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Structural studies of some mono- and bi-nuclear heteroleptic trispyrazolyborate complexes containing eight-co-ordinated europium and gadolinium †

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The X-ray crystal structures of two heteroleptic dimeric carboxylate complexes, $[Eu(HBpz_3)_2(\mu\text{-}O_2CPh)]_2$ and $[Eu(HBpz_3)(\mu\text{-}O_2CPh)_2]_2$ have been determined, together with those of the known mononuclear complexes $[Eu(HBpz_3)_2\{OC(Me)CHC(Me)O\}]$ and $[Eu(HBpz_3)_2\{OC(Ph)CHC(Ph)O\}]$. A fifth complex, $[\{Gd(HBpz_3)_2\}_2\{\mu\text{-}1,4\text{-}(O_2C)_2C_6H_4\}]$ whose structure has also been determined, contains two gadolinium centres linked by a ditopic 1,4-benzenedicarboxylate ligand. The solid angle sum (s.a.s.) values of complexes within the series $[Ln(HBpz_3)_2(dik)]$ [dik = OC(Me)CHC(Me)O, Ln = Ce, Eu, Yb; dik = OC(Ph)CHC(Ph)O, Ln = Eu; dik = $1\text{-O-}2\text{-(OCH)-}4\text{-(OMe)}C_6H_3$, Ln = Eu; dik = $2\text{-}O_2CC_5H_4NO$, Ln = Tb] vary linearly with Ln^{3+} ionic radius. In structures containing a non-bridging κ^2 carboxylate ligand, the s.a.s. values fall below the trend line for $[Ln(HBpz_3)_2(dik)]$. However, for the two binuclear complexes containing bridging carboxylate ligands the s.a.s. values lie above this trend line.

The largely ionic character of the bonding in lanthanide complexes means that the ability of a ligand set to efficiently fill the metal co-ordination sphere is an important factor in determining complex stability. Thus the concept of steric saturation is an important tool for informative discussions of lanthanide complex structure and reactivity.[1,2] Steric saturation can be quantified by assigning solid angle factor (s.a.f.) values to ligands and solid angle sum (s.a.s.) values to complexes.[1] Because of the lanthanide contraction s.a.s. values vary across the lanthanide series.[2] Structural studies of related complexes from different regions of the lanthanide series are useful in demonstrating this variation. Such studies can also reveal how structural changes may occur to optimise s.a.s. values. One such series consists of heteroleptic complexes having the general formula $[Ln(Tp)_2(X)]$ [Tp^- = hydrotrispyrazol-1-ylborate; Ln = a lanthanide element or yttrium; X = a uninegative bidentate ligand such as pentane-2,5-dionate ($acac^-$),[3] tropolonate[4] ($trop^-$), oxalate (ox^{2-}),[5] acetate,[4] or benzoate[4]]. Despite the fact that they undergo quite rapid intermolecular ligand exchange reactions,[6] the complexes $[Ln(Tp)_2(\beta\text{-diketonate})]$ are remarkably stable towards disproportionation to the homoleptic species[7] $[Ln(Tp)_3]$ and form mononuclear complexes across the complete lanthanide ion size range.[3] Sterically less demanding carboxylate ligands X, typically form monomeric complexes with only the smaller lanthanide ions. The larger lanthanide ions produce insoluble compounds of uncertain formulation and intermediate sized ions such as Sm^{3+} and Y^{3+} have been shown by structural studies to form the dimeric species $[Sm(Tp)_2(\mu\text{-}O_2CPh)]_2$[8] and $[Y(Tp)(\mu\text{-}O_2CMe)_2)]_2$.[9,10] In contrast $[Eu(Tp)_2(mosal)]$ (mosal-H = methoxysalicylaldehyde), which contains an intermediate sized lanthanide ion with a β-diketonate like co-ligand, is mononuclear.[11] In this work these structural results have been extended to include two mononuclear europium complexes containing β-diketonate ligands X (compounds **1** and **2**), two dimeric europium complexes, $[Eu(Tp)_2(\mu\text{-}O_2CPh)]_2$ (**3**) and $[Eu(Tp)(\mu\text{-}O_2CPh)_2)]_2$ (**4**), which contain differing types of carboxylate bridging arrangement, and a binuclear gadolinium complex containing two essentially mononuclear $\{Gd(Tp)_2\text{-}(O_2C)\}$ fragments in which the carboxylate is non-bridging but the two fragments are linked by a 1,4-disubstituted aryl ring (**5**). These results have allowed the variation in s.a.s. values with Ln^{3+} ionic radius to be examined.

Experimental

General details

Potassium hydrotrispyrazolylborate[12] was prepared using a previously described method. Hydrated lanthanide trichlorides were obtained from Ventron GMBH and used without further purification.

FT-IR spectra were recorded from KBr pellets using a Perkin-Elmer 1600 series FT-IR spectrometer and LSIMS mass spectra using a Kratos MS80RF instrument, ions being produced by fast atom bombardment from a 3-nitrobenzyl alcohol matrix. The complexes $[Eu(Tp)_2\{OC(Me)CHC(Me)O\}]$, $[Eu(Tp)_2\{OC(Ph)CHC(Ph)O\}]$ and $[Eu(Tp)_2(O_2CPh)]$ were prepared according to previously described methods.[3,4]

Crystallisations

$[EuTp_2(acac)]$, 1. A sample of crude $[EuTp_2(acac)]$ was dissolved in dichloromethane, a similar volume of *n*-hexane was then placed in a layer on top of this solution and the system left to evaporate slowly giving colourless crystals suitable for X-ray diffraction studies.

$[EuTp_2\{OC(Ph)CHC(Ph)O\}]$, 2. This complex was crystallised in the same way as $[EuTp_2(acac)]$ giving yellow crystals suitable for X-ray diffraction studies.

$[Eu(Tp)_2(O_2CPh)]_2$, 3. A sample of $[Eu(Tp)_2(O_2CPh)]$ was dissolved in chloroform (4 cm^3), the resulting solution was filtered into a small sample tube, a loop of wire was then attached to the neck of this tube and it was lowered into a large sample

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† Electronic Supplementary Information (ESI) available: co-ordination polyhedra for complexes **2**, **3**, **4** and **5**. See http://www.rsc.org/suppdata/dt/b1/b100896j/

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Table 1 Crystallographic data

	1	**2**	**3**	**4**	**5**
Formula	$C_{23}H_{27}N_{12}O_2B_2Eu$	$C_{33}H_{31}N_{12}O_2B_2Eu$	$C_{50}H_{50}N_{24}O_4B_4Eu_2$	$C_{46}H_{40}N_{12}O_8B_2Eu_2$	$C_{44}H_{44}N_{24}O_4B_4Gd_2 \cdot 4CH_2Cl_2$
M	677.1	801.3	1398.3	1214.4	1670.5
a/ Å	14.927(7)	16.994(5)	14.164(4)	12.659(5)	11.676(2)
b/ Å	12.871(6)	11.179(4)	19.502(5)	17.638(8)	16.091(4)
c/ Å	15.254(6)	18.466(7)	22.227(5)	11.937(6)	18.162(4)
α/ deg	90	90	90	105.47(1)	90
β/ deg	102.09(2)	90.24(1)	104.08(2)	102.25(2)	97.51(1)
γ/ deg	90	90	90	75.64(2)	90
V/ Å^3	2866(2)	3508(2)	5955(3)	2458(2)	3383(1)
Z	4	4	4	2	2
Space group	$P2_1/a$	$C2/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
ρ_{calcd}/ g cm^{-3}	1.569	1.517	1.560	1.641	1.640
μ(Mo-Kα)/ mm^{-1}	2.233	1.837	2.152	2.593	2.320
$R_w(F_o^2)$[a]	0.0612	0.0463	0.0735	0.0887	0.1729
$R(F_o)$[b]	0.0275	0.0185	0.0483	0.0409	0.0634

[a] $R_w(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [b] $R(F_o) = \Sigma(|F_o - F_c|)/\Sigma|F_o|$ for observed reflections.

tube containing petroleum ether (14 cm^3; boiling range 40–60 °C) and a cap was placed on this tube. After 12 days colourless crystals of [Eu(Tp)$_2$(O$_2$CPh)]$_2$ had been deposited upon the inner walls of the tube. Anal. Found: C, 43.0; H, 3.47; N, 23.5. Calcd. for $C_{50}H_{50}B_4N_{24}O_4Eu_2$: C, 43.0; H, 3.60; N, 24.0%. (+)-LSIMS: *m*/*z* (relative intensity): 678 (10%), 585 (100%), 576 (90%), 532 (20%), 482 (25%), 432 (20%), 366 (45%). IR data (KBr disc) ν_{max}: 2466w; 1621m; 1609s; 1565vs; 1502m; 1402vs; 1300s; 1217m; 1196w; 1120m; 1065w; 1050s; 975m; 760m; 724s; 670m; 621w; 437w cm^{-1}.

[Eu(Tp)(O$_2$CPh)$_2$]$_2$, 4. A sample of crude [Eu(Tp)$_2$(O$_2$CPh)] was dissolved in dichloromethane, the solution filtered, and a similar volume of *n*-hexane was placed in a layer over the resulting filtrate. Slow evaporation led to the deposition of colourless crystals of [Eu(Tp)(O$_2$CPh)$_2$]$_2$. Anal. Found: C, 44.7; H, 3.21; N, 16.2. Calcd. for $C_{46}H_{40}B_2N_{12}O_8Eu_2$: C, 45.5; H, 3.32; N, 13.8%. (+)-LSIMS: *m*/*z* (relative intensity): 678 (8%), 585 (100%), 575 (99%), 532 (15%), 482 (15%), 432 (40%), 366 (50%). IR data (KBr disc) ν_{max}: 2469m; 1621w; 1607vs; 1564vs; 1502s; 1400vs; 1300s; 1218s; 1197m; 1120s; 1065m; 1050vs; 974s; 760s; 723vs; 670s; 621m; 560w cm^{-1}.

[{Gd(Tp)$_2$}$_2${1,4-(O$_2$C)$_2$C$_6$H$_4$}], 5. Terephthalic acid (0.08 g, 0.5 mmol) was dissolved in ammonia solution (15 cm^3; 0.18 mol dm^{-3}). KTp (0.50 g, 2 mmol) was then added, followed by water (10 cm^3). The resulting solution was then added to a stirred solution of gadolinium trichloride hydrate (1 mmol) in water (10 cm^3). Stirring was continued for 30 min, and the precipitate which formed was collected by filtration, and allowed to dry in air overnight. The crude precipitate was dissolved in dichloromethane (15 cm^3), the solution filtered, and *n*-hexane (15 cm^3) was added as a layer onto the filtrate. Slow evaporation led to the deposition of the product as white crystals (0.06 g, 5%). IR data (KBr disc) ν_{max}: 2458m; 1576m; 1560m; 1539m; 1504s; 1404vs; 1390vs; 1300vs; 1215s; 1120s; 1065m; 1050vs; 976m; 759s; 723s; 669m; 622m cm^{-1}.

Structure determinations

Cell dimensions and intensity data for the five complexes, **1**–**5** were measured on a Rigaku R-AXIS II area detector diffractometer at room temperature using Mo-Kα radiation, $\lambda = 0.71073$ Å. The structures were determined[13a] by direct methods and refined[13b] by least-squares on F^2 using anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed in calculated positions. Details are given in Table 1. Diagrams were drawn with ORTEP;[13c] thermal ellipsoids are at the 30% probability level.

CCDC reference numbers 157715–157719.

See http://www.rsc.org/suppdata/dt/b1/b100896j/ for crystallographic data in CIF or other electronic format.

Results and discussion

Crystal formation

A crude sample[4] of the previously reported complex [Eu(Tp)$_2$(O$_2$CPh)] was recrystallised from two different solvent systems to give two sets of crystals shown by X-ray diffraction studies to be complexes **3** and **4**. Crystals of **3** were obtained by vapour diffusion from chloroform–petroleum ether (bp 40–60 °C) and their IR spectrum contains ν_{max}(BH) at 2466 cm^{-1}, along with two strong bands at 1609 and 1565 cm^{-1} attributable to ν_{max}(CO) from the carboxylate group. Crystals of **4** were obtained by slow evaporation of a CH$_2$Cl$_2$–*n*-hexane solution and their IR spectrum (KBr) similarly contains ν_{max}(BH) at 2469 cm^{-1}, along with two strong bands at 1607 and 1564 cm^{-1} attributable to ν_{max}(CO) from the carboxylate group. We have previously suggested that these bands are due to a bridging benzoate ligand, this has now been confirmed structurally. The observation of a band at 1607 cm^{-1} is consistent with the report[8,10] by Reger *et al.*, that [(Y(Tp){O$_2$CMe}$_2$)$_2$] contains a band at 1600 cm^{-1} due to a bridging acetate ligand. The IR spectra of crude [Eu(Tp)$_2$(O$_2$CPh)], **3** and **4** are very similar and could not be used to distinguish between these compounds.

The mass spectra (LSIMS) of **3** and **4** were also obtained and again are quite similar. Neither was found to contain a molecular ion corresponding to {(Eu(Tp)(O$_2$CPh)$_2$)$_2$}$^+$ or {(Eu(Tp)$_2$(O$_2$CPh))$_2$}$^+$. The most prominent ions in both spectra, and that of crude [Eu(Tp)$_2$(O$_2$CPh)], appear at *m*/*z* 585 and 366; these may be attributed respectively to {Eu(Tp)$_2$(H$_2$O)}$^+$ and {Eu(Tp)}$^+$. It is not possible to distinguish the two structural types of europium benzoate complex on the basis of LSIMS data. Added to the similarities between the IR spectra in KBr of crude [Eu(Tp)$_2$(O$_2$CPh)], **3** and **4**, these observations illustrate the difficulties of distinguishing the structural types in these complexes by a method other than X-ray diffraction. Ligand exchange in solution phase or reactions with the medium used to make the measurement (*e.g.* KBr under pressure) is always a ubiquitous problem in making spectroscopic measurements of such compounds.

The new complex **5** was obtained in very low yield by recrystallisation of the precipitate formed from an aqueous mixture of gadolinium trichloride, KTp and terephthalic acid. The IR spectrum of this compound contains ν_{max}(BH) at 2458 cm^{-1} and several bands at *ca.* 1560 cm^{-1} attributable to ν_{max}(CO) from the carboxylate groups. Compound **5** was shown by X-ray diffraction studies to be [{Gd(Tp)$_2$}$_2${μ-1,4-(O$_2$C)$_2$C$_6$H$_4$}] in which each Gd^{3+} ion is bound to two Tp

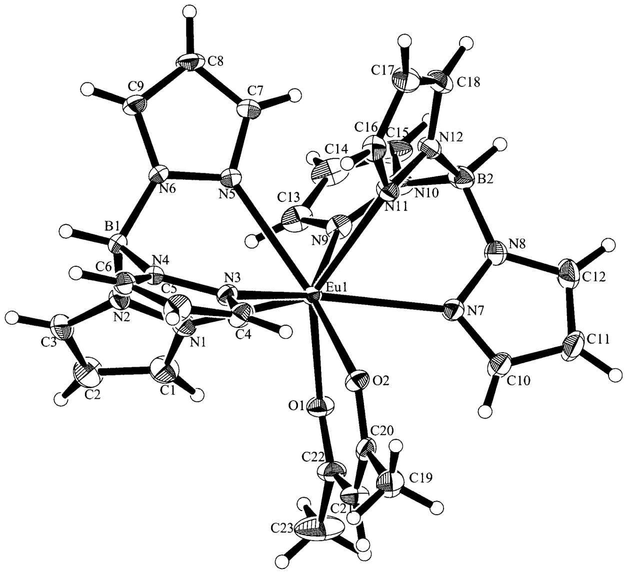

Fig. 1 View of [Eu(Tp)$_2${OC(Me)CHC(Me)O}] **1**.

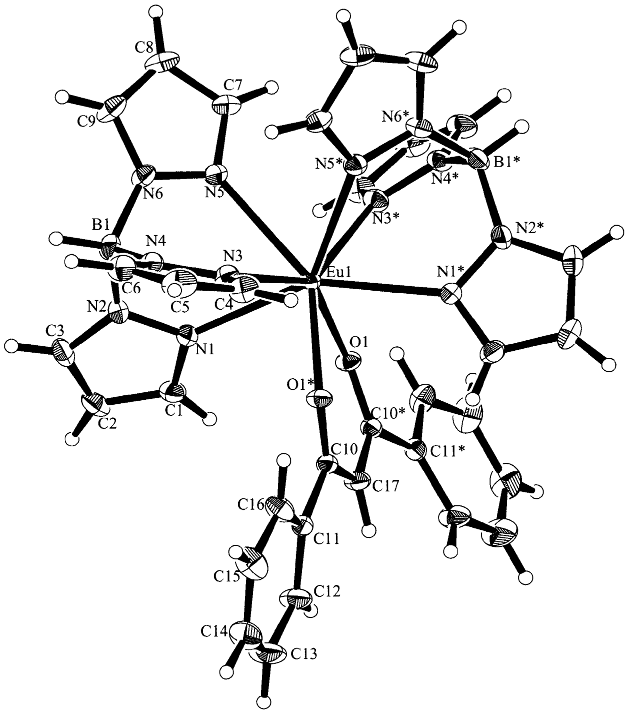

Fig. 2 View of [Eu(Tp)$_2${OC(Ph)CHC(Ph)O}] **2**. Starred atoms are related to the corresponding unstarred atoms by a 2-fold rotation (C_2) axis.

ligands and a single bidentate carboxylate, in contrast to the situation in **3** and **4**.

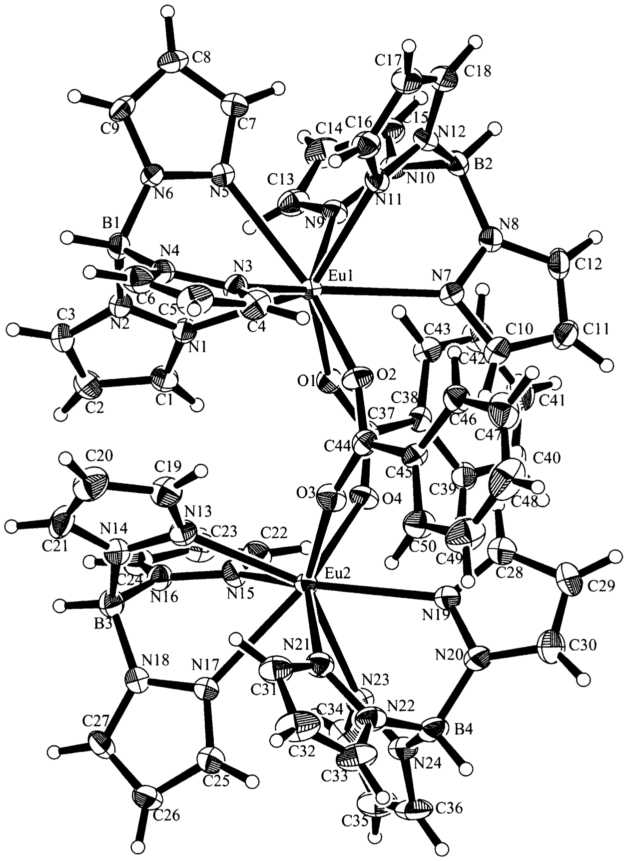

Fig. 3 View of [Eu(Tp)$_2$(O$_2$CPh)]$_2$ **3**.

Structural studies

Views of the complexes **1–5** are shown in Figs. 1–5, and selected geometric parameters are listed in Table 2. In every case the metal ion is eight-co-ordinated. Complex **2** has crystallographic 2-fold rotation symmetry, **4** crystallizes with two independent centrosymmetric molecules in the unit cell and complex **5** is also centrosymmetric. While the general composition of these complexes is of the form [Ln(Tp)$_2$(X)] (X = diketonate or benzoate), the dimeric complex **4** has the composition [Eu(Tp)(O$_2$CPh)$_2$]$_2$. The complex **3** is also dimeric with two bridging benzoate ligands. Although the gadolinium complex **5** is binuclear, each metal ion is complexed in a mononuclear manner (Fig. 5). The molecules exist as discreet entities with no significant intermolecular interactions, apart from structure **5**, where there is possibly weak C–H···O hydrogen bonding between two different solvent dichloromethane molecules and the benzoate oxygen atoms (H···O1 2.44 Å, H···O2 2.51 Å, with C–H···O angles of 169 and 150°, respectively).

Analysis[14] of selected dihedral angles of the co-cordination polyhedra of the complexes allows assessment of the metal co-cordination geometries in terms of their conformity to one or other of three standard eight-co-ordinate polyhedra, corresponding to local energy minima, the dodecahedron (DOD), the square antiprism (SAP) or the bicapped trigonal prism (BCTP). The results, in terms of four δ angles, $\delta 1$–$\delta 4$, and two φ angles, φ_1–φ_2, as defined in ref. 14 are listed in Table 3, together with these values for the idealised polyhedra. Although none of the polyhedra are "ideal", each can be considered to approximate to one of the standard geometries as shown in Table 3. Deviations from ideality are probably mostly due to the constraints imposed by the rigidity and steric bulk of the tridentate Tp ligand, but may also be a result of the well established fluxional behaviour[9,15] of such complexes in solution, so that the geometry actually observed lies on the reaction pathway between ideal polyhedra. Thus, although the co-ordination geometry in complex **2** approximates most closely to SAP (mean deviation 4.6°), the non-zero δ_1 and δ_2 values, together with slightly reduced φ_1 and φ_2, indicate some movement towards DOD. The other deviations from ideality cannot be readily rationalised in these terms. The geometry of **1** differs in an apparently random manner from ideal BCTP and those at the two metal centres in the dimeric complex **3** differ similarly from ideal DOD, with mean deviations 5.0–5.8°. The co-cordination polyhedra in the two independent molecules of **4** deviate more seriously from ideality, respectively by 10.3° from BCTP in molecule A, and by 10.55° from DOD in molecule B. Complex **5** also has a distorted co-cordination polyhedron, with mean deviation of 8.6° from ideal SAP. Considering related eight-co-ordinated complexes, in [Ce(Tp)$_2${OC(Me)CHC(Me)O}],[3] the co-ordination polyhedron is BCTP; in [Yb(Tp)$_2${OC(Me)CHC(Me)O}],[3] it is

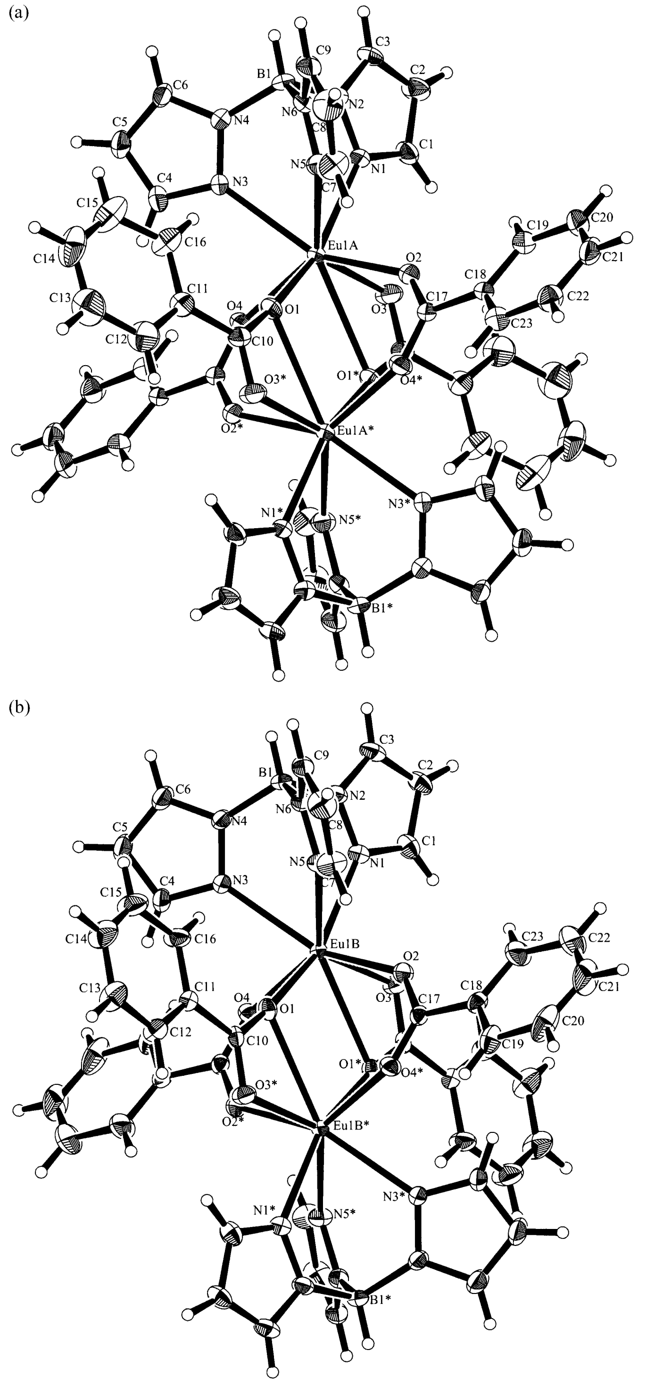

Fig. 4 Views of the two independent $[Eu(Tp)(O_2CPh)_2]_2$ molecules **4**. Starred atoms are related to the corresponding unstarred atoms by an inversion centre.

DOD for molecule A and BCTP for molecule B; in $[Yb(Tp)_2\{OC(Bu^t)CHC(Bu^t)O\}]$[9] and $[Yb(Tp)_2(O_2CPh)]$ (two independent molecules in the crystal),[4] the co-cordination polyhedron is SAP in each case; in $[Eu(Tp)_2(mosal)]$[11] it is DOD and in the dimeric $[Sm(Tp)_2(\mu\text{-}O_2CPh)]_2$,[8,11] the geometry is DOD at one metal centre, but too irregular for description in terms of standard geometry at the other. The three standard polyhedra are almost equally represented (DOD 6, SAP 6 and BCTP 4), in agreement with calculations indicating that these have similar energies,[15] although the first two geometries are, in general, more common for eight-co-ordination.[14c]

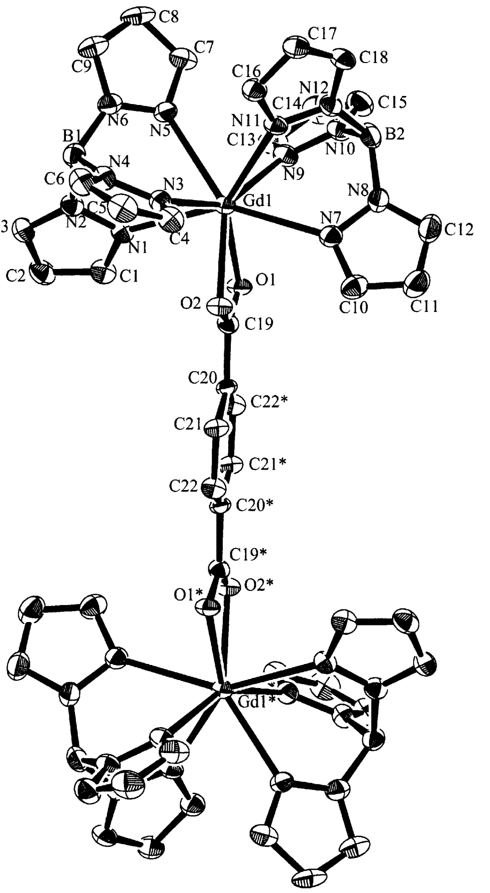

Fig. 5 View of $[\{Gd(Tp)_2\}_2\{\mu\text{-}1,4\text{-}(O_2C)_2C_6H_4\}]$ **5**. Starred atoms are related to the corresponding unstarred atoms by an inversion centre.

Metal–ligand bond lengths (Table 2) show considerable variation. Eu–N lengths range from 2.479 to 2.649 Å, and excluding the long bridging Eu–O bond in the dimeric complex **4** of 2.833(4) Å in molecule A and 2.782(4) Å in molecule B, Eu–O distances are in the range 2.300–2.381 Å. In $[Y(Tp)(O_2CMe)_2]_2$,[10] which is structurally analogous to **4**, the corresponding bridging Y–O distance is too long at 3.227 Å for a significant bonding interaction, and the Y^{3+} ion is only seven-co-ordinated. As had been noted previously[3,6,11] in co-ordination polyhedra with BCTP geometry, the longest metal–ligand distances are generally to the two capping atoms. This is the case in our study. Complex **1** has N5 and N7 at 2.607(3) and 2.619(3) Å (Fig. 6), and in molecule A of complex **4**, N5 and O1* are at 2.555(6) and 2.833(4) Å from the metal (Fig. 7). The Gd–N bonds of complex **5** average 2.506(15) Å, compared with mean Eu–N values of 2.522–2.565 Å in complexes **1–4**, at least qualitatively consistent with the approximately 0.013 Å smaller radius of gadolinium.[16] The Gd–O lengths are, however, longer than those in the europium complexes, averaging 2.398(3) Å, compared with a mean of 2.330(6) Å for the europium complexes. A short C ··· Gd contact of 2.765(7) Å within the four-ring GdO_2C moiety may be the reason for the long Gd–O bonds. In $[Yb(Tp)_2(O_2CPh)]$,[4] which contains an analogous YbO_2C moiety, the C ··· Yb contact distance is a comparable 2.69 Å and the Yb–O lengths are relatively long, averaging 2.331(11) Å.

We have carried out s.a.s calculations to assess the degree of crowding at the metal centres.[1] The results are summarised in Table 4. The steric angle factor (s.a.f) values for the Tp and dioxo ligands are listed separately. The s.a.s values are all within the range 0.758–0.786 and compare with the mean value of 0.766(51) for 58 eight-co-ordinated structures given in ref. 1. The low value found for complex **5** is unexpected on the basis of a slightly smaller metal centre, but may be rationalised by the small s.a.f. of the carboxylate ligand due to the long Gd–O bonds and the very small O–Gd–O angle of 54.4(2)°. The eight-co-ordinate dodecahedral complex[11] $[Eu(Tp)_2(mosal)]$ has s.a.s of 0.768, within the range of values found for our europium complexes. The dimeric $[Sm(Tp)_2(O_2CPh)]_2$ has s.a.s values of

0.787 and 0.776 at the two metal centres,[8] very similar to the s.a.s values in the analogous europium complex **3**. Taken together with previous structural studies, the structural data reported here allow the s.a.s. values of complexes of formula $[Ln(Tp)_2(X)]$ to be compared across the lanthanide series for comparable ligands X, in which X forms a six membered chelate ring with Ln^{3+}. Thus a plot of s.a.s. values against Ln^{3+} effective ionic radius [*r*(Ln)/ Å][16] for the complexes $[Ln(Tp)_2(acac)]$ (Ln = Ce, Eu, Yb), $[Tb(Tp)_2(pca)]$ (pca = $2\text{-}O_2CC_5H_4NO$),[17] $[Eu(Tp)_2\{OC(Ph)CHC(Ph)O\}]$ and $[Eu(Tp)_2(mosal)]$ reveals a linear correlation in which s.a.s. = 1.526–0.707*r*(Ln) with correlation coefficient $R^2 = 0.9708$ (Fig. 8). The s.a.s. values for the two structures $[Ln(Tp)_2(O_2CR)]_n$ ($n = 1$, Ln = Yb, R = Ph; $n = 2$, Ln = Gd, R = C_3H_2) follow a similar trend but lie below the line for the larger chelate ring size systems. The plot in Fig. 8 shows how, by forming carboxylate bridged dimers, the complexes $[Ln(Tp)_2(O_2CPh)]_2$ (Ln = Sm, Eu) can achieve higher s.a.s. values, whilst maintaining the N_6O_2 donor atom set, than is found in **5** where the structural constraints imposed by the terephthalate ligand have prevented dimerisation. A linear correlation between solid angle sum and ionic radius for homologous series of lanthanide complexes had been predicted earlier,[2] an expectation confirmed by these experimental results.

Table 2 Selected bond lengths (Å) for complexes **1–5**

Complex **1**			
Eu(1)–O(1)	2.341(2)	Eu(1)–N(7)	2.619(3)
Eu(1)–O(2)	2.336(2)	Eu(1)–N(9)	2.502(3)
Eu(1)–N(1)	2.563(3)	Eu(1)–N(11)	2.537(3)
Eu(1)–N(3)	2.564(3)	O(1)–C(22)	1.256(4)
Eu(1)–N(5)	2.607(3)	O(2)–C(20)	1.269(4)
Complex **2**			
Eu(1)–O(1)	2.308(1)	Eu(1)–N(5)	2.607(2)
Eu(1)–N(1)	2.571(2)	O(1)–C(10)#1	1.268(2)
Eu(1)–N(3)	2.479(2)		
Complex **3**			
Eu(1)–O(1)	2.327(4)	Eu(2)–O(3)	2.316(4)
Eu(1)–O(2)	2.301(4)	Eu(2)–O(4)	2.308(4)
Eu(1)–N(1)	2.512(5)	Eu(2)–N(13)	2.527(5)
Eu(1)–N(3)	2.532(5)	Eu(2)–N(15)	2.513(5)
Eu(1)–N(5)	2.647(5)	Eu(2)–N(17)	2.649(5)
Eu(1)–N(7)	2.577(5)	Eu(2)–N(19)	2.599(5)
Eu(1)–N(9)	2.512(5)	Eu(2)–N(21)	2.497(6)
Eu(1)–N(11)	2.510(5)	Eu(2)–N(23)	2.536(5)
O(1)–C(37)	1.265(7)	O(3)–C(44)	1.259(7)
O(2)–C(44)	1.244(7)	O(4)–C(37)	1.257(7)
Complex **4**			
Eu(1A)–O(1A)	2.300(4)	Eu(1B)–O(1B)	2.309(4)
Eu(1A)–O(1A)#2	2.833(4)	Eu(1B)–O(1B)#3	2.782(4)
Eu(1A)–O(2A)	2.328(4)	Eu(1B)–O(2B)	2.332(4)
Eu(1A)–O(3A)	2.381(5)	Eu(1B)–O(3B)	2.355(4)
Eu(1A)–O(4A)	2.361(4)	Eu(1B)–O(4B)	2.348(4)
Eu(1A)–N(1A)	2.483(5)	Eu(1B)–N(1B)	2.515(5)
Eu(1A)–N(3A)	2.510(5)	Eu(1B)–N(3B)	2.526(5)
Eu(1A)–N(5A)	2.555(6)	Eu(1B)–N(5B)	2.543(5)
Eu(1A) · · · Eu(1A)#2	3.936(2)	Eu(1B) · · · Eu(1B)#3	3.928(1)
O(1A)–C(10A)	1.257(8)	O(1B)–C(10B)	1.265(7)
O(2A)–C(17A)	1.263(7)	O(2B)–C(17B)	1.267(7)
O(3A)–C(10A)#2	1.261(7)	O(3B)–C(10B)#3	1.257(7)
O(4A)–C(17A)#2	1.253(7)	O(4B)–C(17B)#3	1.247(7)
Complex **5**			
Gd(1)–O(1)	2.401(5)	Gd(1)–N(7)	2.546(7)
Gd(1)–O(2)	2.395(5)	Gd(1)–N(9)	2.456(7)
Gd(1)–N(1)	2.534(6)	Gd(1)–N(11)	2.501(6)
Gd(1)–N(3)	2.472(7)	O(1)–C(19)	1.263(9)
Gd(1)–N(5)	2.525(7)	O(2)–C(19)	1.271(9)

[n] #1 refers to symmetry related position $-x, y, 1/2 - z$. #2 refers to symmetry related position $1 - x, -y, -z$. #3 refers to symmetry related position $-x, 1 - y, 1 - z$.

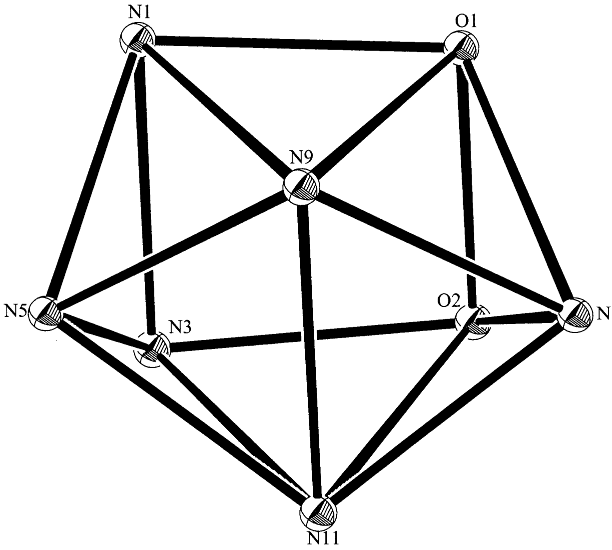

Fig. 6 The metal co-ordination polyhedron of complex **1**.

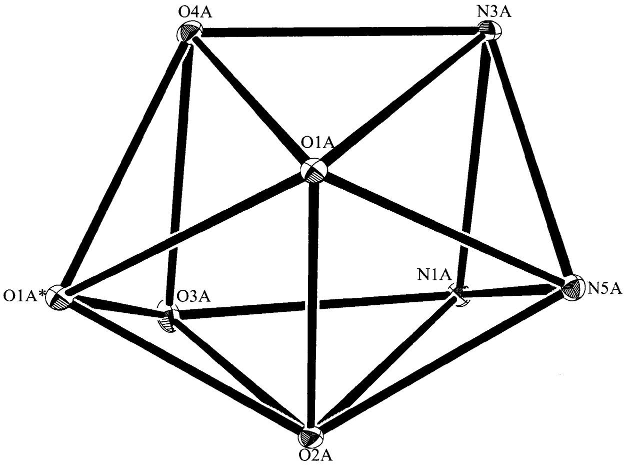

Fig. 7 The metal co-ordination polyhedron in molecule A of complex **4**.

Table 3 Values of δ and φ (°) from shape analysis of co-ordination polyhedra of complexes **1–5**

			3		**4**			**DOD**	**SAP**	**BCTP**
	1	**2**	Eu1	Eu2	A	B	**5**	Idealised polyhedra		
δ_1	37.8	9.1	24.0	23.2	39.5	49.1	18.1	29.5	0.0	21.8
δ_2	1.2	9.0	30.7	33.3	5.5	27.7	15.4	29.5	0.0	0.0
δ_3	46.6	49.3	39.5	38.6	29.8	12.0	50.2	29.5	52.4	48.2
δ_4	38.9	49.5	22.3	21.1	38.3	43.2	45.6	29.5	52.4	48.2
φ_1	9.6	21.3	4.6	3.5	8.0	7.2	16.4	0.0	24.5	14.1
φ_2	16.3	23.8	1.7	2.7	18.4	3.5	25.3	0.0	24.5	14.1
Assigned geometry										
	BCTP	SAP	DOD	DOD	BCTP	DOD	SAP			
Mean deviation between observed and ideal values (°)										
	5.8	4.6	5.0	5.6	10.3	10.55	8.6			

Table 4 Results of solid angle sum (s.a.s.) calculations for complexes **1–5**

			3		**4**		
	1	**2**	Eu1	Eu2	A	B	**5**
Solid angle factor for Tp ligands	0.566	0.572	0.574	0.582	0.296	0.293	0.596
Solid angle factor for dioxo ligand	0.199	0.205	0.204	0.204	0.462	0.467	0.163
Solid angle sum (s.a.s)	0.765	0.777	0.778	0.786	0.758	0.760	0.759

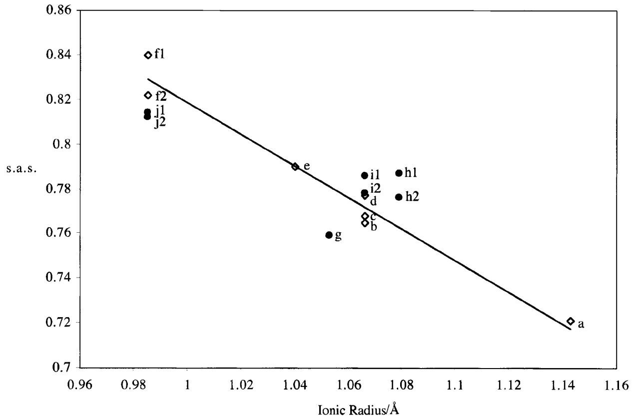

Fig. 8 Plots of s.a.s. against effective ionic radius, *r* (Å). Key: ◇ 1st Series β-diketonate and related co-ligands: **a**, [Ce(Tp)$_2${OC(Me)-CHC(Me)O}]; **b**, [Eu(Tp)$_2${OC(Me)CHC(Me)O}] (**1**); **c**, [Eu(Tp)$_2$-{OC$_6$H$_3$(OMe)CHO}]; **d**, [Eu(Tp)$_2${OC(Ph)CHC(Ph)O}] (**2**); **e**, [Tb(Tp)$_2$(ONC$_5$H$_4$CO$_2$-2)]; **f1** and **f2**, [Yb(Tp)$_2${OC(Me)CHC(Me)-O}]*. • 2nd Series carboxylate co-ligands excluding **4**: **g**, [{Gd(Tp)$_2$}$_2$-{μ-1,4-(O$_2$C)$_2$C$_6$H$_4$}] (**5**); **h1** and **h2**, [Sm(Tp)$_2$(O$_2$CPh)]$_2$; **i1** and **i2**, [Eu(Tp)$_2$(O$_2$CPh)]$_2$ (**3**; **j1** and **j2**, [Yb(Tp)$_2$(O$_2$CPh)]*. *Two independent molecules are present in the unit cell.

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