Studies on Rare-earth Compounds. Part I. The Magnetic Anisotropy of and Crystal Field in Cerous Magnesium Nitrate, $Ce_2Mg_3(NO_3)_{12},24H_2O$

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The average magnetic susceptibility and magnetic anisotropy of cerous magnesium nitrate over the temperature range 80—300 K are reported. These results, together with the previously reported *g*-values, have been interpreted in terms of a point-charge crystal-field model with the inclusion of an orbital reduction parameter *k*. Values of the radial parameters ρ2, ρ4 and ρ6 for both a 12- and 6-co-ordinate model have been determined. The value of *k* required by both models is in the range 0·93—0·96. The possible reasons for this parameter being less than unity are discussed.

THERE has been a recent upsurge of interest in the relationship between the detailed geometries and electronic structures of *d*-transition-metal ions [1] and of rare-earth ions.[2] As part of our investigations into the electronic properties of rare-earth complexes we now report the magnetic anisotropy of cerous magnesium nitrate, $Ce_2Mg_3(NO_3)_{12},24H_2O$, and its interpretation in terms of a simple crystal-field model.

Cerous mangesium nitrate has been shown to crystallise with a hexagonal unit cell [3] in which each cerium(III) ion is surrounded by six nitrato-groups. The arrangement of the nitrato-groups, as shown in Figure 1, is such that the oxygen atoms are at the corners of an irregular icosahedron. There are two sets of six Ce^{III}–O distances, each set constituting a trigonally distorted octahedron. The symmetry of the Ce^{III} environment closely approximates to that of the D_{3d} point-group.

In contrast to hexakis(antipyrine)cerium(III) tri-iodide, for which small structural phase changes have been detected [4] and also small changes in interbond angles invoked to explain the magnetic susceptibilities,[2] it seems unlikely that there will be any major changes in the molecular geometry with temperature since the unit cell dimensions change very little over the temperature range 302—4·2 K [5] (at 302 K, $a = 11·035$ and $c = 34·640$ Å, whilst at 4·2 K, $a = 10·986$ and $c = 34·068$ Å).

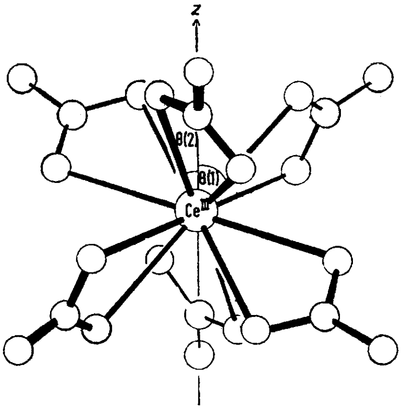

FIGURE 1 The molecular geometry of the $[Ce(NO_3)_6]^{3-}$ unit

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E.s.r. measurements at 4·2 K and 3·33 cm^{-1} are reported to give $g_{\parallel} = 0{\cdot}25 \pm 0{\cdot}05$ and $g_{\perp} = 1{\cdot}84$.[6]

Cerous magnesium nitrate should provide a suitable opportunity to test the suggestion that the effect of bidentate ligands of a short ' bite ', *e.g.* nitrate and acetate, may be approximated by the replacement of the donor atoms by a single atom located at the mean position of the two oxygen atoms.[7]

EXPERIMENTAL

Preparation.—Crystals, as hexagonal plates, were grown from aqueous solution containing equimolar amounts of cerous nitrate (B.D.H., low in other rare-earths) and magnesium nitrate (Found: Ce, 18·3; H, 3·1; Mg, 4·7; N, 10·6. Calc. for $Ce_2H_{48}Mg_3N_{12}O_{60}$: Ce, 18·3; H, 3·1; Mg, 4·7; N, 11·0%).

Magnetic Susceptibility Measurements.—Powder magnetic susceptibilities and magnetic anisotropies were measured over the temperature range 80—300 K by the Gouy and Krishnan ' critical torque ' methods on an apparatus described previously.[8] The fibre for the ' critical torque ' method was calibrated with crystals of both triphenylbenzene[9] and Cs_3CoCl_5.[10] The results, summarised in Table 1, are the mean values obtained from two different preparations for the powder susceptibility, and four crystals selected from these preparations for the anisotropy measurements. The values of $\bar{\mu}$ agreed to within 0·5%, whilst the magnetic anisotropies were all within 2% of the mean values reported in the Table.

TABLE 1

The variation in the magnetic susceptibility with temperature of $Ce_2Mg_3(NO_3)_{12},24H_2O$

χ is expressed in c.g.s. units $\times 10^6$ and μ, calculated from $\mu = 2{\cdot}828\sqrt{\chi \times T}$, is in B.M.

T (K)	$\bar{\chi}_{Ce}$	$\Delta\chi$	$\chi_{\perp}$	$\chi_{\parallel}$	$\bar{\mu}$	$\mu_{\perp}$	$\mu_{\parallel}$
300	2278	350	2395	2045	2·34	2·40	2·22
280	2398	392	2529	2137	2·32	2·38	2·19
260	2558	450	2708	2258	2·31	2·37	2·17
240	2747	533	2925	2392	2·29	2·37	2·14
220	2981	618	3185	2569	2·29	2·37	2·13
200	3252	732	3496	2764	2·27	2·36	2·10
180	3584	897	3883	2986	2·27	2·36	2·07
160	3984	1130	4361	3231	2·26	2·36	2·03
140	4495	1428	4971	3543	2·24	2·36	1·99
120	5155	1895	5787	3892	2·22	2·36	1·93
100	6024	2635	6902	4267	2·19	2·35	1·85
85	6920	3325	8028	4703	2·17	2·34	1·79

The magnetic anisotropy of this compound has been reported previously[11] and our results show the same general trend with temperature, but are *ca.* 10% higher. However, our principal susceptibilities differ considerably from those already reported which were based on the determination of the anisotropy, together with one of the principal crystal susceptibilities, at various temperatures. The values of $\bar{\mu}$ calculated from this information do not agree with those directly determined by us. The reason for this discrepancy is not known but, since the measurement of powder susceptibilities is reliable, we base our subsequent arguments on our present results.

DISCUSSION

The principal magnetic moments, μ, and the g-values have been interpreted in terms of a simple point-charge crystal-field model. The expression for crystal-field potential appropriate to f-electron systems, having 6 point-charges arranged with D_{3d} symmetry, has been given by Gerloch and Mackey.[2] This potential is easily modified to accommodate 12 point-charges, in an analogous manner to that [1a] described for d-electron systems. The eigenvalues and eigenfunctions arising from the perturbation of the $4f^1$ configuration by the Hamiltonian,

$$\mathscr{H} = V_{D\ d} + \lambda[k_{\parallel}\hat{1}_z\hat{s}_z + k_{\perp}/2(\hat{1}_+\hat{s}_- + \hat{1}_-\hat{s}_+)] + \hat{\mu}$$

[where k is the orbital reduction parameter, and $\hat{\mu}$ is $k_{\parallel}\beta H(\hat{1}_z + 2{\cdot}0023\hat{s}_z)$ or $k_{\perp}\beta H(\hat{1}_x + 2{\cdot}0023\hat{s}_x)$ for the parallel (c) and perpendicular directions respectively] were obtained numerically by diagonalising the matrix for various combinations of the radial parameters ($\rho 2 = \frac{Ze^2r^{-2}}{a^3}$, $\rho 4 = \frac{Ze^2r^{-4}}{a^5}$, and $\rho 6 = \frac{Ze^2r^{-6}}{a^7}$ where a is the metal–ligand distance), the angles θ(1) and θ(2), k, and the magnetic field H. The spin-orbit coupling constant, λ, was kept constant at 640 cm^{-1}.

In order to make the calculation of the susceptibilities as general as possible, the rate of change of the eigenvalues with magnetic field was calculated, and the magnetic susceptibilities obtained, from the equation:

$$\chi = \frac{-N\sum_i \frac{\partial W_i}{\partial H} \cdot \exp(-W_i/kT)}{H\sum_i \exp(-W_i/kT)}$$

The variation of the magnetic properties within the six-co-ordinate model has been discussed in detail.[2] It was found that for any particular angle θ, $\bar{\mu}$ depends mainly on ρ4, whilst the anisotropy depends on ρ2. The radial parameter ρ6 has only a small effect on either of these magnetic properties. The results described below show that an entirely analogous situation holds for the twelve-co-ordinate model.

The Interpretation of the Magnetic Results using a Twelve-co-ordinate Model.—The initial approach was to use the mean values of θ(1) = 74·57°, θ(2) = 40·80°, $R\left(= \frac{\text{Ce–O(1)}}{\text{Ce–O(2)}}\right) = 0{\cdot}9842$ obtained from the crystallographic data, with $k_{\parallel} = k_{\perp} = 1{\cdot}0$ as fixed parameters. The radial parameter ρ6 was also kept constant at 200 cm^{-1}. Since ρ4 determines the value of $\bar{\mu}$ an arbitrary value of ρ2 = 2000 cm^{-1} was chosen and ρ4 varied until

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$\bar{\mu}$ at 300 K was reproduced. Using this value of ρ4 (*ca.* 300 cm^{-1}), ρ2 was varied until the anisotropy at 300 K was correctly predicted. The results summarised in Table 2 indicate that ρ2 *ca.* 500 cm^{-1} is a reasonable choice. Using these parameters the variation of the μ values with temperature, and also the *g* values for the lowest Kramers doublet, were next calculated. The results of this are summarised in Figure 2(a). It can be seen that the reproduction of the low-temperature experimental data is completely inadequate. The predicted variation of the μ values is much greater than, and the anisotropy smaller than that observed. Also both *g* values are incorrect.

TABLE 2

The variation of μ at 300 K and *g* with (a) ρ4 and (b) with ρ2 using the twelve-co-ordinate model with ρ6 = 200 cm^{-1}, θ(1) = 74·57°, θ(2) = 40·80°, R = 0·9842, $k_{\parallel} = k_{\perp}$ = 1·00, and λ = 640 cm^{-1}

(*a*) ρ2 = 2000 cm^{-1}					
ρ4 (cm^{-1})	200	300	400	500	600
$\bar{\mu}$ (B.M.)	2·42	2·35	2·24	2·14	2·02
$\mu_{\parallel}$ (B.M.)	1·88	1·83	1·76	1·69	1·61
$\mu_{\perp}$ (B.M.)	2·69	2·61	2·48	2·37	2·22
$g_{\parallel}$	0·35	0·35	0·18	0·32	0·40
$g_{\perp}$	2·19	1·98	1·80	1·65	1·51
(*b*) ρ4 = 300 cm^{-1}					
ρ2 (cm^{-1})		200	500	1000	2000
$(\chi_{\perp} - \chi_{\parallel}) \times 10^6$		166	377	815	1442
$\bar{\mu}$ (B.M.)		2·39	2·37	2·36	2·35
$\mu_{\parallel}$ (B.M.)		2·33	2·24	2·08	1·83
$\mu_{\perp}$ (B.M.)		2·41	2·44	2·50	2·61
$g_{\parallel}$		1·32	1·02	0·58	0·35
$g_{\perp}$		1·33	1·47	1·68	1·98

This situation can be corrected if we assume that the radial parameters ρ2 and ρ4 are temperature dependent. An increase in the value of ρ2 as the temperature decreases would result in an increase in the calculated anisotropy at the lower temperatures, but in order to increase the value of $\bar{\mu}$ the value of ρ4 would have to decrease. This is unsatisfactory for two reasons: (i) if ρ2 and ρ4 were temperature dependent due to changes in metal–ligand distances they should both vary in the same sense, since $\rho 2 \propto \frac{1}{a^3}$ and $\rho 4 \propto \frac{1}{a^5}$, (ii) the small changes in the unit cell dimensions over the temperature range 300—4·2 K suggest that major changes in *a*, and hence in ρ2 and ρ4, are unlikely. A similar problem was encountered in the case of hexakis(antipyrine)cerium(III) tri-iodide [2] where the preferred solution was to allow the parameters ρ2 and θ to vary with temperature, in such a manner that $\frac{3}{2}\rho 2\ (3\cos^2\theta - 1)$ was constant, the values of the other parameters being temperature independent.

An investigation of the effect of varying θ(1) and θ(2) in the ranges 72·5 to 76·5° and 38·8 to 42·8° respectively, with ρ2 = 500 cm^{-1}, ρ4 = 300 cm^{-1}, ρ6 = 200 cm^{-1} and $k_{\parallel} = k_{\perp}$ = 1·00, did not improve the agreement. It was not possible, for any combination of θ values, to reproduce the observed *g* values or the rates of variation of the μ values with temperature. Again a solution to the problem within the above limits of θ could only be found by allowing ρ2 and ρ4 to vary in the opposite sense to each other as discussed above.

An alternative approach to the problem is to retain the geometry determined crystallographically and allow *k* to be less than unity. Isotropy in *k* has been assumed for simplicity. The effect of this reduction in *k* is twofold, namely, a reduction in the magnitude of $\bar{\mu}$ at 300 K, and more importantly, a lessening of the temperature variation of all the μ values. The reduction in the magnitude of $\bar{\mu}$ at 300 K can be compensated for by using smaller values of ρ4. This has allowed very good fits to the observed magnetic anisotropy and also the *g* values to be obtained. A summary of the parameters required to reproduce either the experimental μ and /or *g* values is given in Table 3, and one example of a satisfactory fit to *both* the μ and *g* values is shown in Figure 2(b). The range of parameters which will fit the μ values alone to ±2% is ρ2 *ca.* 400—450 cm^{-1}, ρ4 *ca.* 80—100 cm^{-1}, ρ6 *ca.* 50—200 cm^{-1}, and $k_{\parallel} = k_{\perp}$ *ca.* 0·95—0·93. To fit the *g* and μ values simultaneously then the parameters are more closely defined, ρ2 = 450 cm^{-1}, ρ4 = 80 cm^{-1}, ρ6 = 50—100 cm^{-1}, and $k_{\parallel} = k_{\perp}$ = 0·94—0·93 giving the best fits.

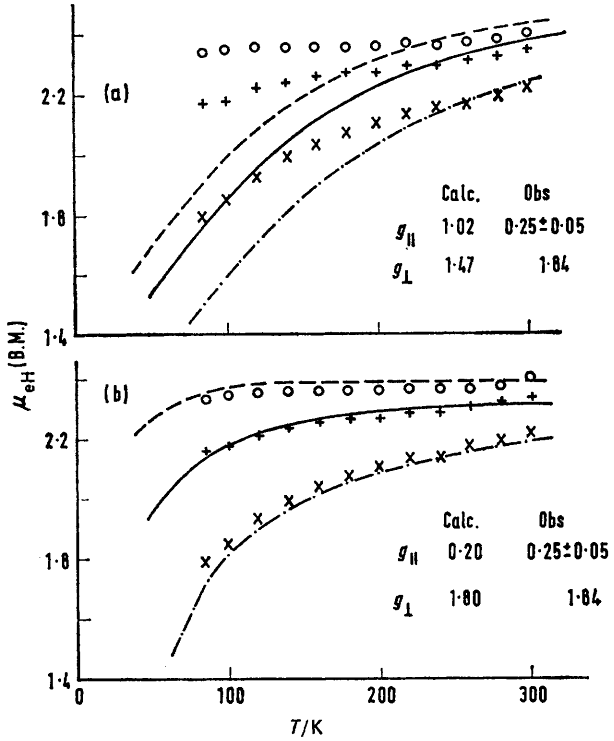

FIGURE 2 The variation of μ with temperature for the 12-co-ordinate model with (a) ρ2 = 500 cm^{-1}, ρ4 = 300 cm^{-1}, ρ6 = 200 cm^{-1}, θ(1) = 74·57°, θ(2) = 40·80°, R = 0·9842, λ = 640 cm^{-1}, $k_{\parallel} = k_{\perp}$ = 1·0.
(b) ρ2 = 450 cm^{-1}, ρ4 = 80 cm^{-1}, ρ6 = 50 cm^{-1}, θ(1) = 74·57°, θ(2) = 40·80°, R = 0·9842, λ = 640 cm^{-1}, $k_{\parallel} = k_{\perp}$ = 0·93. Experimental, ○ $\mu_{\perp}$, + $\bar{\mu}$, × $\mu_{\parallel}$. Calculated, - - - - $\mu_{\perp}$ —— $\bar{\mu}$, — · — · — · — $\mu_{\parallel}$

Although the simultaneous agreement with both magnetic susceptibility and e.s.r. measurements has led to a narrow range of crystal-field parameters it is desirable to obtain further confirmation of these values. Direct measurement of the energy separations arising from the perturbation by the crystal-field and spin-orbit coupling would provide this. The calculated energy separations for one of the acceptable sets of parameters are listed in Table 4. In this typical case the total spread of the f^1 manifold is 2239 cm^{-1}. The i.r. spectrum of a Nujol mull of this compound showed no features which were not present in the lanthanum(III) analogue, and thus provided no evidence to support the chosen values of the parameters.

TABLE 3

Crystal-field parameters required to fit the g and μ values for $Ce_2Mg_3(NO_3)_{12},24H_2O$ using a 12-co-ordinate model

$\theta(1) = 74{\cdot}57^\circ$, $\theta(2) = 40{\cdot}80^\circ$, $\lambda = 640$ cm^{-1}

				Calculated							
						$T = 300$ K			$T = 100$ K		
$\rho 2$ (cm^{-1})	$\rho 4$ (cm^{-1})	$\rho 6$ (cm^{-1})	k	$g_\parallel$	$g_\perp$	$\bar{\mu}$ (B.M.)	$\mu_\parallel$ (B.M.)	$\mu_\perp$ (B.M.)	$\bar{\mu}$ (B.M.)	$\mu_\parallel$ (B.M.)	$\mu_\perp$ (B.M.)
400	70	50	0·93	0·19	1·81	2·32	2·20	2·38	2·22	1·88	2·38
,,	,,	,,	0·94	0·20	1·83	2·36	2·23	2·43	2·43	1·91	2·42
,,	,,	100	0·93	0·20	1·80	2·30	2·20	2·35	2·21	1·89	2·37
,,	,,	,,	0·94	0·20	1·83	2·36	2·23	2·42	2·25	1·92	2·42
450	,,	50	0·92	0·09	1·83	2·30	2·16	2·38	2·18	1·81	2·37
,,	,,	,,	0·93	0·09	1·86	2·32	2·19	2·38	2·21	1·84	2·40
,,	,,	100	0·92	0·09	1·82	2·27	2·16	2·33	2·18	1·82	2·36
,,	,,	,,	0·93	0·10	1·85	2·31	2·19	2·37	2·21	1·85	2·39
400	80	50	0·93	0·30	1·75	2·30	2·20	2·35	2·19	1·86	2·36
,,	,,	,,	0·94	0·31	1·77	2·35	2·24	2·40	2·23	1·89	2·40
450	,,	,,	0·93	0·20	1·80	2·32	2·18	2·39	2·19	1·82	2·38
,,	,,	,,	0·94	0·21	1·82	2·36	2·21	2·43	2·22	1·85	2·41
,,	,,	100	0·94	0·21	1·82	2·34	2·22	2·40	2·22	1·86	2·41
400	90	50	0·94	0·40	1·72	2·34	2·23	2·40	2·20	1·87	2·37
,,	,,	,,	0·95	0·41	1·75	2·36	2·26	2·42	2·23	1·89	2·40
450	,,	,,	0·94	0·30	1·77	2·34	2·22	2·41	2·20	1·83	2·38
,,	,,	,,	0·96	0·31	1·82	2·41	2·28	2·47	2·26	1·88	2·45
400	100	50	0·94	0·48	1·67	2·36	2·23	2·42	2·18	1·85	2·35
,,	,,	,,	0·95	0·49	1·70	2·37	2·25	2·43	2·21	1·87	2·38
			Observed	0·25	1·84	2·34	2·22	2·40	2·19	1·85	2·35

$\theta = 56{\cdot}42^\circ$ $\lambda = 640$ cm^{-1}

TABLE 4

The energy separations and eigenfunctions calculated using the 12-co-ordinate model with $\rho 2 = 450$ cm^{-1}, $\rho 4 = 80$ cm^{-1}, $\rho 6 = 50$ cm^{-1}, and $k_\parallel = k_\perp = 0{\cdot}93$

Ground-state eigenfunctions					
	$\mp 0{\cdot}4290\,\lvert\pm 3, \mp\tfrac{1}{2}\rangle$	$\pm 0{\cdot}1810\,\lvert\pm 2, \pm\tfrac{1}{2}\rangle$	$-0{\cdot}5936\,\lvert 0, \mp\tfrac{1}{2}\rangle$	$+0{\cdot}6562\,\lvert\mp 1, \pm\tfrac{1}{2}\rangle$	$\pm 0{\cdot}0109\,\lvert\mp 3, \mp\tfrac{1}{2}\rangle$
Energy separation (cm^{-1})			Eigenfunctions		
73	$\mp 0{\cdot}0102\,\lvert\pm 2, \mp\tfrac{1}{2}\rangle$	$\mp 0{\cdot}0158\,\lvert\pm 1, \pm\tfrac{1}{2}\rangle$	$-0{\cdot}5405\,\lvert\mp 1, \mp\tfrac{1}{2}\rangle$	$+0{\cdot}8411\,\lvert\mp 2, \pm\tfrac{1}{2}\rangle$	
132	$0{\cdot}0278\,\lvert\pm 3, \pm\tfrac{1}{2}\rangle$	$\mp 0{\cdot}3596\,\lvert\pm 1, \mp\tfrac{1}{2}\rangle$	$\pm 0{\cdot}2957\,\lvert 0, \pm\tfrac{1}{2}\rangle$	$-0{\cdot}3354\,\lvert\mp 2, \mp\tfrac{1}{2}\rangle$	$+0{\cdot}8185\,\lvert\mp 3, \pm\tfrac{1}{2}\rangle$
2069	$\pm 0{\cdot}1164\,\lvert\pm 3, \mp\tfrac{1}{2}\rangle$	$\pm 0{\cdot}3095\,\lvert\pm 2, \pm\tfrac{1}{2}\rangle$	$+0{\cdot}6538\,\lvert 0, \mp\tfrac{1}{2}\rangle$	$+0{\cdot}5879\,\lvert\mp 1, \pm\tfrac{1}{2}\rangle$	$-0{\cdot}3430\,\lvert\mp 3, \mp\tfrac{1}{2}\rangle$
2144	$0{\cdot}5405\,\lvert\pm 2, \mp\tfrac{1}{2}\rangle$	$+0{\cdot}8411\,\lvert\pm 1, \pm\tfrac{1}{2}\rangle$	$\mp 0{\cdot}0102\,\lvert\pm 1, \mp\tfrac{1}{2}\rangle$	$\pm 0{\cdot}0158\,\lvert\mp 2, \pm\tfrac{1}{2}\rangle$	
2163	$0{\cdot}3002\,\lvert\pm 3, \mp\tfrac{1}{2}\rangle$	$+0{\cdot}7536\,\lvert\pm 2, \pm\tfrac{1}{2}\rangle$	$\mp 0{\cdot}0481\,\lvert 0, \mp\tfrac{1}{2}\rangle$	$\mp 0{\cdot}0647\,\lvert\mp 1, \pm\tfrac{1}{2}\rangle$	$+0{\cdot}5792\,\lvert\mp 3, \mp\tfrac{1}{2}\rangle$
2239	$-0{\cdot}2058\,\lvert\pm 3, \mp\tfrac{1}{2}\rangle$	$-0{\cdot}4371\,\lvert\pm 2, \pm\tfrac{1}{2}\rangle$	$\pm 0{\cdot}3611\,\lvert 0, \mp\tfrac{1}{2}\rangle$	$\pm 0{\cdot}3004\,\lvert\mp 1, \pm\tfrac{1}{2}\rangle$	$+0{\cdot}7389\,\lvert\mp 3, \mp\tfrac{1}{2}\rangle$

The Interpretation of the Magnetic Results using a Six-co-ordinate Model.—The procedure described for the twelve-co-ordinate model was adopted, in that the parameters required to fit the data at 300 K were found initially with $\theta = 56{\cdot}42^\circ$. These are summarised in Table 5. Values of $\rho 2 = \rho 4 = 400$ cm^{-1} give a reasonable reproduction of the μ values at 300 K. However, as in the previous model, the calculated μ values fall much more rapidly with temperature than the experimental values and the g values are incorrect, see Figure 3(a).

The investigation of the effect of varying θ in the range $54{\cdot}74^\circ < \theta < 58^\circ$ lead to the same general conclusions as for the twelve-co-ordinate model. The value of $\bar{\mu}$ at a fixed value of $\rho 4$ is not very sensitive to variations in θ in the above range. Thus, in order to obtain the correct value of $\bar{\mu}$ at low temperature, $\rho 4$ has to be reduced. Increasing the value of θ increases the anisotropy at all temperatures, thus values of θ could be found which would predict the anisotropies at low temperatures, allowing $\rho 2$ to remain constant at 400 cm^{-1}. Alternatively, θ could be kept constant whilst $\rho 2$ is increased with decreasing temperature. As in the case of the twelve-co-ordinate model this is unsatisfactory as it seems unreasonable that $\rho 2$ should vary in a different sense to $\rho 4$.

This problem can be resolved, as for the twelve-co-ordinate model, by allowing $k_\parallel$ and $k_\perp$ to be less than unity. For simplicity we have again assumed isotropy in k. Qualitatively, the effects of reducing k are the same as in the twelve-co-ordinate model. The major difference between the two models is that the radial parameter, ρ4, needs to be different. The parameters required to fit either the observed μ and/or g values are given in Table 6, and one example of a satisfactory fit to both the μ and g values is shown in Figure 3(b). The energy separations in the $4f^1$ manifold are very similar to those predicted by the twelve-co-ordinate model, making a definite choice between the two models difficult.

TABLE 5

The variation of μ at 300 K and g with (a) ρ4 and (b) ρ2 using a six-co-ordinate model with $\rho6 = 400$ cm^{-1}, $\theta = 56{\cdot}42°$, $\lambda = 640$ cm^{-1}, and $k_{\parallel} = k_{\perp} = 1{\cdot}00$

(a) $\rho2 = 400$ cm^{-1}

ρ4 (cm^{-1})	200	300	400	600	800
$\bar{\mu}$ (B.M.)	2·49	2·44	2·36	2·16	1·98
$\mu_{\parallel}$ (B.M.)	2·38	2·32	2·24	2·08	1·91
$\mu_{\perp}$ (B.M.)	2·54	2·50	2·42	2·20	2·01
$g_{\parallel}$	0·86	1·02	1·09	1·11	1·06
$g_{\perp}$	1·75	1·62	1·54	1·39	1·26

(b) $\rho4 = 400$ cm^{-1}

ρ2 (cm^{-1})	400	800	1600
$(\chi_{\perp} - \chi_{\parallel}) \times 10^6$	346	574	1139
$\bar{\mu}$ (B.M.)	2·36	2·34	2·34
$\mu_{\parallel}$ (B.M.)	2·24	2·14	1·93
$\mu_{\perp}$ (B.M.)	2·42	2·44	2·55
$g_{\parallel}$	1·09	0·79	0·31
$g_{\perp}$	1·54	1·69	1·93

Thus, in the present system, it is possible to give a good account of the effects of the nitrato-groups on the electronic properties of cerium(III) using both the twelve- and six-co-ordinate models. This provides some support for the view that the effect of such ligands on the electronic properties of metal ions may be approximated by a single atom located at the mean position of the two oxygen atoms. This result contrasts with the general observation noted for dodecahedral complexes of d-transition-metal ions.[1a]

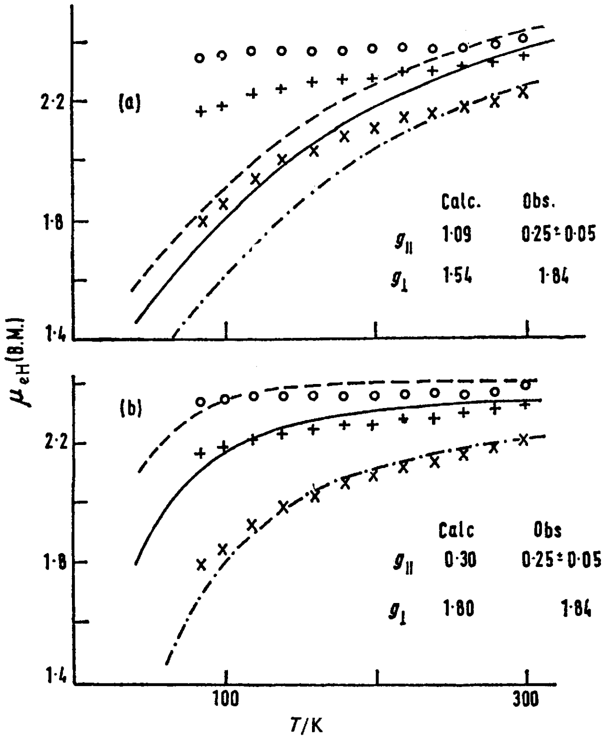

FIGURE 3 The variation of μ with temperature for the six-co-ordinate model with (a) $\rho2 = 400$ cm^{-1}, $\rho4 = 400$ cm^{-1}, $\rho6 = 400$ cm^{-1}, $\theta = 56{\cdot}42°$, $\lambda = 640$ cm^{-1}, $k_{\parallel} = k_{\perp} = 1{\cdot}0$.
(b) $\rho2 = 500$ cm^{-1}, $\rho4 = 120$ cm^{-1}, $\rho6 = 100$ cm^{-1}, $\theta = 56{\cdot}42°$, $\lambda = 640$ cm^{-1}, $k_{\parallel} = k_{\perp} = 0{\cdot}94$. Experimental, ○ $\mu_{\perp}$, + $\bar{\mu}$, × $\mu_{\parallel}$. Calculated, ------ $\mu_{\perp}$, —— $\bar{\mu}$, —·—·—·— $\mu_{\parallel}$.

The Orbital Reduction Parameter, k.—The values of k required by our model call for some comment. It is generally assumed that, for complexes of the lanthanides,

TABLE 6

Crystal-field parameters required to fit the g and μ values for $Ce_2Mg_3(NO_3)_{12},24H_2O$ using a six-co-ordinate model
$\theta = 56{\cdot}42°$, $\lambda = 640$ cm^{-1}

				Calculated							
						$T = 300$ K			$T = 100$ K		
ρ2 (cm^{-1})	ρ4 (cm^{-1})	ρ6 (cm^{-1})	k	$g_{\parallel}$	$g_{\perp}$	$\bar{\mu}$ (B.M.)	$\mu_{\parallel}$ (B.M.)	$\mu_{\perp}$ (B.M.)	$\bar{\mu}$ (B.M.)	$\mu_{\parallel}$ (B.M.)	$\mu_{\perp}$ (B.M.)
400	120	50	0·93	0·44	1·67	2·31	2·22	2·35	2·14	1·85	2·28
,,	,,	,,	0·94	0·45	1·70	2·34	2·24	2·39	2·17	1·87	2·32
450	,,	,,	0·93	0·36	1·72	2·30	2·19	2·35	2·13	1·81	2·30
,,	,,	,,	0·94	0·37	1·74	2·34	2·24	2·39	2·17	1·84	2·33
,,	,,	,,	0·96	0·38	1·80	2·40	2·30	2·45	2·23	1·89	2·40
,,	,,	100	0·93	0·37	1·73	2·32	2·20	2·38	2·14	1·81	2·31
,,	,,	,,	0·94	0·38	1·76	2·35	2·22	2·41	2·17	1·84	2·34
500	,,	50	0·94	0·29	1·78	2·34	2·22	2·39	2·16	1·80	2·34
,,	,,	,,	0·96	0·30	1·84	2·40	2·28	2·45	2·22	1·85	2·41
,,	,,	100	0·94	0·30	1·80	2·35	2·22	2·42	2·17	1·80	2·35
,,	,,	,,	0·96	0·31	1·85	2·40	2·27	2·47	2·23	1·85	2·42
400	130	50	0·94	0·50	1·67	2·33	2·24	2·38	2·15	1·85	2·29
,,	,,	100	0·94	0·51	1·69	2·35	2·25	2·40	2·15	1·86	2·30
500	,,	50	0·94	0·35	1·75	2·33	2·21	2·39	2·14	1·78	2·34
,,	,,	,,	0·96	0·36	1·80	2·39	2·27	2·45	2·20	1·83	2·39
,,	,,	100	0·94	0·35	1·76	2·34	2·21	2·40	2·14	1·78	2·33
,,	,,	,,	0·96	0·37	1·82	2·39	2·27	2·46	2·20	1·83	2·39
			Observed	0·25	1·84	2·34	2·22	2·40	2·19	1·85	2·35

the $4f$ electrons are so well shielded from the ligands that any interaction between them would be entirely electrostatic. Thus k is generally expected to be unity, as suggested by Gerloch and Mackey.[2] However, Englehardt and Figgis[12] have suggested that the experimental susceptibilities of some lanthanide complex oxides and fluorides may be fitted better with k *ca.* 0·95. If the assumption of the D_{3d} point group for the present molecule is a good one, then the reasons for k being less than unity may be twofold. (i) There can be mixing, *via* σ-bonding, between ligand orbitals, which transform as a_{1g}, a_{2u}, e_g and e_u, and cerium a_{2u} and e_u $4f$ orbitals. As in the case of d orbitals this should lead to a reduction in k,[13,14] primarily through the dilution of the $4f$ orbitals by ligand orbitals. If we make the approximation that $1 - k$ represents the total ligand contribution to the $4f$ orbitals then this would amount to *ca.* 5% in the present compound.

(ii) The mixing between cerium f and p orbitals is allowed in D_{3d} symmetry. A simple perturbation calculation, using $\rho 2$ and $\rho 4$ required, for example, by the six-co-ordinate model as estimates for the radial parameters

$$\int_0^\infty R(4f)\, R(Np)\, \frac{r_<^n}{r_>^{n+1}}\, r^2 dr$$

where N is the principal quantum number of the p orbitals, and the ground-state eigenfunctions after spin-orbit coupling, leads to the admixed p functions being only *ca.* 5000 cm^{-1} above the ground-state when $k = 0{\cdot}94$. This seems unreasonably close to the ground-state when in the free-ion the $4f^1$ to $4f^05d^1$ separation is of the order of 50,000 cm^{-1}.[15] Thus, providing our model is valid, it seems probable that the major contribution to k arises from ligand orbital admixture rather than f–p mixing, although it is difficult to completely separate the two effects.

The simple point-charge crystal-field model with the inclusion of an orbital reduction factor, k, gives a good description of the magnetic properties and hence of the electronic structure of cerous magnesium nitrate. The reasons for k being significantly less than unity are not at present understood and work on related systems is in hand in an attempt to clarify this problem.

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