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A Comment on the Jahn–Teller Effect in the Complex $K_2PbCu(NO_2)_6$

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Recently copper(II) complexes with axial or higher site symmetry at room temperature have arisen a great interest[1-6] owing to their reversible properties to show a larger magnetic anisotropy at low temperature than that allowed by crystal symmetry. Up to date, single crystal esr investigations have been reported for the complexes $K_2PbCu(NO_2)_6$[3,7] (T_h site symmetry), $Cu(OMPA)_3(ClO_4)_2$ (D_3)[2] and $Cuen_3SO_4$ (D_3)[6]. Quite lately Billing[8] published a letter mainly concerned with the properties of the complexes $Cuen_3SO_4$ and $K_2PbCu(NO_2)_6$ using single crystal esr data published by our group. The data regarding the latter compound, however, were preliminary, a more complete and exhaustive research having been published thereafter by Pilbrow and Harrowfield.[3] Billing's disregard of the latter communication induced us to compare the temperature dependence of the esr data of these compounds and to report a few characterizing properties of single crystals of $K_2PbCu(NO_2)_6$.

Cubic crystals of $K_2PbCu(NO_2)_6$[9] experience two phase transitions at 273 K and 281 K.[6,10] The latter temperature corresponds to that at which the esr spectra suddenly become anisotropic.[3,7] Pilbrow and Harrowfield showed that below 281 K the complex undergoes a tetragonal distortion which is isooriented within domains. The esr spectra reported show the presence of two signals of different intensities indicating the coexistence of two domains not equally populated. They are misaligned by 90° within the experimental error of the esr technique. Application of a stress parallel to the tetragonal axis of the crystal changes the relative population of the domains. The authors proposed that the distortion is a compression.

In contrast of the behaviour of the $K_2PbCu(NO_2)_6$, the single crystal esr spectra of $Cu(OMPA)_3(ClO_4)_2$ and $Cuen_3SO_4$ at low temperature always show three signals of equal intensity.[2,6] The directions of the three unique ($g_\parallel$) magnetic axes are orthogonal to each other and the three non equivalent magnetic sites are related by the symmetry operations of the C_3 and D_3 point groups respectively. This suggests that the trapping out of the three distortions may be 1) statistical at the molecular level in such a way that the unit cell does not change when the compound becomes anisotropic; 2) statistical with respect to small domains each of them containing only one type of distortion; 3) ordered in the crystal with a new unit cell containing the three distortions. Preliminary X-ray data on $Cu(OMPA)_3(ClO_4)_2$ indicate[2] the presence of three triclinic ($P\bar{1}$) cells related by a C_3 symmetry axis. This can be interpreted as consistent with the possibility (2). The fact that the compound is opaque at low temperature[4] can be considered a support of this hypothesis.

Low temperature X-ray data are missing for $Cuen_3SO_4$; however, at the liquid N_2 temperature it is transparent, always extinguished on the (001) face, although a phase transition has been observed when it became anisotropic.

In the case of $K_2PbCu(NO_2)_6$ the polymeric structure through NO_2 groups linking both Cu and Pb may account for large cooperative effects which force the copper chromophores to distort in the same way within a domain. This mechanism is probably responsible for the different population of the domains.

It is within this framework that we have studied the effect of changing the cooling conditions on the esr spectra of $K_2PbCu(NO_2)_6$. Actually, whereas the

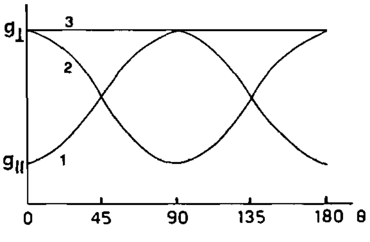

Fig. 1. Three different esr spectra, recorded under different cooling conditions, of $K_2PbCu(NO_2)_6$. The spectra were recorded with the crystal aligned in such a way that a C_2 axis is parallel to the oscillating magnetic field vector. · · · · Crystal cooled by sinking into liquid nitrogen (θ = 30°, θ being the angle between the magnetic field and the closest C_2); —— crystal cooled with a nitrogen stream passing through liquid nitrogen (θ = 0°); - - - - crystal cooled with a nitrogen stream passing through melting ice (θ = 40°).

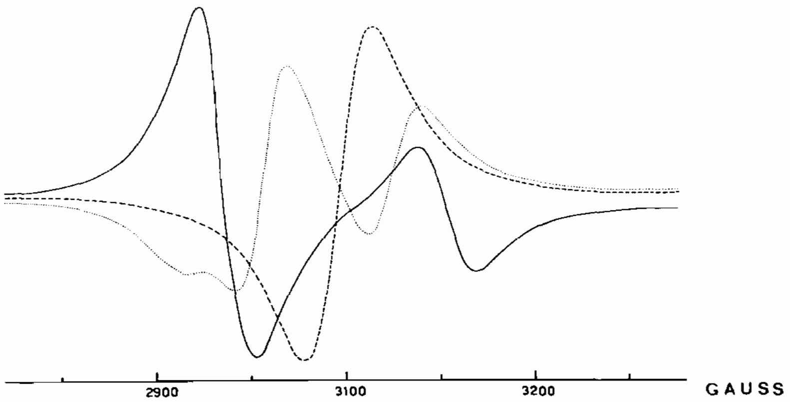

Fig. 2. The variation of the g values for each of the three independent magnetic sites by rotation around the tetragonal crystal axis. θ is the angle of the direction of the magnetic field with a C_2 crystal axis.

spectra below 281 K are not temperature dependent, apart from the usual narrowing of the signals, a change in the cooling conditions may result in a dramatic variation of the spectrum shape. For example, if the crystal is cooled by sinking it into liquid nitrogen it shows three signals, two of them of comparable intensity. If, on the contrary, the crystal is cooled under the mildest conditions, *i.e.* by cooling the crystal with an ice-cooled nitrogen stream, only one signal is observed. As previously reported, two signals are often observed under the usual low temperature recording conditions, *i.e.* by cooling the nitrogen stream with liquid nitrogen. In conclusion, as shown in Figure 1, one, two or three signals can be obtained depending on the cooling conditions. Despite the variability of the signals' intensities with the cooling conditions, the resonance positions can well be accounted for on the basis of the structural data. When three signals are observed, it may be assumed that a three domain structure has been trapped out. By rotating along one crystallographic C_2 axis, one signal varies between $g_{\parallel}$ and $g_{\perp}$, the second between $g_{\perp}$ and $g_{\parallel}$, and the third is not orientation dependent. The extrema g values ($g_{\parallel} = 2.061$; $g_{\perp} = 2.145$) of the orientation dependent signals are found along the other two C_2 axes. Therefore the $g_{\parallel}$ direction is coincident with one Cu–N bond. The behaviour of the signal positions under a rotation is shown in Fig. 2. When only one signal is observed it may behave as any one of the three shown in Fig. 2, that is it may vary between the extreme g values or remain in the $g_{\perp}$ position along a full rotation. If one looks at the g values, a $g_{\parallel} < g_{\perp}$ pattern is observed for the hexanitro[3,13] and tris ethylenediamine complexes[6] whereas the more common reverse pattern is found for the tris octamethylpyrophosphoramide[2] as well as for the trigonal tris bipyridine complex.[14] The assignment of a *trans* compressed structure to the former complexes,[3,8,15,16] and an elongated one to the latter complexes[17] seems now sound, although the factors determining the type of distortions are not understood. The problem of $g_{\parallel}$ being larger than 2.00 in the case $g_{\parallel} < g_{\perp}$ is better accounted for by the zero point motion[18] than by assuming unusual values[8] of the orbital reduction parameter $K_{\parallel}$.

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