Synthesis of the New Tripodal Ligand Tris-[3-(2′-pyridyl)pyrazol-1-yl]hydroborate, and the Crystal Structure of its Europium(III) Complex

Angelo J. Amoroso, Alexander M. Cargill Thompson, John C. Jeffery, Peter L. Jones, Jon A. McCleverty* and Michael D. Ward*

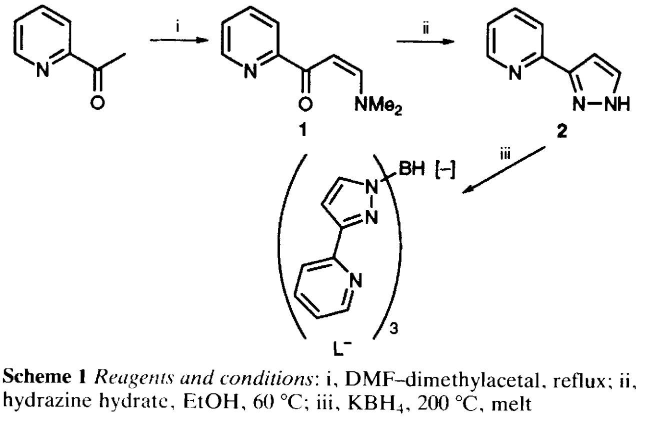
School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK BS8 1TS

The new tripodal ligand tris-[3-(2′-pyridyl)pyrazol-1-yl]hydroborate (L^-), comprising three *N,N*-bidentate chelating arms linked by the apical boron atom, has been synthesized; the crystal structure of $[EuL(MeOH)_2F][PF_6]$ reveals the nine-coordinate metal lying within the hexadentate ligand cavity.

Tripodal ligands (podands) in which three polydentate coordinating arms are attached to a central linking group are popular ligands for conferring high stability on metal complexes. This is exemplified in nature by the siderophore ligands which complex Fe^{III} very effectively.[1] Synthetic tris-chelate podands have been prepared containing a wide variety of side-arms based on chelating groups such as 2,2′-bipyridine,[2] catechol,[3] salicylaldimine[4] and 1,2-diaminoethane.[5] We describe here the synthesis and coordination behaviour of tris-[3-(2′-pyridyl)pyrazol-1-yl]hydroborate, L^-, a new potentially tris-chelating podand ligand based on the well-known tris(pyrazol-1-yl)hydroborate core.[6] Attachment of bulky substituents to the 3-position of the pyrazole rings of tris(pyrazol-1-yl)hydroborates is a popular strategy for preparing complexes in which the metal centre is efficiently shielded, and can result in low coordination numbers and/or unusual patterns of reactivity,[6] but this is the first example of attachment of a ligating group in this position to give a podand with three chelating side-arms linked at the apical boron atom.

The synthesis of the ligand is outlined in Scheme 1† and follows the usual pattern for preparation of substituted tris(pyrazol-1-yl)hydroborates. Molecular modelling studies suggested that second/third row transition metal or lanthanide ions might be a good fit for the cavity of L^-, and accordingly complexes were prepared in methanol using lanthanide ions as their nitrate or chloride salts. Reaction of KL with one equiv. of $EuCl_3 \cdot 6H_2O$ in methanol afforded a clear, colourless solution from which a precipitate appeared slowly on addition of KPF_6. Recrystallisation from MeCN–MeOH–Et_2O afforded X-ray quality crystals of a material whose FAB mass spectrum (*m/z* = 597, 616) suggested the formation of a complex with a 1 : 1 metal : ligand ratio ([EuL] = 597) and a coordinated fluoride ion ([EuLF] = 616). Similar 1 : 1 complexes were obtained with a variety of lanthanides. The X-ray structure‡ of the Eu^{III} complex (Fig. 1) revealed the complex to be $[EuLF(MeOH)_2][PF_6]$, in which the Eu^{III} is nine-coordinated by the six donor atoms of L^-, two methanol ligands and one fluoride (extracted from hexafluorophosphate). The unit cell contains two independent complex units, one in a general position and one astride a mirror plane; only the former is depicted in Fig. 1 and used as a basis for the discussion of the structure, but the bond lengths and angles of the complex unit on the mirror plane are similar. The bonds to the three pyrazolyl nitrogens at the 'top' of the cavity (average length 2.54 Å) are significantly shorter than those to the pyridyl nitrogen atoms at the 'bottom' of the cavity (average length 2.67 Å) which seems to be due to the steric limitations of the ligand—since the three coordinating arms are diverging, closer coordination of the pyridyl donors would cause considerable ligand strain. The ligand is considerably distorted away from C_3 symmetry, particularly in the disposition of the pyridyl rings: whereas the three apical N–B–N angles are fairly similar, the separation between N(121) and N(161) is much less than those between N(121)–N(141) and N(141)–N(161). This allows methanol ligands to attach to the metal in the spaces between N(121) and N(141), and between N(161) and N(141): in fact N(121), N(161), O(172), N(141) and O(171) very roughly describe a pentagonal plane. The coordination geometry of the Eu^{III} is mono-capped square antiprismatic, with N(111), N(151), N(121) and N(161) forming one square plane, N(131), the two oxygen donors and the fluoride ion the next square plane, and N(141) being the cap.

Complexes of Eu^{III} with cryptands and podands containing aromatic nitrogen-based donors are of interest for their luminescence properties, since luminescence from the metal can be sensitised by energy-transfer following excitation of a fully-allowed ligand-based $\pi \rightarrow \pi^*$ transition.[7,8] The emission spectrum (degassed MeOH solution, 293 K) of $[EuLF(MeOH)_2]$ $[PF_6]$ is in Fig. 2. Although the spectrum is not as



Scheme 1 *Reagents and conditions*: i, DMF–dimethylacetal, reflux; ii, hydrazine hydrate, EtOH, 60 °C; iii, KBH_4, 200 °C, melt

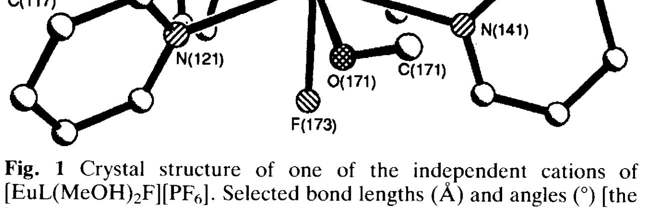


Fig. 1 Crystal structure of one of the independent cations of $[EuL(MeOH)_2F][PF_6]$. Selected bond lengths (Å) and angles (°) [the bond lengths in square brackets are for the equivalent bonds in the other complex cation]: Eu(1)–N(111) 2.533(11) [2.549(10)], Eu(1)–N(131) 2.529(10) [2.492(14)], Eu(1)–N(151) 2.551(10) [2.549(10)], Eu(1)–N(121) 2.648(11) [2.659(10)], Eu(1)–N(141) 2.659(11) [2.660(14)], Eu(1)–N(161) 2.690(10) [2.659(10)], Eu(1)–O(171) 2.466(9) [2.549(8)], Eu(1)–O(172) 2.509(9) [2.549(8)], Eu(1)–F(173) 2.193(7) [2.197(8)]; N(111)–Eu(1)–N(131) 72.7(3), N(111)–Eu(1)–N(151) 65.2(3), N(131)–Eu(1)–N(151) 70.8(3), N(111)–Eu(1)–N(121), 61.6(3), N(131)–Eu(1)–N(141) 61.5(3), N(151)–Eu(1)–N(161) 61.8(3), N(121)–Eu(1)–N(141) 135.7(3), N(121)–Eu(1)–N(161) 79.6(3), N(141)–Eu(1)–N(161) 129.5(3), N(112)–B(1)–N(132) 110.0(11), N(132)–B(1)–N(152) 108.9(11), N(112)–B(1)–N(152) 115.6(11).

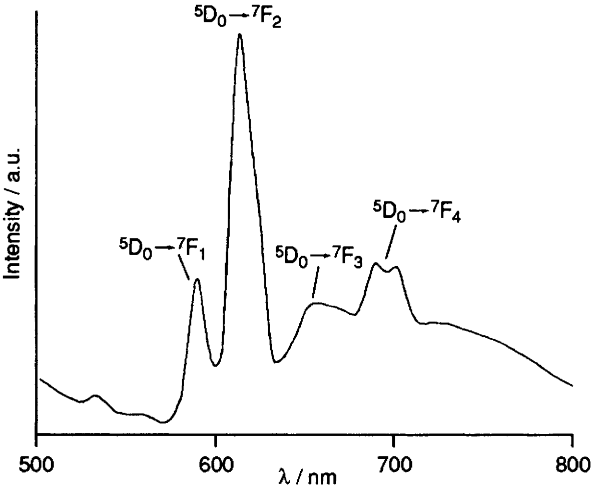


Fig. 2 Luminescence spectrum of $[EuL(MeOH)_2F][PF_6]$ in degassed methanol solution at 293 K

well resolved as those of fully-encapsulated cryptand complexes,[7] probably due to partial deactivation of the excited state by exchange of coordinated solvent molecules, four of the expected five components of the $^5D_0 \rightarrow {}^7F_{0-4}$ transition are present.[8] Identical spectra were obtained on excitation of either of the two ligand-based $\pi \rightarrow \pi^*$ transitions (λ_{max} = 244 and 286 nm).

The presence of three monodentate ligands on the metal suggests that suitable bridging ligands containing chelating acetylacetonate or catecholate sites may be able to bind to the metal allowing buildup of polynuclear complexes; thus attachment of the pendant catechol group of $[Ru(terpy)\{4'\text{-}(3,4\text{-dihydroxyphenyl})terpy\}]^{2+}$ (terpy = 2,2′ : 6′,2″-terpyridine)[9] to a {EuL} fragment would afford a binuclear species containing two photoactive chromophores. We are currently examining this possibility.

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Footnotes

† *Preparation* of **1** and **2**: A solution of 2-acetylpyridine (24.2 g, 0.2 mol) in DMF–dimethylacetal (40 cm^3) was heated to reflux for 16 h (ref. 10). After concentration *in vacuo*, the resulting crude solid was recrystallised from $CHCl_3$–hexane to give 22.8 g (65%) of crystalline **1**. A mixture of **1** (22.0 g, 0.125 mol), hydrazine hydrate (40 cm^3) and ethanol (30 cm^3) was then heated to 60 °C with stirring for 30 min. After addition of water (150 cm^3) and overnight refrigeration the resulting off-white precipitate was filtered off, dried and recrystallised from CH_2Cl_2–hexane to give 11.5 g (63%) of crystalline **2**. Both **1** and **2** gave satisfactory ^{1}H NMR and EI mass spectra.

Preparation of KL: A mixture of **2** (5.8 g, 40 mmol) and KBH_4 (0.54 g, 10 mmol) was heated to 200 °C for 1 h. The melt was then cooled, excess **2** was dissolved in toluene, and the remaining white solid was collected and dried. Yield 80%; IR ν_{B-H}/cm^{-1} (KBr disc) 2444; EI MS *m/z* = 444 (L^-); ^{1}H NMR ([$^2H_6$] acetone) δ 8.54 (1 H, ddd, *J* 4.8, 1.8, 1.0 Hz, pyridyl H^6), 7.7–7.8 (3 H, m, pyridyl H^3/H^5 and pyrazolyl H^4 or H^5), 7.15 (1 H, ddd, *J* 7.3, 4.8, 1.5 Hz, pyridyl H^4), 6.66 (1 H, d, *J* 2.2 Hz, pyrazolyl H^5 or H^4). Satisfactory analytical data (C, H, N) were obtained.

‡ *Crystal data*: $[Eu\{HB(C_8N_3H_6)_3\}(MeOH)_2F]_{1.5}[PF_6]_{1.5}\cdot MeOH\cdot Et_2O\cdot(H_2O)_2$, colourless blocks, M = 1374.7, orthorhombic, space group *Pbnm* [non-standard setting of *Pnma* (no. 62)], a = 13.175(7), b = 19.544(11), c = 43.41(3) Å, U = 11177(11) Å^3, Z = 8, D_{calc} = 1.639 g cm^{-3}, Mo-Kα radiation ($\bar{\lambda}$ = 0.71073 Å), μ(Mo-Kα) = 1.811 mm^{-1}. The crystal was sealed in a capillary containing some of the recrystallisation solvent to prevent facile loss of lattice solvent. 7432 independent reflections were collected at 293 K on a Siemens R3m/V four-circle diffractometer with $2\theta_{max}$ = 45°. The structure was solved by conventional heavy-atom methods and was refined by full-matrix least-squares analysis on all F^2 data (using SHELX93). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic thermal parameters (1.5 × U_{iso} of the parent carbon atoms). Refinement converged at R_1 = 0.065, wR_2 = 0.188. Potential problems with overlapping low-angle reflections due to the long *c*-axis were minimised by using a narrow detector aperture. The asymmetric unit contains 1.5 molecules of the complex, one in a general position with no imposed symmetry and the other astride a mirror plane.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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