

CONCERNING THE LOCATION OF THE PRINCIPAL MAGNETIC AXIS IN
LANTHANIDE SHIFT-REAGENT ADDUCTS.

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ABSTRACT: The fact that the crystal field symmetry does not necessarily lead to the lanthanide-donor bond being colinear with the principal magnetic axis is noted. The conditions for the existence of such an axis, and a means for its location are described.

If information is required concerning the geometry of an adduct \underline{LAS} , formed by the co-ordination of a substrate \underline{S} to a tris-(β -diketonato) lanthanide(III) molecule \underline{LA} , then attention must be paid not only to the distances, r_i , of protons from the metal ion, but also to either the angles χ_i , that the proton-lanthanide vectors make with the principal magnetic axis, or to two sets of angles [1,2] if the symmetry of the magnetic susceptibility is non-axial [2]. In order to avoid the problem of locating the magnetic susceptibility axes, either the angle term [3] or even the location of the metal [4,5] are frequently neglected. If the magnetic susceptibility axes are given consideration then axial symmetry is assumed [6], use then being made of the geometric factor appropriate to such a situation; namely, $(3\cos^2\chi_i - 1)r_i^{-3}$ [2]. Furthermore, the principal magnetic axis, the principal symmetry axis and the lanthanide to donor bond are all taken as colinear [6].

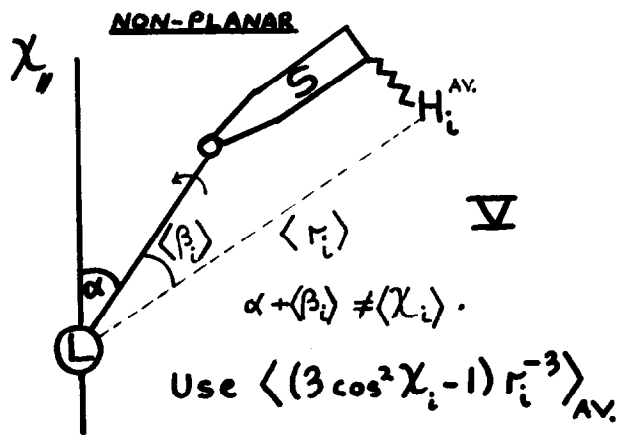
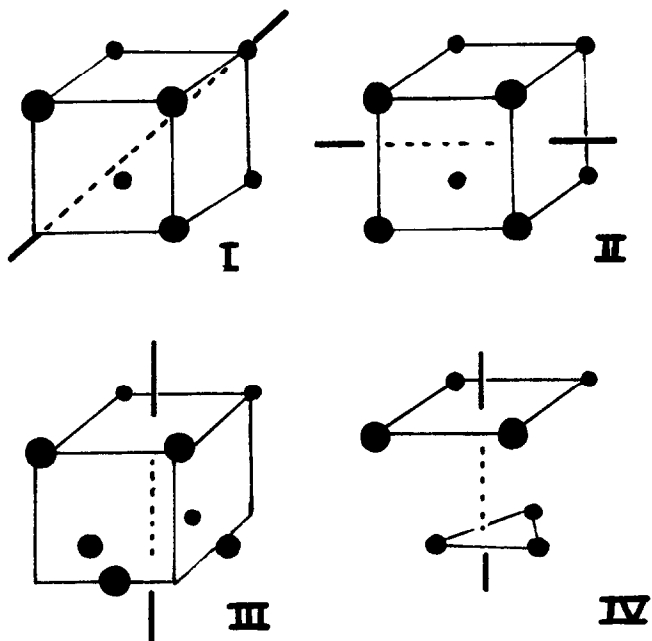
The location of the principal symmetry axis is ambiguous in a rigid tris-complex of a simple chelate ligand. In tris-(acetylaceto) europium(III), the crystal field symmetry is O_h , and the principal crystal field symmetry axis is a C_4 axis through the apices of the octahedron. The molecular symmetry is D_3 , with the principal molecular symmetry axis [7] a C_3 axis through the opposite faces of the crystal field octahedron. The use of the crystal field symmetry, together with the assumption that the magnetic susceptibility axes are colinear with the crystal field symmetry axes is still considered satisfactory in

many cases[7]. The insensitivity of the 4f electrons to the environment, by virtue of their tight binding, suggests that we can adopt the useful assumption concerning the colinearity of the two sets of axes. These will now be termed "the symmetry axes". There are feasible crystal fields[8] in a simplified LAS unit in which, despite high(axial) symmetry, the principal symmetry axis does not coincide with the lanthanide to donor bond.

There is ample evidence to show that the inner co-ordination sphere of the lanthanide (III) ions can consist of from six to ten donor atoms, with ready expansion from six[8,9]. We will consider the simplest case of a monomeric LA unit, in which the co-ordination sphere is expanded to seven or eight donor oxygen atoms via a substrate with one donor oxygen atom. In structure (I) the location of the substrate's donor atom is important, because there are two types of site: that along the principal symmetry axis, and those not along it. Neither structures (II) or (III) require knowledge about the location of the substrate because all eight sites are now equivalent. In these two cases the principal symmetry axis (or principal magnetic axis under our present assumption) does not involve the substrate's donor atoms, and the angles χ_i cannot be defined using the metal-donor bond. In structure (IV) the situation is complicated by the fact that the crystal field is non-axial. We have indicated a sensible choice for one of the magnetic susceptibility axes which does contain a mirror plane. In this circumstance of non-axial symmetry one cannot only use the r_i and the χ_i ; a further angle is involved[2]. A set of axes must first be chosen, and the location of the substrate donor atom with respect to them determined before the required angles can be defined[2].

The splitting of the J levels will be different in the four cases discussed above [10]. If, for example, Eu(III) is placed in environment (II) there will be no splitting of the first excited, thermally populated level (J=1) and the second order paramagnetism therefrom will be isotropic [11,12]. Such an environment in europium shift reagents seems inappropriate, for some anisotropy is required if a pseudocontact interaction is to be observed [2,11]. Environments I,II and IV would split this J=1 level into 2,2 and 3 sublevels respectively [10], with the possibility of an anisotropic magnetic susceptibility [11]. Some surprise that such crystal field splitting can give rise to sufficient anisotropy has recently been expressed [12].

Recently, a structure for a LA dimer has been proposed, with the metal ions in a D_{4d} environment [8]. We suggest that it is possible to attach



substrate donor atoms along the S_4 axis of the dimer giving nine-fold co-ordination and a crystal field symmetry. The principal symmetry axis is retained, whilst the symmetry is sufficiently low to give the required splitting of the $J=1$ level of europium(III) ions.

The location of the principal symmetry axis relative to a substrate of known structure can be determined in the following way if the crystal field symmetry is of cubic, tetragonal or hexagonal type [9,10]. A reasonable estimate of the geometry can be made (see V) defining a set of β_i and r_i for the i hydrogen atoms; the equality of $\alpha + \beta_i$ with χ_i is unlikely. The ratios of $\langle (3\cos^2\chi_i - 1)r_i^{-3} \rangle$ [2], which may be averaged for free or restricted rotation, can be used in conjunction with the experimental PMR shift ratios to discover whether there is a constant value of α (see V). A value of $\alpha \sim 0$ would support the assumption in vogue [6].

It should be emphasised that, because europium is a second order paramagnetic [11,12], and has a very high spin orbit coupling constant [9], the equations for pseudocontact interactions derived for first order paramagnetics [2] in terms of the expectation value of S_z and assumed relaxation and correlation times, are not directly applicable in the present context.

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