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On the Principal Axes of the g- and A-Tensors of Cu(II)-Ions Substituted in Low-Symmetry Sites

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The introduction of paramagnetic metal ions into a diamagnetic host crystal can give rise either to a genuine substitution process or to an interstitial insertion. The determination of the eigenvalues and the eigenvectors of the g- and A-tensors can be used in the elucidation of the coordination sphere of the guest ion. We report on three cases of Cu^{2+} *ion doping, where the study of the eigenvectors is essential in the determination of the local environment of the guest ion.*

Introduction

When a paramagnetic ion is located in a low-symmetry environment, the principal directions of th g- and A-tensors are not imposed by symmetry, and the actual determination of these directions is by no means trivial [1–3]. Such a situation frequently arises when a diamagnetic salt is doped with paramagnetic ions, particularly in the case of non-isomorphism: the substitution will almost certainly induce distortions of unknown magnitude. Obviously in these cases, it is important to reproduce by calculation not only the three principal values of g and A, but also the orientation of the two corresponding tensors.

One possibility is that the tensors, obtained from theory and from experiment, are found to coincide on the basis of a calculation that assumes the ligand positions of the host crystal. Obviously, this fact constitutes an argument in favor of a simple substitution process, where the original diamagnetic metal ion has been replaced by the paramagnetic entity, without any observable change in its coordination sphere. Another possibility is that the tensors, obtained from theory and experiment can be made to concide on the basis of a calculation that accounts for certain small displacements of the ligands in the host crystal. This result still constitutes substantial evidence in favor of a substitution process, and in addition, it provides an idea on the extent of the distortion, associated with the substitution. A final possibility is that theoretical and experimental tensors cannot be made to coincide for any conceivable distortion of the coordination sphere; if so, one has to conclude that no substitution has taken place, and that therefore the paramagnetic ion is situated in an interstitial position.

Experimental Data

Examples of the three possibilities, mentioned in the Introduction, are offered by the three cases that will be treated in this note. In each case, Cu(II)-ions are introduced into non-isomorphic host crystals, namely tetrakis(salicylate)tetraaquodicadmium(II), a seven-coordinated complex [4], bis(β-alanine)zinc(II)nitrate tetrahydrate, a six-coordinated complex [5], and bis(salicylato)strontium(II) dihydrate, an eight-coordinated complex [6]. Figures 1–3 show the three structures, as determined from X-Ray crystallographic data [5–7]. Tables I–III resume the angular positions of the coordinating atoms and the experimental data on the EPR–tensors in the doped crystals. In a number of previous communications [4–6], the g- and A-values were simply calculated along the experimental eigenvectors, assuming an idealized environmental symmetry. It is the purpose of the present paper to extend this earlier work, so as to incorporate the calculation of the tensor orientations in the discussion of the substitution process.

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TABLE I. Angular Coordinates of the Coordinating Atoms in Tetrakis(salicylate)tetra-aquodicadmium(II) or Sal–Cd for short. O(7) and O(8) correspond to Water Ligands.

	O(1)	O(4)	O(2)	O(5)	O(7)	O(8)	O(4')
θ	93.9	95.8	39.3	42.9	95.7	93.7	171.4
ϕ	−10.9	−178	−12.3	−178.3	−97.4	83.9	175.5

Experimental EPR-parameters in Sal–Cd. More details can be found in ref. [4].

$g_1 = 2.432$	$A_1 = (105.6)\ 10^{-4}\ \text{cm}^{-1}$	$\vec{g}_1, \vec{A}_1 \parallel z$
$g_2 = 2.100$	$A_2 = (30.4)$	$\vec{g}_2, \vec{A}_2 \parallel x$
$g_3 = 2.076$	$A_3 = (24.2)$	$\vec{g}_3, \vec{A}_3 \parallel y$

TABLE II. Angular Coordinates of the Coordinating Atoms in bis(β-alanine)-zinc(II) nitrate tetrahydrate, or Ala–Zn for short. O(1), O(1'), O(2) and O(2') correspond to Water Ligands.

	O(1)	O(1')	O(3)	O(3')	O(2)	O(2')
θ	90	90	90	90	1.25	178.75
ϕ	89	269	0	180	109	289

Experimental EPR-parameters in Ala–Zn

$g_1 = 2.400$	$A_1 = (135)\ 10^{-4}\ \text{cm}^{-1}$	$\vec{g}_1, \vec{A}_1 \parallel z$
$g_2 = 2.097$	$A_2 = (22)$	$\vec{g}_2$ at 78° from x, $\vec{A}_2$ near y
$g_3 = 2.084$	$A_3 = (24)$	$\vec{g}_3$ at −12° from x, $\vec{A}_3$ near x

TABLE III. Angular Coordinates of the Coordinating Atoms in Bis(salicylato)strontium(II) dihydrate, or Sal–Sr for short; w indicates a Water Ligand.

	O^1 (10)	O^6 (w)	O^2 (10)	O^5 (w)	O^3 (10)	O^3 (9)	O^4 (10)	O^4 (9)
θ	75.5	53.4	75.5	53.4	136	131.6	136	131.6
ϕ	317	35	137	215	0	70	180	250

Experimental EPR-parameters in Sal–Sr

$g_1 = 2.296$	$A_1 = (150.5)\ 10^{-4}\ \text{cm}^{-1}$	$\vec{g}_1, \vec{A}_1$ near x
$g_2 = 2.076$	$A_2 = (27.7)$	$\vec{g}_2$ near y, $\vec{A}_2$ at ~25° from $\vec{g}_2$
$g_3 = 2.047$	$A_3 = (21.7)$	$\vec{g}_3$ near z, $\vec{A}_3$ at ~25° from $\vec{g}_3$

Methods and Parameters

The calculations will be carried out in terms of ligand field theory; in its angular overlap version, this theory associates two parameters σ and π to each metal–ligand interaction. As for the calculation of the g- and A-tensors, use was made of a computer program, written by Bencini and Gatteschi [8], which is based on the work of Gerloch and Meeking [9]; in the calculation of the hyperfine structure, one needs to introduce the parameters κ and P. Table IV shows the optimal values of the different parameters, that reproduce the experimental g- and A-values as closely as possible.

For the second complex, Ala–Zn, a more detailed analysis was possible than for the other two molecules. Indeed for Ala–Zn, optical spectra were available and the band envelope at ~12.3 kK was

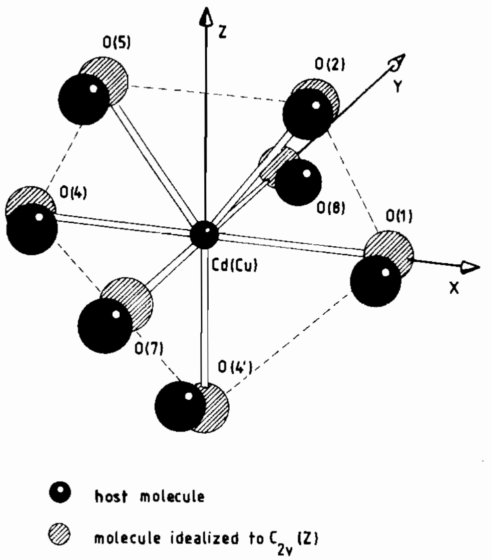

Fig. 1. Tetrakis(salicylate)tetra-aquodicadmium(II) (or Sal–Cd). Full circles: host molecule; shaded circles: idealized C_{2v}(z)-structure.

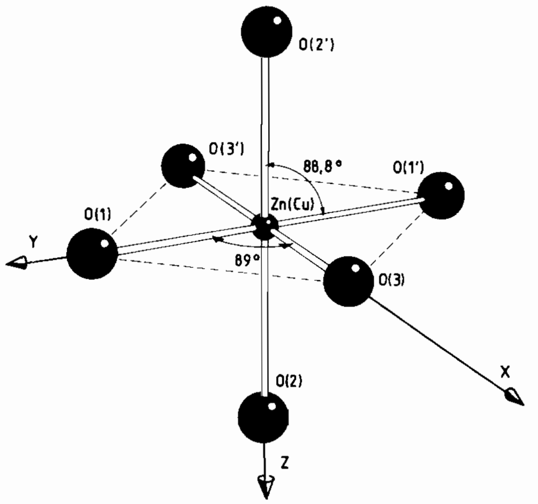

Fig. 2. Bis(β-alanine)zinc(II)nitrate tetrahydrate (or Ala–Zn). The different distortions of the host molecule (axial and equatorial perturbations) are discussed in the text.

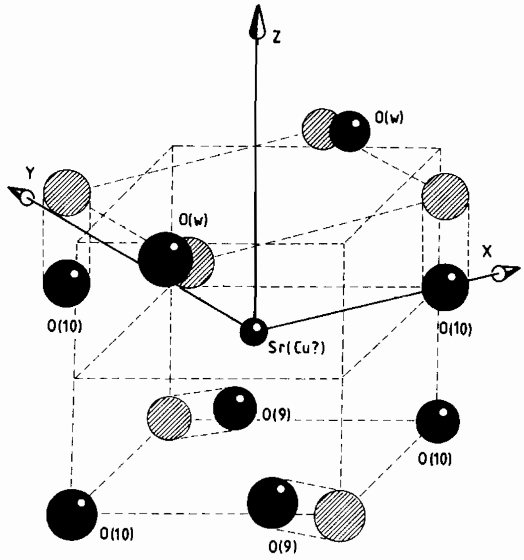

Fig. 3. Bis(salicylato)strontium-dihydrate (or Sal–Sr). Full circles: host molecule; shaded circles: idealized C_{4v}-structure.

interpreted [5] as being composed of the three transitions xz, yz, xy → $x^2 - y^2$. This assignment implies a σ value for the equatorial ligands in the neighbourhood of 5400 cm^{-1} – if at least the ratio $\pi/\sigma \cong 0.2$, which appears to be an average ratio for metal–oxygen bonds. In Table IV, the difference between the σ-parameters for the different oxygen ligands was introduced in order to account for the observed differences in bond-distances: for instance, the experimental values in the host crystal were 2.082 Å for Zn–O(1) *versus* 2.072 Å for Zn–O(3). If the above values of σ are adopted the experimental values of the g-factors cannot be obtained theoretically, unless an orbital reduction factor k is introduced. The numerical value k = 0.86 falls in line with similar studies of Cu(II)-compounds [10]. In Table IV, the values of κ and P for Ala–Zn are slightly different from the values in ref. [5]. This is due to the fact that the Bencini–Gatteschi-program [8] incorporates the orbital reduction factor in the hyperfine coupling operator as well; in

TABLE IV. Optimal Parameters for the Three Considered Complexes. The Ligand Labels in the Second Case (Ala–Zn) refer to Fig. 2.

Complex	σ (in cm^{-1})	π/σ	$k_x = k_y$	k_z	κ	P (in cm^{-1})
Sal–Cd	–4500	0.2	0.75	0.88	0.4	(240) 10^{-4}
Ala–Zn	–4700:O(2) –5420:O(3) –5380:O(1)	0.2	0.86		0.3	(320) 10^{-4}
Sal–Sr	~–4000	~0.2	–	–	–	–

ref. [5], k was introduced only in the Zeeman operator.

For the other two complexes, no optical spectra are available, but since the average metal–ligand distances are larger than in Ala–Zn, it seems reasonable to use smaller σ-values. For sal–Cd, this leads to the parameter set, shown in Table IV; this set is different from what was used in ref. [4], where the calculations were carried out without introducing orbital reduction factors. Both parameter sets might be considered as valid alternatives for the sal–Cd molecule; for reasons of internal consistency, the parameters of Table IV are preferable in the present context.

For sal–Sr, no reasonable complete parameter set could be derived, so as to reproduce the experimental EPR-data. This point will be commented upon in more detail in the next Section.

Results and Discussion

1. Substitution without Distortion: Cu in Sal–Cd

Figure 1 shows that the seven ligands constitute a distorted pentagonal biprism, which can be looked upon as an octahedral wedge, where the sixth ligand of a parent octahedron (at + z) has been replaced by two ligands, separated by a wedge angle of ~80°. The experimental g- and A-tensors are found to have parallel orientations; $\vec{g}_1$ practically bisects the wedge angle, while $\vec{g}_2$ and $\vec{g}_3$ nearly contain the O(4)- and O(7)-atoms respectively.

In our previous work [4], the geometry of the coordination sphere was idealized so as to obtain a C_{2v}-chromophore, where three of the five atoms of the pentagon were situated on the coordinate axes, while the wedge atoms O(2) and O(5) were in the xz-plane, at 40° from the z-axis (see Fig. 1). In a C_{2v}-structure, the principal axes of the tensors are symmetry-determined and oriented along the coordinate system of Fig. 1. The calculated eigenvalues are:

$g_z = 2.434$ $A_z = (108)\ 10^{-4}\ \mathrm{cm}^{-1}$
$g_x = 2.104$ $A_x = (36)$
$g_y = 2.077$ $A_y = (15)$

which compare quite favorably with the experimental values of Table I. When one uses the angular coordinates of the non-idealized host molecule (θ and ϕ of Table I), one finds very small changes in the numerical eigenvalues of g and A, while the directions of the principal axes are modified as follows: $\vec{g}_1$ is at 4° from z, $\vec{g}_2$ at 6° from x, $\vec{g}_3$ at 5° from y, while $\vec{A}_1$ is at 5° from z, $\vec{A}_2$ at 8° from x, and $\vec{A}_3$ at 7° from y. This means that the calculated directional variations are of the same order of magnitude as the experimental uncertainty (±5°). Idealizing the chromophore to the higher C_{2v}-symmetry hardly affects the orientation of the g- and A-tensors. The angular displacements, necessary to realize this idealization are also of the order of 5° to 10°. Since the orientation of the two tensors in the crystal is apparently rather insensitive to displacements of this magnitude, it seems reasonable to conclude that the doped Cu(II)-ion occupies a Cd(II)-position, without observable distortions of its environment.

2. Substitution with Accompanying Distortion: Cu in Ala–Zn

Figure 2 shows the distorted octahedral structure, where the two axial ligands O(2) and O(2′) are at a larger distance (2.165 Å) from the metal than the four equatorial ligands (2.072 Å for O(1) and 2.082 Å for O(3)).

Furthermore, the host molecule differs from the elongated octahedron in two respects: on the one hand, one observes a small equatorial distortion (the angles O(1)–Zn–O(3) and O(1′)–Zn–O(3′) are 89° instead of 90°), and on the other hand the axial ligands are slightly inclined with respect to the z-axis (for O(2), θ = 1.25° and ϕ = 109°). The effective symmetry of the complex is C_i.

The experimental $\vec{g}_1$ and $\vec{A}_1$ vectors are perpendicular to the equatorial (xy)-plane; the $\vec{g}_2$ and $\vec{g}_3$ vectors are found in the equatorial plane at ϕ = +78° and −12° respectively. The directions of $\vec{A}_2$ and $\vec{A}_3$ could not be determined with equal precision, but they are definitely closer to the bond axes than to the bisectors of these bond axes.

Using the coordinates of the host molecule (Table II) and the parameters of Table IV, one calculates

$g_1 = 2.399$ $A_1 = (134)\ 10^{-4}\ \mathrm{cm}^{-1}$
$g_2 = 2.096$ $A_2 = (17)$
$g_3 = 2.083$ $A_3 = (24)$

which is in very good agreement with the experimental values of Table I. These calculated values are very sensitive to small variations in the σ-parameters. For instance, in order to reproduce the experimentally observed $\Delta g = g_y - g_x = 0.013$, it is essential to maintain the equatorial anisotropy between O(1) and O(3) at very nearly the values given in Table IV.

The agreement between theory and experiment is much less sastisfactory as far as the principal directions of the g-tensor are concerned. Indeed, although $\vec{g}_1$ and $\vec{A}_1$ are calculated to be along the z-axis, one finds $\vec{g}_3$ at +10°, instead of the experimentally observed angle of −12°.

If the equatorial bond angles were 90° and if the equatorial anisotropy were only due to $\sigma_x - \sigma_y$ (symmetry D_{2h}), the 3 principal directions would be symmetry-determined and be situated along the x-, y- and z-axes. On the other hand, if there were no

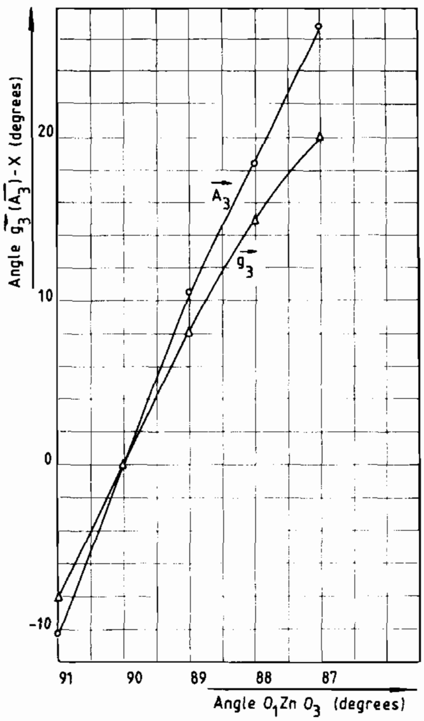

Fig. 4. Variations of the angle between $\vec{g}_3(\vec{A}_3)$ and the x-axis, as a function of the equatorial angle O(1)–Zn–O(3); the two axial ligands were positioned on the z-axis, so that the structure at 90° is characterized by three orthogonal axes.

σ-anisotropy in the equatorial plane, and if the bond angles are different from 90°, the symmetry is again D_{2h}, but now the two equatorial principal directions are along the bisectors of the x- and y-axes. If both perturbations are operative at the same time – as in the present case – the balance of the two effects determines the exact orientation of the tensor. At the same time, a certain influence can be expected from the axial perturbation (the inclination of the O(2)–O(2′)-axis w.r.t.: the z-axis). In order to reproduce the experimental situation, the variation of three different angular coordinates was studied. None of these variations has a significant effect on the g- and A-values, but the consequences for the tensor-orientations were important.

a) *Equatorial perturbation*

Figure 4 shows the result of the calculated rotation of the g- and A-tensors as a function of the equatorial bond angle O(1)–Zn–O(3). At θ = 90°, one obtains the D_{2h}-structure, characterized by orthogonal axes and a different σ-strength for each axis. Obviously, the orientation of the two tensors is a very sensitive function of the angle O(1)–Zn–O(3): one degree in the equatorial angle induces a rotation of ~10° of the $\vec{g}$- and $\vec{A}$-tensors.

b) *Axial perturbation*

In a similar way, the orthogonal D_{2h}-structure can be modified by varying θ (at constant ϕ), or by varying ϕ (at constant θ) of the two axial ligands. As long as θ remains comparatively small ($\theta < 2°–3°$), the effect of these axial perturbations is extremely small: the $\vec{g}_1$- and $\vec{A}_1$-vectors do not depart from the z-axis to any significant extent, and the $\vec{g}_2$- and $\vec{A}_2$-vectors are calculated to change their orientation by at most two or three degrees as a function of θ ($0 \rightarrow 3°$) and ϕ ($0 \rightarrow 180°$). Obviously, the axial ligands, being at a larger distance from the metal center, have only a minor effect on the orientation of the tensor axes. The much stronger equatorial field effectively determines the position of the g- and A-tensors. Therefore, the present calculations confirm the conclusions of previous work [5] on the substitution of a Cu(II)-ion in a Zn(II)-site. The anisotropy of the σ-parameters for O(1) and O(3) remains essential to obtain agreement between calculated and observed g- and A-values. But the additional point of the present work is that a very small in-plane displacement of the equatorial water ligands is sufficient to account for the observed tensor orientations as well; if O(1)–Zn–O(3) = 91.5° (instead of 89° as in the host crystal), the $\vec{g}_3$- and $\vec{g}_2$-vectors rotate over 22° so as to reproduce the experimental directions.

3. *Non-substitution: Cu in Sal–Sr*

Figure 3 shows the host crystal structure where the Sr(II)-ion is surrounded by eight oxygen atoms, arranged in an approximate square antiprismal geometry. While the symmetry of the idealized structure is C_{4v}, the actual symmetry of the complex is only C_2; in Fig. 3, the two-fold axis coincides with the z-axis.

The experimental g-tensor has its principal directions at ~10° from the three coordinate axes of Fig. 3. Although the approximate C_{4v}-symmetry suggests that the two g-factors in the (x,y)-plane will be closer to each other than to g_z, by far the largest g-value is found to be g_1, at ~10° from the x-axis.

In reference [6], the g-values were calculated along the x-, y- and z-directions. The correct order of the g-values could be reproduced more or less satisfactorily by assuming a certain reorganisation of the molecule: as a consequence of the substitution, the water molecules O(w) were supposed to be subject to certain displacements. It was concluded that the Cu(II)-ion was situated in a distorted Sr(II)-site.

From the present work, we are led to reject this earlier suggestion. Indeed, the principal directions of the g-tensor, calculated for the distorted geometry of ref. [6], are at some 35° from the experimentally observed axes!

A more systematic investigation of the different conceivable distortions only confirms this conclusion: it is apparently impossible to obtain satisfactory agreement between calculated and observed results, for both the g-values and the $\vec{g}$-directions.

Certain authors [11–16] introduced an anisotropy in the π-parameters of non-linearly coordinating ligands, such as pyridine, quinoline, water, etc. This allows one to distinguish between the π-bonding properties in the molecular plane of the ligand (where the p-orbitals are also involved in sp^2-hybridization) and perpendicular to the molecular plane. Introducing this anisotropy into the present calculations does not modify the conclusion. While anisotropy factors of the order of 10 are able to improve the orientation of the g-tensor, they do not lead to the correct sequence of the A eigenvalues: $A_1 \gg A_2 \cong A_3$. If more reasonable anisotropy factors (of the order of 3) are introduced, the principal directions of the g-tensor remain at more than 30° from the experimentally observed axes.

Therefore, one concludes that the Cu(II)-ions are probably not situated in the Sr(II)-locations, but rather in some interstitial position. This idea does not appear unreasonable in view of the large difference in ionic radius between the Cu(II)- and Sr(II)-ions.

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