Molecular Nature of the g Anomalies in Bis(diselenocarbamate)copper(II) Complexes

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It is pointed out that from the measured principal g values in single crystals of bis(diethyldiselenocarbamate)copper(II) it is possible to deduce the g values for the single molecular unit. By a reasonable choice of its principal directions it turns out that the g tensor is axial along the bisecting line of the major angle between the Cu–Se bonds, with $g_{\|} \sim 2.05$ and $g_{\perp} \sim 2.01$. These values seem to confirm the presence, also in the pure Cu crystals, of the main g anomaly, recently observed in the Cu : Ni diluted crystals. Therefore, one can infer that the anomaly is essentially due to the nature of the Cu–Se bonds and not to distortions produced by the Ni diamagnetic matrix.

Introduction

Some recent papers [1–4] have shown interesting magnetic anomalies in Cu(II) : Ni(II)bis(diselenocarbamate) diluted crystals, where Cu metal coordinates four Se atoms in a rectangular planar arrangement. The g tensor is approximately axial with its maximum value $g_2 \sim 2.05$ along a direction lying in the molecular plane (y axis, see Fig. 1) and not, as usual, perpendicular to that plane. The other two values (very close to the free electron value, e. g. $g_1 \sim 1.995$, $g_3 \sim 2.005$), are found in directions forming angles of about 45° with the molecular plane.

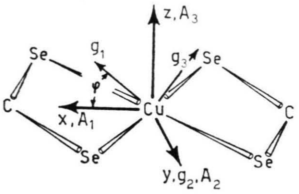

Fig. 1. Molecular structure and principal axes of the g and A tensor in the Cu-bis(diselenocarbamate) complex.

On the other hand, the A tensor shows a quite "normal" behaviour: in fact, it is approximately axial with its maximum value along a direction perpendicular to the molecular plane.

The question is whether these anomalies are inherent of the molecule Cu + 4 Se or due to distortions produced by an eventual difficulty of the Ni diamagnetic matrix to accomodate the cupric ion.

In this paper we try to clarify this question by an ESR study on Cu-bis(diethyldiselenocarbamate) single crystals, which show a dimeric molecular arrangement, contrary to the monomeric arrangement of the Ni-compound.

The crystals of Cu-bis(diethyldiselenocarbamate), $C_{10}H_{20}CuN_2Se_4$, are monoclinic [5] (space group $P\,2_1/c$), with $a = 9.883$, $b = 10.860$, $c = 17.173$ Å, $\beta = 113°12'$ and $Z = 4$.

Single-ion g Values

In spite of the presence of two magnetically unequivalent ions in the elementary cell, the ESR spectra of Cu-bis(diethyldiselenocarbamate) crystals consist of only one line for all the possible orientations of the static magnetic field, both in the X and Q-band.

Two cases are possible: either the relevant line width (from 250 to 550 gauss) does not allow resolution of the resonances of the two unequivalent ions [6], or a strong isotropic exchange interaction produces only one resonance line with a g value averaged from those of the two ions [7].

However, it is possible in both cases to relate the experimental principal values of g in the ac plane of symmetry ($g_{\mathrm{ac},1}$, $g_{\mathrm{ac},2}$) and along the b axis (g_{b}) to the principal values of the single magnetic ion (g_1, g_2, g_3), if one assumes as known the directions of the latter ones.

The former seems to be the case of the compound under study, owing to the large dimer-to-dimer distance (~ 10 Å). Therefore, one can apply the well known formula for the single ion [8]

$$g^2 = g_1^2\, l^2 + g_2^2\, m^2 + g_3^2\, n^2\,, \qquad (1)$$

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where l, m, n are the direction cosines of the static magnetic field with respect to g_1, g_2 and g_3.

Relating the single-ion direction to three orthogonal axes X, Y, Z (Y coincident with b crystal axis), it follows that the g values in the ac plane can be expressed by

$$\begin{aligned} g_{\mathrm{ac}}^2(\Theta) &= g_1^2 (R_{1X} \sin\Theta + R_{1Z}\cos\Theta)^2 \\ &\quad + g_2^2 (R_{2X}\sin\Theta + R_{2Z}\cos\Theta)^2 \\ &\quad + g_3^2 (R_{3X}\sin\Theta + R_{3Z}\cos\Theta)^2 \end{aligned} \tag{2}$$

where $R_{i\alpha}$ is the direction cosine of g_i with respect to the α-axis and Θ is the counterclockwise angle (around the Y axis) measured from the Z axis to the direction of the static magnetic field.

The experimental principal g values, therefore, are obtained by

$$g_{\mathrm{b}}^2 = g_1^2 R_{1Y}^2 + g_2^2 R_{2Y}^2 + g_3^2 R_{3Y}^2, \tag{3 a}$$

$$g_{\mathrm{ac},1}^2 = g_{\mathrm{ac}}^2(\overline{\Theta}), \tag{3 b}$$

$$g_{\mathrm{ac},2}^2 = g_{\mathrm{ac}}^2(\overline{\Theta} + \pi/2) \tag{3 c}$$

where

$$\tan(2\overline{\Theta}) = \tag{4}$$
$$= \frac{2(R_{1X}R_{1Z}g_1^2 + R_{2X}R_{2Z}g_2^2 + R_{3X}R_{3Z}g_3^2)}{(R_{1Z}^2 - R_{1X}^2)g_1^2 + (R_{2Z}^2 - R_{2X}^2)g_2^2 + (R_{3Z}^2 - R_{3X}^2)g_3^2}$$

As one can see, Eqs. (3) and (4) allow to deduce the values of g_1, g_2 and g_3 from the experimental values of $g_{\mathrm{ac},1}$, $g_{\mathrm{ac},2}$, g_{b} and $\overline{\Theta}$, if the $R_{i\alpha}$ terms are known, i. e. in case it is possible to make a reasonable choice of the directions of the principal axes of the single-ion g tensor. There is one equation in excess, which may be used as a test for the correctness of the procedure. For instance, the values of g_1, g_2 and g_3, calculated by means of the set (3), allow to obtain, from (4), a value for the angle $\overline{\Theta}$ to be compared with the experimental result. Only a reasonable agreement between these two values can assure that $g_{\mathrm{ac},1}$ and $g_{\mathrm{ac},2}$ are the limiting values (in the ac plane) for the single-ion g tensor, as required from experimental data.

Results and Discussion

The ESR spectra were obtained by means of an X-band Varian V 4502 spectrometer with 100 kHz field modulation, equipped with the Varian conversion kit for the Q-band. The static magnetic field was measured by means of a nuclear resonance probe, for the X-band, and a DPPH marker, for the Q-band.

The experimental principal values of g, at room temperature, are

$$g_{\mathrm{ac},1} = 2.043 \pm 0.003, \quad g_{\mathrm{ac},2} = 2.012 \pm 0.001, \quad g_{\mathrm{b}} = 2.023 \pm 0.002, \tag{5}$$

and are found [9] along the directions shown in Figure 2. The relevant errors are due to the large line width.

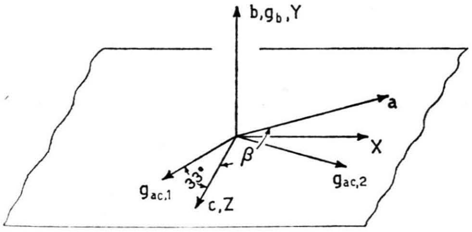

Fig. 2. Experimental principal directions of g in Cu-bis(diethyldiselenocarbamate) crystals.

At this point it is necessary to fix the axes of the single-ion g tensor. With the Cu + 4 Se molecular unit in mind, the following two choices appear possible.

(i) Taking into account the relevant D_{2h} symmetry of the molecular unit and the C_{2h} character (with y the main axis) evident in the ESR data of the Cu : Ni diluted compounds, it is reasonable to assume that one of the principal single-ion g values (g_2) is along the y molecular axis. Nothing can be said, however, about the other two principal directions: in fact, there is no "a priori" reason why the feeble anomaly shown by the Cu:Ni diluted compounds (g_1 and g_3 at ca. 45° from the plane) should be present also in the Cu pure compound.

In Fig. 3(a), the principal single-ion g values, deduced from Eqs. (3), are plotted versus the angle φ, which g_1 and g_3 may form with the molecular axes (see Figure 1). The values of the angle $\overline{\Theta}$, deduced from Eq. (4) using the calculated g values, are also plotted as a check of the procedure. For all values of φ, except for a narrow range near a singularity ($\varphi \sim 10° \pm 1°$), the calculated $\overline{\Theta}$ is in very good agreement with the experimental value $\overline{\Theta}_{\mathrm{ex}} \sim -33°$, measured assuming the Z axis coincident with the c axis.

It is evident that the single-ion g tensor turns out to be almost axial, with its maximum value along the y molecular axis, whichever direction, among those possible, g_1 and g_3 may have. Moreover, the principal values are similar to those of the diluted com-

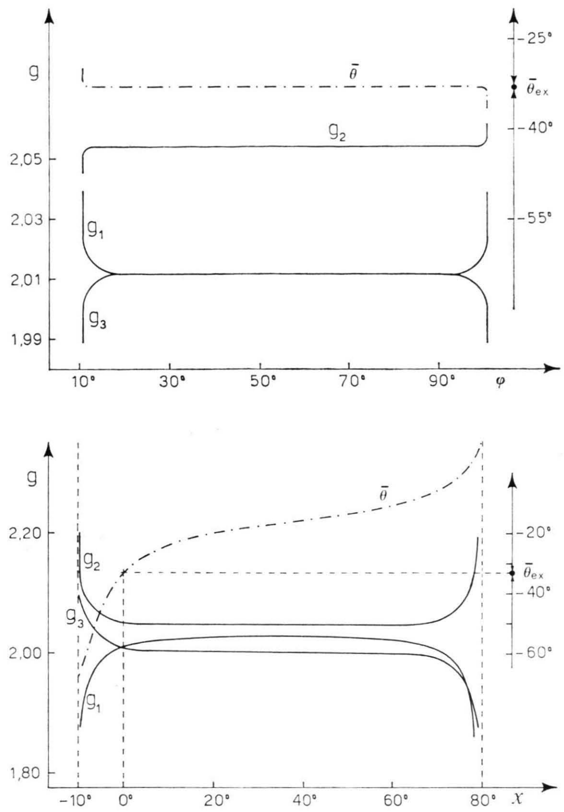

Fig. 3. Single-ion g values deduced from Eqs. (3) and corresponding $\bar{\Theta}$ values deduced from Equation (4). (a) y molecular axis is assumed as g_2 direction and φ is the counterclockwise angle by which g_1 and g_3 are rotated with respect to x and z molecular axes. (b) z molecular axis is assumed as g_3 direction and χ is the counterclockwise angle by which g_1 and g_2 are rotated with respect to x and y. For φ and χ values outside the ranges shown, it is obvious that $g_1(\varphi \pm \pi/2) = g_3(\varphi)$ and $g_2(\varphi \pm \pi/2) = g_2(\varphi)$ (case a); $g_1(\chi \pm \pi/2) = g_2(\chi)$ and $g_3(\chi \pm \pi/2) = g_3(\chi)$ (case b).

pounds, taking into account also the experimental uncertainty of $g_{\mathrm{ac},1}$, $g_{\mathrm{ac},2}$ and g_{b}.

(ii) Alternatively, assuming for the molecular unit a magnetic D_{4h} symmetry with eventual C_{2h} distortions (with z the main axis), as more usual for copper planar complexes, it appears reasonable to fix a single-ion g axis (g_3) orthogonal to the molecular plane. As one can see in Fig. 3 (b) (where χ is the counterclockwise angle by which g_1 and g_2 are rotated with respect to the molecular in-plane axes), we obtain coherent solutions for Eqs. (3) and (4) only when one of the other principal directions is very close to the y axis. Such a situation coincides with that for $\varphi \sim 0^\circ$ of Fig. 3 (a) and, therefore, this result supports the previous hypothesis of C_{2h} symetry.

From both cases, (i) and (ii), it follows that the main g-anomaly is present also in the pure Cu-crystals and, therefore, we may consider such an anomaly as essentially due to the copper-selenium bond and not to distortions produced by the host diamagnetic nickel matrix *. As supposed in Ref. [4], this is probably due to an anomalous spin-orbit quenching, deriving from both the highly covalent character of the unpaired electrons (2/3 of which are shared by the Se ligands) and the large one-electron spin orbit constant of the Se ligands (about twice that of the Cu (II) ion).

There is a last point worthy of discussion. In the decomposition of the experimental g values, we have assumed one single-ion g axis coincident with a direction characteristic of the Cu + 4 Se molecule (y or z), disregarding the dimeric nature of the complex ion. A priori, this is correct only if the two magnetically equivalent units of the dimeric complex do not interact or interact by isotropic exchange. In fact, in both cases the only resonance line is centered at the same g values of the single unit. When anisotropic exchange is present, the center of gravity of the unresolved fine structure lines does not necessarily correspond to the g value of the single unit. This correspondence is still valid, however, if the anisotropic part of the exchange interaction is of perturbative order with respect to the Zeeman interaction of the dimeric complex.

Owing to the large line width observed, we cannot exclude a presence of unresolved fine structure, up to $\sim$200 gauss of separation. In this limit, however, the perturbative character of the anisotropy is undoubted, compared with the Zeeman interaction (up to 12.000 gauss using Q-band). The maximum uncertainty of g, due to an exchange anisotropy ΔJ, can be calculated as [10]

$$\Delta g \sim \frac{g}{32}\left(\frac{\Delta J}{g\,\beta\,H}\right)^2 \sim \frac{2}{32}\left(\frac{200}{12.000}\right)^2 \sim 0.001\,, \quad (6)$$

and therefore does not seem able to invalidate our results.

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[6] This is supported by the presence, in the ESR spectra, of feeble shoulders, that vanish in the ac plane of symmetry.

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[8] In presence of a very strong isotropic exchange, the expression of *g* would be linear rather than quadratic, as we shall discuss in detail in a future paper. However, the numerical results for the two cases almost coincide, owing to the low *g* anisotropy of the compound under study.

[9] We thank Dr. A. Mangia, of the Parma Istituto di Chimica Generale e Inorganica, for kindly furnishing the necessary X-ray information.

[10] This formula has been deduced, in the limit $\Delta J \ll g \beta H$, from A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Clarendon, Oxford 1970, England, p. 502.

* *Note in proofs:* In a recent publication (G. Agastini, P. L. Nordio, L. Pasimeni, and U. Segre, J. C. S. Faraday II, **70,** 621 [1974] analogous conclusions are deduced from a study of Cu-bis (diethyldiselenocarbamate) dissolved in nematic solvents.