Single-crystal Polarized Electronic and Electron Spin Resonance Spectra of Dichlorobis(triphenylphosphine oxide)copper(II)

By **Ivano Bertini, Dante Gatteschi,** and **Giacomo Martini,** Istituto di Chimica Generale e di Chimica-fisica, Laboratorio C.N.R., 39 via Nardi, 50132 Firenze, Italy

The polarized single-crystal electronic and e.s.r. spectra of dichlorobis(triphenylphosphine oxide)copper(II) have been recorded and the spectral properties have been interpreted on the basis of a compressed tetrahedral geometry in C_2 symmetry.

PSEUDOTETRAHEDRAL copper(II) complexes are not numerous and in all the known instances the chromophores have been found to be distorted towards square-planar geometry.[1] The electronic properties of the pseudotetrahedral $CuCl_4^{2-}$ complex have been accounted for by assuming the d_{xy} orbital to be the most destabilized orbital,[2] whereas it has been suggested that the $d_{x^2-y^2}$ orbital might be the highest energy one for the bis(2,2'-bipyridylamine)copper(II) complex cation, which has a similar geometry.[3] Recently the X-ray structure determination of the dichlorobis(triphenylphosphine oxide)copper(II) complex $[Cu(Ph_3PO)_2Cl_2]$ has been reported.[4] We have recorded polarized electronic and e.s.r. spectra of $Cu(Ph_3PO)_2Cl_2$ with the aim of contributing to the knowledge of the energy level order in this kind of copper(II) complex.

EXPERIMENTAL

Crystallographic Data.—Single crystals of $Cu(Ph_3PO)_2Cl_2$ were obtained as previously described;[5] they are rhombic,[4] space group $Fdd2$, $a = 31·961$, $b = 20·839$, $c = 9·886$ Å, $Z = 8$, with the copper(II) ion in a C_2 site symmetry (C_2 is parallel to c). The crystals were prismatic in shape, elongated along c, with the (100) and (010) most highly developed faces. A schematic drawing of the chromophore is shown in Figure 1.

Electronic Spectra.—The electronic spectra were recorded with the apparatus previously described[6] on the (100) and (010) faces at 77 and 300 K along the a, b, and c directions.

E.S.R. Spectra.—The e.s.r. measurements were performed using a Varian V 4502 X-band 100 kHz field-modulation
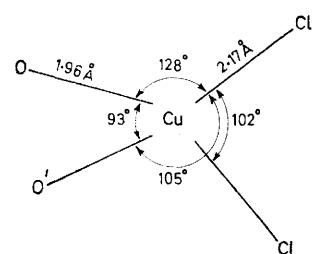

FIGURE 1 A schematic drawing of the CuO_2Cl_2 chromophore

spectrometer equipped with a variable temperature assembly. Measurements of the static magnetic field were done by means of a proton resonance. The g-factors were calibrated using a $10^{-2}M$ aqueous solution of manganese(II). The crystals were mounted on a quartz capillary using silicon grease and the spectra were recorded at every rotation of 15° around the three crystallographic axes.

RESULTS

Electronic Spectra.—The electronic spectra recorded on the (010) and (100) faces at 77 K are reported in Figure 2. The spectra recorded on the (100) face are of poorer quality

[1] L. Helmholtz and R. F. Kruh, *J. Amer. Chem. Soc.*, 1952, **74**, 1176; B. Morosin and E. C. Lingafelter, *J. Phys. Chem.*, 1961, **65**, 50; P. L. Orioli and L. Sacconi, *J. Amer. Chem. Soc.*, 1966, **88**, 277; T. P. Cheeseman, D. Hall, and T. N. Waters, *J. Chem. Soc.* (A), 1966, 1396; C. Panattoni, G. Bombieri, and R. Graziani, *Acta Cryst.*, 1967, **A23**, 537; J. E. Johnson, T. A. Beineke, and R. A. Jacobson, *J. Chem. Soc.* (A), 1971, 1327.

[2] J. Ferguson, *J. Chem. Phys.*, 1964, **40**, 3406; C. Furlani, E. Cervona, F. Calzona, and B. Baldanza, *Theor. Chim. Acta*, 1967, **7**, 375.

[3] R. J. Dudley, B. J. Hathaway, and P. G. Hodgson, *J.C.S. Dalton*, 1972, 882.

[4] J. A. Bertrand and A. R. Kalyanaraman, *Inorg. Chim. Acta*, 1971, **5**, 341.

[5] D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.* (A), 1961, 2298.

[6] I. Bertini, D. Gatteschi, and F. Mani, *Inorg. Chem.*, 1972, **11**, 2464.

due to the thinness of the crystals. The spectra recorded along a and b are very similar to each other with respect to the position and the shape of the bands, with a maximum at 10·4 kK, and two shoulders, in the low frequency range, at 8·5 and 6·5 kK. However the intensities of the bands are different in the two spectra, the spectrum recorded along a being more intense, as revealed by the comparison with the spectrum recorded along c both on the (100) and (010) faces. The latter shows only one broad band, with maximum at 7·2 kK. Minor changes in the position of the maxima with temperature in the a and b spectra are observed. They are probably due to some changes in the relative intensities of the transitions and/or to a change of ligand field strength, as X-ray powder photographs at room and low temperature revealed no change in the structural parameters.

E.S.R. Spectra.—The single crystal e.s.r. spectra have been recorded at 77 K. In all the orientations of the sample in the magnetic field only one signal was observed, as expected on the basis of the structural data. The linewidth increases drastically with temperature so that at room temperature no signal is practically observable. The
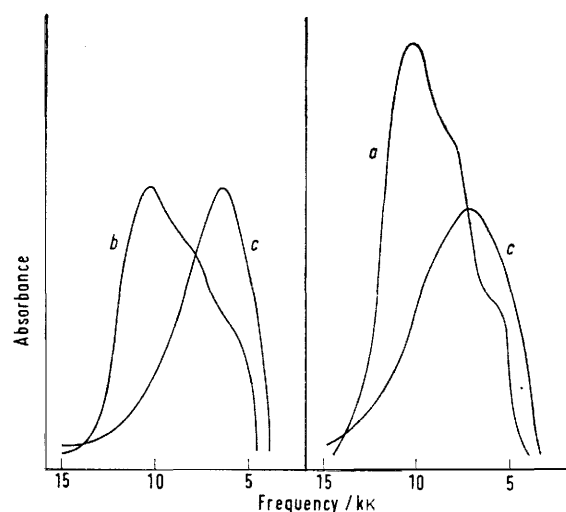

FIGURE 2 Single-crystal polarized electronic spectra of the CuO_2Cl_2 chromophore recorded at 77 K on the (100) and (010) faces

principal magnetic directions of the crystal coincide with the crystallographic axes, the g-values being (± 0.001) $g_a = 2.385$, $g_b = 2.091$, $g_c = 2.071$. Also powder spectra were recorded at 77 K; due to the small difference in the g_b and g_c values an apparent two g-value spectrum was obtained, $g_{\parallel} = 2.389$, $g_{\perp} = 2.078 \pm 0.003$. In this case too, line broadening with increasing temperature was observed, so that no spectra were recorded at room temperature.

DISCUSSION

The co-ordination polyhedron has been described[4] as derived from a tetrahedron affected by two different distortions, elongation along the C_2 axis and twisting of the interplanar angles (Cl–Cu–Cl' and O–Cu–O' see Figure 1) from 90 to 71°. Neglecting the latter distortion, it was suggested to describe the geometry of the chromophore as an elongated tetrahedron. In our opinion the polyhedron may be merely considered as a tetrahedron compressed along the axis bisecting the Cl–Cu–O' and

Cl'–Cu–O angles (pseudo-S_4 axis). These angles in fact are larger than 109° 28' (the tetrahedral value) while the other four angles are smaller than this value, as is expected for a compressed tetrahedron. The interplanar angle around the pseudo-S_4 axis is 86°, which compares well with the values found in other compressed tetrahedral copper(II) complexes.[1] The pseudo-S_4 axis lies in the ab plane, forming an angle of 15° with the a axis.

The site-symmetry of the copper(II) ion is C_2, however a symmetry as high as D_{2d} could be assumed to be operative if the inequivalence of chlorine and oxygen donor atoms and minor angular distortions were neglected. In this case, the pseudo-S_4 axis forming an angle of 15° with the a axis, the spectra recorded along c and b would be expected to be almost identical. This is contrary to what is observed. On the other hand the different intensities of the spectra recorded along a and b rule out the possibility that the c axis be the S_4 of the elongated tetrahedron.

Therefore the assignment of the spectra can be attempted only on the basis of the C_2 symmetry. The five d orbitals are split into three A and two B levels by a C_2 ligand field and since one transition is polarized parallel to the C_2 axis whereas three are normally polarized, the 7·2 kK is assigned to the $B \rightarrow B$ transition, and the other three bands at 10·4, 8·5, and 6·5 kK to $B \rightarrow A$ transitions. Because of the low symmetry of the chromophore it is difficult to specify which orbital contributes most to each level. Further light can be shed on the problem by comparison with the assignment of the spectra of the $CuCl_4$ chromophore. Choosing the z molecular axes coincident with the S_4 or pseudo-S_4 axes of $CuCl_4$ and $Cu(Ph_3PO)_2Cl_2$ respectively and labelling as y the C_2 axis of the latter complex the following correlation holds

	D_{2d}	C_2
d_{z^2}	A_1	A
$d_{x^2-y^2}$	B_1	A
d_{xy}	B_2	B
$d_{xz,yz}$	E	$A + B$

The assignments for the two chromophores, which are reported in the Table, agree quite closely, the only

The assignments of the polarized single-crystal electronic spectra of the CuO_2Cl_2[a] and $CuCl_4$[b] chromophores.

CuO_2Cl_2			$CuCl_4$		
$B \longrightarrow A$		6·7 kK	$B_2 \longrightarrow E$		5·5 kK
B		7·2			
A		8·5		B_1	7·4
A		10·4		A_1	9·0

[a] C_2 Symmetry. [b] D_{2d} Symmetry.

difference being the high frequency shift of the bands of $Cu(Ph_3PO)_2Cl_2$. This may be due either to the inequivalence between oxygen and chlorine donor atoms or to the larger planar distortion[7] operative in the latter complex [the angle θ between the pseudo-S_4 axis and the bond directions is *ca.* 64° in $Cu(Ph_3PO)_2Cl_2$ and 62° in $CuCl_4$].

[7] D. W. Smith, *J. Chem. Soc. (A)*, 1970, 2900.

The e.s.r. data yield immediately only the g_y molecular value, equal to the g_c crystallographic value, since the C_2 axes of all the eight molecules are aligned along the c crystal axis (space group $Fdd2$, C_2 site symmetry [8]) whereas the g_x and g_z values cannot be determined due to the different angles made by the molecular axes with the crystallographic axes in the ab plane. The molecules however may be divided into two sets having opposite direction cosines relative to the crystallographic axes, so that the relations between the molecular and the crystal g values are

$$g_a{}^2 = \cos^2\alpha\, g_z{}^2 + \mathrm{sen}^2\alpha\, g_x{}^2$$
$$g_b{}^2 = \mathrm{sen}^2\alpha\, g_z{}^2 + \cos^2\alpha\, g_x{}^2$$

where α is the angle of the z axis with the a axis. These equations obviously cannot be used to establish the directions of the molecular axes, however they can provide useful information. It can be seen that for $\alpha = 45°$ the equations do not admit any solution and for α values close to $45°$ one g value is less than 2. Since this does not

seem reasonable [9] α values ranging from 25 to 65° have to be discarded. If the magnetic axes are chosen coincident with those of the electronic spectra $\alpha = 15°$ and consequently $g_z = 2\cdot408$, $g_x = 2\cdot064$, and $g_y = 2\cdot071$. These values compare quite well with those reported for CuCl$_4$ [10] and with the magnetic anisotropy data for the latter complex.[11]

In conclusion, it is well established that the d_{xy} orbital is the ground orbital (hole formalism). Moreover in the present case the magnetic axes are either coincident with the optical axes or quite close to them. It is remarkable that the g values are quite close to the values expected for a D_{2d} symmetry, whereas the electronic spectra require a C_2 symmetry.

[8] A. Abragam and B. Bleaney, 'Electron Paramagnetic Resonance of Transition Ions,' Clarendon, Oxford, 1970.
[9] B. J. Hathaway and D. E. Billing, *Co-ordination Chem. Rev.*, 1970, **5**, 143.

[10] M. Sharnoff, *J. Chem. Phys.*, 1964, **41**, 2203.
[11] B. N. Figgis, M. Gerloch, J. Lewis, and R. C. Slade, *J. Chem. Soc. (A)*, 1968, 2028.