A dinuclear double-helical complex of potassium ions with a compartmental bridging ligand containing two terdentate N-donor fragments

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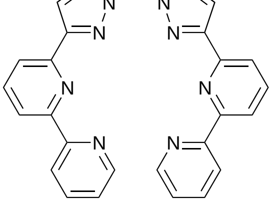
The compartmental bridging ligand bis{3-[6′-(2,2′-bipyridyl)]pyrazol-1-yl}hydroborate (L^-), which contains two chelating terdentate N-donor arms linked by an anionic $-BH_2-$ bridge, forms a dinuclear double-helical complex K_2L_2 with K^+ ions.

Recently helicates have become a well known structural motif in supramolecular coordination chemistry.[1–4] They are of particular interest not just for their appealing structures but also because of the processes of molecular recognition and self-assembly that are required for their formation. Their formation requires (*i*) ligands which contain several discrete metal-ion binding domains, and (*ii*) metal ions with specific preferences for particular coordination geometries that match the ligand binding sites. It is the appropriate combination of these two factors which dictates the outcome of the self-assembly process. Thus, a ligand which has two terdentate domains might give a double helicate with a transition-metal ion (coordination number six) but a triple helicate with a lanthanide (coordination number nine).[2–5] In contrast, linear oligopyridines can partition themselves according to the dictates of the metal ion, and give different structures with Cu^I (when the ligand is partitioned into bidentate domains) and Cd^{II} or Ni^{II} (when it is split into terdentate domains).[1]

The requirement of the metal ion for a specific geometry or coordination number is principally controlled by charge/size effects: thus Cu^I and Ag^I have a preference for (usually) four-coordination, whereas transition-metal dications generally prefer six-coordination and lanthanides prefer approximately nine-coordination.[1–5] In contrast the use of s-block metals in double helicates is virtually unknown. The only certain example, recently published by Bell and Jousselin, is a 2 : 2 complex of Na^+ with a 'heterohelicene' ligand which is preorganised into a helical shape and therefore inevitably imposes a helical structure on its complexes.[6] The complex was characterised by NMR spectroscopy and mass spectrometry, but not crystallographically. It is also possible that the 1 : 1 adduct of 2,2′ : 6′,2″ : 6″,2‴ : 6‴,2⁗-quinquepyridine with $LiClO_4$ is a double helicate.[7] Cram and coworkers recently described a macrocyclic ligand containing two phenanthroline binding sites that was twisted into a helically chiral conformation by virtue of binaphthyl groups incorporated into the cycle; this imposes a helically chiral geometry on alkali-metal cations due to its preorganisation.[8]



L^-

We describe here the preparation of the new compartmental bis-terdentate ligand bis{3-[6′-(2,2′-bipyridyl)]pyrazol-1-yl}-hydroborate (L^-) as its potassium salt KL, and the crystal structure of this salt which reveals a double-helical complex of stoichiometry K_2L_2. The ligand was prepared by reaction of 6-(3-pyrazolyl)-2,2′-bipyridine[9] with KBH_4,† which is the usual route for preparing bidentate bis(pyrazol-1-yl)hydroborates[10] and tridentate tris(pyrazol-1-yl)hydroborates[11] from substituted pyrazoles. All of the spectroscopic and analytical data were consistent with formation of KL, in which two terdentate N-donor arms are linked by an anionic $-BH_2-$ fragment. Even using a fourfold excess of the pyrazole, we found that only the bis(pyrazolyl)borate was obtained, and this is the first example of a bis(pyrazolyl)borate functionalised in this manner so that each arm becomes chelating rather than monodentate. The compound was crystallised by slow evaporation from chloroform to give colourless prisms; the crystal structure is in Fig. 1,‡ and reveals that in the solid state the

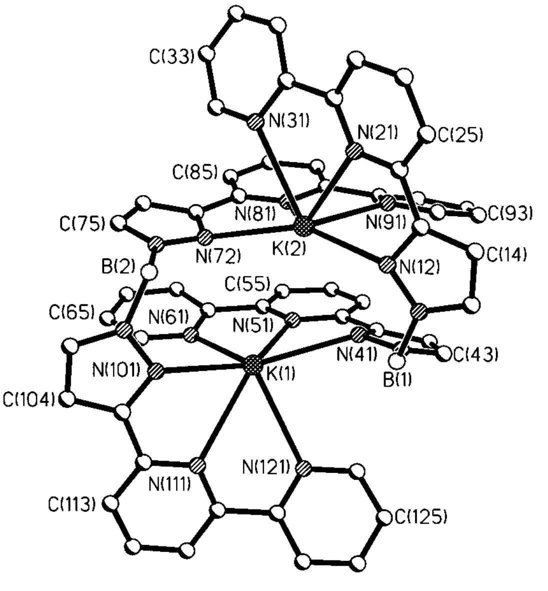


Fig. 1 Crystal structure of K_2L_2. Selected bond lengths (Å) and angles (°): K(1)–N(101) 2.772(5), K(1)–N(41) 2.784(6), K(1)–N(61) 2.816(6), K(1)–N(51) 2.857(5), K(1)–N(111) 2.927(5), K(1)–N(121) 2.956(6), K(2)–N(72) 2.766(6), K(2)–N(12) 2.777(6), K(2)–N(91) 2.802(6), K(2)–N(81) 2.855(6), K(2)–N(31) 2.877(6), K(2)–N(21) 2.890(6), K(1)···K(2) 3.954(2); N(101)–K(1)–N(41) 150.1(2), N(101)–K(1)–N(61) 84.2(2), N(41)–K(1)–N(61) 116.1(2), N(101)–K(1)–N(51) 139.3(2), N(41)–K(1)–N(51) 59.2(2), N(61)–K(1)–N(51) 57.4(2), N(101)–K(1)–N(111) 57.3(2), N(41)–K(1)–N(111) 134.9(2), N(61)–K(1)–N(111) 95.4(2), N(51)–K(1)–N(111) 132.5(2), N(101)–K(1)–N(121) 111.9(2), N(41)–K(1)–N(121) 80.3(2), N(61)–K(1)–N(121) 115.3(2), N(51)–K(1)–N(121) 97.8(2), N(111)–K(1)–N(121) 56.4(2), N(72)–K(2)–N(12) 150.1(2), N(72)–K(2)–N(91) 116.3(2), N(12)–K(2)–N(91) 85.4(2), N(72)–K(2)–N(81) 58.8(2), N(12)–K(2)–N(81) 141.5(2), N(91)–K(2)–N(81) 58.1(2), N(72)–K(2)–N(31) 80.7(2), N(12)–K(2)–N(31) 114.4(2), N(91)–K(2)–N(31) 105.8(2), N(81)–K(2)–N(31) 89.2(2), N(72)–K(2)–N(21) 135.8(2), N(12)–K(2)–N(21) 59.4(2), N(91)–K(2)–N(21) 88.5(2), N(81)–K(2)–N(21) 124.7(2), N(31)–K(2)–N(21) 56.6(2).

compound is in fact a double-helical complex K_2L_2. The double-helical structure is emphasised in Fig. 2.

Each K^+ ion is coordinated in an irregular six-coordinate environment by two terdentate arms, one from each of the two ligands. The K–N bond distances around K(1) lie in the range 2.77–2.96 Å and those around K(2) lie in the range 2.77–2.89 Å, which are comparable to those found for the K^+ complex of one of Bell's cyclic torand ligands based on pyridyl donors[12] and for $[K(phen)_3][BPh_4]$.[13] There are additional weak interactions between K(1) and N(72) [3.469(5) Å] and between K(2) and N(41) [3.437(5) Å], which probably just arise from the steric constraints of the complex and do not represent true bridging behaviour by N(41) and N(71). Each ligand donates one terdentate arm to each of the two metal ions, a binding mode which is facilitated by the flexible $-BH_2-$ 'hinge' at the centre of each ligand. The N–B–N angles are 111.0(6)° at B(1) and 110.3(5)° at B(2), both very close to the ideal tetrahedral value which indicates that this mode of coordination is not imposing any steric strain on the ligands: this is no doubt facilitated by the ability of K^+ to tolerate a highly irregular coordination environment. The two terdentate fragments of each ligand are therefore approximately mutually perpendicular.

The structure appears to be stabilised by aromatic π-stacking interactions (3.2–3.6 Å) between near-parallel, overlapping sections of the two ligands. This is a common feature of helical complexes[1–4] but one which is not essential for helicate formation: the matching of metal-ion coordination geometry and ligand donor properties is probably more important.[14] The metal–metal separation [3.954(2) Å] is shorter than that in metallic potassium (4.54 Å) but significantly longer than the sum of two ionic radii for K^+ ions (*ca.* 2.7 Å). The crystal contains opposite enantiomers in the unit cell, related by an inversion centre. As with all 'supramolecular' structures based on labile metal ions, the solid-state structure is not necessarily wholly representative of the solution behaviour which could be considerably more complex.

This complex has several unusual features. First, it is to date the only structurally characterised double-helical complex with an s-block metal. Secondly, unlike the helical complexes described by Bell and Jousselin[6] and Cram and coworkers,[8] the helical geometry is not imposed by a preorganised ligand but arises naturally from the assembly of achiral ligands around the metal ions, as normally occurs for the transition-metal and lanthanide based helicates.[1–5] Thirdly, it is an unusual example of alkali-metal coordination by an open-chain nitrogen donor ligand.[13] Although several examples of alkali-metal complexes with exclusively N-donor ligands are known, they usually require highly preorganised ligands such as torands,[12,15] macrocycles[16] and cryptands,[17] where the cavity size is a particularly good match for an alkali-metal cation, and the coordination geometry is particulary unsuited to a transition-metal ion, neither of which is true in K_2L_2. It is probable that, considering the predominantly ionic nature of the complex, the affinity of L^- for K^+ is enhanced by the negative charge of the ligand.

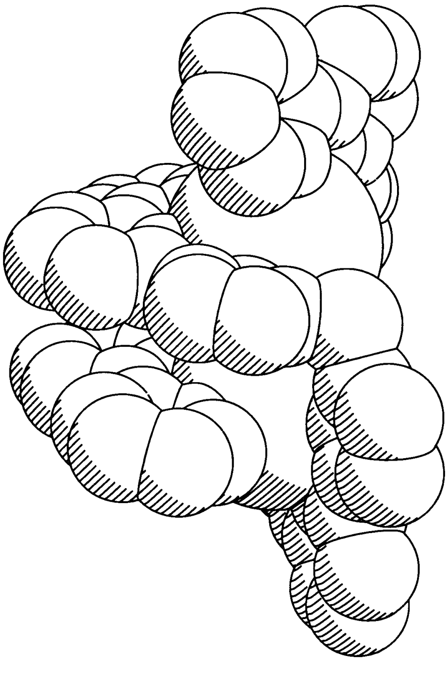


Fig. 2 Space-filling diagram of K_2L_2

Footnotes

† *Preparation* of K_2L_2: a mixture of 6-(3-pyrazolyl)-2,2′-bipyridine (0.25 g, 1.13 mmol) and KBH_4 (0.015 g, 0.28 mmol) was finely ground together in a mortar to ensure intimate mixing. The solid mixture was then heated to 190 °C under N_2 for 3 h (it melted at *ca.* 120 °C and H_2 evolution was observed to start at *ca.* 150 °C). After cooling the mixture the solid was washed with toluene to remove excess unreacted 6-(3-pyrazolyl)-2,2′-bipyridine; the remaining solid was collected by filtration and dried to give KL (0.040 g, 30%). Negative-ion electrospray MS: *m/z* 455 (100%, L^-). A satisfactory elemental analysis was obtained.

‡ *Crystal data* for K_2L_2: $C_{52}H_{40}B_2K_2N_{16}$, colourless prisms, crystal size 0.40 × 0.25 × 0.10 mm, $M = 988.82$, triclinic, space group $P\bar{1}$, $a = 9.858(2)$, $b = 13.566(2)$, $c = 18.4766(12)$ Å, $\alpha = 87.541(10)$, $\beta = 85.050(9)$, $\gamma = 83.102(9)$°, $U = 2442.5(6)$ Å^3, $Z = 2$, $D_c = 1.345$ g cm^{-3}, μ(Mo-Kα) = 0.25 mm^{-1}. Using a Siemens SMART diffractometer and graphite-monochromated Mo-Kα X-radiation, 11128 data were collected at −100 °C with $2\theta_{max} = 46.5$°, and merged to give 6871 unique data ($R_{int} = 0.067$). The data were corrected for absorption effects by an empirical method based on multiple measurements of equivalent reflections. The structure was solved by direct methods, and refined on all F^2 data using the SHELX suite of programs (version 5.03). All non-hydrogen atoms were refined with anisotropic thermal parameters. Aromatic C–H hydrogen atoms were included in calculated positions with isotropic thermal parameters 20% higher than those of the parent atoms; the four B–H hydrogen atoms were located directly and their thermal parameters refined freely. Refinement of 665 parameters using 6616 data converged at $R_1 = 0.088$, $wR_2 = 0.207$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this information should quote the full literature citation and the reference number 182/364.

References

1 E. C. Constable, *Prog. Inorg. Chem.*, 1994, **42**, 67.
2 D. Philp and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1155.
3 D. S. Lawrence, T. Jiang and M. Levett, *Chem. Rev.*, 1995, **95**, 2229.
4 D. B. Amabilino and J. F. Stoddart, *Chem. Rev.*, 1995, **95**, 2725.
5 B. Hasenknopf and J.-M. Lehn, *Helv. Chim. Acta*, 1996, **79**, 1643; C. Piguet, J.-C. G. Bünzli, G. Bernardinelli, G. Hopfgartner and A. F. Williams, *J. Am. Chem. Soc.*, 1993, **115**, 8197.
6 T. W. Bell and H. Jousselin, *Nature*, 1994, **367**, 441.
7 G. Oepen and F. Vögtle, *Liebigs Ann. Chem.*, 1979, 2114.
8 J. K. Judice, S. J. Keipert and D. J. Cram, *J. Chem. Soc., Chem. Commun.*, 1993, 1323.
9 J. C. Jeffery, P. L. Jones, K. L. V. Mann, E. Psillakis, J. A. McCleverty, M. D. Ward and C. M. White, *Chem. Commun.*, 1997, 175.
10 S. Trofimenko, J. C. Calabrese and J. S. Thompson, *Inorg. Chem.*, 1992, **31**, 974 and references therein.
11 S. Trofimenko, *Chem. Rev.*, 1993, **93**, 943.
12 T. W. Bell, P. J. Cragg, M. G. B. Drew, A. Firestone and D.-I. A. Kwok, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 345.
13 G. Bombieri, G. Bruno, M. D. Grillone and G. Polizzotti, *Acta Crystallogr., Sect. C*, 1984, **40**, 2011.
14 E. C. Constable, M. J. Hannon and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1993, 1883.
15 T. W. Bell, P. J. Cragg, M. G. B. Drew, A. Firestone, A. D.-I. Kwok, J. Liu, R. T. Ludwig and A. T. Papoulis, *Pure Appl. Chem.*, 1993, **65**, 361.
16 E. C. Constable, M. J. Doyle, J. Healy and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1988, 1262.
17 J.-M. Lehn and J. B. R. De Vains, *Helv. Chim. Acta*, 1992, **75**, 1221 and references therein.

Received, 25th November 1996; Com. 6/07984I