# Crystal Structure of Gadolinium(III) Acetate Tetrahydrate. Stereochemistry of the Nine-co-ordinate [M(bidentate ligand)$_3$(unidentate ligand)$_3$]$^{x\pm}$ System

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The crystal structure of the title compound has been determined by single-crystal *X*-ray diffraction at 295(1) K and refined by least squares to a residual of 0.034 for 2 874 ' observed ' reflections. Crystals are triclinic, space group $P\bar{1}$, with $a$ = 10.790(2), $b$ = 9.395(3), $c$ = 8.941(3) Å, $\alpha$ = 60.98(2), $\beta$ = 88.50(2), $\gamma$ = 62.31(2)°, and $Z$ = 2. The compound is isostructural with its erbium analogue and comprises a dimeric species with the two rare-earth metal atoms bridged by acetate oxygen atoms; the co-ordination number of each rare-earth metal atom is nine, through the three bidentate acetate groups, two water molecules, and a bridging oxygen from one of the adjoining acetates. Bond lengths (Gd–O) range from 2.368(6) to 2.571(4) Å. The co-ordination stereochemistry for the [M(bidentate)$_3$(unidentate)$_3$]$^{x\pm}$ is examined in terms of a repulsion model.

THIS paper reports the single-crystal *X*-ray structure determination of gadolinium(III) acetate tetrahydrate, and discusses the nine-co-ordinate stereochemistry of the [M(bidentate)$_3$(unidentate)$_3$]$^{x\pm}$ entity in terms of electron-pair repulsion theory.

## EXPERIMENTAL

*Crystal Data.*—$C_6H_{17}GdO_{10}$, $M$ = 406.5, Triclinic, space group $P\bar{1}$ ($C_i^1$, no. 2), $a$ = 10.790(2), $b$ = 9.395(3), $c$ = 8.941(3) Å, $\alpha$ = 60.98(2), $\beta$ = 88.50(2), $\gamma$ = 62.31(2)°, $U$ = 678.0(7) Å$^3$, $D_m$ = 2.00(1), $Z$ = 2, $D_c$ = 1.99 g cm$^{-3}$, $F(000)$ = 394, monochromatic Mo-$K_\alpha$ radiation, $\lambda$ = 0.710 69 Å, $\mu$ = 47.4 cm$^{-1}$, specimen size 0.27 × 0.45 × 0.34 mm.

*Structure Determination.*—A unique data set measured to $2\theta_{\max.}$ 55° on a Syntex $P\bar{1}$ four-circle diffractometer was obtained, yielding 3 126 independent reflections, 2 874 with $I > 3\sigma(I)$ being considered ' observed ' and used in the structure solution and refinement after correction for absorption. The structure was solved by the heavy-atom method, and refined by 9 × 9 block-diagonal least squares, but with hydrogen-atom parameters included in the same block as the parent C and O atoms. Residuals: $R$ = 0.034, $R'$ = 0.046, $S$ 2.5. The weighting scheme used was $[\sigma^2(F_o) + 0.000\,5(F_o)^2]^{-1}$. Neutral atom scattering factors were employed for Gd corrected for anomalous dispersion ($\Delta f'$,$\Delta f''$).[1-3] Calculations were carried out using the ' *X*-RAY ' '76 program system,[4] on a CYBER 73 computer. The final positions of all the atoms are given in Table 1. The anisotropic thermal parameters for the non-hydrogen atoms, isotropic parameters for the hydrogen atoms, and structure factors are contained in Supplementary Publication No. SUP 22657 (16 pp.).†

The structure is isomorphous with that of the erbium analogue (previously reported).[5] The unit cell has been reoriented, and atoms have been relabelled in order to aid description of the molecular geometry. The environment of the gadolinum atom contains a pseudo-three-fold axis and the three segments about this axis are labelled a, b, and c, with atoms within each segment being labelled as shown in Figure 1; the metal co-ordination stereochemistry is a good approximation to a tricapped trigonal prism. The contents of the unit cell are shown in Figure 2.

## DISCUSSION

The crystal structure of gadolinium acetate tetrahydrate is isomorphous with that of the erbium analogue.[5] The gadolinium atom is nine-co-ordinated by the oxygen atoms of three bidentate acetate ligands, two water molecules, and a bridging oxygen atom from an acetate ligand of an adjacent molecule [O(a), ($\bar{x}$, $1 - y$, $\bar{z}$)] at distances ranging between 2.368(6) and 2.571(4) Å (Tables 2 and 3). A projection of the gadolinium environment is shown in Figure 1 and suggests the presence of local pseudo-three-fold symmetry: each acetate ligand together with one of the water or bridging-oxygen atoms makes a reasonable approxim-

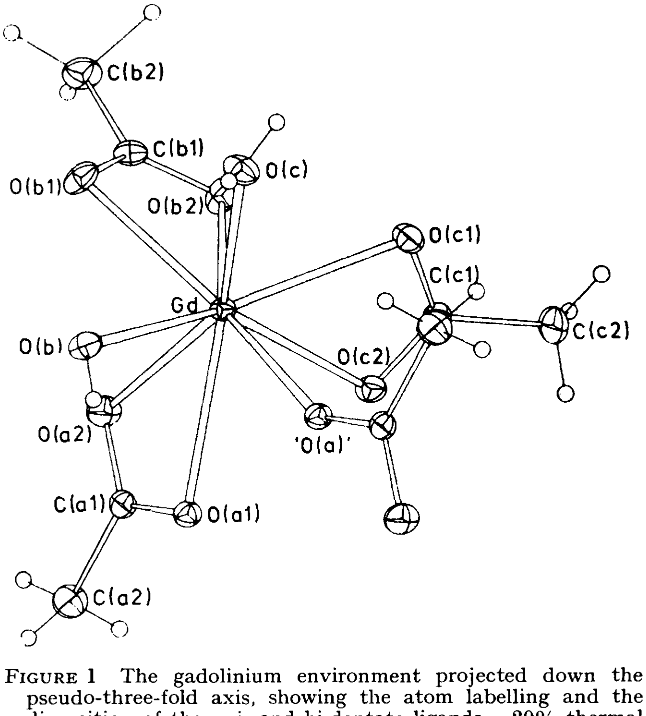

FIGURE 1 The gadolinium environment projected down the pseudo-three-fold axis, showing the atom labelling and the disposition of the uni- and bi-dentate ligands. 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms are shown with an arbitrary radius of 0.1 Å

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

ation to a planar ' blade ' of a three-bladed propeller configuration (Table 4). Of the three ligand atoms of each blade, O(*n*) have the shortest Gd–O distance ($2.38_6$ Å). The other two Gd–O (acetate) distances are longer and unequal, the mean (equatorial) Gd–O(*n*1) distance being 2.51 Å, and the mean Gd–O(*n*2) distance $2.45_4$ Å. Within the first two triads, the Gd–O(a) and Gd–O(a1) distances are longest, a consequence of the bridging nature of that oxygen atom. The deviations of the gadolinium atom from the three co-ordination planes O(*n*), O(*n*1), and O(*n*2) are 1.61, —0.35, and —1.63 Å respectively; the angles between their normals are O(*n*)—O(*n*1) 8.2, O(*n*)—O(*n*2) 13.1, and O(*n*1)—O(*n*2) 5.6°. Within the acetate ligands all C(1)–O(1) distances are longer (mean $1.26_6$ Å) than the C(1)–O(2) distances (mean $1.25_4$ Å); the significance of each individual difference is not high but the consistency of the overall trend is convincing. However, the long C(1)–O(1) distances are also associated with the longer Gd–O(1) distances, and on this basis the difference must be treated with some caution. The acetate geometries are otherwise generally as expected.

TABLE 1

Atomic fractional cell co-ordinates $\times 10^3$ for H, $\times 10^4$ for other atoms with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Gd | 897.9(3) | 3 141.6(3) | 2 750.9(3) |
| (*i*) Acetate group a | | | |
| O(1) | 996(4) | 5 492(6) | −274(5) |
| O(2) | 2 679(5) | 4 181(7) | 2 028(6) |
| C(1) | 2 141(6) | 5 283(8) | 386(7) |
| C(2) | 2 821(8) | 6 328(12) | −767(10) |
| H(2α) | 340(9) | 560(12) | −120(11) |
| H(2β) | 186(13) | 788(18) | −146(16) |
| H(2γ) | 364(7) | 605(10) | −7(9) |
| (*ii*) Acetate group b | | | |
| O(1) | 952(5) | 278(6) | 3 251(6) |
| O(2) | 2 087(5) | 1 340(6) | 1 345(5) |
| C(1) | 1 674(6) | 185(8) | 2 130(8) |
| C(2) | 2 048(13) | −1 335(14) | 1 727(13) |
| H(2α) | 148(15) | −37(20) | 48(20) |
| H(2β) | 324(15) | −254(18) | 221(16) |
| H(2γ) | 182(10) | −221(13) | 229(12) |
| (*iii*) Acetate group c | | | |
| O(1) | 1 863(5) | 2 749(6) | 5 503(6) |
| O(2) | 3 067(5) | 423(6) | 5 089(6) |
| C(1) | 2 947(6) | 1 129(8) | 6 011(7) |
| C(2) | 4 085(9) | 48(12) | 7 705(10) |
| H(2α) | 417(13) | −141(18) | 843(16) |
| H(2β) | 482(11) | −16(14) | 766(13) |
| H(2γ) | 372(12) | 72(16) | 848(15) |
| (*iv*) Co-ordinated water molecules | | | |
| O(b) | −825(6) | 2 849(8) | 4 384(7) |
| H(bα) | −84(8) | 199(11) | 499(10) |
| H(bβ) | −170(14) | 375(19) | 402(17) |
| O(c) | −674(5) | 6 246(6) | 2 217(6) |
| H(cα) | −127(11) | 713(15) | 120(15) |
| H(cβ) | −122(15) | 738(20) | 268(18) |
| (*v*) Lattice water molecules | | | |
| O(d) | 5 040(6) | 3 194(9) | 4 238(9) |
| H(dα) | 443(12) | 368(16) | 329(16) |
| H(dβ) | 542(13) | 236(17) | 443(17) |
| O(e) | 3 716(6) | 4 596(9) | 6 455(9) |
| H(eα) | 394(13) | 411(19) | 592(17) |
| H(eβ) | 418(17) | 558(23) | 577(20) |

TABLE 2

Interatomic distances (Å) and angles (°) within the complex molecule with estimated standard deviations in parentheses

[O(a) ≡ O(a1)($\bar{x}$, 1 − *y*, $\bar{z}$)]

| | Ligands *n* | | |
|---|---|---|---|
| | a | b | c |
| (*i*) Gadolinium environment * | | | |
| M–O(*n*) | 2.402(5) | 2.368(6) | 2.389(5) |
| M–O(*n*1) | 2.571(4) | 2.476(7) | 2.485(6) |
| M–O(*n*2) | 2.476(6) | 2.460(6) | 2.427(4) |
| O(*n*) · · · O(*n* + 1) | 3.191(7) | 2.904(9) | 3.020(9) |
| O(*n*) · · · O(*n*1) | 2.659(8) | 2.917(9) | 3.101(5) |
| O(*n*) · · · O(*n* + 1 1) | 3.092(5) | 3.039(10) | 2.974(7) |
| O(*n*1) · · · O(*n*2) | 2.169(7) | 2.185(7) | 2.173(8) |
| O(*n*1) · · · O(*n* + 1 2) | 3.007(7) | 2.937(10) | 3.024(7) |
| O(*n*2) · · · O(*n* + 1 2) | 3.330(10) | 3.100(8) | 3.073(7) |
| O(*n*)–Gd–O(*n* + 1) | 84.0(2) | 75.3(2) | 78.2(2) |
| O(*n*1)–Gd–O(*n* + 1 1) | 120.3(2) | 113.3(2) | 120.6(2) |
| O(*n*2)–Gd–O(*n* + 1 2) | 84.8(2) | 78.7(2) | 77.6(2) |
| O(*n*)–Gd–O(*n*1) | 64.5(2) | 74.0(2) | 79.0(2) |
| O(*n*)–Gd–O(*n*2) | 115.4(2) | 125.4(2) | 131.0(2) |
| O(*n*1)–Gd–O(*n*2) | 50.9(2) | 52.6(2) | 52.5(2) |
| O(*n*)–Gd–O(*n* + 1 1) | 78.7(2) | 77.5(2) | 73.6(2) |
| O(*n*)–Gd–O(*n* − 1 1) | 153.6(1) | 139.3(1) | 143.0(2) |
| O(*n*)–Gd–O(*n* + 1 2) | 76.4(2) | 97.9(2) | 84.2(2) |
| O(*n*)–Gd–O(*n* − 1 2) | 150.4(2) | 148.4(3) | 144.5(1) |
| O(*n*1)–Gd–O(*n* + 1 2) | 73.4(2) | 73.6(2) | 75.1(2) |
| O(*n*1)–Gd–O(*n* − 1 2) | 122.4(2) | 132.0(2) | 129.9(1) |
| (*ii*) Acetate ligands | | | |
| C(1)–O(1) | 1.270(9) | 1.265(9) | 1.263(7) |
| C(1)–O(2) | 1.255(7) | 1.250(10) | 1.258(11) |
| C(1)–C(2) | 1.488(12) | 1.512(17) | 1.509(10) |
| C(2)–H(2α) | 0.9(1) | 1.0(1) | 1.1(2) |
| C(2)–H(2β) | 1.2(1) | 1.2(1) | 0.7(1) |
| C(2)–H(2γ) | 0.9(1) | 0.9(1) | 1.1(2) |
| Gd–O(1)–C(1) | 92.9(3) | 92.8(5) | 92.7(5) |
| Gd–O(2)–C(1) | 97.8(5) | 93.9(4) | 95.6(3) |
| O(1)–C(1)–C(2) | 120.5(5) | 120.0(8) | 120.6(8) |
| O(2)–C(1)–C(2) | 121.0(7) | 119.3(8) | 120.3(6) |
| O(1)–C(1)–O(2) | 118.5(6) | 120.7(8) | 119.1(6) |
| C(1)–C(2)–H(2α) | 106(7) | 92(12) | 102(8) |
| C(1)–C(2)–H(2β) | 101(8) | 118(10) | 119(8) |
| C(1)–C(2)–H(2γ) | 110(5) | 122(8) | 111(5) |
| H(2α)–C(2)–H(2β) | 133(9) | 126(11) | 105(11) |
| H(2β)–C(2)–H(2γ) | 115(11) | 88(10) | 108(14) |
| H(2γ)–C(2)–H(2α) | 91(9) | 114(14) | 110(10) |
| (*iii*) Co-ordinated water molecules | | | |
| O–H(α) | | 0.7(1) | 0.9(1) |
| O–H(β) | | 0.8(1) | 1.2(2) |
| H(α)–O–H(β) | | 105(12) | 88(12) |

* Gd–O(a)–Gd($\bar{x}$, 1 − *y*, $\bar{z}$) = 115.5(2)°; Gd–O(a)–C(a)-($\bar{x}$, 1 − *y*, $\bar{z}$) = 151.7(4)°.

*Stereochemistry of the Tricapped Trigonal Prism.*—The tricapped trigonal-prismatic stereochemistry for a metal atom surrounded by nine unidentate ligands has been examined by Kepert,[6] King,[7] Guggenberger and Muetterties,[8] and Robertson.[9] If all ligands are considered to lie on the surface of a sphere of unit radius (Figure 3), the stereochemistry is defined by the angle $\phi$ the six

TABLE 3

Close interspecies hydrogen bonds (O · · · H ⩽2.0 Å)

| Linkage | *r*(O–H)/Å * | O–H · · · O (°) * |
|---|---|---|
| H(cα) · · · O(b2$^{\text{I}}$) | 1.9(1) | 161(12) |
| H(cβ) · · · O(c1$^{\text{II}}$) | 1.7(2) | 133(12) |
| H(bβ) · · · O(e$^{\text{II}}$) | 1.9(1) | 169(15) |
| H(dα) · · · O(a2) | 2.0(2) | 152(13) |
| H(eβ) · · · O(d$^{\text{III}}$) | 1.7(2) | 153(16) |

Transformations of the asymmetric unit (*x*,*y*,*z*): I ($\bar{x}$, 1 − *y*, $\bar{z}$); II $\bar{x}$, 1 − *y*, 1 − *z*; III 1 − *x*, 1 − *y*, 1 − *z*. * Estimated standard deviations are given in parentheses.

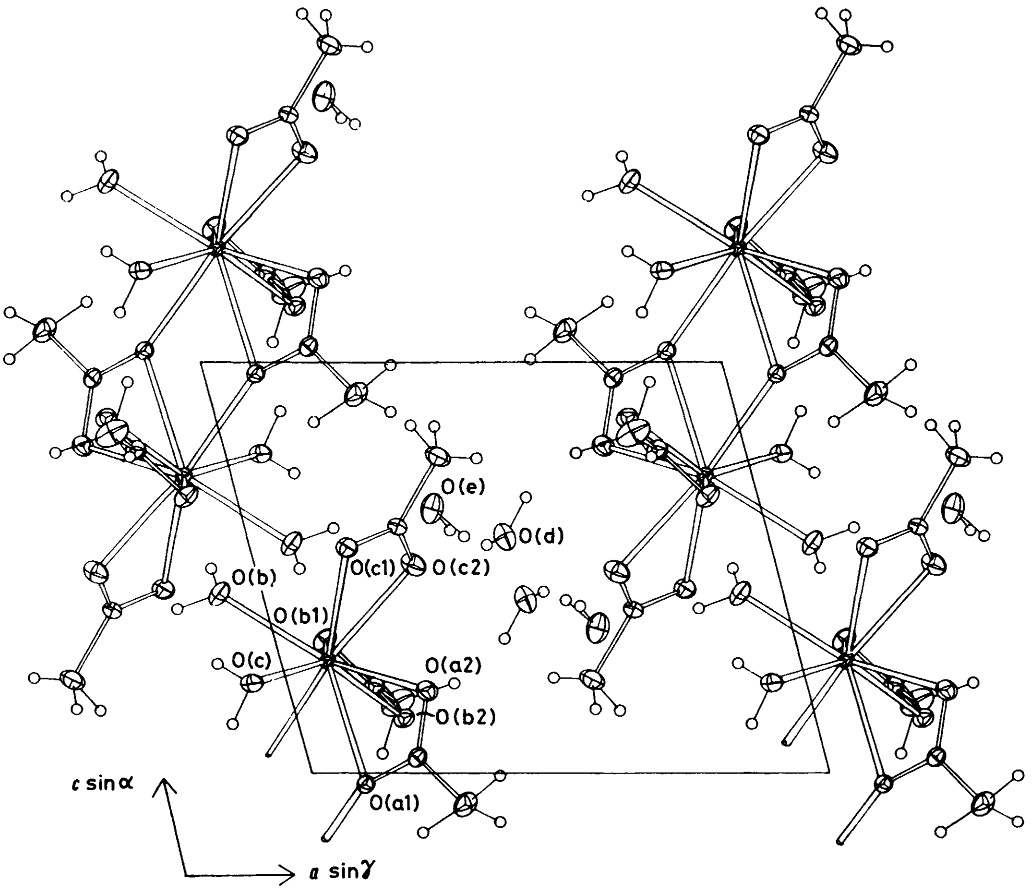

FIGURE 2 Unit-cell contents projected down *b*, showing ligand labelling and lattice water molecules, together with the dimeric nature of the complex species

' prismatic ' metal–ligand bonds make with the three-fold axis. For a ' hard-sphere model ', each unidentate ligand is in contact with four neighbouring unidentate ligands, $\phi = \arcsin(\frac{2}{3}) = 41.8°$, the polyhedral edge lengths being $AB = AD = 2/(3)^{\frac{1}{2}} = 1.154\,7$ and $AG = (\frac{2}{3})5^{\frac{1}{2}} = 1.490\,7$. Each ' prismatic ' atom therefore has four neighbours at 1.154 7 and one at 1.490 7, while each ' capping ' atom has four neighbours at **1.154 7** and two at $3^{\frac{1}{2}} = 1.732\,1$.

For the polyhedron formed by minimisation of the total repulsion energy,[6] $\phi$ is increased by several degrees (to 45.3° for $n = 1$, 44.7° for $n = 6$, and 43.9° for $n = 12$) resulting in a decrease in all four ligand–ligand distances to each capping atom, but increasing two and decreasing

TABLE 4

Least-squares planes [a]

| | Ligand *n* | | | | | |
|---|---|---|---|---|---|---|
| | a | | b | | c | |
| Plane [b] | (i) | (ii) | (i) | (ii) | (i) | (ii) |
| $10^4p$ | −1 732 | −1 874 | 6 323 | 5 735 | 8 405 | 8 884 |
| $10^4q$ | 7 592 | 7 532 | −6 156 | −5 672 | 4 271 | 3 371 |
| $10^4r$ | 6 274 | 6 306 | 4 704 | 5 910 | −3 335 | −3 117 |
| $s$ | 3.709 | 3.640 | 2.079 | 2.287 | 1.584 | 1.760 |
| σ [c] | 0.000 | 0.005 | 0.000 | 0.123 | 0.000 | 0.079 |
| δO(1) [c] | *0.000* | *0.004* | *0.000* | *0.095* | *0.000* | *−0.055* |
| δO(2) | *0.000* | *−0.004* | *0.000* | *−0.114* | *0.000* | *0.074* |
| δO | −0.048 | *−0.004* | −0.585 | *−0.098* | 0.429 | *0.061* |
| δC(1) | *0.000* | −0.011 | *0.000* | −0.076 | *0.001* | 0.065 |
| δC(2) | *0.000* | −0.033 | *0.000* | −0.237 | *0.000* | 0.193 |
| δGd | −0.030 | *0.004* | −0.105 | *0.117* | 0.095 | *−0.080* |
| θ [d] | 0.9 | | 8.2 | | 6.0 | |

Angles (°) between the normals to planes (ii): a–b 80.7; a–c 83.7; b–c 82.3. [a] Plane equations are given in the form $pX + qY + rZ = s$. [b] Plane (i) defined by the $C_2O_2$ skeleton of the acetate group and plane (ii) defined by each $O_2GdO(n)$ unit are given relative to the orthogonal Å frame $(X,Y,Z)$ with $X$ parallel to $a$ and $z$ in the $ac$ plane. [b] Atom deviations are given in Å as are estimated standard deviations of the defining atom σ; defining atom deviations are italicised. [d] θ (°) is the angle between planes (i) and (ii).

two ligand–ligand distances to each prismatic atom. For example, for $n = 6$, AB = 1.218 1, AD = 1.138 7, and AG = 1.421 8. Each capping atom therefore experiences greater repulsion than does each prismatic atom, for example for $n = 6$, $Y_D/Y_A = 1.14$ [$Y_D$ is the repulsion energy associated with the unidentate ligand D, $Y_A$ that associated with the unidentate ligand A]. This resultant increase in metal–capping atom bond length will lead to a further increase in $\phi$.[6]

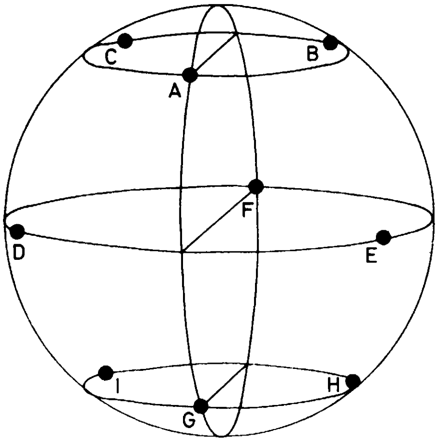

FIGURE 3 Tricapped trigonal-prismatic [M(unidentate)$_9$]

When the results of these calculations were first reported,[6] there was insufficient experimental data to test these bond-angle and relative bond-length predictions. More recently the geometry of the nona-aqualanthanoid(III) complexes have been more accurately determined, the structural parameters being in excellent agreement with predictions (Table 5).

These stereochemical calculations are now extended to the case of [M(bidentate)$_3$(unidentate)$_3$]$^{x\pm}$, as in [Gd(O$_2$CMe)$_3$]·4H$_2$O. For compounds containing different metal–ligand bonds, it is possible to fit experimental structures to calculations involving an empirical parameter $R$, which may be considered to be the distance between the central atom and the centre of repulsion of the metal–unidentate bond, divided by the distance between the central atom and the centre of repulsion of the metal–bidentate bond. The results quoted below were obtained using a value of $n = 6$ in the repulsion law; similar results were obtained for $n = 1$ and 12. The calculations were carried out as a function of the ' normalised bite ' of the bidentate ligand $b$, which is defined as the distance between the donor atoms divided by the metal–ligand distance.

TABLE 5

Capped trigonal-prismatic [M(unidentate)$_9$] complexes

| Complex | $\phi$ | MD/MA | Ref. |
|---|---|---|---|
| [Pr(OH$_2$)$_9$][BrO$_3$]$_3$ | 47.4 | 1.01 | *a* |
| [Yb(OH$_2$)$_9$][BrO$_3$]$_3$ | 47.5 | 1.05 | *a* |
| [Pr(OH$_2$)$_9$][SEtO$_3$]$_3$ | 45.1 | 1.05 | *a* |
| [Ho(OH$_2$)$_9$][SEtO$_3$]$_3$ | 45.4 | 1.04 | *b* |
| [Yb(OH$_2$)$_9$][SEtO$_3$]$_3$ | 45.1 | 1.08 | *a* |

[a] J. Albertson and I. Elding, *Acta Cryst.*, 1977, **B33**, 1460.
[b] C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, *Acta Cryst.*, 1974, **B30**, 2613.

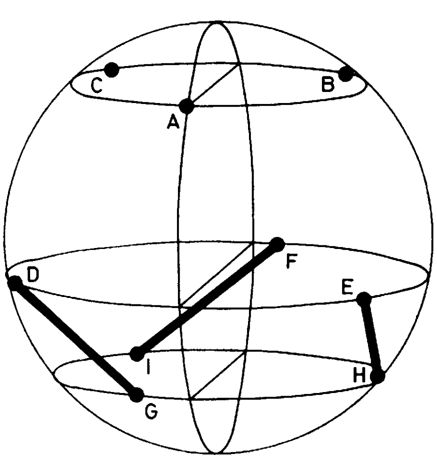

FIGURE 4 Tricapped trigonal-prismatic [M(bidentate)$_3$-(unidentate)$_3$]

The principal axis is chosen to be normal to the plane containing the three unidentate ligands A, B, and C, so that $\phi_A = \phi_B = \phi_C$ and $\theta_A = 0$. The stereochemistry corresponding to the minimum in the repulsion energy is always found to contain a three-fold axis (Figure 4), $\phi_D = \phi_E = \phi_F$, $\phi_G = \phi_H = \phi_I$, $\theta_B = 120^\circ$, $\theta_C = 240^\circ$, $\theta_F = \theta_E + 120^\circ = \theta_D + 240^\circ$, and $\theta_I = \theta_H + 120^\circ = \theta_G + 240^\circ$. The variation of the angular co-ordinates $\phi_A$, $\phi_D$, $\phi_G$, $\theta_D$, and $\theta_E$ with normalised bite $b$, and bond length ratio $R$, is shown in Figure 5 for $n = 6$. As the normalised bite is reduced from $b = 1.138\ 7$, the regular tricapped trigonal prism at $\phi_A = 44.7$, $\phi_D = 90.0$, $\phi_G = 135.3$, $\theta_D = 300.0$, and $\theta_G = 360.0^\circ$ is distorted

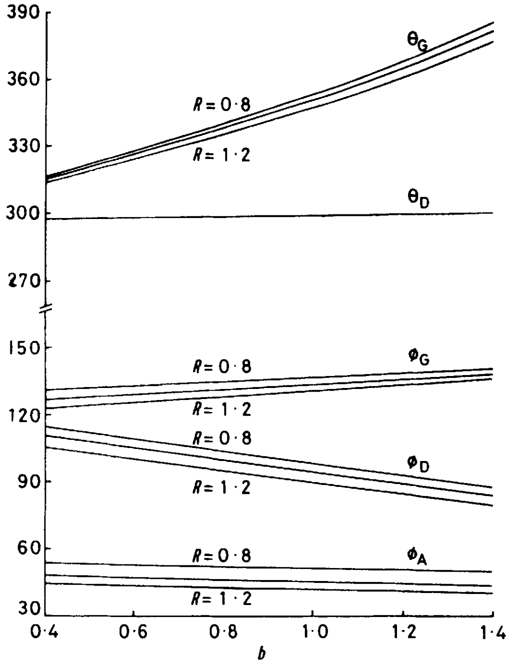

FIGURE 5 Angular co-ordinates (°) for tricapped trigonal prismatic [M(bidentate)$_3$(unidentate)$_3$] as a function of normalised bite $b$ and bond-length ratio $R$ ($n = 6$)

TABLE 6

Capped trigonal-prismatic [M(bidentate)$_3$(unidentate)$_3$] complexes

| | $b$ | MD/ME | $\phi_A$ | $\phi_D$ | $\theta_D$ | $\phi_E$ | $\theta_E$ | $\alpha$ | $R$ | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| [Gd(O$_2$CMe)$_3$]·4H$_2$O | 0.88 | 1.02 | 47.4 | 98.1 | 297.2 | 131.8 | 341.7 | 87.3 | 1.0 | *a* |
| [Er(O$_2$CMe)$_3$]·4H$_2$O | 0.87 | 1.04 | 49 | 97 | 300 | 131 | 343 | 86 | 1.0 | 5 |
| [Er(NO$_3$)$_3$(OSMe$_2$)$_3$] | 0.91 | 1.04 | 48 | 100 | 297 | 135 | 345 | 88 | 0.9 | *c* |
| [Yb(NO$_3$)$_3$(OSMe$_2$)$_3$] | 0.86 | 1.02 | 50 | 101 | 298 | 134 | 342 | 88 | 0.9 | *d* |
| [Lu(NO$_3$)$_3$(OSMe$_2$)$_3$] | 0.89 | 1.06 | | | | | | | | *e* |
| [Nd(NO$_3$)$_3$(O=CNPhNMeCMe=CH)$_3$] | 0.84 | 1.01 | 50 | 103 | 301 | 135 | 346 | 90 | 0.8 | *f* |

Units of θ, $\phi$, and α are degrees.

[a] This work. [c] L. A. Aslanov, L. I. Soleva, and M. A. Porai-Koshits, *J. Struct. Chem.*, 1972, **13**, 1021. [d] K. K. Bhandary, H. Manohar, and K. Venkatesan, *J.C.S. Dalton*, 1975, 288. [e] L. A. Aslanov, L. I. Soleva, and M. A. Porai-Koshits, *J. Struct. Chem.*, 1973, **14**, 998. [f] K. K. Bhandary, H. Manohar, and K. Venkatesan, *Acta Cryst.*, 1976, **B32**, 861.

by a large decrease in $\theta_G$, the other angular parameters remaining relatively constant. That is, the major effect of reducing $b$ is to twist the triangular end GHI of the prism. Decreasing the metal–unidentate effective bond length ratio $R$ increases all the $\phi$ angular parameters as intuitively expected, with a smaller increase in $\theta_G$. A notable feature of the stereochemistry is that the dihedral angle α between any two bidentate ligands is close to 90° (Figure 6). The three bidentate ligands can therefore be considered to form half an icosahedron, whereas the three unidentate ligands form half an octahedron.

It is predicted that each bidentate ligand will be asymmetrically bonded to the metal atom, the capping site experiencing greater repulsion than the prismatic site (Figure 7).

Structural parameters for molecules of the type [M(bidentate)$_3$(unidentate)$_3$] with this stereochemistry are shown in Table 6. In agreement with predictions, the bidentate ligands are asymmetrically bonded to the metal atom, the metal–capping atom bond length being *ca.* 3% longer than the metal–prismatic atom bond length. The angular parameters found for [Gd(O$_2$CMe)$_3$]·4H$_2$O are in good agreement with those calculated using $n = 6$, $b = 0.88$, and $R = 1.0$, $\phi_A = 46.0$, $\phi_D = 97.1$, $\theta_D = 299.2$, $\phi_E = 132.0$, and $\theta_E = 343.1°$. Similar fits of the structural parameters with those calculated lead to the $R$ values shown in Table 6.

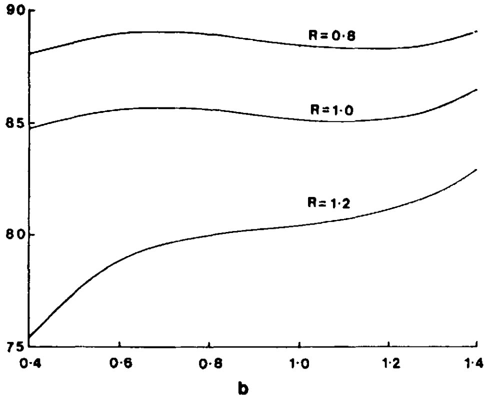

FIGURE 6 Dihedral angle α (°) between the bidentate ligands for tricapped trigonal-prismatic [M(bidentate)$_3$(unidentate)$_3$] as a function of normalised bite $b$ and bond-length ratio $R$ ($n = 6$)

The only other compound of the type [M(bidentate)$_3$(unidentate)$_3$] which is monomeric is [Eu(NO$_3$)$_3${OC(NMe$_2$)$_2$}$_3$],[10] which has a tricapped trigonal-prismatic stereochemistry with the three unidentate ligands on the same rectangular face of the trigonal prism, that is sites A, B, and G of Figure 3. The non-existence of the isomer with three-fold symmetry may be due to unfavourable steric interactions which arise if three tetramethylurea groups are placed on the same triangular face of the tricapped trigonal prism.

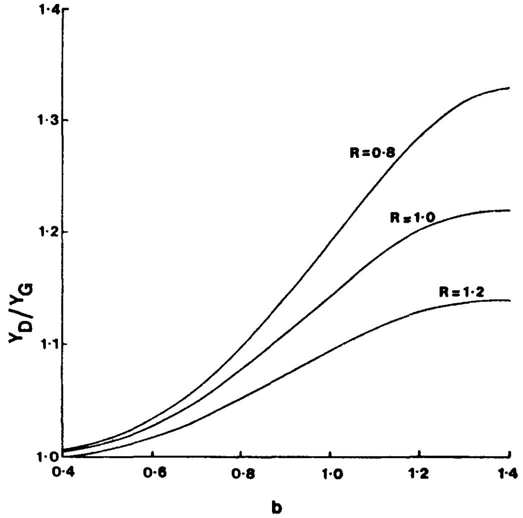

FIGURE 7 Ratio of individual atom repulsion coefficients for the two ends of each bidentate ligand in the tricapped trigonal-prismatic [M(bidentate)$_3$(unidentate)$_3$] ($n = 6$)

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