2, \quad (v_3) \qquad (V)$$

$$\rightarrow (xz)^1(yz)^2(xy)^2(z^2)^2(x^2-y^2)^2. \quad (v_4)$$

The reflection spectrum (Fig. 5/2) contains a wide band $v_{max}=13.40$ kK, the spectrum of the aqueous solution $(v_{max}=13.10)$ is only slightly different, and in pyridine the band is shifted to 15.15 kK. The decrease in the coupling constants (0.78—0.86) indicates mainly ionic bonding [69].

Though the elongated rhombic form is more frequent, there are examples (e.g. Ba_2CuF_6, $Cu(dien)_2(NO_3)_2$) of the compressed version, too. The spectrum of the dien complex has been investigated by STEPHENS [17]. From the rhombic-type (symmetry: C_2) e.s.r. spectrum, $g_1=2.0266$, $g_2=2.1440$ and $g_3=2.1570$ [52]; the ground orbital is z^2.

In the single-crystal spectrum the presence of three bands can be detected, at 8.00, 12.00 and 16.00 kK; these are assigned to the $x^2-y^2 \rightarrow z^2$, $xy \rightarrow z^2$ and $xz,yz \rightarrow z^2$ transitions [7]. The one-electron orbital sequence is $z^2 > x^2-y^2 > xy > xz, yz$. The broad band observed in the reflection spectrum can be resolved into three Gaussian curves, at 12.10, 14.00 and 16.00 kK (Fig. 6/3). In water or in pyridine, only one, nearly symmetric band is measurable, at 16.20 and 17.05 kK, respectively.

4. Trigonal structure

$Cu(dip)_3Br_2$ and $Cu(en)_3SO_4$ have trigonally-distorted structures. The en complex has an isotropic e.s.r. spectrum, $g=2.13$ [24]; the symmetry is D_3; the ground orbital is xy (see Fig. 2/b).

The single-crystal spectrum of $Cu/Zn(dip)_3Br_2 \cdot 6 \ H_2O$ shows three bands, at 6.40, 14.40 and 14.70 kK; in xy- and z-polarization the spectra are similar. The reflection spectrum of $Cu(en)_3SO_4$ yields only one band, at 15.60 kK. In aqueous solution this band is shifted considerably $(v_{max}=18.20$ kK). The spectrum of $Cu(dip)_3Br_2$ (Fig. 5/3) also contains a single wide band, the maximum being at 12.70 kK. The spectral character of the aqueous solution is similar, but the band is shifted to 14.00 kK. The structures of the spectra of aqueous and pyridine solutions are of the same character.

When interpreting the properties of these compounds, the JAHN—TELLER theorem has to be taken into account. According to this theorem, with a lower than octahedral symmetry a more stable structure is formed and consequently the degeneracy of the ground-state is removed. Hence, in the spectra there are more bands than is to be expected from the simple term-scheme.

5. *Cis-octahedral structure*

In the $Cu(dip)_2ONO.NO_3$ molecule (CuN_4O_2 chromophore) the lengths of the four Cu—N bonds are between 1.98 and 2.10 Å, and those of the two Cu—O bonds are 2.27 and 2.35 Å [36]. The symmetry of the molecule is C_{2v}. The complex is paramagnetic, with 1.89 B.M. [68]. From the rhombic-type *e.s.r.* spectrum, $g_1 = 2.029$, $g_2 = 2.170$ and $g_3 = 2.205$ [36]; the ground orbital is z^2.

The crystal spectrum changes with the direction of the polarization; the bands lie between 9.5 and 15.00 kK. These bands, according to the C_{2v} symmetry, are assigned to the transitions (see Fig. 2/d) [72]:
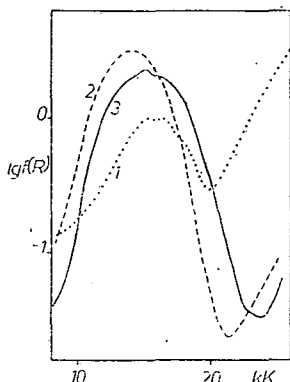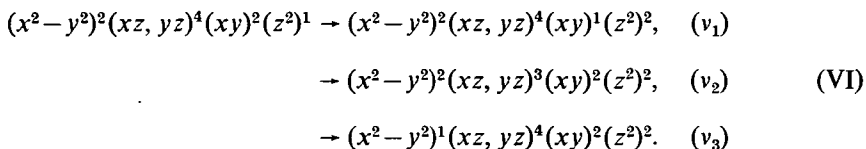
$$(x^2-y^2)^2(xz, yz)^4(xy)^2(z^2)^1 \rightarrow (x^2-y^2)^2(xz, yz)^4(xy)^1(z^2)^2, \quad (\nu_1)$$

$$\rightarrow (x^2-y^2)^2(xz, yz)^3(xy)^2(z^2)^2, \quad (\nu_2) \qquad \text{(VI)}$$

$$\rightarrow (x^2-y^2)^1(xz, yz)^4(xy)^2(z^2)^2. \quad (\nu_3)$$

Fig. 6. Reflection spectra.
1: $Cu(dip)_2ONO \cdot NO_3$;
2: $CaCu(CH_3COO)_4 \cdot 6 H_2O$;
3: $Cu(dien)_2(NO_3)_2$.

The reflection spectrum is also strongly complex (Fig. 6/1), and the aqueous spectrum is only slightly changed in comparison with the reflection spectrum.

IV. *Eight-coordination*

Distorted dodecahedral structure

According to the structure investigations [21] on $CaCu(CH_3COO)_4 \cdot 6 H_2O$, there are four shorter (1.97 Å) and four longer (2.79 Å) Cu—O bonds. The symmetry is D_{2d}. From the rhombic-type *e.s.r.* spectrum, $g_1 = 2.079$, $g_2 = 2.109$ and $g_3 = 2.383$ can be calculated [71].

The single-crystal spectrum was investigated by BILLING *et al.* [73], and by GLIEMANN and MORYS [74]. The results are similar, but as regards the ground-states, the assignments and the one-electron orbital sequences the opinions are divided. The reflection (Fig.6/2) and the absorption spectra of the aqueous solution are very similar; the band is at around 14 kK.

7. *Conclusions*

It can be stated that by the sole use of magnetic moments, the reflection or the absorption spectrum, structure determinations of Cu(II) complexes are quite impossible. Success can only be expected if multiple investigations of single-crystal polarization spectra, *e.s.r.* spectra and quantum-chemical calculations are carried out.

The maximum in the reflection spectrum can be taken as a measure of the in-plane field [75]; this increases with decrease of the axial field.

As expected for complexes with D_{4h} symmetry, $10\,Dq$ varies inversely with the ratio r_p/r_a. Due to extremely complicated solvation equilibria, the spectra of solutions are even more difficult to interpret.

In most cases the ligand field calculations do not give exact orbital sequences. For the square-planar arrangement, for instance, it cannot be decided whether the z^2 orbital lies above or below the xy, xz and yz orbitals. It can be determined, however, which orbital has the highest energy and which will contain the odd electron. The following example [76] illustrates how the relation between the axial and in-plane fields affects the orbital sequences. In the case of elongated geometries:

$$r_p/r_a = 1.0 - 0.79: \quad (xz, yz) < xy < z^2 < x^2 - y^2,$$

$$= 0.75 \quad : \quad (xz, yz) < z^2 < xy < x^2 - y^2.$$

For compressed geometries:

$$r_p/r_a = 0.82 \quad : \quad xy < x^2 - y^2 < (xz, yz) < z^2.$$

The real one-electron orbital sequence can only be given by quantum-chemical calculations.

The investigation of *e.s.r.* spectra is very important, as it allows determination of the molecular symmetry and of the ground orbitals on which the unpaired electron dwells. In the knowledge of the optical and *e.s.r.* spectra, the spin-orbit coupling constant λ can be calculated, and by using this conclusions can be drawn on the character of the bonds.

It is important to mention that a relationship was found between the degree of tetragonal distortion and the square of the frequency of the Cu—L stretching vibration [77].

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СПЕКТРЫ, СТЕРЕОХИМИЯ И ЭЛЕКТРОННАЯ СТРУКТУРА КОМПЛЕКСОВ МЕДИ (II)

Й. Часар и Я. Балог

Обсуждаются зависимость между спектральными свойствами и стерической структурой медных (II) комплексов.