

## Single Crystal ESR Study of the $\text{Cu}(\text{en})_3\text{SO}_4$ Complex

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(Received July 23, 1974)

Copper(II) complexes having a site symmetry larger than that allowed by the Jahn-Teller theorem, as  $\text{Cu}(\text{en})_3^{2+}$ ,  $\text{Cu}(\text{bipy})_3^{2+}$ ,  $\text{Cu}(\text{OMPA})_3^{2+}$  and  $\text{Cu}(\text{NO}_2)_3^{3-}$ , still represent a puzzle for inorganic chemists.<sup>1</sup> We wish to report the results of the investigation on the compound  $\text{Cu}(\text{en})_3\text{SO}_4$ , by means of low temperature single crystal esr spectroscopy. The  $\text{Cu}(\text{en})_3^{2+}$  complex has  $D_3$  symmetry (space group  $P\bar{3}1c$ ,  $Z = 2$ )<sup>2</sup> and electronic spectra very close to those of  $\text{Cu}(\text{bipy})_3^{2+}$  and  $\text{Cu}(\text{phen})_3^{2+}$  both in number of bands and polarizations properties.

The powder esr spectra at room temperature give an isotropic signal with a  $g$  value at 2.12, while single crystal data provided  $g_{\parallel} = 2.126$  and  $g_{\perp} = 2.110$ .<sup>6</sup> At the liquid nitrogen temperature the powder spectrum is largely anisotropic allowing to estimate two  $g$  values,  $g_{\parallel} = 2.06$  and  $g_{\perp} = 2.16$ . The transition from the isotropic to the anisotropic spectrum occurs within 2 K at 180 K. The single crystal spectra recorded at 77 K show more than one resonance signal and in some orientation three magnetically non equivalent sites are evidenced. In every case the spectrum was resolved into three lorentian components by a curve fitting program. By rotating the crystal perpendicularly to the (100) face two signals of intensity 1:2 are observed. The former varies between the extrema values  $g_1 = 2.053$  and  $g_3 = 2.159$  the angles of the  $g$  directions with the  $C_3$  axis being 55 and 145° respectively. Assuming these axes to be two main  $g$  directions, the esr spectra were recorded by rotating the crystal along a direction parallel to the  $g_1$  direction.

The positions of the signals for this rotation ( $r$ ), calculated through the curve fitting program, are reported in Figure 1. The main features of these spectra are: i) every 90° the extrema  $g_1$  value appears; ii) every 180° an extremating  $g$  value,  $g_3 = 2.159$

appears but with a phase difference from the previous signal of 45°; iii) another  $g$  value,  $g_2$  appears at 90° from the  $g_3$  direction with the value of 2.134.

These data are accounted for by assuming a model with three magnetically non equivalent sites. The existence of three sites indicates that the symmetry of the crystal at low temperature has to be lower than trigonal, since in the room temperature cell only two molecules are present. Further one has to assume that no exchange coupling is operative in these non-diluted copper(II) crystals. The three  $g_1$  directions are related by the  $C_3$  axis of the room temperature coordinate system, forming an angle of 55° with it, one of the  $g_1$  directions lying on the (100) face. Also the  $g_2$  and  $g_3$  directions of the three sites are related by the  $C_3$  axis,  $g_2$  being coincident with the crystallographic  $C_2$  axis orthogonal to  $g_1$ . The relative orientations of the main  $g$  directions for the three sites, as referred to a cube, are shown in Figure 2. Within the experimental error such directions are related by the symmetry operations of the  $D_3$  point group, that is the same point group of the molecule site symmetry.

Referring to the cube of Figure 2, it appears evident that during the rotation ( $r$ ) (Figure 1) the signal of site I varies between  $g'_2$  and  $g'_3$  whereas the other two signals vary between  $g_1$  and  $[(g_2)^2 + (g_3)^2]/2$ .<sup>1/2</sup>. The same pattern is obtained when the rotation is performed along the other two  $g_1$  directions. Furthermore, when the crystal is rotated normally to the (100) face, that is along a  $C_2$  axis, the  $g$  values of site I vary between  $g_1$  and  $g_3$  whereas the  $g$  values of sites II and III are coincident. Finally, by rotating along the  $C_3$  axis, the same spectrum is obtained every 120°.

Willing to refer the  $g$  directions to the molecule, there are two possibilities due to the uncertainty of the sense of the  $c$  axis, *i.e.* to the uncertainty of labelling the face containing  $a$  and  $b$  (001) or (00 $\bar{1}$ ).<sup>7</sup> In both cases  $g_2$  is coincident with the molecular  $C_2$  axis; however in the first case  $g_1$  is coincident with one of the three Cu-N axes. In the second case,  $g_1$  and  $g_3$  are rotated, with respect to the former case, by 110° around  $C_2$  through  $C_3$ . Although the first possibility is more tempting there is no way at the moment to choose on a sound base.

If one remembers that the complex is isotropic at room temperature, the present model is consistent

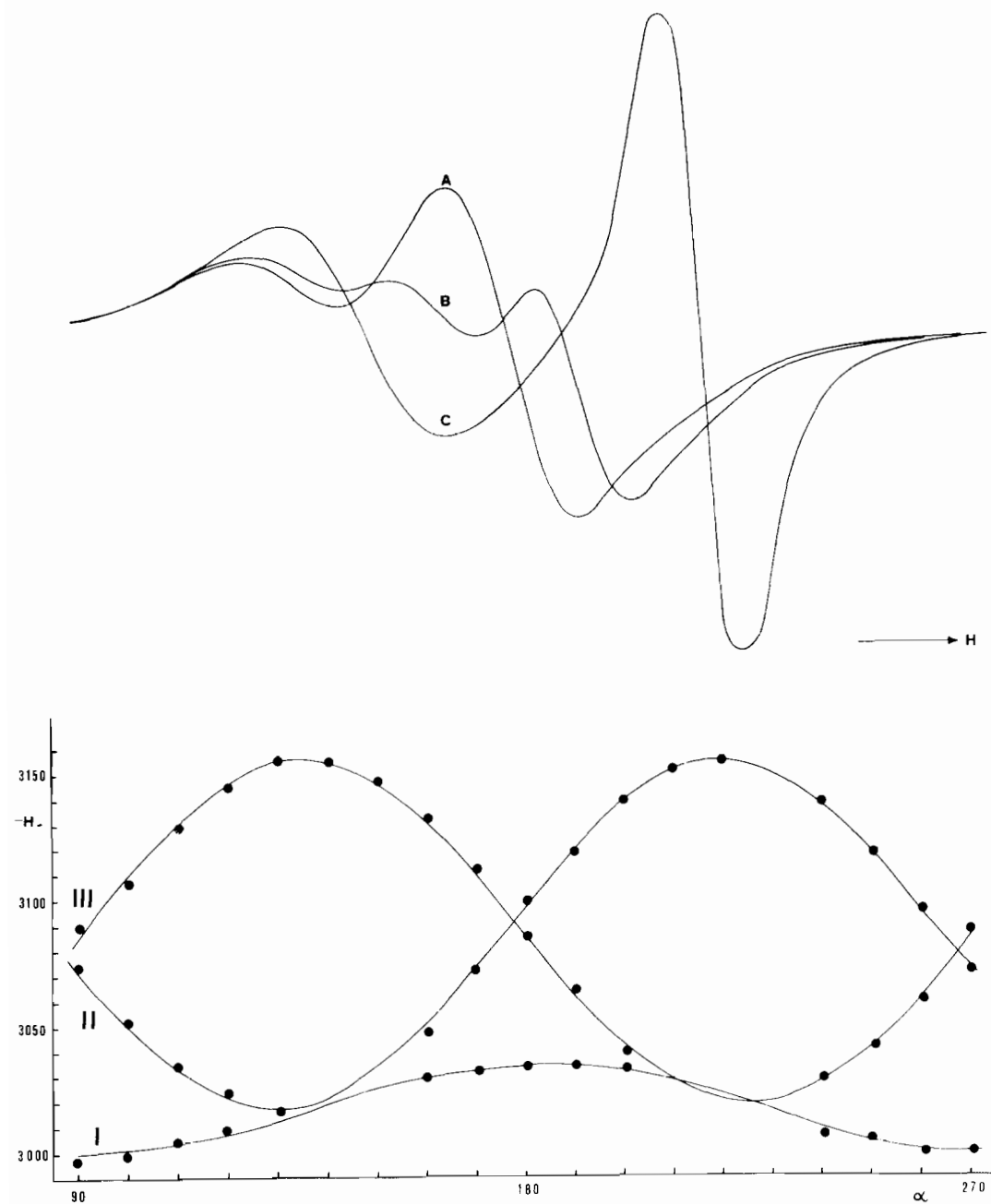
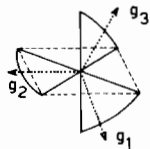
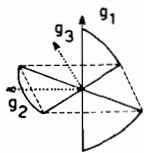


Fig. 1. Above, single crystal esr spectra of the  $\text{Cu}(\text{en})_3\text{SO}_4$  complex recorded rotating about the  $g'_1$  direction (see text). The angles between the magnetic field and the (100) face are: A,  $90^\circ$ ; B,  $100^\circ$ ; C,  $130^\circ$  and  $220^\circ$ . Below, the variation of the resonating fields with the angle. The dots are the points obtained by the Lorentzian analysis.



with a static-dynamic Jahn-Teller effect.<sup>8,9</sup> The  $g$  values pattern is somewhat unusual and cannot be straightforwardly related to a stereochemistry. It is different from that shown by the trigonal  $\text{Cu}(\text{bipy})_3^{2+}$ <sup>10</sup> and  $\text{Cu}(\text{OMPA})_3^{2+}$ <sup>7</sup> but is similar to

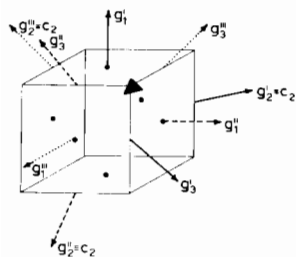


Fig. 2. A scheme of the relative orientations of the crystallographic axes at room temperature and of the  $g$  directions for the three sites at low temperature. The axes have been referred to a cube for clarity purposes.

that shown by  $\text{Cu}(\text{NO}_2)_6^{3-}$ .<sup>11</sup> Before trying to relate the  $g$  values with the type of distortion experienced by the complex, both low temperature X-ray investigations and more single crystal esr data on other complexes are needed. A similar research on trigonal and triclinic  $\text{Cu}(\text{bipy})_3^{2+}$  complexes is now in progress in our laboratories.

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