

Complexes of the Podand Ligand Tris[3-(2-pyridyl)-pyrazol-1-yl]borate with Lanthanoids and Actinoids: Rare Examples of Icosahedral N₁₂ Coordination

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The title ligand [L¹]⁻ forms 2 : 1 complexes [M^{III}(L¹)₂]⁺ (M = Sm, U) in which the metal ions are in an icosahedral N₁₂ coordination environment from the two interleaved hexadentate ligands.

The tris(pyrazol-1-yl)hydroborate ligand system [HB(3-R-5-R'-pz)₃] has become popular with synthetic chemists, in part owing to the ease with which attachment of substituents at the 3- and 5-positions of the pyrazolyl ring has allowed the synthesis of a wide variety of ligands and a plethora of complexes.¹ Particularly noteworthy has been the introduction of bulky substituents at the 3-position: the resultant sterically hindering ligands are uniquely suited for stabilization of low-coordination metal environments and important bioinorganic model compounds.² The elaboration of the tris(pyrazolyl)hydroborate ligands with potentially coordinating groups attached to the pyrazolyl 3-position has lagged behind, but recently we communicated the synthesis of the first such podand ligand, tris[3-(2-pyridyl)-pyrazol-1-yl]hydroborate, L¹,³ and have shown it to be remarkably versatile, permitting *inter alia* the encapsulation of a triangular Ag₃ cluster and self-assembly of tetramers with first-row transition metals.⁴ We now report the crystal structures of bis-ligand complexes with f-block elements, [Sm(L¹)₂][BPh₄]⁻ **1** and [U(L¹)₂][I]⁻ **2**, which are very rare examples of twelve-coordination with N-donor ligands, complex **2** being the first reported case for an actinoid ion.

In the previously reported 1 : 1 complex [Eu(L¹)F(MeOH)₂]⁺ the coordinated fluoride was extracted from a [PF₆]⁻ ion.³ We were interested to see how the ligand L¹ would coordinate to lanthanoids in the absence of strong competing ligands, and accordingly used [BPh₄]⁻ as the anion. Reaction of KL¹ with SmCl₃·6H₂O in methanol followed by addition of aqueous NaBPh₄ afforded a white solid [Sm(L¹)₂][BPh₄]⁻ **1**;† absence of competing fluoride has permitted coordination of a second equivalent of L¹. The investigations with actinoids began with U₂(thf)₄,⁵ with a view to comparing the binding properties of the podand L¹ with those of its simpler 3,5-dimethyl cousin L².⁶ Analysis of the products from the reaction indicated formation of [U(L¹)₂]⁺ **2** and [U(L¹)₂][BPh₄]⁻ **2a** where, as with the Sm^{III} analogue, two potentially hexadentate ligands are attached to the U^{III} centre.† This contrasts with U(L²)₂I where the iodide ligand is retained bonded to uranium.⁷

The crystal structures of **1** and **2** are depicted in Figs. 1 and 2.‡ As a consequence of the same charge and similar size of the metals, and lack of stereoelectronic preferences, the structures are very similar. Each metal ion is 12-coordinate and has an approximately icosahedral (3 : 6 : 3') coordination geometry, with 3 and 3' denoting mutually staggered sets of pyrazolyl donor atoms, and the 6 denoting the puckered arrangement of 6 pyridyl donor atoms interleaved around the equator.⁸ The main

distortion in the icosahedral geometry is a compression along the B–M–B axis, such that the dihedral angles between the faces either side of the six pyridyl–pyridyl edges are *ca.* 130° instead of the ideal 138°. Both **1** and **2** have crystallographically imposed inversion symmetry at the metal. The metal–pyridyl bonds (average length 2.95 Å in both **1** and **2**) are *ca.* 0.29 Å longer than the metal–pyrazolyl bonds (average 2.66 Å in both **1** and **2**), which is a steric consequence of having six pyridyl ligands around the equator of the complex; in [Eu(L¹)F(MeOH)₂][PF₆], the average Eu–pyridyl distance is only 0.13 Å more than the average Eu–pyrazolyl distance. The apical N–B–N bonds of the ligands in **1** and **2** are 109–110°, indicating that the ligand is not having to strain to accommodate the large metal ions. The bite angles of the N,N-chelating fragments are all between 57 and 59°.

Although twelve coordination is well-known in lanthanoid(III) complexes, it is largely confined to complexes containing bidentate oxyanion ligands such as nitrates in which the two donor atoms are very close together: [La(18-crown-6)(NO₃)₃]⁹ and [Nd(18-ane-N₆)(NO₃)₃]¹⁰ are typical examples. The only 12-coordinate lanthanoid complexes with solely N-donor ligands are [M(napy)₆][ClO₄]₃ (napy = 1,8-naphthyridine; M = La, Ce, Pr)¹¹ and [La(ctthb)₄][ClO₄]₃ (ctthb = *cis*-triazza-tris-

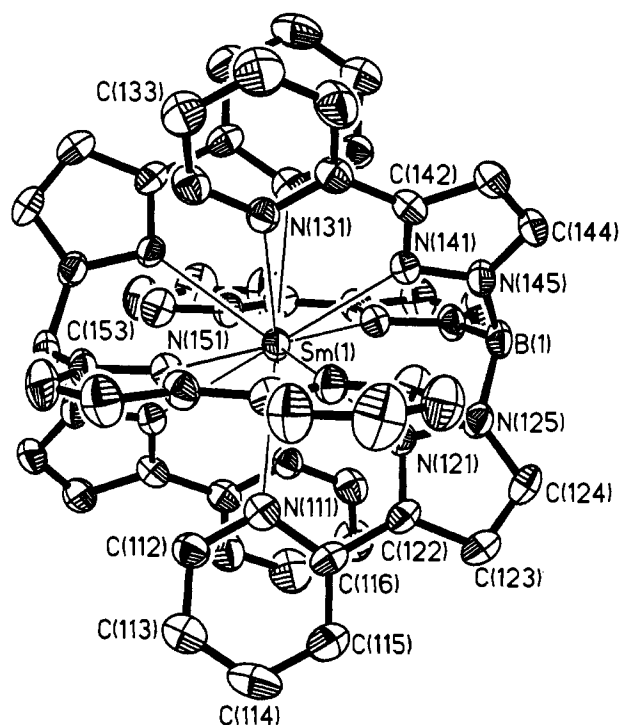
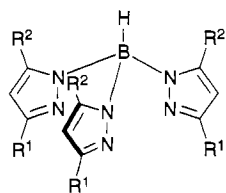


Fig. 1 Crystal structure of the cation of [Sm(L¹)₂][BPh₄]⁻ **1** with thermal ellipsoids at 35% probability. Selected bond lengths (Å) (the values in square brackets are for the independent complex cation): Sm(1)–N(121) 2.661(5) [2.636(5)], Sm(1)–N(141) 2.652(5) [2.651(6)], Sm(1)–N(161) 2.667(6) [2.678(5)], Sm(1)–N(111) 2.935(6) [2.913(6)], Sm(1)–N(131) 2.929(6) [2.976(6)], Sm(1)–N(151) 2.972(6) [2.973(6)].



L¹, R¹ = 2-pyridyl, R² = H
L², R¹ = R² = Me

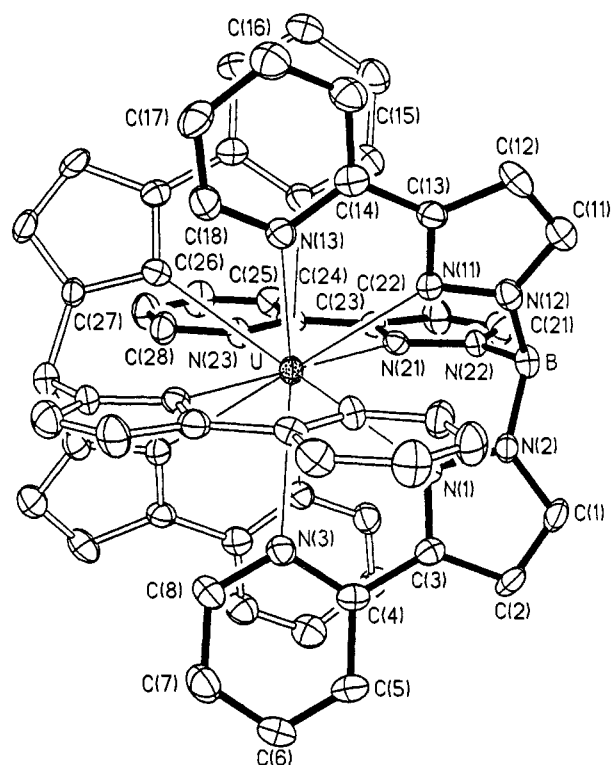


Fig. 2 Crystal structure of the cation of $[U(L^1)_2]I$ **2** with thermal ellipsoids at 35% probability. Selected bond lengths (\AA): U–N(1) 2.693(7), U–N(11) 2.671(7), U–N(21) 2.704(7), U–N(3) 2.981(9), U–N(13) 2.933(8), U–N(23) 2.938(6).

σ -homobenzene; 1,2:3,4:5,6-triiminocyclohexane; 3,6,9-triazatetrayclo[6.1.0.0^{2,4}.0^{5,7}]nonane,¹² in both of which the high coordination number was ascribed to the unusual proximity of the N-donor atoms within each ligand. With more conventional ligands such as polypyridines, coordination numbers of 8 or 9 are more common.¹³

The coordination chemistry of U^{III} is not well developed,¹⁴ in part because of the ease with which the metal can be oxidized to the +4 state, and recent interest in the +3 oxidation state has mostly focused on its organometallic chemistry.¹⁵ Complex **2** is therefore doubly unusual in that it is a rare example of a well defined and structurally characterized U^{III} coordination complex,¹⁶ and it is the first example of an actinoid with N_{12} coordination.¹⁷ The chemistry of the related 1:1 complex $[U(L^1)I(thf)_n]^+$ is currently being developed.

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Footnotes

† Preparations **1**: a mixture of KL^1 (1 mmol) and $SmCl_3 \cdot 6H_2O$ (0.5 mmol) in MeOH (20 cm^3) was stirred for 1 h, after which time an aqueous solution containing excess of $NaBPh_4$ was added. Concentration *in vacuo* produced an off-white precipitate which was collected by filtration and recrystallised by diffusion of ether into a concentrated acetone solution to give colourless blocks. FAB-MS: m/z (%): 1041 (100) $\{[Sm(L^1)_2]^+\}$; IR (KBr disc): $\nu(B-H)/cm^{-1}$ 2480, 2455.

2: solid KL^1 (1 mmol) was added to a slurry of $UI_3(thf)_4$ (0.5 mmol) in thf. The mixture was stirred for 15 min, resulting in almost complete precipitation of product, $[U(L^1)_2]I$ **2** and KI. Addition of $TiBPh_4$ (1 mmol) to the residue followed by filtration gave a turquoise solution. Concentration of the solution produced a dark green microcrystalline solid $[U(L^1)_2][BPh_4]$ **2a**; hexane diffusion into the supernatant solution gave a further crop of **2a** for a combined yield of 0.29 g (72%); IR (KBr disc): $\nu(B-H)/cm^{-1}$ 2482, 2453. Green-black crystals of **2** suitable for X-ray analysis were obtained by slow evaporation of a thf solution.

Repeated attempts at elemental analyses for **1** and **2** consistently gave results with the %N being too low (even with X-ray-quality single crystals) although the %C and %H figures were acceptable. However the IR spectra of the crystals were in each case identical to those of the bulk sample.

‡ Crystal data: (a) $[Sm(L^1)_2][BPh_4] \cdot (Et_2O) [1 \cdot Et_2O]$, $C_{76}H_{68}B_3N_{18}OSm$: $M = 1432.26$, monoclinic, $P2_1/c$, $a = 12.254(2)$, $b = 24.847(4)$, $c = 22.718(4)$ \AA , $\beta = 97.90(1)^\circ$, $V = 6851(2)$ \AA^3 , $Z = 4$, $D_c = 1.389$ $g\ cm^{-3}$, $\mu = 9.18$ cm^{-1} , 6331 unique reflections ($2\theta_{max} = 40^\circ$) were collected at 293 K. Refinement (data: parameter ratio, 7.1) using SHELX93 on all F^2 data converged at $R_1 [F > 4\sigma(F)] = 0.037$, wR_2 (all data) = 0.107. Maximum/minimum residual electron density: +0.36, –0.63 $e\ \text{\AA}^{-3}$. The asymmetric unit contains two independent half-molecules, each astride an inversion centre.

(b) $[U(L^1)_2]I$ **2a**, $C_{48}H_{38}B_2IN_{18}U$: $M = 1253.51$, monoclinic, C_2/c , $a = 21.715(4)$, $b = 12.119(2)$, $c = 18.552(3)$ \AA , $\beta = 107.78(2)^\circ$, $V = 4649(2)$ \AA^3 , $Z = 4$, $D_c = 1.793$ $g\ cm^{-3}$, $\mu = 42.19$ cm^{-1} . 2920 unique reflections ($2\theta_{max} = 46^\circ$) were collected at 244 K. Refinement (data: parameter ratio, 6.1) using SHELXTL-PLUS using 1958 data with $F > 4\sigma(F)$ converged at $R_1 [F > 4\sigma(F)] = 0.033$, wR_2 (all data) = 0.044. Maximum/minimum residual electron density: +0.91, –0.89 $e\ \text{\AA}^{-3}$. The uranium atom lies on an inversion centre, and the iodine atom on a twofold axis.

Crystals of **1** lost solvent rapidly and were mounted in a capillary tube with some of the crystallisation solvent. Both data sets were collected using graphite-monochromatised Mo-K α radiation ($\lambda = 0.71073$ \AA) and were collected for Lorentz, polarisation and absorption effects. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in calculated positions and refined isotropically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information of Authors, Issue No. 1.

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