Heteroleptic Poly(pyrazolyl)borate Derivatives of the Lanthanide Ions. The Synthesis of Tropolonate and Carboxylate Complexes and the *X*-Ray Crystal Structures of $[Yb\{HB(C_3N_2H_3)_3\}_2(O_2C_7H_5)]$ and $[Yb\{HB(C_3N_2H_3)_3\}_2(O_2CPh)]$ †

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The new heteroleptic hydrotris(pyrazol-1-yl)borato lanthanide complexes $[Ln\{HB(C_3N_2H_3)_3\}_2X]$ (X = tropolonate, Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Tb, Yb, or Lu; X = benzoate, Ln = Y, Sm, Eu, Yb, or Lu; X = acetate, Ln = Y, Eu, Gd, Yb, or Lu) have been synthesised. The complexes $[Ln\{HB(C_3N_2H_3)_3\}_2(O_2CMe)]$ (Ln = Ce and Sm) were prepared but appeared to be unstable in solution, disproportionating to $[Ln\{HB(C_3N_2H_3)_3\}_3]$. Crystal and molecular structures of $[Yb\{HB(C_3N_2H_3)_3\}_2(O_2C_7H_5)]$ and $[Yb\{HB(C_3N_2H_3)_3\}_2(O_2CPh)]$ have been determined by *X*-ray diffraction methods and are eight-co-ordinate, unsolvated monomers. They have an approximately C_2 molecular symmetry with a distorted square-antiprismatic co-ordination geometry. Their steric angle sums are 0.819 and 0.814 respectively. The steric angle factors for the tropolonate and benzoate ligands in these structures are respectively 0.209 and 0.174. The steric angle factor for $HB(C_3N_2H_3)_3$ in $[Yb\{HB(C_3N_2H_3)_3\}_2(O_2CPh)]$ is anomalously high (0.320 compared with an average of 0.305 for three other examples) as a result of the shorter Yb–N and longer Yb–O distances compared to those found in the related systems $[Yb\{HB(C_3N_2H_3)_3\}_2\{OC(Me)CHC(Me)O\}]$ and $[Yb\{HB(C_3N_2H_3)_3\}_2(O_2C_7H_5)]$.

The homoleptic polypyrazolylborate complexes $[LnL_3]$ [Ln = Y, La, Ce, Pr, Sm, Gd, Er, Yb, or Lu; L = hydrotris(pyrazol-1-yl)borate] were first reported by Bagnall *et al.*[1] A subsequent structural characterisation[2] of $[YbL_3]$ established that the Yb^{3+} ion was eight-co-ordinate, having one bi- and two tri-dentate ligands L completing an approximately bicapped trigonal prismatic co-ordination geometry about Yb. This finding prompted us to investigate[3] whether stable heteroleptic complexes containing the LnL_2^+ fragment and having the formula $[LnL_2X]$ (X = a bidentate uninegative ligand other than L) could be isolated. Thus the air- and moisture-stable complexes $[LnL_2(acac)]$ (Hacac = pentane-2,4-dione) were isolated for yttrium and all of the lanthanides except Pm. The complexes with Ln = Ce and Yb were also structurally characterised by *X*-ray diffraction methods.[4] The compound containing the larger Ce^{3+} ion had an approximately bicapped trigonal prismatic (b.t.p.) co-ordination geometry, while that containing the smaller Yb^{3+} ion was closer to a square antiprismatic (s.a.) arrangement,[5] a similar structure having been reported by Takats and co-workers[6] for $[YbL_2\{OC(Bu^t)CHC(O)Bu^t\}]$.

The stabilities and structures of lanthanide-ion complexes are highly sensitive to the extent to which the ligand set around the ion can sterically saturate its co-ordination sphere.[7] It is thus of interest to assess the effect of variations in the size of the co-ligand, X, on the steric saturation of the metal co-ordination sphere in $[LnL_2X]$. The complexes $[LnL_2(acac)]$ are soluble in polar organic solvents and stable towards ligand disproportionation across the whole of the lanthanide series.[5] In these compounds the acac ligand forms a six-membered chelate ring with the Ln^{3+} ion. The use of other bidentate uninegative ligands allows the effects of reducing the size of the chelate ring formed between the lanthanide ion and X in $[LnL_2X]$ to be assessed. Thus the use of 2-hydroxycyclohepta-2,4,6-trien-1-one (Htrop) in place of Hacac may result in the formation of five-membered chelate rings,[8] while the use of carboxylic acid ligands may result in the formation of four-membered chelate rings.[9]

Both of these ligand types are known to form complexes with the lanthanide ions. Homoleptic tropolonate complexes were studied by Muetterties and Wright[10] in 1965. The larger lanthanide ions form insoluble, unsolvated complexes, $[Ln(trop)_3]$ (Ln = La—Ho) while the smaller ions afford the complexes $[HLn(trop)_4]$ (Ln = Er—Lu) which lose tropolone at 170 °C to form $[Ln(trop)_3]$. Although both $[HSc(trop)_4]$ and $[Sc(trop)_3]$ have been structurally characterised by *X*-ray diffraction methods,[11,12] $[YbL_2(trop)]$ is the first tropolonate complex with a lanthanide to be structurally characterised.[8]

In the case of carboxylate ligands, the larger lanthanide ions form mono-, sesqui-, and di-hydrated tris(acetato) complexes while the tetrahydrates predominate for the smaller lanthanide ions from samarium to lutetium.[13] Among the latter series $[Ln(O_2CMe)_3(H_2O)_2]\cdot 2H_2O$ (Ln = Ho, Er, or Gd) have been structurally characterised.[14,15] The tetrahydrate consists of nine-co-ordinate lanthanide ions surrounded by three bidentate acetate ions, two water molecules, and one oxygen of an acetate ligand bound to a neighbouring lanthanide ion. Benzoate complexes of the lanthanides have been reported[16] but the only unsubstituted benzoate complex which has been structurally characterised[17] is $[Dy(\mu\text{-}O_2CPh)(O_2CPh)_2(H_2O)_4]\cdot H_2O$. The structure of this complex consists of eight-co-ordinate dysprosium ions with a b.t.p. co-ordination geometry. The trigonal prism is formed by two monodentate benzoate ligands and four water molecules, and two square faces of the trigonal prism are capped by bridging benzoate ligands, forming infinite chains.

Bis(cyclopentadienyl)lanthanide acetates, benzoates, and formates were first reported in 1963.[18] These were found to be dimeric, as were the bis(cyclopentadienyl)ytterbium carboxylates $[\{Yb(cp)_2(O_2CR)\}_2]$ where R = Me, C_6F_5, or

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† Bis{hydrotris(pyrazol-1-yl)borato}tropolonatoytterbium(III) and benzoatobis{hydrotris(pyrazol-1-yl)borato}ytterbium(III)

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

C_5H_4N.[19] The pentamethylcyclopentadienyl derivatives, $[\{Yb(C_5Me_5)_2(O_2CR)\}_n]$, were reported to be monomeric when R = CF_3 but oligomeric when R = Bu^t.[20] The complexes $[\{Yb(cp)_2(O_2CR)\}_2]$ (R = Ph or C_6F_5) are doubly benzoate-bridged dimers.[19,21] Recently, Reger *et al.*[22,23] have reported the syntheses of $[LnL_2Cl(H_2O)]$ (Ln = Y or La), $[YL_2Cl(C_3N_2H_4)]$, and $[\{YL(\mu\text{-}O_2CMe)_2\}_2]$, all three yttrium complexes having been structurally characterised by *X*-ray studies. In $[YL_2Cl(C_3N_2H_4)]$ the Y^{3+} ion is in a distorted s.a. co-ordination environment while in the dimer $[\{YL(\mu\text{-}O_2CMe)_2\}_2]$ a monocapped trigonal prismatic arrangement was found.

Results and Discussion

Synthetic and Spectroscopic Studies.—The anhydrous heteroleptic polypyrazolylborate complexes $[LnL_2(trop)]$ (Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Tb, Yb, or Lu) precipitate from a basic ethanol–water solution containing $LnCl_3$, KL, and Htrop. The complexes containing Y and Nd—Lu are freely soluble in polar organic solvents such as CH_2Cl_2, $CHCl_3$, or tetrahydrofuran (thf) and can be purified by recrystallisation. The complexes which contain La, Ce, or Pr are sparingly soluble in these solvents and cannot be recrystallised. However, purified microcrystalline samples may be obtained by sublimation *in vacuo* at 250 °C. The cerium complex decomposes in solution to a black material on exposure to air but the complexes containing Nd—Lu appear stable to air for a period of weeks at least. These complexes appear similar in properties to their acac-containing counterparts except that the larger ions La, Ce, and Pr afford products which exhibit low solubilities in polar organic solvents as found for $[LnL_3]$.[1]

The chemistry of the carboxylate complexes $[LnL_2(O_2CR)]$ (R = Me or Ph) proved to be less tractable than that of $[LnL_2(acac)]$ or $[LnL_2(trop)]$. An aqueous solution containing Y^{3+}, $MeCO_2^-$, and L^- in a 1:1:2 ratio rapidly precipitates a white powder. The i.r. and ^1H n.m.r. spectral properties of this material are consistent with its formulation as the complex $[YL_2(O_2CMe)]$. Ytterbium and lutetium ions undergo a similar reaction, but the resulting complexes have i.r. spectra which are substantially different from that of the yttrium complex. Samarium, europium, and gadolinium ions also undergo a similar reaction but in these cases the products give i.r. spectra which are different again from those of the yttrium- and of the ytterbium- and lutetium-containing materials. Substantial amounts of $[LnL_3]$ (Ln = Sm, Eu, or Gd) are also formed in these reactions. Since the aqueous synthetic method did not give promising results with acetate as the co-ligand a non-aqueous synthesis was also investigated. Silver acetate, KL, and anhydrous yttrium trichloride were mixed in dry thf under nitrogen to give $[YL_2(O_2CMe)]$ as the only soluble product. Ytterbium trichloride reacts in a similar fashion forming the complex $[YbL_2(O_2CMe)]$, which has an i.r. spectrum identical to that of the complex formed in aqueous solution. A cerium complex was also prepared using this anhydrous method. The solid-state i.r. spectrum of this material contains a broad band at 1 590—1 610 cm^{-1} attributable to the C–O stretching vibration of an acetate ligand. This becomes a sharp band at 1 585 cm^{-1} in CH_2Cl_2 solution and a $CDCl_3$ solution of the supposed $[CeL_2(O_2CMe)]$ gives a satisfactory 270 MHz ^1H n.m.r. spectrum containing signals, each of relative area 6, due to the pyrazolyl protons at δ 6.33, 3.55, and 1.72. The acetate methyl protons appear as a signal of relative area 3 at δ −0.08 but this complex slowly decomposes in solution.

When benzoate was used as the co-ligand the aqueous synthetic route afforded precipitates which were soluble in, and could be recrystallised from, polar organic solvents for Ln = Y, Sm, Eu, Yb, or Lu. However, only poorly soluble materials resulted from the reactions involving the larger lanthanides Ln = La—Nd.

The i.r. spectra of the tropolonate complexes $[LnL_2(trop)]$ (Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Tb, Yb, or Lu) are superimposable. The spectra are also similar to those of $[LnL_2(acac)]$ and contain ν(B–H) at 2 460 cm^{-1} and a sharp band attributable to ν(C=O) at 1 595 cm^{-1}. The characteristic polypyrazolylborate bands in the region 1 500—600 cm^{-1} are also present.

The i.r. spectra of the acetate complexes $[LnL_2(O_2CMe)]$ (Ln = Y, Eu, Gd, Yb, or Lu) are all essentially the same as for $[LnL_2(trop)]$ except for the region between 1 650 and 1 500 cm^{-1} where $\nu(CO_2)$ appears. These solid-state spectra fall into three groups. First yttrium forms a complex which has a strong band at 1 600 cm^{-1} when isolated from CH_2Cl_2–hexane mixtures. This contrasts with the value of 1 560 cm^{-1} reported[23] for this compound when isolated from benzene solutions. Secondly, the larger lanthanide ions Eu and Gd have two equally intense strong bands at 1 595 and 1 550 cm^{-1}. Thirdly the smaller lanthanide ions Yb and Lu form complexes with a weak band at 1 635 cm^{-1} and a stronger band at 1 535 cm^{-1}. The solution (CH_2Cl_2) spectrum of the yttrium complex is different from that obtained in the solid state but has the same appearance as the solid-state spectra of the ytterbium and lutetium complexes. The solution (CH_2Cl_2) spectrum of the ytterbium complex is the same as found in the solid state as is the case for the europium complex also.

The i.r. spectra of the benzoate complexes $[LnL_2(O_2CPh)]$ (Ln = Y, La, Nd, Sm, Eu, Yb, or Lu) differ from the spectra of the other complexes in two respects. First, the B–H stretch in the spectra of complexes containing the larger lanthanide ions, La, Nd, Sm, and Eu, is similar to that in all of the acetylacetonate, tropolonate, and acetate complexes referred to above in that it appears as a sharp band at 2 460 cm^{-1}. However, in the solid-state spectra of the benzoate complexes containing the smaller lanthanide ions, Y, Yb, and Lu, there is an additional band at 2 510 cm^{-1} which is approximately half the intensity of the band at 2 460 cm^{-1}. Solution studies show that the presence of this band at 2 510 cm^{-1} is a solid-state effect. Secondly, the C=O stretching region can again be used to divide the spectra into three types. In the first type, the yttrium complex has two strong bands at 1 610 and 1 515 cm^{-1} and two weaker bands at 1 595 and 1 565 cm^{-1}. This spectrum remains essentially unchanged in solution (CH_2Cl_2). In the second group, the solution and solid-state spectra of the benzoate complexes of ytterbium and lutetium are simpler, containing only a strong band at 1 525 cm^{-1} and a weak broad band at 1 625 cm^{-1} attributable to $\nu(CO_2)$. These bands at 1 625 and 1 525 cm^{-1} can be assigned to the carboxylate group by analogy to the acetate spectra of ytterbium and lutetium. In the third group the solid-state spectra of the benzoate complexes of the larger lanthanides, La, Nd, Sm, and Eu, have two very strong bands at 1 605 and 1 560 cm^{-1} similar to the spectra of related acetate complexes. Again these bands are unchanged in a solution (CH_2Cl_2) spectrum of the europium complex.

It is difficult to make detailed assignments relating the carboxylate vibrational frequencies to specific carboxylate bonding modes, since there are so few reports of i.r. information in conjunction with *X*-ray structural data. The three most important bonding modes for carboxylate ligands are monodentate, bidentate, and bridging. The band in the region 1 530—1 510 cm^{-1} has been assigned to a carboxylate antisymmetric stretch.[16] The structural study described below establishes that the antisymmetric stretch at 1 535—1 525 cm^{-1} and the weak band at 1 635—1 625 cm^{-1}, observed in the spectra of $[LnL_2(O_2CMe)]$ (Ln = Yb or Lu in solid and solution; Ln = Y in solution) and $[LnL_2(O_2CPh)]$ (Ln = Yb or Lu), can be assigned to a bidentate carboxylate. It is possible

Table 1. Proton n.m.r. spectral data for $[LnL_2(trop)]$ and $[LnL_2(O_2CR)]$ (R = Me or Ph)[a]

Ln	Pyrazolyl resonances			Co-ligand resonances		
Tropolonate complexes				H_α	H_β	H_γ
Y	7.62(d)	7.04(d)	5.95(t)	7.18(d)	7.36(t)	6.85(t)
La[b]	7.65(d)	7.13(s)	5.98(t)	7.17(d)	7.37(t)	6.87(t)
Ce[b]	9.21(s)	6.17(s)	2.22(br)	16.4(s)	13.8(s)	12.5(t)
Pr[b]	7.91(s)	6.67(s)	6.22(s)	31.9(s)	23.1(s)	19.7(t)
Nd[c]	10.03(s)	7.36(s)	4.03(s)	17.1(d)	14.6(t)	12.6(t)
Sm	8.60(d)	5.81(t)	3.71(d)	8.65(d)	8.41(t)	8.01(t)
Eu	12.2(s)	3.56(s)	2.61(s)	−0.49(d)	−0.01(t)	2.10(t)
Tb	9.6(s)	−5.8(s)	−95.6(s)	181(s)	115(s)	104(s)
Yb	25.4(br)	6.56(s)	5.05(s)	−24.5(d)	−11.2(t)	−10.3(t)
Lu[c]	7.64(d)	7.03(d)	5.97(t)	7.18(d)	7.36(t)	6.85(t)
Acetate complexes[d]				Me		
Y	7.66(d)	7.11(d)	6.02(t)	2.07(s)		
Eu	10.3(br)	3.35(s)	2.60(s)	−7.45(br)		
Yb	33.5(s)	7.19(s)	2.15(s)	−44.4(s)		
Lu	7.66(d)	7.08(d)	6.02(t)	2.06(s)		
Benzoate complexes[e]					Ph	
Y	7.64(d)	7.12(d)	5.97(t)	8.13(br)	7.3—7.4(br)	
Sm	8.35(d)	5.83(s)	5.48(br)	7.08(br)	6.69(br)	
Eu	9.55(br)	3.08(s)	2.38(s)	7.39(br)	6.40(br)	
Yb	33.1(s)	6.94(s)	1.86(s)	−4.89(s)	−24.2(s)	−2.60(s)
Lu	7.65(d)	7.11(d)	5.99(t)	8.14(d)	7.38(t)	7.47(t)

[a] All spectra were recorded in $CDCl_3$ at 270 MHz unless otherwise specified. The pyrazolyl proton resonances were each of relative area 6 while the tropolonate resonances were of relative area 2 for each of H_α and H_β and 1 for H_γ; s = singlet, d = doublet, t = triplet, and br = broad. In all cases ^3J(H–H) was 2Hz. [b] Saturated solutions used. [c] Recorded at 400 MHz. [d] Relative area of acetate methyl resonance = 3. [e] Total relative area of benzoate phenyl resonances = 5.

that the two strong bands at 1 600 and 1 555 cm^{-1} in the spectra of acetate and benzoate complexes of the larger lanthanides may be due to a bridging bonding mode. This would be consistent with the reported[23] value of 1 600 cm^{-1} for $\nu(CO_2)$ in the acetate-bridged dimer $[\{YL(\mu\text{-}O_2CMe)_2\}_2]$.

Osmometric solution molecular weight determinations, using $CHCl_3$ as the solvent, gave values of 703, 630, 877, and 943 for $[YbL_2(O_2CMe)]$, $[LuL_2(O_2CMe)]$, $[YbL_2(O_2CPh)]$, and $[LuL_2(O_2CPh)]$ compared with the expected respective values of 658, 660, 720, and 722. These values are consistent with monomeric formulations for the acetate complexes in $CHCl_3$ solutions. However, the figures for the benzoate complexes are somewhat higher than expected and, although more consistent with a monomeric rather than a dimeric formulation, suggest that association may be occurring to some extent in these solutions.

The 270-MHz ^1H n.m.r. spectra of the new complexes are presented in Table 1. In solution the complexes $[LnL_2(trop)]$ undergo ligand reorganisation processes which are fast on the ^1H n.m.r. time-scale as observed for the complexes $[LnL_2(acac)]$. In each case only three pyrazolyl proton environments are observed, the chemical shifts of these resonances being similar to those observed for $[LnL_2(acac)]$ complexes. For example the three pyrazolyl proton environments in $[YL_2(acac)]$ are at δ 7.61, 7.05, and 5.96 and in $[YL_2(trop)]$ occur at 7.62, 7.05, and 5.95; in each case the coupling constant is 2 Hz. The tropolonate resonances consist of a doublet integrating for two protons, and two triplets, one integrating for two protons and the other for one proton. These may be assigned to the α, β, and γ protons of the cycloheptatrienyl ring respectively. In the spectra of complexes containing the diamagnetic lutetium and yttrium ions, these α, β, and γ protons have respective chemical shifts of δ 7.18, 7.36, and 6.85 with a coupling constant of 10 Hz. The paramagnetic ions paramagnetically shift the proton resonances of the tropolonate ligands, and in some cases the coupling is not resolved. The terbium complex gives the only spectrum in which the γ proton coupling is not resolved. The β proton of the tropolonate ligand in $[EuL_2(trop)]$ has a chemical shift of δ −0.01 which was confirmed by acquiring a spectrum without $SiMe_4$ and referencing to the proteo impurities in deuteriochloroform. The ^1H n.m.r. spectra of the poorly soluble complexes $[LnL_2(trop)]$ (Ln = La, Ce, or Pr) were obtained by prolonged pulsing of the sample to reduce the signal-to-noise ratio. A qualitative observation made during the acquisition of these three spectra was that these complexes are increasingly soluble as the ionic radius is reduced, lanthanum forming the least-soluble complex and praseodymium forming the most soluble complex.

The complexes $[LnL_2(O_2CMe)]$ (Ln = Y or Lu) give diamagnetic spectra which are essentially identical. Each contains a singlet of relative area 3 H attributable to the acetate methyl and three pyrazolyl proton resonances with similar chemical shifts to those found for the analogous complexes containing acac and trop co-ligands. The diamagnetic complexes $[LnL_2(O_2CPh)]$ (Ln = Y or Lu) also exhibit only three pyrazolyl proton resonances. The phenyl resonances are well resolved in the spectrum of the lutetium complex, but in that of the yttrium complex they appear as broad signals, possibly due to dynamic processes. The europium and samarium complexes also exhibit poorly resolved spectra. The methyl or phenyl and one of the pyrazolyl proton resonances appear as broad signals which do not show any reduction in line width on lowering the temperature to −60 °C.

The paramagnetic shift of the pyrazolyl protons, which is dependent upon the distance between the proton and the ytterbium atom, in $[YbL_2(O_2CMe)]$ and $[YbL_2(O_2CPh)]$ is greater than in the analogous complexes containing acac

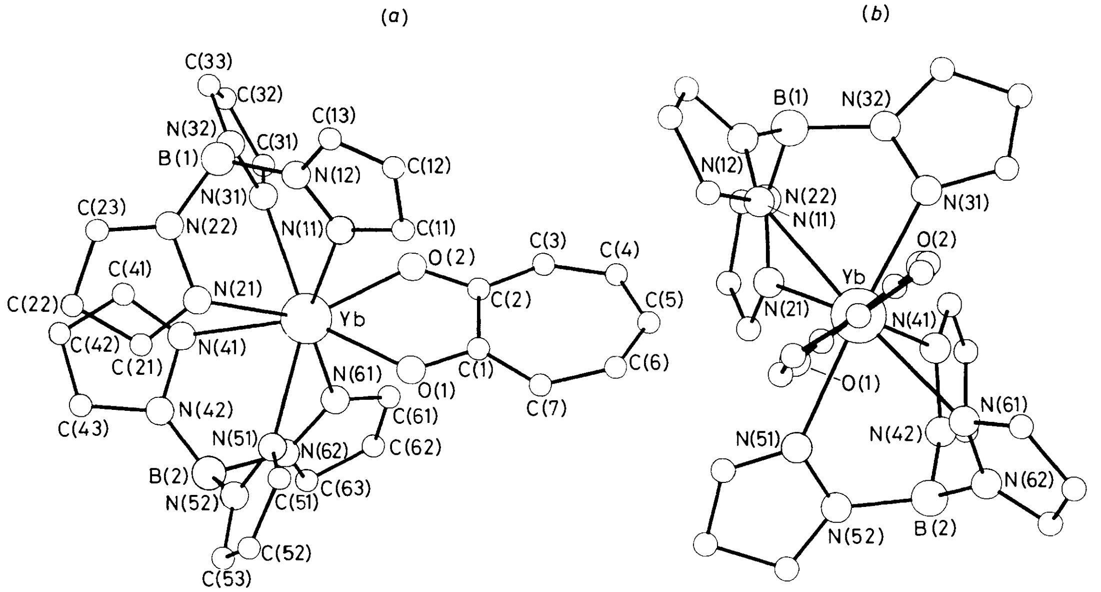

Figure 1. The molecular structure of [YbL_2(trop)]. (*a*) A general view of the molecule showing the atom numbering. (*b*) A view along the axis bisecting the O–Yb–O angle. Hydrogen atoms have been omitted for clarity. The plotting routine used was PLUTO (W. D. S. Motherwell, Program for Plotting Molecular and Crystal Structure, Cambridge Crystallographic Files, University of Manchester Regional Computer Centre, Manchester, 1981)

or trop as the co-ligand. The 3 proton in the pyrazolyl ring has a chemical shift of δ 33.1 in [$YbL_2(O_2CPh)$] and 33.5 in [$YbL_2(O_2CMe)$] whereas in [YbL_2(acac)] it is 10 and in [YbL_2(trop)], 25.4. This finding is consistent with the solid-state structure of [$YbL_2(O_2CPh)$] described below in which the ligand L is closer to the central ion than in the analogous complexes containing acac or trop as the co-ligand.

Electron-impact mass spectra of the complexes [LnL_2(trop)] exhibit molecular ions of the correct isotopic pattern. Common fragment ions which are also observed include [LnL{HB(pz)$_2$}(trop)]$^+$ (pz = $C_3N_2H_3$), [LnL_2]$^+$, [LnL(pz)]$^+$, and [Ln(pz)$_2$]$^+$. In the mass spectra of all acetate and benzoate complexes an ion of one mass unit smaller than the molecular ion is observed. Other common fragment ions include [LnL_2]$^+$, [LnL(pz)]$^+$, and [Ln(pz)$_2$]$^+$. In the spectra of the acetate complexes ions at higher *m*/*z* than the molecular ion are also observed indicating that oligomers may be present.

Structural Studies.—In order to assess the structural effect of reducing the size of the chelate ring formed between Ln and the co-ligand X in [LnL_2X] *X*-ray diffraction studies of two representative complexes were carried out. In order to facilitate comparisons between previously reported structures of lanthanide compounds containing L, complexes of ytterbium were chosen. Unfortunately, crystals of the acetate complex fractured upon removal from the mother-liquor and repeated attempts to mount crystals in capillaries containing the solvent of crystallisation failed to solve this problem. However, the benzoate complex formed more robust crystals so that the structure of [$YbL_2(O_2CPh)$] was determined.

The complex [YbL_2(trop)] crystallises in the orthorhombic space group $P2_12_12_1$ which is a non-centrosymmetric space group. The crystal structure consists of discrete molecular units, one molecule in the asymmetric unit and four molecules in the unit cell. The complex has a similar structure to [YbL_2(acac)] with two tridentate L ligands and one bidentate tropolonate ligand as illustrated in Figure 1. Fractional atomic co-ordinates are presented in Table 2 and selected bond distances and angles in Table 3. The molecule does not possess a plane of symmetry but has an approximate two-fold axis of rotation through C(5) on the tropolonate ligand and the ytterbium ion. The point group is therefore C_2, and the molecule is chiral. In the non-centrosymmetric space group the other enantiomer is not generated by operating on the symmetry elements of the crystal. By comparison of the *R* values for models of the two possible enantiomers the one which gave the lowest *R* value was taken to be correct, and is pictured in Figure 1.

The ytterbium ion is eight-co-ordinate and the co-ordination geometry is best described as s.a. but a loss of planarity in one of the 'squares' means that the structure is on the geometric pathway to b.t.p. The co-ordination polyhedron dimensions are given in Table 4. The relatively short Yb–O bond distances and small bite distance of the tropolonate ligand lead to an apparent tilt of the square planes from parallel, since the tropolonate ligand spans between the two 'squares.' The closest apices of the two 'squares' consist of the two tropolonate oxygen atoms, and the acute angle between the two least-squares planes is 11.5°. The use of normalised co-ordinates removes the anomaly due to these short Yb–O distances and the angle between the least-squares planes reduces to zero. The polytopal analysis values,[24] δ and φ, are given in Table 5. The rectangular face made up of O(1), N(11), N(21), and N(51) is essentially planar (δ = 4°, which reduces to 0.4° for normalised co-ordinates).[25] The other 'square,' made up of O(2), N(31), N(41), and N(61), is distorted from planarity (δ = 14.5°) but not as much as for previous examples of the b.t.p. geometry {[YbL_3], δ = 34.2° and [CeL_2(acac)], δ = 42.5°}. The φ values of 26.6 and 25.7° are close to that of 24.5° calculated for a square antiprismatic geometry.

The longest Yb–O bond distance is to O(2), 2.267(8) Å, and the longest Yb–N distance is to N(41), 2.55(1) Å, both of which are capping atoms if the co-ordination geometry is described as b.t.p. The longest 'square' diagonal distance is 4.25 Å between these two atoms. The 'square' diagonal distance between N(31) and N(61), of 4.01 Å, would have to be much shorter, about 3.0 Å, in order for b.t.p. to be an applicable description. For normalised co-ordinates the square diagonal distances across the planar 'square' are both 1.7 Å but the distorted 'square' has diagonal distances of 1.76 Å between the capping atoms O(2) and N(41) and 1.64 Å between N(31) and N(61). The mean bite distance of 3.02 Å for the co-ordinated nitrogen atoms of L is similar to that of [YbL_3], and [YbL_2(acac)], which both have

Table 2. Fractional atomic co-ordinates (× 10^4) for [YbL_2(trop)] with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Yb	−1 621.8(5)	−1 995.1(3)	−2 908.5(2)	C(52)	−2 736(19)	−96(13)	−4 417(10)
O(2)	−2 330(8)	−3 203(5)	−2 780(4)	C(53)	−1 433(18)	−397(10)	−4 718(8)
O(1)	−3 831(9)	−2 162(5)	−3 323(5)	C(41)	1 979(14)	−1 409(8)	−2 699(7)
B(2)	465(17)	−1 395(12)	−4 362(11)	C(42)	3 034(12)	−990(9)	−3 009(9)
B(1)	−1 099(16)	−1 415(9)	−1 140(8)	C(43)	2 699(19)	−949(10)	−3 677(11)
N(61)	−845(14)	−2 620(7)	−3 985(6)	C(21)	−615(16)	−176(8)	−2 576(8)
N(62)	83(15)	−2 292(8)	−4 458(6)	C(22)	131(14)	293(7)	−2 069(9)
N(51)	−1 934(12)	−1 067(7)	−3 820(6)	C(23)	−14(16)	−145(8)	−1 473(8)
N(52)	−982(14)	−936(8)	−4 317(7)	C(31)	760(16)	−3 012(10)	−1 909(8)
N(41)	983(11)	−1 602(8)	−3 113(6)	C(32)	1 489(18)	−3 014(10)	−1 289(12)
N(42)	1 309(12)	−1 304(7)	−3 766(6)	C(33)	824(24)	−2 467(10)	−916(9)
N(21)	−1 137(11)	−785(6)	−2 320(5)	C(11)	−4 651(13)	−1 946(10)	−1 802(9)
N(22)	−736(11)	−777(7)	−1 605(6)	C(12)	−4 931(22)	−1 815(13)	−1 109(8)
N(31)	−185(14)	−2 444(6)	−1 950(6)	C(13)	−3 843(18)	−1 574(10)	−811(7)
N(32)	−169(12)	−2 114(6)	−1 310(6)	C(2)	−3 586(13)	−3 423(7)	−2 996(7)
N(11)	−3 190(11)	−1 847(6)	−1 868(5)	C(1)	−4 458(13)	−2 820(7)	−3 311(7)
N(12)	−2 736(12)	−1 603(6)	−1 260(6)	C(7)	−5 827(17)	−2 896(10)	−3 605(10)
C(61)	−924(18)	−3 327(9)	−4 209(9)	C(6)	−6 749(17)	−3 527(9)	−3 593(10)
C(62)	−114(17)	−3 420(9)	−4 784(8)	C(5)	−6 437(22)	−4 261(12)	−3 433(11)
C(63)	510(16)	−2 754(9)	−4 928(7)	C(4)	−5 238(19)	−4 551(9)	−3 144(10)
C(51)	−2 906(14)	−585(8)	−3 890(7)	C(3)	−4 118(18)	−4 127(9)	−2 968(9)

Table 3. Selected bond distances (Å) and angles (°) for [YbL_2(trop)] with e.s.d.s in parentheses

Yb–O(1)	2.222(9)	O(1)–C(1)	1.31(2)
Yb–O(2)	2.267(8)	O(2)–C(2)	1.30(2)
Yb–N(11)	2.501(10)	C(1)–C(2)	1.48(2)
Yb–N(21)	2.482(11)	C(2)–C(3)	1.35(2)
Yb–N(31)	2.425(12)	C(3)–C(4)	1.33(2)
Yb–N(41)	2.548(10)	C(4)–C(5)	1.35(3)
Yb–N(51)	2.439(11)	C(5)–C(6)	1.38(3)
Yb–N(61)	2.474(11)	C(6)–C(7)	1.41(2)
		C(7)–C(1)	1.40(2)
pz(C–C) *	1.37(6)		
pz(C–N) *	1.33(5)		
pz(N–N) *	1.38(4)		
pz(N–B) *	1.54(8)		
O(1)–Yb–O(2)	69.2(3)	N(21)–Yb–N(51)	76.4(4)
N(11)–Yb–O(2)	81.0(3)	N(51)–Yb–O(1)	73.7(4)
N(11)–Yb–N(31)	74.7(4)		
N(21)–Yb–N(31)	80.5(4)	O(2)–Yb–N(31)	76.2(3)
N(21)–Yb–N(41)	70.1(4)	N(31)–Yb–N(41)	71.9(4)
N(51)–Yb–N(41)	79.2(4)	N(41)–Yb–N(61)	73.5(4)
N(51)–Yb–N(61)	74.3(4)	N(61)–Yb–O(2)	75.4(4)
O(1)–Yb–N(61)	84.5(4)		
		O(1)–Yb–N(21)	116.7(3)
O(1)–Yb–N(11)	76.6(3)	N(51)–Yb–N(11)	116.3(3)
N(11)–Yb–N(21)	69.1(3)	O(2)–Yb–N(41)	123.6(4)
		N(61)–Yb–N(31)	109.7(4)

* Mean value.

Table 4. Square-antiprismatic dimensions (Å) for [YbL_2(trop)]

Edge	Polyhedron	Normalised polyhedron
(*i*) Square edges		
O(1)–N(11)	2.94	1.24
N(11)–N(21)	2.83	1.13
N(21)–N(51)	3.04	1.24
N(51)–O(1)	2.80	1.20
O(2)–N(31)	2.90	1.23
N(31)–N(41)	2.92	1.17
N(41)–N(61)	3.01	1.20
N(61)–O(2)	2.90	1.22
(*ii*) Triangular edges		
O(1)–O(2)	2.55	1.14
N(11)–O(2)	3.10	1.30
N(11)–N(31)	2.99	1.21
N(21)–N(31)	3.17	1.29
N(21)–N(41)	2.89	1.15
N(51)–N(41)	3.18	1.27
N(51)–N(61)	2.97	1.21
O(1)–N(61)	3.16	1.34
(*iii*) Square diagonals		
O(1)–N(21)	4.01	1.70
N(51)–N(11)	4.20	1.70
O(2)–N(41)	4.25	1.76
N(61)–N(31)	4.01	1.64

a mean bite distance of 3.00 Å. The bite distance of the tropolonate ion is 2.55 Å which is about 0.17 Å shorter than the acac bite distance in [YbL_2(acac)]. The mean bite distance of trop in [Th(trop)$_4$(dmf)] (dmf = dimethylformamide) is 2.54(2) Å and in [Sc(trop)$_3$] and [HSc(trop)$_4$] is 2.523(2) and 2.54(2) Å respectively.[11,12,26] The average Yb–O bond length of 2.24(3) Å is within one standard deviation of 2.22(3) Å found in [YbL_2(acac)].

Solid-angle factor (s.a.f.) calculations[7] give s.a.f. values of 0.305 and 0.209, for L and trop respectively. Thus the solid-angle sum (s.a.s.) for this ytterbium complex is 0.819 compared with 0.833 for [YbL_2(acac)]. The s.a.f. value of 0.305 for L is the same as the average of the s.a.f. for this ligand in [YbL_3] and [YbL_2(acac)]. The standard s.a.f. value for the tropolonate ligand can only be estimated, since there is no structural information for the ligand bound to a larger lanthanide ion, but a value of about 0.19 would seem reasonable.

The complex [YbL_2(O_2CPh)] crystallises in the triclinic space group $P\bar{1}$. The crystal structure consists of discrete molecular units, there are two independent molecules in the asymmetric unit and four molecules in the unit cell. Both molecules contain eight-co-ordinate ytterbium ions bound to a bidentate benzoate ligand and two tridentate ligands L as illustrated in Figure 2. Fractional atomic co-ordinates are given in Table 6 and selected bond distances and angles in Table 7. At first sight the structure appears to be similar to those of [YbL_2(acac)] and [YbL_2(trop)]. There is however one very

Table 5. Values of δ and φ (°) for [YbL$_2$(trop)]

	Polyhedron	Normalised polyhedron	Dodecahedron	s.a.	b.t.p.
δ O(2)[N(61)N(31)]N(41)	14.5	13.2	29.5	0.0	21.8
δ O(1)[N(11)N(51)]N(21)	4.0	0.38	29.5	0.0	0.0
δ O(1)[N(61)N(51)]N(41)	60.3	58.1	29.5	52.5	48.2
δ O(2)[N(11)N(31)]N(21)	58.8	56.1	29.5	52.5	48.2
φ N(31)–O(2)–O(1)–N(51)	26.6	26.6	0.0	24.5	14.1
φ N(61)–N(41)–N(21)–N(11)	25.7	25.7	0.0	24.5	14.1

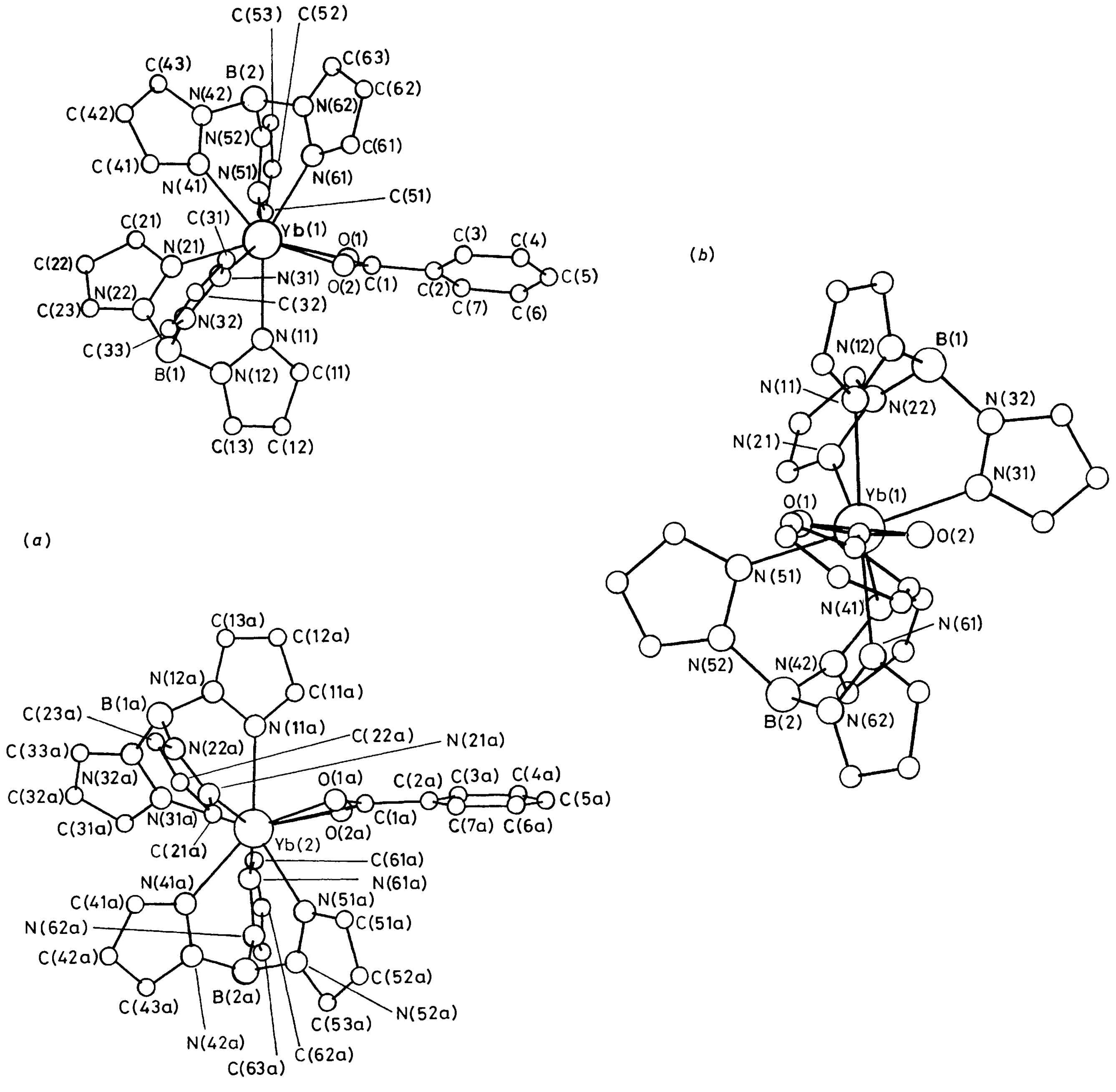

Figure 2. The molecular structure of [YbL$_2$(O$_2$CPh)]. (*a*) A general view of molecules (1) and (2) showing the atom numbering, molecule (2) is distinguished by having the letter a appended after each number. (*b*) A view of molecule (1) along the axis bisecting the O–Yb–O angle. The plotting routine used was PLUTO

Table 6. Fractional atomic co-ordinates (× 10^4) for [$YbL_2(O_2CPh)$] with e.s.d.s in parentheses

Molecule (1)				Molecule (2)			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Yb(1)	3 736.6(3)	1 289.2(2)	2 582.4(2)	Yb(2)	1 451.7(3)	6 294.0(2)	2 644.1(2)
B(1)	1 960(10)	1 045(6)	4 209(5)	B(1a)	3 087(10)	6 062(6)	4 255(5)
B(2)	7 384(11)	1 319(7)	1 925(5)	B(2a)	−2 077(10)	6 233(7)	1 974(6)
O(1)	2 669(6)	2 169(3)	1 694(3)	O(2a)	3 410(6)	5 867(3)	1 991(3)
O(2)	1 965(6)	836(4)	1 886(3)	O(1a)	2 473(6)	7 174(4)	1 738(3)
N(31)	2 788(7)	110(4)	3 332(3)	N(11a)	3 575(7)	6 916(4)	3 104(3)
N(32)	2 155(7)	177(4)	3 939(3)	N(12a)	4 014(6)	6 656(4)	3 753(3)
N(21)	4 310(6)	1 680(4)	3 687(3)	N(31a)	2 363(7)	5 110(4)	3 404(3)
N(22)	3 457(7)	1 427(4)	4 249(3)	N(32a)	2 966(7)	5 186(4)	4 008(3)
N(11)	1 529(7)	1 920(4)	3 059(3)	N(21a)	744(7)	6 724(4)	3 731(3)
N(12)	1 047(6)	1 665(4)	3 703(3)	N(22a)	1 557(7)	6 474(4)	4 301(3)
N(41)	6 056(7)	561(4)	2 947(3)	N(51a)	−404(7)	7 338(4)	2 317(3)
N(42)	7 351(7)	791(4)	2 634(3)	N(52a)	−1 637(7)	7 167(4)	1 984(3)
N(51)	5 463(7)	2 374(4)	2 291(3)	N(41a)	−842(7)	5 560(4)	3 026(3)
N(52)	6 765(7)	2 247(4)	1 968(4)	N(42a)	−2 111(7)	5 724(4)	2 665(3)
N(61)	4 996(8)	704(4)	1 654(3)	N(61a)	461(7)	5 625(4)	1 734(3)
N(62)	6 440(7)	877(5)	1 484(4)	N(62a)	−953(8)	5 762(5)	1 544(3)
C(31)	2 749(9)	−722(5)	3 249(4)	C(11a)	4 572(8)	7 479(5)	2 814(4)
C(32)	2 092(10)	−1 188(5)	3 808(5)	C(12a)	5 624(9)	7 596(5)	3 276(5)
C(33)	1 744(10)	−608(5)	4 240(5)	C(13a)	5 236(8)	7 065(5)	3 864(5)
C(21)	5 538(9)	1 973(6)	3 912(5)	C(31a)	2 411(9)	4 283(5)	3 336(5)
C(22)	5 490(10)	1 926(6)	4 609(5)	C(32a)	3 020(11)	3 801(6)	3 908(5)
C(23)	4 162(10)	1 578(6)	4 814(4)	C(33a)	3 354(10)	4 395(6)	4 325(5)
C(11)	546(8)	2 523(5)	2 780(4)	C(21a)	−514(8)	7 041(6)	3 953(5)
C(12)	−559(9)	2 648(5)	3 245(5)	C(22a)	−501(10)	7 036(6)	4 645(5)
C(13)	−215(9)	2 091(6)	3 821(5)	C(23a)	812(10)	6 660(5)	4 852(4)
C(41)	6 409(10)	33(6)	3 517(5)	C(51a)	−381(11)	8 189(5)	2 286(5)
C(42)	7 938(10)	−86(6)	3 552(5)	C(52a)	−1 622(11)	8 561(6)	1 924(5)
C(43)	8 502(9)	399(6)	2 973(5)	C(53a)	−2 358(10)	7 894(6)	1 740(5)
C(51)	5 279(10)	3 233(5)	2 247(5)	C(41a)	−1 227(10)	5 083(6)	3 605(5)
C(52)	6 467(11)	3 646(6)	1 904(5)	C(42a)	−2 755(10)	4 938(6)	3 625(5)
C(53)	7 361(10)	2 989(6)	1 741(5)	C(43a)	−3 252(9)	5 352(6)	3 018(5)
C(61)	4 590(11)	159(6)	1 235(5)	C(61a)	1 063(10)	5 100(6)	1 330(5)
C(62)	5 747(14)	−41(7)	810(5)	C(62a)	39(13)	4 866(6)	893(5)
C(63)	6 918(11)	439(7)	987(5)	C(63a)	−1 264(12)	5 302(6)	1 044(4)
C(1)	1 963(8)	1 551(5)	1 520(4)	C(1a)	3 304(8)	6 565(5)	1 583(4)
C(2)	1 178(9)	1 699(5)	869(4)	C(2a)	4 110(9)	6 695(5)	913(4)
C(3)	916(11)	1 021(6)	521(5)	C(7a)	4 151(11)	7 524(7)	553(5)
C(4)	250(13)	1 189(7)	−99(6)	C(6a)	4 885(13)	7 607(8)	−79(6)
C(5)	−177(11)	2 030(6)	−371(5)	C(5a)	5 469(13)	6 923(7)	−330(6)
C(6)	57(12)	2 683(7)	−20(5)	C(4a)	5 440(12)	6 093(7)	36(5)
C(7)	793(10)	2 540(6)	589(5)	C(3a)	4 721(11)	6 000(6)	665(5)

important difference between these two structures and that of [$YbL_2(O_2CPh)$]. In the benzoate complex the co-ordinating nitrogen atoms of the ligands L are closer to the ytterbium ion and to compensate for this the oxygen atoms of the benzoate ligand are more distant from Yb than those in the acac or trop complexes. The mean Yb–N bond distance is 2.43 Å [ranges: molecule (1), 2.369(6)—2.462(7); molecule (2), 2.363(6)—2.481(6) Å] for [$YbL_2(O_2CPh)$] compared with 2.49 Å [range: 2.401(7)—2.601(6) Å][2] for [YbL_3], 2.49 Å [ranges: molecule (1), 2.444(10)—2.576(11); molecule (2), 2.432(14)—2.526(13) Å][5] for [YbL_2(acac)], and 2.48 Å [range 2.425(12)—2.548(10) Å] for [YbL_2(trop)]. The mean Yb–O bond distance to the benzoate ligand in [$YbL_2(O_2CPh)$] is 2.33 Å [ranges: molecule (1), 2.310(5)—2.360(6); molecule (2), 2.319(5)—2.336(5) Å], compared with 2.22 Å [ranges: molecule (1), 2.199(11)—2.258(9); molecule (2), 2.200(9)—2.238(9) Å][5] to acac and 2.24 Å [range 2.222(9)—2.267(8) Å] to trop respectively in [YbL_2(acac)] and [YbL_2(trop)]. The co-ordination geometry of [$YbL_2(O_2CPh)$] is best described as s.a. with distortion of both 'squares' so that it is on the geometric pathway from s.a. to dodecahedral. This contrasts with the situation in [YbL_2(trop)] which has only one 'square' distorted so that it is on the geometric pathway from s.a. to b.t.p. The two 'squares' are made up of atoms O(1)–N(11)–N(21)–N(51) and O(2)–N(31)–N(41)–N(61). Polytopal analysis values δ and φ are given in Table 8. Since the Yb–O distances in [$YbL_2(O_2CPh)$] are similar to the Yb–N distances, the normalisation of bond distances has much less effect on the δ and φ values. The 'squares' are all substantially bent, δ values ranging from 14.4 to 26.5° compared with an ideal dodecahedral value of 29.5°. However the other δ values range from 48.5 to 56.0° and the φ values range from 13.3 to 24.0°. These values are more similar to those expected for s.a., of 52.4 and 24.5° respectively.

The co-ordination polyhedron dimensions for [$YbL_2(O_2CPh)$] are given in Table 9. The shortest cross 'square' diagonal distances should be approximately 3.1 Å if dodecahedral is to be a suitable description of the co-ordination polyhedron, in fact the diagonal distances range from 3.78 to 4.37 Å, only a range of 0.3 Å either side of a mean value of 4.1 Å appropriate for s.a. The mean bite distances of L in this structure are 2.98 and 2.99 Å for molecules (1) and (2) respectively. This compares with mean bite distances of 2.99—3.02 Å for other ytterbium hydrotris(pyrazol-1-yl)borate complexes. The bite distance of the benzoate ligand is 2.20 Å

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

		Molecule (1)	Molecule (2)		Molecule (1)	Molecule (2)
Yb–O(1)		2.310(5)	2.319(5)	O(1)–Yb–O(2)	56.2(2)	56.5(2)
Yb–O(2)		2.360(6)	2.336(5)	N(11)–Yb–O(2)	80.7(2)	76.8(2)
Yb–N(11)		2.459(6)	2.463(7)	N(11)–Yb–N(31)	77.2(2)	78.6(2)
Yb–N(21)		2.462(7)	2.447(7)	N(21)–Yb–N(31)	78.3(2)	78.6(2)
Yb–N(31)		2.390(6)	2.375(6)	N(21)–Yb–N(41)	72.0(2)	72.6(2)
Yb–N(41)		2.456(6)	2.481(6)	N(51)–Yb–N(41)	77.2(2)	76.2(2)
Yb–N(51)		2.369(6)	2.363(6)	N(51)–Yb–N(61)	81.4(2)	82.5(2)
Yb–N(61)		2.448(7)	2.448(7)	O(1)–Yb–N(61)	81.3(2)	81.4(2)
pz(C–C)*		1.391(12)	1.393(18)	O(1)–Yb–N(11)	74.4(2)	75.0(2)
pz(C–N)*		1.352(11)	1.345(10)	N(11)–Yb–N(21)	71.0(2)	71.2(2)
pz(N–N)*		1.367(9)	1.373(9)	N(21)–Yb–N(51)	77.9(2)	79.0(2)
pz(N–B)*		1.539(19)	1.536(21)	N(51)–Yb–O(1)	76.5(2)	75.6(2)
O$_2$CPh	O(1)–C(1)	1.283(10)	1.277(10)	O(2)–Yb–N(31)	80.4(2)	81.0(2)
	O(2)–C(1)	1.254(9)	1.276(9)	N(31)–Yb–N(41)	81.0(2)	78.7(2)
Yb	··· C(1)	2.688(7)	2.685(8)	N(41)–Yb–N(61)	68.8(2)	69.8(2)
	C(2)–C(1)	1.490(11)	1.509(11)	N(61)–Yb–O(2)	71.4(2)	71.8(2)
	Ph(C–C)*	1.390(17)	1.393(22)			
	O(1)–C(1)–O(2)	120.1(7)	119.3(7)	O(1)–Yb–N(21)	126.6(2)	125.6(2)
				N(51)–Yb–N(11)	108.9(2)	111.9(2)
				O(2)–Yb–N(41)	128.0(2)	130.4(2)
				N(61)–Yb–N(31)	107.4(2)	103.4(2)

* Mean value.

Table 8. Values of δ and φ (°) for [YbL$_2$(O$_2$CPh)]

	Molecule (1)		Molecule (2)				
	Polyhedron	Normalised polyhedron	Polyhedron	Normalised polyhedron	Dodecahedron	s.a.	b.t.p.
δ 1(57)3	21.6	21.2	26.5	26.3	29.5	0.0	21.8
δ 2(68)4	18.1	17.2	14.4	13.4	29.5	0.0	0.0
δ 2(58)3	50.5	49.7	48.5	48.7	29.5	52.4	48.2
δ 1(67)4	56.0	55.6	54.4	53.5	29.5	52.4	48.2
φ 7-1-2-8	24.0	24.0	20.7	20.7	0.0	24.5	14.1
φ 5-3-4-6	13.9	13.9	13.3	13.2	0.0	24.5	14.1

Polyhedra vertices were defined thus: 1 [O(2), O(2a)], 2 [O(1), O(1a)], 3 [N(4), N(4a)], 4 [N(2), N(2a)], 5 [N(6), N(6a)], 6 [N(1), N(1a)], 7 [N(3), N(3a)], 8 [N(5), N(5a)].

compared with 2.55 Å for tropolonate and 2.72 Å for acetylacetonate. The carboxylate carbon [C(1)] to ytterbium distances are 2.688(7) and 2.685(8) Å, but the O(1)–C(1)–O(2) angles for benzoate are 120.1(7) and 119.3(7)° for molecules (1) and (2) respectively so the geometry of the carboxylate carbon is undistorted upon co-ordination to ytterbium.

Due to the shorter Yb–N bonds in [YbL$_2$(O$_2$CPh)] the s.a.f. value for the ligands L in this complex is anomalously high. The mean s.a.f. value calculated from three ytterbium hydrotris(pyrazol-1-yl)borate complexes {[YbL$_3$], [YbL$_2$(acac)], and [YbL$_2$(trop)]} is 0.305(3), whereas that for L in this complex is 0.320. The s.a.f. value for the benzoate ligand is calculated to be 0.174. The s.a.s. value for the complex is therefore 0.814, which is only slightly smaller than the respective values for [YbL$_2$(acac)] and [YbL$_2$(trop)] of 0.833 and 0.819. The reduction of the Yb–N bond length in this benzoate complex is probably driven by the requirement to maximise steric saturation with the ligand set available. The maximisation of steric saturation and therefore the s.a.s. value is counteracted by the minimisation of steric interaction between the ligands around the metal. In the second atom sphere from the metal the benzoate ligand is sterically undemanding, relative to acetylacetonate and tropolonate, having only the carboxylate carbon. The ligand L is sterically demanding in this second-atom sphere, projecting the 3 hydrogen out of the pyrazolyl ring. Therefore in the acetylacetonate and tropolonate complexes a high s.a.s. value can be achieved while allowing the L ligand to lie further away from the metal ion to minimise the interaction of these second-sphere atoms. In the benzoate complex the co-ligand is less sterically demanding in the first co-ordination sphere and, fortuitously, the second-atom sphere can interlock when the two ligands bind at almost the same distance from the metal ion.

This structure determination has revealed that, in addition to the ability of the L ligands to interlock with each other and pack with more or less efficiency, the L ligands can vary their distance from the metal thus modifying their steric demand and the extent to which they interlock with the co-ligand.

Conclusions

These studies have established a clear trend in the solubility properties of the heteroleptic lanthanide complexes [LnL$_2$X]. As the size of the chelate ring formed by X is reduced, so the maximum lanthanide ion radius for which complexes soluble in polar organic solvents may be isolated decreases. Thus for [LnL$_2$(acac)] all of the complexes for Ln = La—Lu are soluble while for [LnL$_2$(trop)] complexes containing the three largest lanthanide ions (Ln = La—Pr) are poorly soluble. When benzoate co-ligands are present in place of tropolonate the

Table 9. Square-antiprismatic dimensions (Å) for $[YbL_2(O_2CPh)]$

	Molecule (1)		Molecule (2)	
	Polyhedron	Normalised polyhedron	Polyhedron	Normalised polyhedron
(*i*) Square edges				
O(1)-N(11)	2.89	1.21	2.91	1.22
N(11)-N(21)	2.86	1.16	2.86	1.16
N(21)-N(51)	3.03	1.26	3.06	1.27
N(51)-O(1)	2.90	1.24	2.87	1.23
O(2)-N(31)	3.06	1.29	3.06	1.30
N(31)-N(41)	3.15	1.30	3.08	1.26
N(41)-N(61)	2.77	1.13	2.82	1.14
N(61)-O(2)	2.81	1.17	2.81	1.17
(*ii*) Triangular edges				
O(1)-O(2)	2.20	0.94	2.20	0.95
N(11)-O(2)	3.12	1.29	2.98	1.24
N(11)-N(31)	3.03	1.25	3.07	1.27
N(21)-N(31)	3.06	1.26	3.05	1.27
N(21)-N(41)	2.89	1.18	2.92	1.18
N(51)-N(41)	3.01	1.25	2.99	1.23
N(51)-N(61)	3.14	1.30	3.17	1.32
O(1)-N(61)	3.10	1.30	3.11	1.30
(*iii*) Square diagonals				
O(1)-N(21)	4.26	1.79	4.24	1.78
N(51)-N(11)	3.93	1.63	4.00	1.66
O(2)-N(41)	4.33	1.80	4.37	1.82
N(61)-N(31)	3.90	1.61	3.78	1.57

complexes of the four largest lanthanide ions (Ln = La—Nd, Pm was not studied) are insoluble. In the cases of the six largest lanthanides (Ln = La—Sm) the complexes $[LnL_2(O_2CMe)]$ appear to be unstable to disproportionation in solution giving the insoluble homoleptic complex $[LnL_3]$.

The *X*-ray diffraction study of $[YbL_2(trop)]$ affords the first structural characterisation of a lanthanide tropolonate complex. The s.a.f. value of the tropolonate ligand bound to ytterbium is 0.209, the standard s.a.f. value is estimated to be 0.19. Furthermore, the *X*-ray diffraction study of $[YbL_2(O_2CPh)]$ provides the first example of a structurally characterised lanthanide complex containing a bidentate benzoate ligand. The s.a.f. value of the bidentate benzoate ligand attached to ytterbium is 0.174. On the basis of i.r. and n.m.r. spectral data, $[LnL_2X]$ (Ln = Yb or Lu, X = O_2CPh or O_2CMe) adopt similar structures in the solid state and in solution.

Experimental

Synthetic and Spectroscopic Studies.—Potassium hydrotris(pyrazol-1-yl)borate was prepared by the literature method.[27] Hydrated lanthanide trichlorides were obtained from Ventron GMBH and anhydrous lanthanide trihalides were obtained by ammonium chloride sublimation.[28] Sodium benzoate, sodium acetate, and silver acetate were obtained from Aldrich Chemicals Ltd. and 2-hydroxy-2,4,6-cycloheptatrien-1-one (tropolone) from Lancaster Synthesis Ltd.; they were used without further purification.

Proton n.m.r. spectra were recorded using JEOL JNM GX270 and Bruker WH400 (SERC Service, University of Warwick) spectrometers. Deuteriated n.m.r. solvents were obtained from Aldrich Chemicals Ltd., and chemical shifts are reported with $SiMe_4$ as internal reference at 293 K. I.r. spectra were recorded using KBr pellets and a Perkin-Elmer 297 spectrometer, mass spectra using a Kratos MS80RF spectrometer, ions being produced by electron impact. Elemental analyses were performed by the Microanalytical Laboratory, School of Chemistry, University of Birmingham.

Bis{hydrotris(pyrazol-1-yl)borato}tropolonatoyttrium(III). The salt $K[HB(C_3N_2H_3)_3]$ (0.5 g, 2 mmol), 2-hydroxy-2,4,6-cycloheptatrien-1-one (0.12 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 $YCl_3{\cdot}6H_2O$ (0.30 g, 1 mmol) in water (15 cm^3). Stirring was continued for 1 h and the resulting yellow precipitate collected by filtration and dried *in vacuo* (0.58 g, 91%). Recrystallisation from CH_2Cl_2–hexane afforded large yellow crystals (0.45 g, 71%), m.p. 268—270 °C.

The corresponding complexes were prepared similarly with Nd, Sm, Eu, Tb, Yb, and Lu; complexes containing La, Ce, and Pr were only sparingly soluble and were purified by sublimation at 250 °C *in vacuo*. Yields, melting points, colours, and elemental analyses are given in Table 10.

Benzoatobis{hydrotris(pyrazol-1-yl)borato}yttrium(III). The salt $K[HB(C_3N_2H_3)_3]$ (0.5 g, 2 mmol) and sodium benzoate (0.15 g, 1 mmol) were dissolved in water (30 cm^3) and added to a stirred solution of $YCl_3{\cdot}6H_2O$ (0.30 g, 1 mmol) in water (15 cm^3); stirring was continued for 10 min. The resulting white amorphous precipitate was collected by filtration (0.51 g, 81%). Recrystallisation from CH_2Cl_2–hexane gave large white crystals (0.40 g, 63%), m.p. 234—235 °C.

The corresponding complexes were prepared similarly with Sm, Eu, Yb, and Lu. Complexes containing La and Nd were only sparingly soluble and the crude powder was not recrystallised. Yields, melting points, colours, and elemental analyses are presented in Table 10.

Acetatobis{hydrotris(pyrazol-1-yl)borato}yttrium(III). The salt $K[HB(C_3N_2H_3)_3]$ (0.5 g, 2 mmol) and sodium acetate (0.08 g, 1 mmol) were dissolved in water (30 cm^3) and added to a stirred solution of $YCl_3{\cdot}6H_2O$ (0.30 g, 1 mmol) in water (15 cm^3); stirring was continued for 10 min. The resulting white amorphous precipitate was collected by filtration (0.46 g, 81%). Recrystallisation from CH_2Cl_2–hexane gave fine white crystals which fractured on drying (0.40 g, 70%), m.p. 229–231 °C.

The corresponding complexes were prepared similarly with Eu, Gd, Yb, and Lu. Yields, melting points, colours, and elemental analyses are presented in Table 10.

An alternative preparation of the acetate complexes $[YL_2(O_2CMe)]$ and $[YbL_2(O_2CMe)]$ was also used as follows.

Acetatobis{hydrotris(pyrazol-1-yl)borato}yttrium(III). Anhydrous yttrium trichloride (0.29 g, 1.5 mmol), $K[HB(C_3N_2H_3)_3]$ (0.76 g, 3 mmol), and silver acetate (0.25 g, 1.5 mmol) were introduced into a Schlenk flask under nitrogen and dry tetrahydrofuran (thf) (20 cm^3) added. The mixture was stirred for 1 h then filtered under nitrogen. The colourless filtrate was taken to dryness *in vacuo* and found to be air-stable by i.r. spectroscopy. Slow fractional crystallisation from CH_2Cl_2–hexane afforded the pure product (0.4 g, 70%) (Found: C, 41.6; H, 4.0; N, 29.1. $C_{20}H_{23}B_2N_{12}O_2Y$ requires C, 41.8; H, 4.0; N, 29.3%). The corresponding ytterbium complex could be prepared similarly (0.33 g, 50%).

Structural Studies.—*Bis{hydrotris(pyrazol-1-yl)borato}tropolonatoytterbium*(III). All of the soluble complexes $[LnL_2(trop)]$ (Ln = Nd—Lu) form large single crystals. Orange crystals of $[YbL_2(trop)]$ were obtained by slow evaporation of a solution of the complex in CH_2Cl_2–hexane.

Crystal data. $C_{25}H_{25}B_2N_{12}O_2Yb$, M = 720.2, orthorhombic, a = 9.280(2), b = 17.840(8), c = 19.393(2) Å, U = 3 211 Å^3, Z = 4, D_c = 1.48 g cm^{-3}, space group $P2_12_12_1$ (no. 19), Mo-K_α radiation (λ = 0.7107 Å, μ = 28 cm^{-1}), T = 293 K.

Data were collected on an Enraf-Nonius CAD4 diffractometer at the Crystallography Unit, Universities of Aston and

Table 10. Yields, melting points, colours, and elemental analyses for $[LnL_2X]$ (X = trop, O_2CMe, or O_2CPh)

				Analysis (%)[a]		
Ln	Yield/g (%)	M.p. (°C)	Colour	C	H	N
Tropolonate complexes						
Y	0.58(91)	271—273	Yellow	46.9 (47.2)	4.1 (4.0)	26.1 (26.4)
La[b]	0.65(95)	275 (decomp.)	Yellow	43.5 (43.8)	3.7 (3.7)	24.7 (24.5)
Ce[b]	0.63(92)	275 (decomp.)	Orange	43.8 (43.7)	3.9 (3.7)	24.45 (24.45)
Pr[b]	0.59(86)	280 (decomp.)	Yellow	43.6 (43.6)	3.9 (3.7)	24.6 (24.4)
Nd	0.63(91)	263—265	Red	43.5 (43.4)	3.8 (3.6)	24.5 (24.3)
Sm	0.60(86)	274—276	Orange	43.3 (43.0)	3.7 (3.6)	24.4 (24.1)
Eu	0.61(87)	257—258	Orange	42.7 (42.9)	3.4 (3.6)	23.8 (24.0)
Tb	0.65(92)	272—274	Yellow	42.6 (42.5)	3.6 (3.6)	23.5 (23.8)
Yb	0.69(96)	263—265	Orange	41.5 (41.7)	3.7 (3.5)	23.2 (23.3)
Lu	0.60(83)	283—285	Yellow	41.3 (41.6)	3.2 (3.5)	23.0 (23.3)
Benzoate complexes						
Y	0.51(81)	234—235	Colourless	47.6 (47.2)	4.2 (4.0)	26.7 (26.4)
La	0.57(83)	330 (decomp.)	Colourless			
Nd	0.58(84)	270—290	Purple			
Sm	0.65(93)	275—276	Colourless	43.1 (43.1)	3.5 (3.6)	23.9 (24.1)
Eu	0.65(93)	269—270	Colourless	41.6 (42.9)	3.9 (3.6)	23.7 (24.0)
Yb	0.51(71)	263—265	Colourless	42.2 (41.7)	3.5 (3.5)	23.6 (23.3)
Lu	0.70(98)	263—265	Colourless	41.8 (41.6)	3.5 (3.5)	23.1 (23.3)
Acetate complexes						
Y	0.46(81)	229—231	Colourless	42.1 (41.8)	4.1 (4.0)	29.3 (29.3)
Eu	0.53(83)	252—254	Colourless	37.4 (37.7)	3.9 (3.6)	26.1 (26.4)
Gd	0.58(91)	252—254	Colourless	37.6 (37.4)	3.9 (3.6)	25.9 (26.1)
Yb	0.58(88)	130	Colourless	36.8 (36.5)	3.7 (3.5)	25.2 (25.5)
Lu	0.60(91)	120	Colourless	36.6 (36.4)	3.8 (3.5)	25.8 (25.5)

[a] Calculated values are given in parentheses. [b] Purified by sublimation at 250 °C *in vacuo* to give *ca.* 25% purified yield.

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 ω scan angle of (1.00 + 0.35 tan θ)°. 5 215 Reflections were measured (2 < 2θ < 55°), giving 2 813 unique reflections with $I > 2.5\sigma(I)$ after merging ($R = 0.0434$). Two standard reflections were measured every hour and showed no variation with time. Data were corrected for Lorentz and polarisation factors. 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,[29] and literature values for scattering factors of neutral atoms and for anomalous dispersion terms.[30,31]

The structure was solved using conventional heavy-atom techniques on the merged data and was refined by full-matrix least-squares methods. Final cycles of refinement were carried out on unmerged data, with all non-hydrogen atoms anisotropic and hydrogens in calculated positions with one, overall, refined μ_{iso} [= 0.11(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 $|F_0|$. The final model with 386 parameters varied refined to R 0.0613 and R' $\{ = [\Sigma w(|F_o| - |F_c|)^2]^{\frac{1}{2}}\}$ 0.0652. The refinement of the other enantiomer converged to a model with R 0.069 and R' 0.074. Least-squares planes were calculated using *X*-RAY 72.[32] Electron density in the final difference map < 1 e Å^{-3}, no unusually close intermolecular contacts.

*Benzoatobis{hydrotris(pyrazol-*1*-yl)borato}ytterbium*(III). Colourless crystals of $[YbL_2(O_2CPh)]$ were obtained by the slow evaporation of a solution in CH_2Cl_2–hexane.

Crystal data. $C_{25}H_{25}B_2N_{12}O_2Yb$, $M = 720.2$, triclinic, $a = 9.148(1)$, $b = 15.796(8)$, $c = 20.089(10)$ Å, $\alpha = 81.57(5)$, $\beta = 88.65(2)$, $\gamma = 88.15(3)$°, $U = 2\,870$ Å^3, $Z = 4$, $D_c = 1.67$ g cm^{-3}, space group $P\bar{1}$ (no. 2), Mo-K_α radiation ($\lambda = 0.7107$ Å, $\mu = 31$ cm^{-1}), $T = 293$ K.

Data were collected, processed, and corrected as for $[YbL_2(trop)]$, to give 10 020 unique reflections. The structure was solved using conventional heavy-atom techniques. Initial refinement was by full-matrix least-squares methods, with isotropic non-hydrogen atoms. In the final stages, block-diagonal least-squares refinement was carried out, in which all non-hydrogen atoms were refined as anisotropic, except for the phenyl carbon atoms which were refined as isotropic. The structure refinement program used had a limit on the number of atoms refined ($N_{iso} + 2N_{aniso} = 160$), this limit had almost been reached because there were two independent molecules in the asymmetric unit, consequently hydrogen positions were not calculated. The centric space group was confirmed by the success of the structure determination. Refinement weights derived from counting statistics gave satisfactory analysis of the variation of $w\Delta^2$ with increasing $(\sin\theta)/\lambda$ and with increasing fractions of $|F_o|$. The final model with 697 parameters varied refined to R 0.0504 and $R'\{[\Sigma w(|F_o| - |F_c|)^2]^{\frac{1}{2}}\}$ 0.0519. Residual electron density in the final difference map < 1 e Å^{-3}; no unusually close intermolecular contacts.

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

Acknowledgements

We are grateful to Dr. A. J. Edwards and Professor W. J. Evans for helpful discussions, to Dr. D. W. Bruce and Ms. S. Bradshaw for the solution molecular weight determinations, to the S.E.R.C. and BP Chemicals for support (to M. A. J. M.), and to NATO for the provision of travel grant No. 175/84.

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Received 19*th May* 1989; *Paper* 9/02115I