Single-crystal Electron Spin Resonance Studies of Gadolinium Trisilylamide and Sodium Gadolinium Dipicolinate (Pyridine-2,6-dicarboxylate)

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The *X*-band e.s.r. spectra of Gd^{3+} doped into single crystals of $Na_3[La(C_7H_3NO_4)_3]\cdot15H_2O$ and into $La[N(SiMe_3)_2]_3$ are reported and interpreted in terms of the same spin Hamiltonian. The zero-field splitting of 4.66 cm^{-1} obtained for $Gd[N(SiMe_3)_2]_3$ appears to be the largest yet reported for Gd^{3+}.

WE have previously reported [1] on the e.s.r. studies of the trisilylamide complexes of chromium(III) and iron(III), where this novel ligand produced large zero-field splittings in the orbitally non-degenerate ground states ^4A and ^6A respectively. A preliminary study [2] on polycrystalline samples of the corresponding gadolinium complex indicated effective g values of 8 and 2. We now report the results of a single-crystal e.s.r. study on gadolinium doped into lanthanum trisilylamide to extend our work to an ^8A (or ^8S) state.

Gadolinium must be one of the most studied atoms in e.s.r. spectroscopy, perhaps because its spectra may easily be observed at room temperature and under most conditions. The emphasis in these studies has been two-fold: to investigate the local structure in different crystals and to try to understand the theoretical mechanisms whereby an S state is split in a crystal field. Accordingly, most studies have been concerned with doping gadolinium into different crystal types rather than with discrete gadolinium compounds. The atoms surrounding the lanthanide have usually been oxygen, fluorine, chlorine, or bromine.[3] We can trace but one other e.s.r. study of gadolinium complexed to nitrogen-donor ligands,[4] *viz.* the complexes of gadolinium nitrate with 1,10-phenanthroline and 2,2′-bipyridine in which the symmetry is low and the effect of the crystal field relatively small. Thus, our study is somewhat unusual in that it is concerned with discrete molecules of low co-ordination and with nitrogen-donor ligands.

In gadolinium trisilylamide the lanthanide is surrounded by three nitrogen atoms with trigonal symmetry as discussed below in more detail. In the absence of comparable studies, as indicated above, we have also investigated the e.s.r. spectra of sodium gadolinium dipicolinate, in which the environment of the lanthanide ion has similarities to the trisilylamide. As the effect of the crystal field in the dipicolinate is not too different to that in previous work we report these results first so as to highlight the peculiarities of the trisilylamide case.

RESULTS

Sodium Gadolinium Dipicolinate.—We presume that the gadolinium and lanthanum compounds, $Na_3[M(C_7H_3NO_4)_3]\cdot15H_2O$, have similar structures to that of neodymium.[5] The space group is $P\bar{1}$, the lanthanide co-ordination polyhedron being a tricapped trigonal prism with carboxylate oxygen atoms at the corners of the prism and nitrogen atoms in the equatorial plane (see Figure 1). To within the accuracy of the X-ray data the nitrogen atoms form an equilateral triangle with the lanthanide atom at the centre.

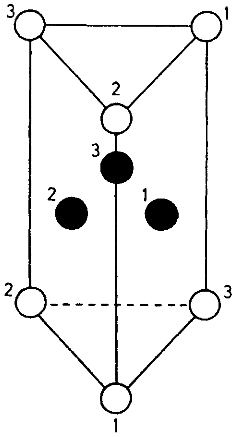

FIGURE 1 The ligand arrangement in sodium gadolinium dipicolinate: ○ = oxygen; ● = nitrogen. Atoms with the same number belong to the same ligand

Thus, if we consider nearest neighbour atoms only, the local symmetry is D_{3h}, whereas the inclusion of the complete ligand drops the symmetry to D_3.

The Gd^{3+} ion is in an $(f^7)^8S_{\frac{7}{2}}$ ground state which is split by the crystal field. The spin Hamiltonian used to represent the e.s.r. results is usually written in the form of equation (1), where the O_l^m are spin operators.[6] The symmetry of the crystal field, and the restriction of the problem to f electrons, limits the possible values of l and m. For D_{3h} symmetry equation (2) is obtained, with the g tensor having two principal components: $g_{\parallel}$ and $g_{\perp}$. For the case of D_3 the additional terms $B_4^3O_4^3$ and $B_6^3O_6^3$ must be added to equation (2). To avoid large numbers the constants B are usually redefined as follows: [7] $b_2^0 = 3B_2^0$, $b_4^0 = 60B_4^0$, $b_6^0 = 1\,260B_6^0$, $b_4^3 = 3B_4^3$, $b_6^3 = 36B_6^3$, $b_6^6 = 1\,260B_6^6$. With the magnetic field parallel to the three-fold axis seven lines should be observed corresponding to the $\Delta S_z = \pm1$ transitions. The positions and relative intensities of these lines are given in Table 1 provided all of the off-diagonal elements of the spin Hamiltonian are small (which may not be the case for the silylamide ligand).

$$\mathscr{H} = \beta\boldsymbol{H}\,.\,\boldsymbol{g}\,.\,\boldsymbol{S} + \sum_{l,\,m} B_l^mO_l^m \qquad (1)$$

$$\mathscr{H} = \beta\boldsymbol{H}\,.\,\boldsymbol{g}\,.\,\boldsymbol{S} + B_2^0O_2^0 + B_4^0O_4^0 + B_6^0O_6^0 + B_6^6O_6^6 \qquad (2)$$

TABLE 1

Theoretical positions and relative intensities of the lines (to first order) for D_3 symmetry when the magnetic field is parallel to the trigonal axis

Transition	Position	Relative intensity
$\pm\frac{7}{2}\leftrightarrow\pm\frac{5}{2}$	$g\beta H = h\nu \mp (6b_2^0 + 20b_4^0 + 6b_6^0)$	1.75
$\pm\frac{5}{2}\leftrightarrow\pm\frac{3}{2}$	$g\beta H = h\nu \mp (4b_2^0 - 10b_4^0 - 14b_6^0)$	3
$\pm\frac{3}{2}\leftrightarrow\pm\frac{1}{2}$	$g\beta H = h\nu \mp (2b_2^0 - 12b_4^0 - 14b_6^0)$	3.75
$-\frac{1}{2}\leftrightarrow+\frac{1}{2}$	$g\beta H = h\nu$	4

Spectra of the pure gadolinium compound exhibit broad lines due to magnetic concentration. Figure 2 shows the spectrum for a single crystal of sodium lanthanum dipicolinate doped with gadolinium (1 : 500) mounted with the magnetic field parallel to the three-fold axis of the molecule.

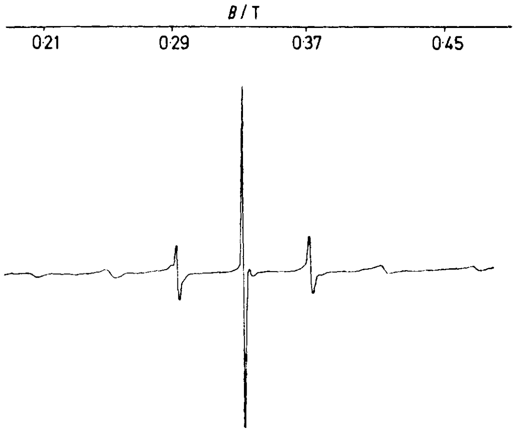

FIGURE 2 X-Band spectrum of a single crystal of $Na_3[La(C_7H_3NO_4)_3]\cdot15H_2O$ doped with Gd^{3+} aligned with the magnetic field parallel to the trigonal axis

This type of spectrum is typical for Gd^{3+}: seven lines with relative intensities approximately as in Table 1. The values of $g_{\|}$, b_2^0, b_4^0, and b_6^0 may be obtained using the experimental line positions and the theoretical expressions; the parameters are listed in Table 2 and the comparison between experimental and calculated line positions given in Table 3 under the $\theta = 0°$ column. The remaining parameters can only be obtained from spectra taken when the angle between the three-fold axis and the magnetic field (θ) is between 0 and 90°. The theoretical line positions must now be calculated by complete diagonalisation of the spin Hamiltonian, but good agreement with experiment could not be obtained. As an example, the best fit for $\theta = 67°$ is shown in Table 3; the parameter values for $g_{\perp}$, b_4^3, b_6^3, and b_6^6 given in Table 2 were used. Certainly the interpretation of the spectra for angles other than $\theta = 0°$ is not as straightforward as for the silylamide. Presumably more spin Hamiltonian parameters are required with, perhaps, the inclusion of terms of odd parity.[8] Nevertheless we have established the main splitting parameters for $Na_3[Gd(C_7H_3NO_4)_3]\cdot15H_2O$ and they are typical for Gd^{3+} (see the discussion below).

TABLE 2

Spin Hamiltonian parameters for $Na_3[Gd(C_7H_3NO_4)_3]\cdot15H_2O$. The energy unit is 10^{-4} cm^{-1} and absolute signs have not been determined

$g_{\|} = 1.9921$ $\quad g_{\perp} \sim 1.9780$
$b_2^0 = 196.9$ $\quad b_4^3 \sim -5$
$b_4^0 = 2.08$ $\quad b_6^3 \sim 1$
$b_6^0 = 0.12$ $\quad b_6^6 \sim -7$

TABLE 3

Comparison between theory and experiment for $Na_3[Gd(C_7H_3NO_4)_3]\cdot15H_2O$ with the parameters in Table 2 (line positions are in T)

$\theta = 0°$		$\theta = 67°$	
Experiment	Theory	Experiment	Theory
0.200 7	0.200 9	0.292 8	0.285 3
0.250 3	0.250 2	0.320 2	0.312 9
0.292 8	0.292 7	0.326 3	0.324 1
0.332 6	0.332 5	0.334 6	0.336 3
0.372 5	0.372 3	0.342 8	0.343 9
0.414 8	0.414 7	0.355 1	0.348 8
0.463 8	0.464 1	0.368 5	0.364 6

Gadolinium Trisilylamide.—The gadolinium and lanthanum compounds, $M[N(SiMe_3)_2]_3$, are taken to have the same structure [9] as that of scandium and europium, which crystallise in the space group $P\bar{3}1c$. The three silylamide ligands by themselves show D_3 symmetry with the metal atom situated out of the plane of the three nitrogen atoms such that the MN_3 moiety has a pyramidal structure with C_{3v} symmetry. The symmetry of an isolated molecule is quite low if the complete ligands are considered. We shall assume C_{3v} symmetry when the spin Hamiltonian considered for D_3 is appropriate.

As for the dipicolinate, the pure gadolinium compound gave broad lines. The spectrum for a single crystal of lanthanum trisilylamide doped with gadolinium (1 : 200) oriented with the field parallel to the trigonal axis ($\theta = 0°$) is shown in Figure 3: the contrast with Figure 2 is great and is a clear indication of much larger spin Hamiltonian parameters. The simplest interpretation, that the line positions are as given in Table 1 with the positive signs, is incorrect in that an additional line at 0.205 8 T is then predicted for the transition ($\frac{3}{2}\leftrightarrow\frac{1}{2}$). To first order the line positions are given in Table 4. As the middle two line positions are related we do not have enough experimental data to find all four theoretical parameters $g_{\|}$, b_2^0, b_4^0, and b_6^0. However, if we assume that b_6^0 is negligible (it is usually small [3]), we obtain the values given in Table 5 under

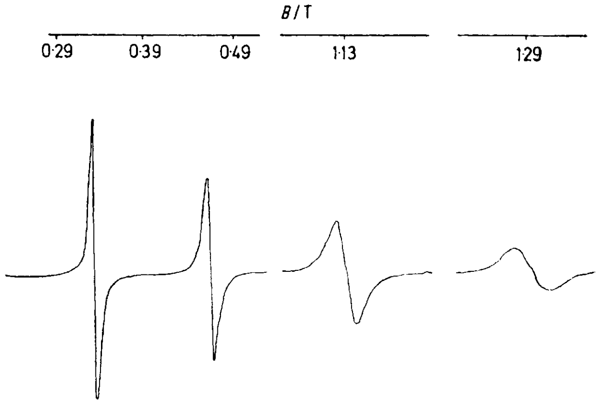

FIGURE 3 X-Band spectrum of a single crystal of $La[N(SiMe_3)_2]_3$ doped with Gd^{3+} aligned with the magnetic field parallel to the trigonal axis

TABLE 4

Theoretical positions and relative intensities (to first order) of the four lines for $Gd[N(SiMe_3)_2]_3$

Transition	Position	Relative intensity
$-\frac{1}{2}\leftrightarrow\ \frac{1}{2}$	$g\beta H = h\nu$	4
$-\frac{1}{2}\leftrightarrow -\frac{3}{2}$	$g\beta H = -h\nu + (2b_2^0 - 12b_4^0 + 14b_6^0)$	3.75
$-\frac{3}{2}\leftrightarrow -\frac{1}{2}$	$g\beta H = h\nu + (2b_2^0 - 12b_4^0 + 14b_6^0)$	3.75
$-\frac{3}{2}\leftrightarrow -\frac{5}{2}$	$g\beta H = -h\nu + (4b_2^0 - 10b_4^0 - 14b_6^0)$	3

the column headed set 1. An alternative interpretation is possible. The mean position of the middle two lines found experimentally (see Table 6, $\theta = 0°$) corresponds to a value of $g_{\parallel}$ of *ca.* 1.99, the most common value for gadolinium complexes. This value cannot fit the experimental data unless we go beyond first-order theory: solution of the complete determinant of the spin Hamiltonian shows that a value of 105.9×10^{-4} cm^{-1} for b_4^3 gives a reasonable fit to the spectrum if b_2^0 and b_4^0 are slightly modified (see Table 5, set 2). The experimental intensities are approximately 4:3.6 : 2.7 : 1.4 in reasonable agreement with theory if allowance is made for the inaccuracy of our field measuring equipment and the inhomogeneity of the field outside the range 0.2—0.6 T.

TABLE 5

Spin Hamiltonian parameters for $Gd[N(SiMe_3)_2]_3$. The energy unit is 10^{-4} cm^{-1} and absolute signs have not been determined

Set 1		Set 2	
$g_{\parallel} = g_{\perp} = 1.975\,4$		$g_{\parallel} = g_{\perp} = 1.991\,8$	
$b_2^0 = 3\,808$	b_4^3 undet.	$b_2^0 = 3\,850$	$b_4^3 = 105.9$
$b_4^0 = 22.2$	b_6^3 undet.	$b_4^0 = 25.8$	$b_6^3 \sim 0$
$b_6^0 = 0$	b_6^6 undet.	$b_6^0 = 0$	b_6^6 undet.

TABLE 6

Comparison of theory and experiment for $Gd[N(SiMe_3)_2]_3$ with the parameters in Table 5 (line positions are in T)

θ°	Experiment	Set 1	Set 2
0	0.335 2	0.335 3	0.335 2
	0.464 8	0.461 6	0.464 8
	1.130 0	1.132 2	1.135 5
	1.292 0	1.292 2	1.293 8
90	0.087 5	0.087 5	0.086 8
	0.308 2	0.309 4	0.308 5
	0.733 0	0.768 1	0.770 4

The line positions obtained for the crystal mounted along its needle axis are shown in Table 6 ($\theta = 90°$), along with the calculated values for both sets of parameters. The agreement is reasonable in that three lines only are predicted at about the right positions. The biggest difference is for the line at 0.733 0 T, but the theoretical position of this line is very sensitive to the value of θ. Thus if the crystal is misaligned by *ca.* 3.5° (*i.e.* $\theta = 86.5°$) this line is predicted to be *ca.* 38 mT downfield of the values in Table 6, with changes of 0.8 mT downfield for the 0.308 2 T line and 0.2 mT upfield for the third line. The technique which had to be used to mount a single crystal of this reactive compound (see Experimental section) makes such a misalignment quite possible, so we conclude that the agreement is good. Unfortunately the misalignment precludes the possibility of finding b_6^6 by rotation about the needle axis.[10]

DISCUSSION

The theory of *g* values[11] and of crystal-field parameters[12] for Gd^{3+} is not sufficiently well developed for us to distinguish on theoretical grounds between the two sets of values in Table 5 for $Gd[N(SiMe_3)_2]_3$. Empirical *g* values tend to be close to 1.99 and $g_{\parallel}$ and $g_{\perp}$ to be equal,[3] although many exceptions are known. It is interesting to note that *g* values apparently less than 1.99 may be due to an insufficiently general variation of the crystal-field parameters.[13] We cannot definitely select the better set but tend to favour the second one because the *g* values are more typical for gadolinium compounds.

In Table 7 we collect the largest known crystal-field parameters for Gd^{3+} in different symmetries and in Table 8 some typical values for Gd^{3+} in trigonal fields. The values found for $Na_3[Gd(C_7H_3NO_4)_3]\cdot15H_2O$ (Table 2) are fairly typical for trigonal symmetry as is the total zero-field splitting of 0.24 cm^{-1}. On the other hand, b_2^0 and the total zero-field splitting of 4.66 cm^{-1} for

TABLE 7

The largest crystal-field parameters (in units of 10^{-4} cm^{-1}) for Gd^{3+} in different symmetries

Host lattice	Symmetry	$\lvert b_2^0\rvert$	$\lvert b_4^0\rvert$	$\lvert b_6^0\rvert$	Ref.
CaF_2	Tetragonal	1 486	23	1	*a*
$La[SO_4]_3\cdot9H_2O$	Hexagonal	639.7	2.6	0.2	*b*
CaF_2 (O_2^-)[c]	Trigonal	2 905.7	12.6	0	*d*
$[CsY][MoO_4]_2$	Lower than trigonal	902.0	22.4	0.2	*e*

[a] J. Sierro and R. Lacroix, *Compt. rend.*, 1960, **250**, 2686. [b] D. R. Johnston, E. Y. Wang, and O. M. Stafsudd, *J. Chem. Phys.*, 1966, **44**, 2693. [c] The extra charge, when Gd^{3+} is substituted for Ca^{2+}, is compensated by an O_2^- ion. [d] Sook Lee, Chi-Chung Yang, and A. J. Bevolo, *Phys. Rev.*, 1974, **B10**, 4515. [e] A. I. Otko, L. N. Pelikh, and A. I. Zvyagin, *Sov. Phys.-Solid State*, 1973, **14**, 2918.

TABLE 8

Some parameters for Gd^{3+} in a trigonal environment (*b* values in 10^{-4} cm^{-1})

Host lattice	$g_{\parallel}$	$g_{\perp}$	b_2^0	b_4^0	b_6^0	b_4^3	b_6^3	b_6^6	Ref.
BaF_2 (O_2^-)[a]	1.992 3	1.992 3	−136.6	24.54	−0.28	−34.661	−0.082 7	−0.60	*b*
SrF_2 (O_2^-)[a]	1.992 7	1.992 7	−2 671.7	11.7	0	−346	22	24	*c*
CaF_2 (O_2^-)[a]	1.991 0	1.991 0	−2 905.7	12.6	0	−547	30	11	*c*
ZnO	1.987	1.978	850.4	15.77	0.464				*d*
Al_2O_3	1.991 2		1 032.9	26.00	1.0	|18.30|	|1.0|	|5.00|	*e*
$La[AlO_3]$	1.990 8	1.986	371.2	6.17	1.0			7.6	*f*
$[Bi_2Mg_3][NO_3]_{12}\cdot24H_2O$	1.991 7	1.998 3	117.9	0.384	0.421 6			5.358 7	*g*
$[La(C_{11}H_{12}N_2O)_6]I_3$[h]	1.993 1		827	2.8	−1.1	8.0	0.8	6.9	*i*
La_2O_3	1.96	1.988	1 310	16	1	10	6	7	*j*

[a] See footnote *c* to Table 7. [b] L. A. Boatner, R. W. Reynolds, and M. M. Abraham, *J. Chem. Phys.*, 1970, **52**, 1248. [c] See footnote *b* of Table 7. [d] A. Hausmann, *Solid State Comm.*, 1969, **7**, 579. [e] Ref. 7. [f] W. Low and A. Zusman, *Phys. Rev.*, 1963, **130**, 144. [g] H. A. Buckmaster, J. C. Dering, and D. J. I. Fry, *J. Phys.*, 1968, **C1**, 599. [h] $C_{11}H_{12}N_2O$ is antipyrine. [i] J. M. Baker and F. I. B. Williams, *Proc. Phys. Soc.*, 1961, **78**, 1340. [j] D. Vivien, A. Kahn, and A. M. Lejus, *Phys. Status Solidi*, 1976, **B73**, 593.

Gd[N(SiMe$_3$)$_2$]$_3$ appear to be the largest values yet reported; the only others which approach it are also for trigonal symmetry: the charge compensated centres in CaF$_2$ and SrF$_2$. We conclude that the silylamide ligands produce the largest zero-field splitting in the ground state of Gd^{3+} yet reported (*cf.* the Cr^{3+} and Fe^{3+} ions [1]) and that this effect is a property of the ligands as a whole rather than the triangular array of nitrogen atoms.

EXPERIMENTAL

Tris[bis(trimethylsilyl)amido]-derivatives of gadolinium and lanthanum were prepared by the method of Bradley *et al.*[2] Single crystals of both the pure gadolinium complex and gadolinium doped in different concentrations into the corresponding lanthanum complex were grown from toluene solutions under an atmosphere of dry nitrogen. The compounds crystallize as thin needles. For the anisotropy studies well formed crystals of 4—5 mm in length were mounted both along the long axis and at right angles to the long axis in Spectrosil tubes under an atmosphere of dry nitrogen in a dry box. The needle axis of the crystal coincides with the trigonal axis of the molecule, so orientation in the cavity with respect to the magnetic field was straightforward.

Trisodium tris(pyridine-2,6-dicarboxylato)-derivatives of lanthanum and gadolinium were prepared by the method of Albertsson.[5] Suitable single crystals, both of the pure gadolinium compound and of gadolinium doped into the lanthanum compound, were grown by slow evaporation from aqueous solutions. The crystals effloresced, and were coated with a thin layer of Durofix. The crystals are triclinic and their Weissenberg *X*-ray photographs were used to orient them in the cavity.

All the spectra were obtained at *X*-band with the samples at room temperature.

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