Single-crystal Magnetic Properties of Lanthanide Complexes. Part VII.[1] Hexakis(antipyrine)europium(III) Tri-iodide

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The principal and average magnetic moments of hexakis(antipyrine)europium(III) tri-iodide (antipyrine is 2,3-dimethyl-1-phenyl-Δ^3-pyrazolin-5-one) have been measured in the temperature range 300—80 K. Approximate values for the powder susceptibilities have also been determined down to 4 K. These are interpreted within a point-change crystal-field model of D_{3d} symmetry, using the free-ion ground term, corrected for the effects of intermediate coupling, as basis. However, the restricted basis of $^7F_0 + {}^7F_1 + {}^7F_2 + {}^7F_3$ was found to be sufficient for present purposes. Sixth-order crystal-field terms cannot operate in the first three states so that no value for ρ_6 could be estimated. Estimates of ρ_4 depend critically upon the energy levels of the very low-lying state of europium(III), so that only a relationship between these has been established. Magnetic anisotropies, however, have fixed a value of $A_2^0\langle r^2\rangle$, related to the second-order potential, of *ca.* 250 cm^{-1}.

EUROPIUM(III) ions take a somewhat special place in the history of the magnetic properties of the lanthanides for, with samarium(III) ions, their experimental moments are not well reproduced by Hund's formula, $\mu = g\sqrt{J(J+1)}$ BM, in which lanthanide moments are taken to be a property of the ground state alone. Van Vleck and Frank[2] successfully modified the theory by including first- and second-order Zeeman effects from nearby excited states. The same problem concerns us in Eu(antip)$_6$I$_3$ (antip = antipyrine = 2,3-dimethyl-1-phenyl-Δ^3-pyrazolin-5-one) being the next in our studies of trigonally distorted octahedral lanthanide complexes.

The ^7F free-ion ground term of the f^6 configuration in europium(III) ions spans an energy spectrum of some 5000 cm^{-1} and is then well separated energetically from the other terms, the nearest being components of ^5D at *ca.* 17,000 cm^{-1}. Mean energy levels observed from spectra of europium chloride, double nitrate, and ethyl sulphate are given in Table 1. These energy levels do not fit a Landé splitting rule at all well; those for the inverse f^8 configuration of terbium(III) were rather better. As usual this behaviour results from the effects of intermediate coupling and Ofelt[3] has fitted these energies and those of higher states by a least-squares fit to an intermediate coupling model parameterized by one interelectronic repulsion parameter, F_2, and ζ, the spin–orbit coupling parameter. The third line in Table 1 gives approximate % parities of the eigenvectors derived in Ofelt's treatment. As often appears to happen for lanthanide ground-terms (but see f^{12}, Part VI[1]) intermediate coupling is manifest in the eigenvalues but not significantly in the eigenvectors.

TABLE 1

Free-ion eigenvalues and eigenvectors for f^6

State	$^7F_0$	$^7F_1$	$^7F_2$	$^7F_3$	$^7F_4$	$^7F_5$	$^7F_6$
Energy/cm^{-1}	0	355	1023	1847	2751	3802	4907
% purity	94	95	96	97	98	98	97

Our calculations as usual involve a D_{3d} symmetry crystal field with the parameters ρ_2, ρ_4, ρ_6 for second-, fourth-, and sixth-order radial parameters in the point-charge formalism: θ, the effective distortion angle, is the angle subtended by any Eu–O bond and the molecular triad. We have considered basis sets spanning the complete ^7F term although we find that all moments are calculated identically for the restricted basis of the four lowest states: $^7F_0 + {}^7F_1 + {}^7F_2 + {}^7F_3$.

EXPERIMENTAL

Powder susceptibilities and crystal anisotropies of Eu(antip)$_6$I$_3$ were measured in the temperature range 80—300 K by the Gouy and Krishnan 'critical torque' techniques, respectively. The results, corrected for the diamagnetic properties of powdered samples and single crystals of the lutetium analogue, are given in Tables 2

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[1] Part VI, M. Gerloch and D. J. Mackey, preceding paper.

[2] J. H. Van Vleck and A. Frank, *Phys. Rev.*, 1929, **34**, pp. 1494, 1625.

[3] G. S. Ofelt, *J. Chem. Phys.*, 1963, **38**, 2171.

and 3. Interpolated principal molecular moments are given in Table 4. Procedures and calibrations are as in ref. 4.

TABLE 2

Experimental mean molecular susceptibilities of $Eu(antip)_6I_3$

T/K	$10^6\bar{\chi}_M'$/ c.g.s.u. mole^{-1}	T/K	$10^6\bar{\chi}_M'$/ c.g.s.u. mole^{-1}
301·0	4865	207·0	5715
292·5	4965	191·5	5845
289·0	5000	174·0	6195
285·0	5015	162·5	6215
276·5	5055	148·5	6320
268·0	5130	132·0	6405
259·5	5205	114·5	6405
239·0	5365	100·0	6620
224·0	5540	90·0	6495

TABLE 3

Experimental molecular anisotropies of $Eu(antip)_6I_3$

T/K	$10^6(\chi_\perp - \chi_\parallel)$/ c.g.s.u. mole^{-1}	T/K	$10^6(\chi_\perp - \chi_\parallel)$/ c.g.s.u. mole^{-1}
291·5	915	189·0	1960
282·0	990	168·5	2260
270·0	1085	148·5	2590
257·0	1190	134·0	2825
245·0	1305	119·0	3035
227·5	1480	103·5	3275
216·0	1610	89·0	3460
200·0	1815		

TABLE 4

Principal magnetic moments of $Eu(antip)_6I_3$

T/K	$\bar{\mu}$/BM	$\mu_\parallel$/BM	$\mu_\perp$/BM
301·0	3·42	3·22	3·51
292·5	3·41	3·19	3·51
289·0	3·40	3·18	3·51
285·0	3·38	3·16	3·49
276·5	3·34	3·11	3·46
268·0	3·32	3·07	3·43
259·5	3·28	3·04	3·41
239·0	3·20	2·92	3·34
224·0	3·15	2·84	3·29
207·0	3·07	2·75	3·23
191·5	2·99	2·64	3·15
174·0	2·94	2·57	3·11
162·5	2·84	2·46	3·02
148·5	2·74	2·34	2·92
132·0	2·60	2·18	2·79
114·5	2·42	1·99	2·61
100·0	2·30	1·88	2·49
90·0	2·16	1·74	2·35

We have also measured the powder susceptibility of $Eu(antip)_6I_3$ in the range 4—100 K using a P.A.R. 150 vibrating sample magnetometer. There is some evidence of slight variation of $\bar{\chi}$ in this temperature range perhaps associated with a hysteresis effect. If real, such an effect might be linked with the reported phase-change in these complexes. The matter is being studied further. We quote here the result that $\bar{\chi}$ is approximately constant below *ca.* 75 K with the value 6500 ± 200 c.g.s.u.

DISCUSSION

The energies of the first four states of trigonally distorted octahedral f^6 ions shown in Figure 1 as functions of the distortion angle θ. States arising from the free-ion $^7F_1$ state approach within 100 cm^{-1} of the ground state but do not cross it for the conditions of Figure 1. There is therefore a $J = 0$, A_{1g} non-magnetic ground-state throughout the angular range.

In Figure 2 we show principal and average moments as functions of θ, calculated using the basis states corrected for intermediate coupling as discussed in the Appendix. If this correction is ignored all moments differ by less than *ca.* 0·08 BM at 100 K or 0·04 BM at 300 K, intermediate coupling serving to raise the moments roughly uniformly across the angular range. The results shown in this Figure derive from the first four states as basis: some repeated calculations in the full-term basis show that all moments are affected by *ca.* 0·06 BM at most, some being raised, others lowered. As usual room-temperature mean moments $\bar{\mu}$(300 K) vary little with θ but $\bar{\mu}$(100 K) varies rather more, especially for $\theta > \theta_{oct}$. $\bar{\mu}$ at 300 or 100 K is independent of ρ_2 for a given θ value (not shown); *i.e.* variations of less than *ca.* 0·02 BM in the range $500 < \rho_2 < 2500$ cm^{-1}. The sign of anisotropy is uniquely determined by the sign of distortion being $\mu_\parallel > \mu_\perp$ for $\theta > \theta_{oct}$ and *vice versa.* Further, as for most members of this series, $\bar{\mu}$ values decrease with decreasing temperature; anisotropy values increase.

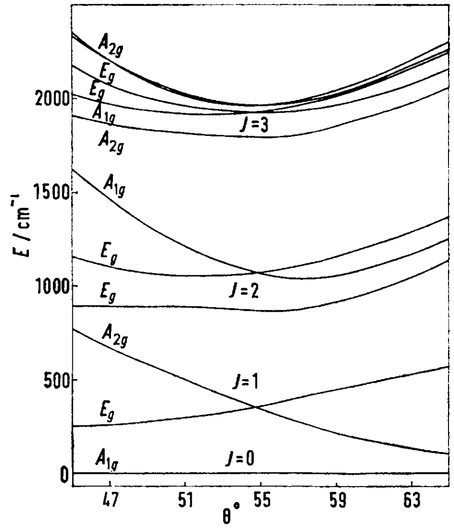

FIGURE 1 Crystal-field splittings for the four lowest states of f^6 as functions of the trigonal distortion angle θ; ρ_2 1500, ρ_4 5000, and ρ_6 200 cm^{-1}

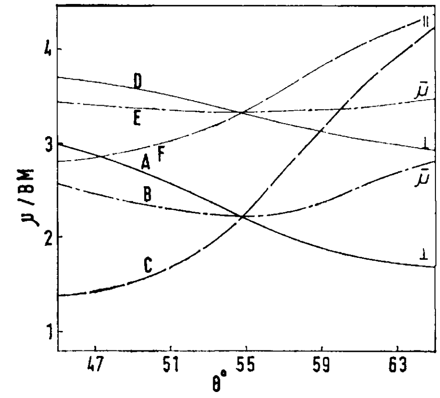

FIGURE 2 Principal and average moments for f^6 systems in D_{3d} at A—C 100 K and D—F 300 K symmetry; ρ_2 1500, ρ_4 500, ρ_6 200 cm^{-1}

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[4] B. N. Figgis, M. Gerloch, J. Lewis, and R. C. Slade, *J. Chem. Soc.* (*A*), 1968, 2028.

All moments change by <0·01 BM as ρ_6 varies in the range $0 < \rho_6 < 500$ cm^{-1} at any temperature. This is obviously due to the first state in which a sixth-order crystal-field harmonic can operate being the $^7F_3$ at 1800 cm^{-1} above ground. Consequently this investigation is unable to determine any value for ρ_6 but equally, estimates of other parameters are unaffected by any ρ_6 value assumed for computational purposes.

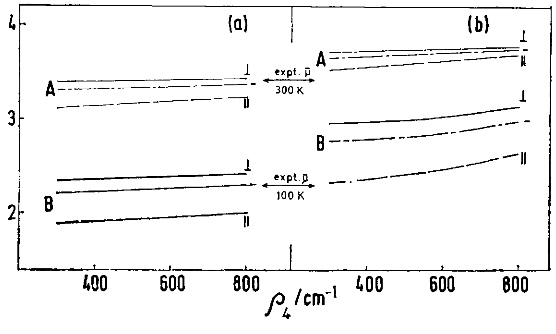

FIGURE 3 Principal and average moments of f^6 systems as functions of ρ_4 at A 300 K and B 100 K. Experimental value for Eu(antip)$_6$I$_3$ are indicated; ρ_2 1500, ρ_6 200 cm^{-1}, and $\theta = 53°$. (a) $\Delta E(^7F_1 - {}^7F_0)$ 355 cm^{-1} (Table 1), and (b) ΔE 220 cm^{-1} corresponding to a Landé interval rule with ζ 1320 cm^{-1}

Figure 3(a) shows principal and mean moments as functions of ρ_4. Again there is not very much variation for a similar reason to that discussed for ρ_6 dependence: the first 'magnetically active' level for fourth-order harmonics is the $^7F_2$ at *ca.* 1000 cm^{-1}. Nevertheless, there remains sufficient dependence of moments on ρ_4 to suggest searching for a fit to the experimental value for Eu(antip)$_6$I$_3$. Figure 3(a), however, shows that the calculated mean moments at 300 K are sufficiently low to require a ρ_4 value in excess of *ca.* 700 cm^{-1} to fit experiment. Such a high value for ρ_4 seems out of place compared with values we have found for other compounds in this series. The curves in Figure 3 are calculated assuming θ 53° but, as discussed earlier, $\bar{\mu}$(300 K) values are so little affected by θ that some θ values as low as, say, 49° might be required to improve the situation in Figure 3(a). Even though we regard θ as an effective distortion angle, we do not favour such low values, especially as other complexes throughout the series could be fitted with θ anywhere in the range 49—54°, say. $\bar{\mu}$ values are independent of ρ_2 and ρ_6 so we must vary something other than the crystal-field parameters.

The ground state is non-magnetic and all contributions to moments are from excited state. The placing of their energy levels is therefore particularly important and doubly so as the first level for europium(III) is only *ca.* 350 cm^{-1} above ground. We recall at this point that the energy values quoted in Table 1 are those for other europium compounds. Van Uitert and Soden[5] have reported that Eu(antip)$_6$I$_3$ fluoresces weakly but do not quote any detailed results. We have tried using Ofelt's spin–orbit coupling coefficient value, ζ 1320 cm^{-1}, to calculate the first energy level assuming a Landé interval rule. This gives the energy of $^7F_1$ as 220 cm^{-1} above ground. The resulting moment, again as functions of ρ_4 are shown in Figure 3(b). Clearly no fits are possible, all calculated moments being too high. It is interesting to recall Van Vleck and Frank's early calculation[2] of the moments of europium(III) compounds. They assumed a Landé interval rule, *i.e.* neglect of intermediate coupling, and adjusted ζ to fit observed moments. They found ζ to be 1530 cm^{-1}, and so put the $^7F_1$ state at 255 cm^{-1} above $^7F_0$ ground.

We do not have experimental energy levels available for Eu(antip)$_6$I$_3$ and clearly cannot parameterize all levels nor, in the light of the spectra of the other europium complexes can we neglect intermediate coupling. We therefore chose to parameterize the energy of the first excited state, which should perhaps have most influence on the magnetic moments, and take the eigenvalues in Table 1 for the others. Varying this energy, $\Delta E(^7F_1 - {}^7F_0)$, we constructed curves like those in Figure 3 and observed what ρ_4 values would then be required to fit experiment. The process is summarized in Figure 4 showing the relation between ΔE and ρ_4 for fit to mean moments. There is obviously great sensitivity of ρ_4 to ΔE, a change of ΔE from 320 to 360 cm^{-1} corresponding to ρ_4 varying from 100 to 700 cm^{-1}.

As temperature is decreased and all excited states depopulate, moments should tend to a limiting value of the temperature-independent paramagnetism. This is found in the calculations and also from the experimental results given. Figure 5 shows plots of the 'limiting value' of $\bar{\chi}$ calculated as function of ρ_4 for a series of assumed $\Delta E(^7F_1 - {}^7F_0)$ values. The experimental value, shown with error bars, intersect the curves in a way that pairs up ρ_4 and ΔE values, *e.g.* ρ_4 400 and ΔE 340 cm^{-1}, or ρ_4 625 and ΔE 355 cm^{-1}. These results are in good agreement with the curve in Figure 4: *i.e.* the very low temperature results, though approximate only, are consistent with the 100—300 K temperature range results. Of course, as $\bar{\mu}$ values (especially at 100 K) vary a little

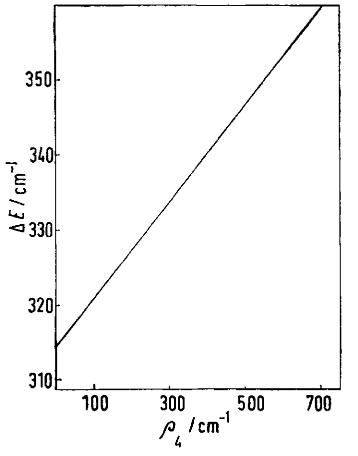

FIGURE 4 Relationship between ΔE and ρ_4 mean moments of Eu(antip)$_6$I$_3$

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[5] L. G. Van Uitert and R. R. Soden, *J. Chem. Phys.*, 1962, **36**, 1797.

with θ, Figures 3—5 will vary also. But the steep dependence of $\bar{\mu}$ on ΔE (Figure 4) or of $\bar{\chi}$ on ΔE (Figure 5) is such that we have here the major influence on mean magnetic properties. Apart from the relationships described in Figures 4 and 5, we cannot define the crystal-field parameter ρ_4.

The magnitude of the magnetic anisotropies $\Delta\mu$, however, do not depend very much on ρ_4 (Figure 3). Nor (Figure 6) do they depend much on ΔE, even at 100 K. Thus, while an estimate of ρ_4, which must derive from a study of mean moments, is linked to the value of ΔE, our usual procedure for estimating second-order crystal-field effects based on anisotropies is not. Accordingly we take ρ_4 400 and ρ_6 200 cm^{-1} for computational purposes, based on values obtained for other complexes in this series and establish combinations of ρ_2 and θ which fit $\Delta\mu$ values for Eu(antip)$_6$I$_3$. As usual we find θ to fit varies a little with temperature but not too much. Table 5 gives values of ρ_2, θ, and $A_2^0\langle r^2\rangle$, related to the coefficient of Y_2^0 in the trigonal potential, which exactly fit the experimental anisotropies at 300, 200, and 100 K. $A_2^0\langle r^2\rangle$ values are essentially independent of ρ_2 in the range $500 < \rho_2 < 2000$ cm^{-1}, but increase (with θ decreasing) a little as temperature decreases, falling in the range 235—280 cm^{-1}.

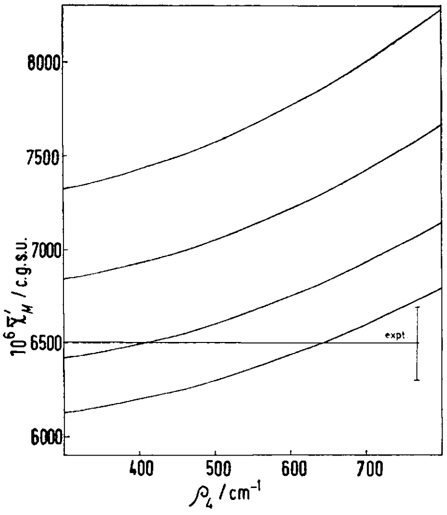

FIGURE 5 Calculated ' limiting ' mean susceptibilities as functions of ρ_4 for family of ΔE values. Experimental results in range 4—75 K for Eu(antip)$_6$I$_3$ are shown

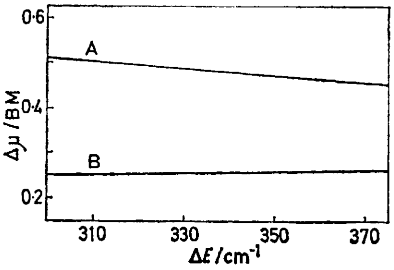

FIGURE 6 Approximate independence of anisotropies on ΔE at A 100 and B 300 K

TABLE 5

Eu(antip)$_6$I$_3$: values of ρ_2, θ, and $A_2^0\langle r^2\rangle$ * to fit anisotropies; ρ_4 400, ρ_6 200 cm^{-1}, see text

T/K	θ/deg.	$A_2^0\langle r^2\rangle$
(*a*) ρ_2 500 cm^{-1}		
300	48·21	249
200	47·85	263
100	47·45	279
(*b*) ρ_2 1000 cm^{-1}		
300	51·62	235
200	51·36	254
100	51·14	272
(*c*) ρ_2 1500 cm^{-1}		
300	52·62	238
200	52·46	250
100	52·32	272
(*d*) ρ_2 2000 cm^{-1}		
300	53·17	235
200	53·03	254
100	52·91	272

* $A_2^0\langle r^2\rangle = \frac{3}{2} \cdot \rho_2(3\cos^2\theta - 1)$.

In summary, then, ρ_6 cannot be determined for europium(III) complexes because sixth-order crystal-field terms only operate within states lying higher than 1800 cm^{-1}, estimates of ρ_4 are very sensitive functions of the energy spectrum of the lowest levels and may be related to the energy of the lowest excited state for convenience and finally, values of ρ_2/θ and $A_2^0\langle r^2\rangle$ for comparison with those for other members of the series could be determined from anisotropies because of the latters' moderate independence of the detailed energy levels in the ^7F term.

APPENDIX

The calculations and strategy of the calculations follows that discussed in previous parts, particularly Part VI.[1] Intermediate coupling f^6 free-ion eigenvectors were taken from Ofelt.[3] Correction factors for the crystal-field reduced matrix elements have been calculated from these and are as follows:

U_2 U_4 U_6	$^7F_0$	$^7F_1$	$^7F_2$	$^7F_3$	$^7F_4$	$^7F_5$	$^7F_6$
$^7F_0$	0 0 0						
$^7F_1$	0 0 0	0·9727 0 0					
$^7F_2$	0·9794 0 0	0·9883 0 0	0·9712 0·9760 0				
$^7F_3$	0 0 0	0·9868 0·9766 0	0·9916 0·9768 0	0·9507 0·9601 1·0184			
$^7F_4$	0 0·9836 0	0 0·9860 0	0·9915 1·0076 0·9926	0·9934 0·9698 0·9872	1·0213 0·9752 0·9838		
$^7F_5$	0 0 0	0 0·9996 1·0073	0 0·9965 1·0001	0·9988 0·9931 0·9947	0·9958 0·9978 0·9819	0·9981 0·9747 0·9765	
$^7F_6$	0 0 1·0045	0 0 1·0020	0 1·0077 0·9960	0 1·0021 0·9840	1·0046 0·9970 0·9824	0·9992 0·9911 0·9678	0·9895 0·9856 0·9515

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