Heteroleptic Poly(pyrazolyl)borate Derivatives of the Lanthanide Ions. The Synthesis of Acetylacetonate Complexes and the Molecular Structures of $[Ln\{HB(C_3N_2H_3)_3\}_2\{MeC(O)CHC(O)Me\}]$ (Ln = Ce or Yb)†

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The air- and moisture-stable complexes $[Ln\{HB(C_3N_2H_3)_3\}_2\{MeC(O)CHC(O)Me\}]$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Tm, Lu, or Y) have been prepared and characterised. Evidence was found that intramolecular ligand reorganisation processes were occurring on the n.m.r. time-scale down to −80 °C. The molecular structures of the compounds with Ln = Ce and Yb have been determined. Polytopal analysis of these structures reveals that a substantial distortion of the near bicapped trigonal prismatic co-ordination geometry, found for the cerium complex, towards square antiprismatic is necessary to allow the ligand set to accommodate the smaller Yb^{3+} ion.

The ionic character of organolanthanide derivatives results in their being extremely air and moisture sensitive.[1,2] This arises from both the oxophilic nature of the lanthanides themselves and the instability of their associated carbanion ligands towards aerial oxidation or protonation by moisture. Despite the difficulties of handling such compounds a rich derivative chemistry of the $[Ln(\eta^5\text{-}C_5R_5)_2]^+$ moiety (typically R = H or Me; Ln = a lanthanide ion, La^{3+} or Y^{3+}) is being developed. A primary function of the cyclopentadienyl ligand in organolanthanide derivatives of this type is sterically to protect the metal ion without fully neutralising its cationic charge. Thus the replacement of the air-sensitive cyclopentadienyl ligand by a sterically similar, but air-stable ligand might be expected to improve the stability and handling properties of organolanthanide derivatives. The tripodal ligand hydrotris-(pyrazolyl)borate, L^-, is similar to $C_5Me_5^-$ in that it is uninegative, sterically bulky, and can occupy three facial co-ordination sites on a metal ion.[3] Thus the $[LnL_2]^+$ moiety would seem a suitable substrate for the preparation of more robust organolanthanide complexes. However, attempts to develop this synthetic strategy using $[LnL_2Cl]$ as a precursor have been hindered by disproportionation reactions leading to the air-stable tris complexes, $[LnL_3]$.[4–6]

The molecular structure of the homoleptic complex $[YbL_3]$ has been determined by *X*-ray methods. The geometry about the eight-co-ordinate Yb^{3+} ion was found to be approximately that of a bicapped trigonal prism (b.t.p.), having one bidentate and two tridentate poly(pyrazolyl)borate ligands.[7] This observation prompted us to investigate whether a new series of stable heteroleptic complexes containing the $[LnL_2]^+$ moiety could be prepared using other bidentate coligands to complete the co-ordination shell of the Ln^{3+} ion[8,9] so that the structural and dynamic properties of such species could be studied. An ideal coligand for this purpose is acetylacetonate (acac⁻); it has oxygen donor atoms and forms a six-membered chelate ring upon co-ordination to a metal ion.[10]

Acetylacetonate complexes of the lanthanide elements have been known since the late 19th century.[11] They are prepared by precipitation from an aqueous solution of a lanthanide salt and a basic solution of acetylacetone. Solid-state structural studies show that eight-co-ordinate complexes, $[Ln(acac)_3(H_2O)_2]$, are formed for Ln = Y and lanthanide ions from La to Tm,[12–14] but the smaller ytterbium ion forms a complex, $[Yb(acac)_3(H_2O)]$, which is seven-co-ordinate in the solid state.[15] In 1979 Bielang and Fischer[16] reported that attempts to prepare complexes of the type $[Yb(\eta^5\text{-}C_5H_5)_2(acac)]$ gave rise to 'badly tractable, non-sublimable products devoid of distinct melting points.' The intractability of these compounds could be due to the fact that they are sterically unsaturated, since the same ligand set forms a stable complex with the smaller Sc^{3+} ion.[17] Subsequently Deacon *et al.*[18] reported that $[Yb(\eta^5\text{-}C_5H_5)_2(acac)]$ is a dimer whereas $[Yb(\eta^5\text{-}C_5H_5)_2(dbzm)]$ (dbzm = dibenzoylmethanide) is a monomer. The L^- ligand is more sterically demanding than $\eta^5\text{-}C_5H_5^-$ so that complexes of the type $[LnL_2(acac)]$ should be more sterically saturated than their cyclopentadienyl analogues, and thus less prone to oligomerisation. In order to examine this point we have investigated the syntheses and structures of complexes having the general formula $[LnL_2(acac)]$.[8,9] The stability, or otherwise, of $[LnL_2(acac)]$ towards disproportionation to give $[LnL_3]$ and $[Ln(acac)_4]^-$ or solvated $[Ln(acac)_3]$ was also of special interest in terms of the apparent instability of species of the type $[LnL_2R(solv)]$ (R = hydrocarbyl, solv = solvent or nothing).

Results and Discussion

Synthetic and Spectroscopic Studies.—The anhydrous complexes $[LnL_2(acac)]$ (Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu) precipitate from a mildly basic aqueous solution containing a 1:2:1 mixture of hydrated lanthanide trichloride, potassium hydrotris(pyrazol-1-yl)borate, and pentane-2,4-dione. The crude precipitates were obtained in essentially quantitative yield, after drying *in vacuo*. These crude powders dissolve readily in polar organic solvents such as CH_2Cl_2, $CHCl_3$, acetone, and tetrahydrofuran (thf), are slightly soluble in hot toluene, but are insoluble in hydrocarbon solvents such as hexane and protic solvents such as water and ethanol. Recrystallisation from CH_2Cl_2–hexane affords highly crystalline, air- and water-stable solids. Despite the apparent stability of the homoleptic complexes $[LnL_3]$ and $[Ln(acac)_3(H_2O)_n]$, a high yield of $[YL_2(acac)]$ was obtained both in the presence of a 4:1 molar excess of KL and a 10:1 molar excess of Hacac.

The solid-state i.r. spectra of these complexes are superimposable and contain ν(BH) at 2 460 cm⁻¹, ν(C=O/C=C) at 1 605 and 1 520 cm⁻¹, plus other bands characteristic of the

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† Acetylacetonatobis[hydrotris(pyrazol-1-yl)borato]-cerium and -ytterbium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Proton n.m.r. data for $[LnL_2(acac)]$[a]

		Pyrazolyl resonances			Acac resonances	
Ln	MHz[b]	Intensity 6	6	6	1	6
Y[c]	270	7.61(d)	7.05(d)	5.96(t)	5.60(s)	2.00(s)
La[c]	100	7.67(d)	7.14(d)	6.03(t)	5.63(s)	2.00(s)
Ce	270	8.9(s)	2.9(s)	6.2(s)	25.1(s)	8.15(s)
Pr	270	9.86(s)	6.66(s)	5.55(s)	48.8(s)	18.8(s)
Nd	100	9.4(s)	5.6(s)	7.3(s)	22.1(s)	7.8(s)
Sm	270	8.26(d)	4.81(d)	5.87(t)	8.98(s)	2.80(s)
Eu	60	7.96(d)	4.25(d)	3.68(t)	−8.2(s)	−3.65(s)
Tb	270	4.1(s)	−4.0(s)	−67.7(s)	337.0(s)	111.0(s)
Ho	270	0.88(s)	−2.2(s)	−13.5(s)	170.4(s)	64.7(s)
Er	270	36.2(s)	4.7(s)	−0.9(s)	−97.1(s)	−32.3(s)
Yb	400	10.0(s)	9.0(s)	5.6(s)	−46.6(s)	−21.4(s)
Lu[c]	100	7.65(d)	7.05(d)	5.99(m)	5.63(s)	2.00(s)

[a] Spectra were recorded in $CDCl_3$. Paramagnetic shift and line-broadening effects led to poorly resolved spectra being obtained in the cases of Dy and Tm. [b] Spectrometer frequency for ^1H. [c] Spectra were recorded in CD_2Cl_2.

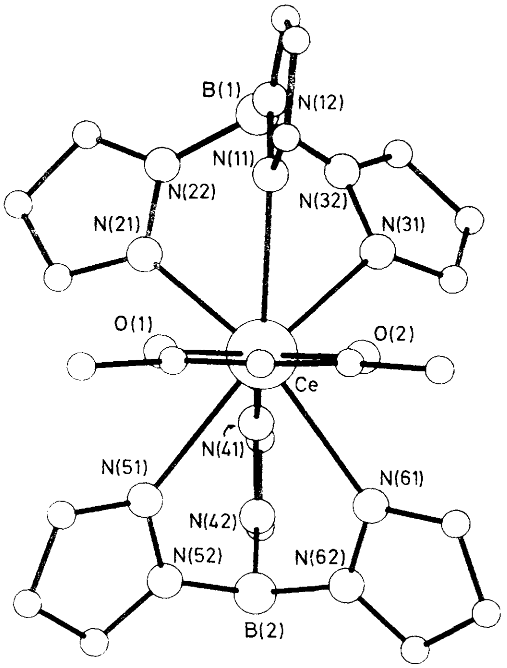

Figure 1. Molecular structure of $[CeL_2(acac)]$ showing connectivity and atom labelling (view bisecting the O(1)–Ce–O(2) angle). The plotting routine used was PLUTO (W. D. S. Motherwell, Program for Plotting Molecular and Crystal Structure, Cambridge Crystallographic Files, University of Manchester Regional Computer Centre, Manchester, 1981)

poly(pyrazolyl)borate ligand. The only point of variance is that for complexes containing the larger lanthanide ions (La to Ho) a band at 890 cm^{-1} is split into a doublet.

The ^1H n.m.r. spectra of the new complexes are summarised in Table 1. The spectra of the complexes containing the diamagnetic ions yttrium, lanthanum, and lutetium are essentially identical. The other lanthanide ions give rise to proton resonances which are subject to temperature-dependent paramagnetic shifts. The proton resonances of complexes containing samarium and europium exhibit relatively small paramagnetic shifts and the coupling on the pyrazolyl proton resonance is still observed. This coupling is unresolved in the spectra of the complexes containing the other paramagnetic lanthanide ions. All of the spectra contain only three pyrazolyl proton resonances, each integrating for six protons. Where coupling is resolved these three resonances appear as two doublets and a triplet (strictly a doublet of doublets) with $J(H-H) = 2$ Hz. The equivalence of the three pyrazolyl residues within each hydrotris(pyrazol-1-yl)borate ligand on the n.m.r. time-scale indicates that the molecules are dynamic at room temperature. The equivalence in the pyrazolyl signals persisted in variable-temperature n.m.r. studies to below −80 °C. This behaviour contrasts with that reported for $[LnL_3]$ (Ln = Yb or Lu) which is rigid in solution on the n.m.r. time-scale,[19] but is in accord with the dynamic spectra reported for $[LnL_2(L')]$ (Ln = Yb or Lu; L′ = 3-trifluoroacetyl-D-bornan-2-onate or 2,2,6,6-tetramethylheptane-3,5-dionate).[20] The spectra of $[LnL_2(acac)]$ also contain two singlets, one integrating for six protons and the other for one proton, due to the methyl protons and the methine proton, respectively, on the acetylacetonate ligand. Proton n.m.r. studies of mixtures of $[CeL_2(acac)]$ and $[LaL_2\{OC(Ph)CH(Me)O\}]$ or of $[YbL_2\{OC(Ph)CH(Me)O\}]$ and $[LuL_2(acac)]$ provided evidence of intermolecular ligand-exchange processes which are slow on the n.m.r. time-scale up to 200 °C at 270 MHz, but which reach equilibrium within minutes at room temperature.[21]

The mass spectra of the new complexes generally contained a molecular ion with the expected isotopic distribution. The most intense fragment ion is attributable to pyrazolyl (pz, $m/z = 67$) and the second most intense fragment corresponds with $[LnL_2]^+$ formed by loss of the β-diketonate coligand. Further fragment ions listed in order of decreasing intensity were found to be $[Ln(pz)]^+$ and $[Ln(pz)_2]^+$ formed by the sequential loss of $HB(pz)_2$.

Structural Studies.—The powder *X*-ray diffraction patterns of the complexes $[LnL_2(acac)]$ were obtained to establish whether their structure varied across the lanthanide series. The patterns for the complexes of the larger lanthanide ions, from lanthanum to dysprosium, are essentially the same. The patterns for complexes containing yttrium and holmium are also essentially the same and only slightly different from those containing lanthanum to dysprosium.

A number of different patterns were obtained for the series of complexes containing erbium to lutetium, the patterns appearing to be dependent upon the speed of crystallisation. These qualitative results indicate that complexes containing La to Dy are isomorphous, as are the complexes containing Y and Ho. However, the series of complexes containing Er to Lu exhibits polymorphism although some of the crystalline forms are common to more than one element.

In order to obtain more detailed structural information about representatives of the two major structural groups, single-crystal *X*-ray diffraction studies were carried out on $[CeL_2(acac)]$ and $[YbL_2(acac)]$. The former was taken as a representative of the larger lanthanide ions, from lanthanum to dysprosium, and the latter as a representative of the smaller lanthanide ions.

The complex $[CeL_2(acac)]$ crystallises from CH_2Cl_2–hexane solution to form yellow, monoclinic, lozenge-shaped crystals of space group $P2_1/c$. Fractional atomic co-ordinates are listed in Table 2 and selected geometrical parameters in Table 3. The molecular structure is illustrated in Figure 1 which also shows the numbering scheme for atoms other than carbon and hydrogen, the first digit of the number assigned to a pyrazolyl nitrogen denoting the pyrazolyl ring number.

The crystal structure consists of discrete molecular units, one molecule in the asymmetric unit and four molecules in the unit cell. The most important result of this structural analysis is that it confirms that the cerium ion is eight-co-ordinate; both of the L ligands are tridentate and the acac ligand is bidentate. The

Table 2. Fractional atomic co-ordinates (× 10^4) for [$CeL_2(acac)$] with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ce	3 400.0(1)	5 524.1(1)	2 285.7(1)	C(21)	5 266(3)	6 056(4)	4 121(3)
B(1)	5 152(3)	3 498(4)	3 139(3)	C(22)	6 035(3)	5 658(4)	4 672(3)
B(2)	3 761(3)	8 079(3)	1 196(3)	C(23)	6 087(3)	4 658(4)	4 384(3)
O(2)	1 937(1)	4 781(2)	1 633(2)	C(31)	4 573(3)	4 207(3)	775(2)
O(1)	2 413(2)	5 700(2)	3 336(2)	C(32)	5 400(3)	3 728(3)	771(3)
N(11)	3 441(2)	3 659(2)	3 026(2)	C(33)	5 717(3)	3 430(3)	1 639(3)
N(12)	4 217(2)	3 076(2)	3 246(2)	C(41)	5 623(2)	6 283(3)	1 865(3)
N(21)	4 856(2)	5 340(2)	3 536(2)	C(42)	6 098(2)	7 018(3)	1 478(3)
N(22)	5 375(2)	4 472(3)	3 701(2)	C(43)	5 472(2)	7 773(3)	1 181(2)
N(31)	4 390(2)	4 206(2)	1 593(2)	C(51)	3 072(3)	7 967(3)	3 352(3)
N(32)	5 111(2)	3 710(2)	2 143(2)	C(52)	3 064(3)	9 023(4)	3 250(3)
N(41)	4 756(2)	6 563(2)	1 807(2)	C(53)	3 299(3)	9 187(3)	2 450(3)
H(42)	4 665(2)	7 496(2)	1 379(2)	C(61)	2 198(2)	6 145(3)	5(2)
N(51)	3 326(2)	7 502(2)	2 652(2)	C(62)	2 054(3)	6 898(3)	−654(2)
N(52)	3 457(2)	8 276(2)	2 087(2)	C(63)	2 602(2)	7 706(3)	−287(2)
N(61)	2 801(2)	6 464(2)	738(2)	C(5)	411(3)	4 220(3)	1 149(3)
N(62)	3 041(2)	7 441(2)	542(2)	C(4)	1 162(2)	4 714(3)	1 842(2)
C(11)	2 760(3)	3 059(3)	3 171(2)	C(3)	965(2)	5 055(3)	2 647(3)
C(12)	3 077(3)	2 092(3)	3 474(3)	C(2)	1 580(3)	5 546(3)	3 329(3)
C(13)	4 000(3)	2 137(3)	3 509(3)	C(1)	1 253(4)	5 932(6)	4 148(4)

Table 3. Selected bond distances (Å) and angles (°) for [$CeL_2(acac)$] with e.s.d.s in parentheses

Ce–O(1)	2.397(2)
Ce–O(2)	2.406(2)
Ce–N(11)	2.664(3)
Ce–N(21)	2.583(3)
Ce–N(31)	2.617(3)
Ce–N(41)	2.659(3)
Ce–N(51)	2.634(3)
Ce–N(61)	2.633(3)
pz(C–C)*	1.37(1)
pz(C–N)*	1.34(1)
pz(N–N)*	1.36(1)
pz(N–B)*	1.54(1)
acac O(1)–C(2)	1.259(4)
O(2)–C(4)	1.267(4)
C(1)–C(2)	1.513(6)
C(2)–C(3)	1.387(6)
C(3)–C(4)	1.387(5)
C(4)–C(5)	1.511(5)

(*i*) Angles subtended by rectangular edges	
O(1)–Ce–O(2)	71.4(1)
N(21)–Ce–N(31)	76.9(1)
N(51)–Ce–N(61)	73.5(1)
(*ii*) Angles subtended by triangular edges	
O(1)–Ce–N(51)	73.0(1)
O(2)–Ce–N(61)	73.0(1)
O(1)–Ce–N(21)	93.5(1)
O(2)–Ce–N(31)	96.5(1)
N(21)–Ce–N(51)	90.1(1)
N(31)–Ce–N(61)	93.6(1)
(*iii*) Angle between capping atoms	
N(11)–Ce–N(41)	128.6(1)
(*iv*) Angles subtended by cap to face edges	
O(2)–Ce–N(11)	75.4(1)
O(1)–Ce–N(11)	76.7(1)
N(11)–Ce–N(21)	70.4(1)
N(11)–Ce–N(31)	67.0(1)
N(21)–Ce–N(41)	71.0(1)
N(31)–Ce–N(41)	72.3(1)
N(41)–Ce–N(51)	68.3(1)
N(41)–Ce–N(61)	70.0(1)

* Mean value.

molecule has an approximate plane of symmetry containing the cerium atom, the two boron atoms, the methine carbon [C(3)] of acac, and rings 1 and 4 of the L ligands. The plane of symmetry is only approximate because of a small rotation of one tris(pyrazolyl)borate ligand, to avoid a close contact between pyrazolyl ring 1 with the pentane-2,4-dionate ligand.

The co-ordination geometry is best described by the ideal polyhedron b.t.p. as shown in Figure 2. Both L ligands span one rectangular edge and cap one retangular face (pyrazolyl rings 1 and 4), and the acac ligand spans the other rectangular edge. The shortest cerium to ligand bond lengths are to the acac ligand, 2.406(2) and 2.397(2) Å, and the longest are to the face-capping nitrogens, 2.664(3) and 2.659(3) Å. The angles subtended by the triangular edges of the uncapped rectangular face are both 73.0(1)°, whereas similar angles for the two capped faces are greater than 90°. The symmetry of the trigonal prism is therefore reduced by the effects of the capping atoms, elongating the triangular edges of the capped rectangular faces. From Table 4, which contains the co-ordination polyhedron dimensions, this elongation is calculated to be 0.63—0.83 Å in magnitude.

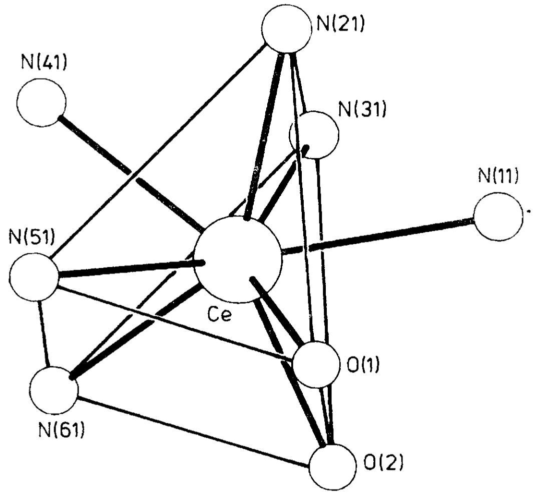

Figure 2. Co-ordination polyhedron of [$CeL_2(acac)$]. The plotting routine used was PLUTO

Polytopal analysis values,[22] δ and φ, are presented in Table 5. The rectangular face of the b.t.p., atoms O(1), O(2), N(51), N(61), is effectively planar with a δ value of 0.41°; this reduces to 0.25° for normalised data, where anomalies due to the shorter Ce–O bonds are removed by setting all cerium to ligand bond lengths to 1 Å. The elongation of the triangular edges of the capped rectangular faces means that the δ value for the unique rectangular edge, N(21)N(31), 40.5°, is much larger than the value calculated on the assumption of a trigonally symmetric b.p.t. The C_{2v} symmetry of the co-ordination polyhedron is reduced to an approximate C_s symmetry in the complex by the tridentate ligands.

Table 4. Bicapped trigonal prism dimensions (Å) for [CeL$_2$(acac)]

Edge	Polyhedron	Normalised polyhedron
(*i*) Rectangular edges		
N(21)–N(31)	3.23	1.24
N(51)–N(61)	3.15	1.20
O(1)–O(2)	2.80	1.17
(*ii*) Triangular edges		
O(2)–N(51)	3.00	1.19
O(2)–N(21)	3.63	1.46
N(21)–N(51)	3.69	1.41
O(1)–N(61)	3.00	1.19
O(1)–N(31)	3.75	1.49
N(31)–N(61)	3.83	1.46
(*iii*) Cap to face edges		
N(11)–O(2)	3.15	1.24
N(11)–N(21)	3.03	1.15
N(11)–O(1)	3.11	1.22
N(11)–N(31)	2.91	1.10
N(41)–N(51)	2.97	1.12
N(41)–N(21)	3.04	1.16
N(41)–N(61)	3.04	1.15
N(41)–N(31)	3.11	1.18
(*iv*) Quadrilateral diagonals		
O(1)–N(61)	4.22	1.68
O(2)–N(51)	4.22	1.67
N(11)–N(41)	4.80	1.80
N(21)–N(31)	3.23	1.24 (see above)

Table 5. Values of δ and φ (°) for [CeL$_2$(acac)] *

	p	n.p.	d	s.a.	b.t.p.
δ N(11)[N(21)N(31)]N(41)	40.5	42.5	29.5	0.0	21.8
δ O(1)[O(2)N(51)]N(61)	0.41	0.25	29.5	0.0	0.0
δ O(1)[N(21)N(51)]N(41)	45.6	43.5	29.5	52.5	48.2
δ N(11)[O(2)N(31)]N(61)	34.9	39.1	29.5	52.5	48.2
φ N(31)–N(11)–O(1)–N(51)	12.4	11.8	0.0	24.5	14.1
φ N(21)–N(41)–N(61)–O(2)	8.3	8.4	0.0	24.5	14.1

* The atom numbering is shown in Figure 4. p = polyhedron, n.p. = normalised polyhedron, d = dodecahedron, s.a. = square antiprism, and b.t.p. = bicapped trigonal prism.

The complex [YbL$_2$(acac)] crystallises from CH$_2$Cl$_2$–hexane solution as colourless, triclinic, crystals of space group $P\bar{1}$. Fractional atomic co-ordinates are presented in Table 6 and selected geometrical parameters in Table 7. The crystal structure consists of discrete molecular units; there are two independent molecules in the asymmetric unit and four molecules in the unit cell. The molecular structure is shown in Figure 3 along with the numbering scheme for the atoms around Yb(1) and Yb(2). This is the same as for [CeL$_2$(acac)] and the numbering in molecule 2 is distinguished by the postscript A after the numbers of the non-metal atoms. Both molecules are eight-co-ordinate and have structures which are distorted with respect to [CeL$_2$(acac)] so that both molecules have C_1 point symmetry. The smaller ionic radius of the ytterbium ion, as compared to cerium, produces a substantial distortion of the co-ordination polyhedron about the metal from b.t.p. This reflects the need for the two tripodal and one bidentate ligands to accommodate to one another while approaching more closely to the centre of the metal ion. The co-ordination geometry of the ytterbium ion in the two molecules cannot be adequately described in terms of an ideal polyhedron. Both may be considered to be derived from a square antiprism, but the shortening of square-diagonal distances coupled with a loss of planarity in the 'squares' takes the geometry along the geometric pathway towards dodecahedral if both squares distort, and b.t.p. if only one square distorts as shown in Figure 4.

As shown in Table 8, the co-ordination polyhedron in molecule 1 has square diagonals ranging from 3.76 to 4.48 Å; the normalised square-diagonal distances of 1.54—1.60 Å approach those of the triangular edges, which is necessary for the geometry to be dodecahedral. The δ values (Table 9) of 14.7 and 26.6° show that neither 'square' is planar. The φ values of 5.71 and 5.78° are quite close to the value of zero required for dodecahedral. The co-ordination polyhedron of molecule 2 has square-diagonal distances ranging from 3.95 go 4.17 Å, a considerably smaller range than for molecule 1. The δ values show that one 'square' is quite flat, δ = 1.46°, and the other is quite bent, δ = 12.8°. The φ values of 15.9 and 15.1° are quite close to those for b.t.p. (14.1°).

The structures of [YbL$_3$][7] and [CeL$_2$(acac)] are similar, in terms of both the disposition of ligands and the co-ordination geometry. The mean bite distance between the co-ordinated nitrogen atoms of L in [YbL$_3$] is 3.00 Å compared to 2.89 Å for [CoL$_2$].[22] The mean bite distance appears to remain constant for a given metal irrespective of the co-ordination geometry, since [YbL$_2$(acac)] has a mean bite distance of 3.00 Å in molecule 1 and 2.99 Å in molecule 2. The mean bite distance would appear to be dependent upon the ionic radius of the metal ion since for [CeL$_2$(acac)] its value is increased to 3.05 Å. Palenik[23] has reported that the mean dimensions of β-diketonates co-ordinated to a particular lanthanide appear to be independent of the β-diketone and whether the complex is a tetrakis(β-diketonato)lanthanide anion or a tris(β-diketonato)-lanthanide bis(base) adduct. The only structurally characterised cerium(III) β-diketonate which we are aware of is the tetrakis[4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionate] complex, in which the mean Ce–O bond is 0.07 Å longer than the mean distance in [CeL$_2$(acac)] of 2.402(5) Å.[24] The dimensions of the acac ligand bonded to ytterbium in [YbL$_2$(acac)] are essentially the same as for the three previous structural determinations of ytterbium acac derivatives.[15,25,26] The mean Yb–O distance of 2.22(2) Å is short in comparison to those in [Yb(acac)$_3$B] [B = H$_2$O or MeC(O)CH$_2$C(NH$_2$)Me] complexes, but because of the quite large estimated standard deviations associated with bond lengths in the [YbL$_2$(acac)] structure this shortening of 0.01—0.03 Å which is within two standard deviations of the previous values, may not be significant.

Solid angle factor (s.a.f.) calculations were carried out[27] and established that [CeL$_2$(acac)] has a solid angle sum (s.a.s.) value of 0.721, in which L has a s.a.f. of 0.267 and acac has a s.a.f. of 0.187. The complex [YbL$_2$(acac)] has a s.a.s. value of 0.833, in which L has a s.a.f. of 0.305 and acac has a s.a.f. of 0.223; [YbL$_3$] has a s.a.s. value of 0.827, in which the bidentate ligand has a s.a.f. value of 0.217. The revised standard s.a.f.s for tridentate and bidentate L are estimated to be 0.284 and 0.204 respectively; previous values reported by Xing-fu and Fischer[28,29] were 0.260 and 0.170 respectively.

The mean s.a.s. value for 58 eight-co-ordinate structures is 0.766 ± 0.051.[27] The structure of [CeL$_2$(acac)] falls within one standard deviation of this mean on the sterically unsaturated side. The structures of both of the molecules of [YbL$_2$(acac)] fall between one and two standard deviations above the mean value, both being sterically overcrowded. Using these first-order steric calculations [YbL$_2$(acac)] is found to be slightly more sterically crowded than [YbL$_3$].

The ability of L ligands bound to a metal ion to interlock

Table 6. Fractional atomic co-ordinates (× 10^4) for [YbL_2(acac)] with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Yb(1)	743.5(5)	2 122.6(4)	805(3)	Yb(2)	7 405.2(5)	3 301.2(4)	6 379.7(3)
B(2)	3 071(14)	2 834(10)	1 381(9)	B(1A)	6 543(14)	4 914(11)	7 558(9)
B(1)	−2 625(15)	2 715(13)	1 403(10)	B(2A)	5 461(22)	1 949(15)	6 155(13)
O(1)	1 597(10)	2 144(7)	−466(5)	O(1A)	9 202(9)	2 418(7)	6 378(6)
O(2)	1 132(9)	768(7)	694(6)	O(2A)	8 699(9)	3 875(7)	5 336(5)
N(41)	1 213(12)	2 131(9)	2 060(6)	N(21A)	6 104(9)	3 429(8)	7 701(6)
N(42)	2 052(10)	2 567(9)	2 091(7)	N(22A)	5 816(9)	4 181(7)	7 967(6)
N(51)	1 648(9)	3 411(5)	428(6)	N(11A)	8 439(10)	3 893(7)	7 084(6)
N(52)	2 481(10)	3 450(7)	770(6)	N(12A)	7 920(10)	4 545(8)	7 476(6)
N(61)	3 045(9)	1 649(8)	736(6)	N(31A)	6 589(11)	4 810(8)	6 186(7)
N(62)	3 677(10)	2 029(6)	1 024(6)	N(32A)	6 243(11)	5 281(8)	6 755(7)
N(21)	−849(9)	3 310(7)	1 434(7)	N(61A)	71 86(12)	2 712(10)	5 288(7)
N(22)	−2 057(10)	3 340(7)	1 640(7)	N(62A)	6 417(13)	2 201(10)	5 369(8)
N(31)	−929(11)	1 419(7)	1 689(7)	N(51A)	6 995(12)	1 864(9)	6 945(7)
N(32)	−2 176(11)	1 790(8)	1 816(6)	N(52A)	6 127(13)	1 551(9)	6 791(8)
N(11)	−1 027(10)	2 612(9)	147(7)	N(41A)	5 145(11)	3 483(8)	6 379(6)
N(12)	−2 214(10)	2 779(9)	521(7)	N(42A)	4 665(12)	2 874(10)	6 307(7)
C(41)	451(14)	1 934(11)	2 776(9)	C(21A)	5 351(13)	2 897(12)	8 199(8)
C(42)	894(16)	2 353(13)	3 269(10)	C(22A)	4 589(14)	3 383(11)	8 762(9)
C(43)	1 851(16)	2 700(13)	2 822(9)	C(23A)	4 909(13)	4 158(10)	8 596(8)
C(51)	1 383(14)	4 137(10)	−68(9)	C(11A)	9 673(12)	3 649(10)	7 189(8)
C(52)	2 005(15)	4 751(10)	−46(9)	C(12A)	9 857(14)	4 193(12)	7 640(9)
C(53)	2 711(14)	4 336(10)	500(9)	C(13A)	8 723(15)	4 745(12)	7 816(9)
C(61)	3 818(11)	975(9)	474(10)	C(31A)	6 332(14)	5 323(12)	5 529(9)
C(62)	4 991(15)	935(12)	597(12)	C(32A)	5 801(18)	6 163(12)	5 684(11)
C(63)	4 879(12)	1 624(10)	947(10)	C(33A)	5 790(17)	6 127(10)	6 464(11)
C(21)	−591(14)	3 944(10)	1 721(9)	C(61A)	7 794(15)	2 886(13)	4 520(9)
C(22)	−1 785(15)	4 320(11)	2 152(10)	C(62A)	7 389(18)	2 401(13)	4 134(11)
C(23)	−2 643(14)	3 950(11)	2 046(10)	C(63A)	6 536(18)	1 953(11)	4 693(11)
C(31)	−872(14)	620(10)	2 112(9)	C(51A)	7 499(18)	1 272(12)	7 491(10)
C(32)	−2 050(21)	487(12)	2 529(12)	C(52A)	6 924(27)	577(16)	7 691(14)
C(33)	−2 856(17)	1 243(12)	2 305(10)	C(53A)	6 025(24)	749(15)	7 267(14)
C(11)	−1 004(13)	2 778(11)	−611(8)	C(41A)	4 188(14)	4 140(12)	6 501(9)
C(12)	−2 233(17)	3 018(14)	−717(10)	C(42A)	3 085(15)	3 937(15)	6 502(9)
C(13)	−2 989(15)	3 014(11)	3(10)	C(43A)	3 399(15)	3 120(16)	6 380(9)
C(1)	2 429(22)	1 923(17)	−1 757(10)	C(1A)	11 201(16)	1 526(12)	6 242(15)
C(2)	1 902(15)	1 551(13)	−883(9)	C(2A)	10 295(14)	2 385(10)	5 921(11)
C(3)	1 847(15)	719(12)	−639(12)	C(3A)	10 672(15)	2 916(12)	5 278(10)
C(4)	1 454(13)	350(11)	157(12)	C(4A)	9 842(16)	3 679(11)	5 018(9)
C(5)	1 544(16)	−614(12)	366(14)	C(5A)	10 325(21)	4 292(14)	4 277(10)

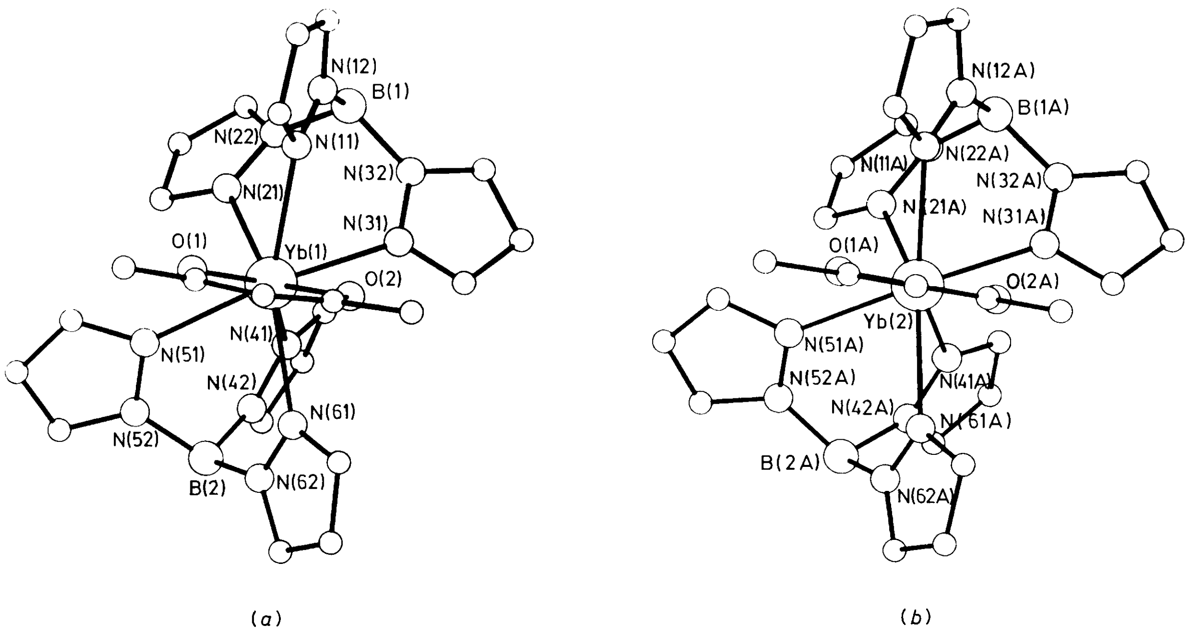

Figure 3. Molecular structure of [YbL_2(acac)]. Views bisecting the O–Yb–O angle in (*a*) molecule 1 and (*b*) molecule 2. The plotting routine used was PLUTO

Table 7. Selected bond distances (Å) and angles (°) for [YbL$_2$(acac)] with e.s.d.s in parentheses

	Molecule 1	Molecule 2[a]
Yb–O(1)	2.258(9)	2.200(9)
Yb–O(2)	2.199(11)	2.238(9)
Yb–N(11)	2.489(12)	2.483(13)
Yb–N(21)	2.576(11)	2.499(10)
Yb–N(31)	2.472(11)	2.388(12)
Yb–N(41)	2.489(13)	2.526(13)
Yb–N(51)	2 444(10)	2.432(14)
Yb–N(61)	2.528(10)	2.504(17)
pz(C–C)[b]	1.40(4)	1.39(3)
pz(C–N)[b]	1.35(2)	1.36(2)
pz(N–N)[b]	1.34(2)	1.34(2)
pz(N–B)[b]	1.54(1)	1.55(4)
acac O(1)–C(2)	1.30(2)	1.30(2)
O(2)–C(4)	1.25(2)	1.27(2)
C(1)–C(2)	1.57(2)	1.61(2)
C(2)–C(3)	1.34(3)	1.36(2)
C(3)–C(4)	1.43(3)	1.39(2)
C(4)–C(5)	1.51(2)	1.53(2)
O(1)–Yb–O(2)	75.8(4)	75.1(3)
O(1)–Yb–N(61)	75.3(4)	89.0(4)
O(2)–Yb–N(11)	96.9(5)	83.2(4)
N(11)–Yb–N(31)	75.0(4)	74.7(4)
N(21)–Yb–N(31)	73.9(4)	79.7(4)
N(21)–Yb–N(41)	71.2(4)	69.8(4)
N(41)–Yb–N(51)	80.6(4)	77.4(4)
N(51)–Yb–N(61)	72.2(4)	74.2(5)
O(1)–Yb–N(11)	74.7(4)	74.8(4)
O(1)–Yb–N(51)	77.6(4)	72.5(4)
N(21)–Yb–N(51)	72.5(3)	75.8(5)
N(11)–Yb–N(21)	70.4(4)	70.4(4)
O(2)–Yb–N(31)	71.0(4)	74.8(4)
O(2)–Yb–N(61)	76.1(4)	75.1(4)
N(41)–Yb–N(61)	69.9(4)	69.9(4)
N(31)–Yb–N(41)	81.4(5)	73.4(4)
O(1)–Yb–N(21)	128.0(4)	114.3(4)
N(11)–Yb–N(51)	100.7(4)	116.3(4)
O(2)–Yb–N(41)	106.4(5)	120.3(4)
N(31)–Yb–N(61)	127.3(4)	109.2(5)

[a] Atom numbers have an A after the digits for atoms in molecule 2. [b] Mean value.

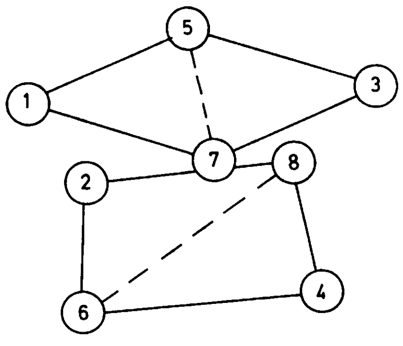

Figure 4. A distorted s.a., if face 1–5–3–7 is bent, and 5–7 is shortened; then the co-ordination geometry is on the geometric pathway to b.t.p., and if both 'square' faces are bent, and both 5–7 and 6–8 are shortened it is on the geometric pathway to a dodecahedron. Polyhedra vertices were defined thus: 1 [N(21), O(2A)], 2 [N(31), N(11A)], 3 [O(1), N(41A)], 4 [N(61), N(51A)], 5 [N(11), N(31A)], 6 [N(41), O(1A)], 7 [N(51), N(61A)], and 8 [O(2), N(21A)]

means that the same ligand set can form stable complexes for the full range of lanthanide ion sizes, which is uncommon. The difference of 0.112 between the s.a.s. values of [YbL$_2$(acac)] and [CeL$_2$(acac)] is more than the s.a.f. value of a monodentate oxygen or nitrogen donor ligand, and it is probably the ability of the L ligand to pack with more or less efficiency that prevents the cerium complex becoming nine-co-ordinate, through solvation, in the solid state.

Conclusions

The results described here have shown that eight-co-ordinate heteroleptic complexes are stable not only to moisture and air but also towards disproportionation. This finding is remarkable in view of the dynamic nature of the complexes as revealed by ^{1}H n.m.r. studies. Attempts to prepare seven-co-ordinate heteroleptic complexes with monodentate coligands were reported by Takats and co-workers[5] to be unsuccessful, although [YL$_2$Cl(OH$_2$)][30] and [YbL$_2$Cl(OC$_4$H$_8$)][20] have since been reported. The complexes [LnL$_2$(acac)] are soluble in polar organic solvents for the full range of lanthanide ionic radii, whereas the homoleptic complexes of the larger lanthanide ions are insoluble.[31] In solution the heteroleptic complexes exhibit intramolecular ligand reorganisation processes which are fast on the n.m.r. time-scale down to at least −80 °C. In contrast the homoleptic complex [YbL$_3$] is stereochemically rigid in solution on the n.m.r. time-scale. We have found that intermolecular exchange of β-diketonate ligands in the series of heteroleptic complexes is slow on the n.m.r. time-scale at room temperature.

The *X*-ray crystal and molecular structure determinations of [CeL$_2$(acac)] and [YbL$_2$(acac)] combined with the spectroscopic evidence show that the L$_2$(acac) ligand set can accommodate the full range of lanthanide ionic sizes. A comparison of the structures of [CeL$_2$(acac)] and [YbL$_2$(acac)] reveals that this ligand set can pack more tightly around a smaller ytterbium ion, by a concerted rotation of both L ligands. The structural data now available for [CeL$_2$(acac)] have allowed a more accurate calculation of the standard s.a.f. value of L (0.284) than was possible with data for the homoleptic ytterbium complex alone. As measured by s.a.f. values, L is significantly more sterically demanding than η-C$_5$Me$_5$.

Experimental

Synthetic and Spectroscopic Studies.—Potassium hydrotris(pyrazol-1-yl)borate was prepared by the literature method.[32] Hydrated lanthanide trichlorides were obtained from Ventron GMBH and acetylacetone from Aldrich Chemicals Ltd.; they were used without further purification. Water was distilled before use. Proton n.m.r. spectra were recorded using Perkin-Elmer R12B, Varian XL-100, JEOL JNM GX270, and Bruker WH400 MHz (University of Warwick) spectrometers. Deuteriated n.m.r. solvents were obtained from Aldrich Chemicals Ltd., and chemical shifts are reported with tetramethylsilane as internal reference at 293 K. Infrared spectra were recorded using potassium bromide pellets and a Perkin-Elmer 297 spectrometer. Mass spectra were obtained using a Kratos MS80RF mass spectrometer, ions being produced by electron impact. Powder *X*-ray diffraction patterns were recorded on a Philips PW 1050/70 powder diffractometer.

Acetylacetonatobis[hydrotris(pyrazol-1-yl)borato]yttrium(III).—The salt K[HB(pz)$_3$] (0.5 g, 2 mmol), pentane-2,4-dione (0.1 g, 1 mmol), ethanol (10 cm^3), and 0.1 mol dm^{-3} aqueous KOH (10 cm^3) were mixed and added to a stirred solution of YCl$_3$·6H$_2$O (0.30 g, 1 mmol) in water (15 cm^3). Stirring was continued for 1 h. The resulting white amorphous precipitate

Table 8. Square antiprismatic dimensions (Å) for [YbL$_2$(acac)]*

	Molecule 1			Molecule 2		
		p	n.p.		p	n.p.
(*i*) Square edges						
O(1)–N(51)	3–7	2.95	1.25	6–4	2.74	1.18
N(51)–N(21)	7–1	2.97	1.18	4–8	3.03	1.23
N(21)–N(11)	1–5	2.92	1.15	8–2	2.87	1.15
N(11)–O(1)	5–3	2.88	1.21	2–6	2.85	1.21
O(2)–N(61)	8–4	2.93	1.23	1–7	2.90	1.22
N(61)–N(41)	4–6	2.88	1.14	7–3	2.88	1.14
N(41)–N(31)	6–2	3.24	1.30	3–5	2.94	1.20
N(31)–O(2)	2–8	2.72	1.16	5–1	2.81	1.21
(*ii*) Triangular edges						
O(1)–O(2)	3–8	2.74	1.23	6–1	2.71	1.22
O(1)–N(61)	3–4	2.93	1.22	6–7	3.30	1.40
N(51)–N(61)	7–4	2.93	1.18	4–7	2.98	1.21
N(51)–N(41)	7–6	3.19	1.29	4–3	3.10	1.25
N(21)–N(41)	1–6	2.95	1.16	8–3	2.88	1.14
N(21)–N(31)	1–2	3.04	1.20	8–5	3.13	1.28
N(11)–N(31)	5–2	3.02	1.22	2–5	2.96	1.21
N(11)–O(2)	5–8	3.52	1.50	2–1	3.14	1.33
(*iii*) Square-diagonal distances						
O(1)–N(21)	3–1	4.35	1.80	6–8	3.95	1.68
N(11)–N(51)	5–7	3.80	1.54	2–4	4.17	1.70
O(2)–N(41)	8–6	3.76	1.60	1–3	4.14	1.73
N(31)–N(61)	2–4	4.48	1.79	5–7	3.99	1.63

* The numbering of vertices is as shown in Figure 4.

Table 9. Values of δ and φ (°) for [YbL$_2$(acac)]*

	Molecule 1		Molecule 2				
	p	n.p.	p	n.p.	d	s.a.	b.t.p.
δ 1(57)3*	26.6	25.0	12.8	10.7	29.5	0.0	21.8
δ 2(68)4	14.7	19.8	1.46	2.02	29.5	0.0	0.0
δ 2(58)3	29.5	30.7	41.8	43.7	29.5	52.4	48.2
δ 1(67)4	38.8	41.6	39.7	39.5	29.5	52.4	48.2
φ 7-1-2-8	5.78	5.74	15.9	16.1	0.0	24.5	14.1
φ 5-3-4-6	5.71	6.09	15.1	15.1	0.0	24.5	14.1

* The numbering of vertices is as shown in Figure 4.

was collected by filtration and dried *in vacuo* (yield = 90%). Recrystallisation from CH_2Cl_2–hexane gave large white crystals (yield = 73%), m.p. = 194 °C.

The corresponding complexes with La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu were prepared similarly using 1 mmol of $LnCl_3 \cdot 6H_2O$. Details of the yields, melting points, and colours of the products are given in Table 10 along with their C, H, and N analyses.

Structural Studies.—Crystal data for [CeL$_2$(acac)]. $C_{23}H_{27}B_2CeN_{12}O_2$, $M = 665.3$, monoclinic, $a = 14.943(2)$, $b = 12.981(2)$, $c = 15.178(2)$ Å, $\beta = 102.02(1)°$, $U = 2\,879$ Å^3, $Z = 4$, $D_c = 1.53$ g cm^{-3}, space group $P2_1/a$ [non-standard setting of $P2_1/c$ (no. 14)], Mo-K_α radiation ($\lambda = 0.7107$ Å, $\mu = 15$ cm^{-1}), $T = 293$ K. Data were collected on an Enraf-Nonius CAD 4 diffractometer at the Crystallography Unit, Universities of Aston and Birmingham. Accurate cell dimensions were obtained by least-squares methods from the setting angles of 25 reflections. Intensities were measured with an ω—2θ scan, a variable scan rate, and an ω scan angle of $(1.00 + 0.35 \tan\theta)°$; 4 607 unique reflections were measured $(2 < 2\theta < 55°)$ with $I > 2.5\sigma(I)$. Two standard reflections were measured every hour and showed no variation with time. Data were corrected for Lorentz and polarisation factors.

Table 10. Yields, melting points, colours, and elemental analyses for [LnL$_2$(acac)]

				Elemental analysis/%		
Ln	Crude yield/g (%)	M.p. (°C)	Colour	C	H	N
Y	0.55 (90)	194	Colourless	44.8 (45.0)	4.3 (4.4)	27.4 (27.4)
La	0.61 (92)	219—220	Colourless	41.9 (41.6)	3.9 (4.1)	25.2 (25.3)
Ce	0.60 (90)	211—212	Yellow	41.8 (41.5)	4.0 (4.1)	25.5 (25.3)
Pr	0.61 (92)	213—215	Green	41.7 (41.5)	3.9 (4.1)	25.3 (25.2)
Nd	0.64 (96)	204	Purple	41.2 (41.3)	4.3 (4.1)	25.4 (25.1)
Sm	0.63 (93)	196—197	Colourless	41.0 (40.9)	3.9 (4.0)	25.6 (24.9)
Eu	0.66 (97)	187	Yellow	41.0 (40.8)	3.9 (4.0)	24.7 (24.8)
Gd	0.64 (94)	185—187	Colourless	40.6 (40.5)	4.2 (4.0)	24.6 (24.6)
Tb	0.65 (95)	174—175	Colourless	40.4 (40.4)	4.2 (4.0)	24.3 (24.6)
Dy	0.63 (92)	173—175	Colourless	39.9 (40.2)	4.0 (4.0)	24.5 (24.4)
Ho	0.64 (93)	183—184	Brown	40.0 (40.0)	3.8 (3.9)	24.4 (24.4)
Er	0.61 (88)	198—200	Pink	41.1 (39.9)	4.2 (3.9)	23.6 (24.3)
Tm	0.61 (87)	194—196	Colourless	41.5 (39.8)	4.1 (3.9)	23.6 (24.2)
Yb	0.63 (90)	197—198	Colourless	39.4 (39.6)	3.6 (3.9)	23.8 (24.1)
Lu	0.62 (86)	197	Colourless	39.2 (39.5)	3.6 (3.9)	23.7 (24.0)

The structure was solved using conventional heavy-atom techniques, and refined by full-matrix least-squares methods. Final cycles of refinement were carried out with all non-hydrogen atoms anisotropic and hydrogens in calculated positions with two, refined U_{iso}, for hydrogens on sp^2 carbons [$U_{iso} = 0.071(3)$ Å^2] and hydrogens on sp^3 carbons [$U_{iso} = 0.18(1)$ Å^2]. Refinement weights derived from counting statistics gave a satisfactory analysis of the variation of $w\Delta^2$ with increasing $(\sin\theta)/\lambda$ and with increasing fractions of $|F_o|$. The final R was 0.0261 and R' $\{= [\Sigma w(|F_o| - |F_c|)^2]^{\frac{1}{2}}\}$ 0.0264. Residual electron density in the final difference map was < 1 e Å^{-3} and no unusually close intermolecular contacts were found. Calculations for this and the following structure were carried out on a Honeywell QUAD DPS 8/70M computer at the University of Birmingham Computer Centre and on a CDC 7600 computer at the University of Manchester Regional Computer Centre using the program SHELX, and literature values for scattering factors of neutral atoms and for anomalous dispersion terms.[33,34]

Crystal data for [YbL$_2$(acac)]. $C_{23}H_{27}B_2N_{12}O_2Yb$, $M = 698.2$, triclinic, $a = 11.422(4)$, $b = 16.361(5)$, $c = 18.237(6)$ Å, $\alpha = 75.92(3)$, $\beta = 74.58(3)$, $\gamma = 75.74(3)°$, $U = 3\,126$ Å^3, $Z = 4$, $D_c = 1.48$ g cm^{-3}, space group $P\bar{1}$ (no. 2), Mo-K_α radiation ($\lambda = 0.7107$ Å, $\mu = 28$ cm^{-1}), $T = 293$ K. Data were collected, processed, and corrected as for [CeL$_2$(acac)] to give 7 661 unique reflections. The data were corrected for absorption effects using DIFABS,[35] a computer program for the determination of empirical absorption corrections; this led to a reduction in R of 3.4%. The structure was solved using conventional heavy-atom techniques.

Full-matrix and block-diagonal least-squares refinement were used, anisotropic thermal parameters were justified by Hamilton's test,[36] and hydrogens were not included. The centrosymmetric space group $P\bar{1}$ was confirmed by the success of the structure determination. Refinement weights derived from counting statistics gave a satisfactory analysis of the variation of $w\Delta^2$ with increasing $(\sin\theta)/\lambda$ and with increasing fractions of $|F_o|$. The final R was 0.0679 and R' 0.0692. Residual electron density in the final difference map was < 1 e Å^{-3} and no unusually close intermolecular contacts were found.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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