

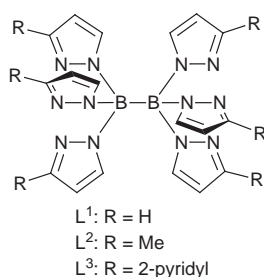
Dinuclear molybdenum and gadolinium complexes of new 'back-to-back' B—B linked bis[tris(pyrazolyl)borate] ligands

Nicholas C. Harden, John C. Jeffery, Jon A. McCleverty,* Leigh H. Rees and Michael D. Ward*

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

Some B—B linked 'back-to-back' bis[tris(pyrazolyl)borate] bridging ligands [(Rpz)₃B—B(Rpz)₃] (where Rpz is 3-R-pyrazolyl) have been prepared: when R = H or Me the ligands have two terdentate compartments, and have been used to prepare a variety of molybdenum complexes; when R = 2-pyridyl, the ligand has two B—B linked hexadentate cavities which each bond a lanthanide(III) ion.

Since their introduction by Trofimenko,¹ the tris(pyrazolyl)borates (Tp)[†] have proven to be a very popular and versatile class of ligand² with applications as diverse as modelling metalloprotein active sites³ and the preparation of complexes with unexpected and manipulable magnetic behaviour and non-linear optical properties;⁴ it appears that the use of tris(pyrazolyl)borates shows no sign of slowing down. The use of the Tp fragment as a component of multinucleating bridging ligands however is almost unknown. This is in strong contrast to *e.g.* oligopyridyl ligands, where it is synthetically straightforward to link together two chelating fragments to give 'back-to-back' ligands for the preparation of multinuclear complexes, and the use of such bridging ligands to study electronic and magnetic metal–metal interactions is now commonplace.⁵ That Tp-based ligands have not been exploited in the same way is due to the lack of simple synthetic methods for functionalisation of the capping BH group. There are just two examples of dinucleating bridging ligands based on Tp fragments: [(C₅H₄[B(pz)₃]₂Fe)²⁻, in which the two Tp fragments are attached to the cyclopentadienyl rings of a central ferrocenyl moiety which therefore acts as a 'ball-bearing' spacer,⁶ and [(pz)₃B—B(pz)₃]²⁻ (L¹), in which the two Tp fragments are linked back-to-back directly by a B—B bond.⁷



Despite the obvious appeal of ligands of the type [(pz)₃B—B(pz)₃]²⁻ as a basis for the preparation of multinuclear complexes only one example, containing two {Pd(η³-allyl)} fragments, was reported ten years ago.⁷ As part of our general interest in metal–metal interactions in multinuclear complexes we have re-investigated this area, and report here our initial results which show that (i) these ligands offer a new route into multinuclear complexes containing redox-active and paramagnetic {TpMo} fragments,^{8–10} and (ii) the synthetic method can be extended to allow preparation of a dodeca-

dentate 'super-podand' ligand containing two B—B linked hexadentate cavities.

Initially we prepared the known ligand L¹ and used it to prepare [Mo(CO)₂(NO)₂(L¹)] (1) in the same way that the mononuclear analogue [Mo(CO)₂(NO)(Tp)] is prepared from Tp.^{8,§} The crystal structure (Fig. 1)[‡] confirmed the dinuclear nature of the complex, and the staggered conformation of the {Mo(CO)₂(NO)(pz)₃} groups with respect to the B—B bond. In principle, this molecule must exist as a number of conformers because of rotation about the B—B bond, but this could not be detected crystallographically because the NO and CO ligands were disordered about the threefold rotation axis. We also prepared the new ligand [(Mepz)₃B—B(Mepz)₃]²⁻ (L²; Mepz = 3-methylpyrazolyl) as a back-to-back analogue of Tp^{Me,Me} because the methyl substituents at the C³ position play an important role in stabilising Mo complexes of this sort, and used L² to prepare

[‡] Crystallographic data. [Mo(CO)₂(NO)₂(L¹)] (1): C₂₂H₁₈B₂Mo₂N₄O₁₆, *M* = 788.0; crystal size 0.1 × 0.1 × 0.1 mm³, rhombohedral, space group *R*3̄, *a* = 13.029(2), *c* = 14.916(4) Å, *U* = 2192.9(7) Å³, *Z* = 3, *D*_c = 1.790 g cm⁻³, *F*(000) = 1170, μ(Mo-Kα) = 0.923 mm⁻¹. Data were collected on a Siemens SMART diffractometer to 2θ_{max} = 55° at -100 °C. Refinement of 2230 unique data (176 parameters, 73 restraints) using the SHELXTL 5.03 package¹¹ converged at *R*₁ = 0.0352, *wR*₂ = 0.0746. The NO and two CO ligands at each metal are disordered about the threefold axis which passes through the B—B bond; thus, each coordination site is occupied by a disordered mixture of CO (site occupancy 0.67) and NO (site occupancy 0.33). The thermal parameters on these disordered atoms, and on some of the pyrazolyl ring atoms, required restraining to keep the refinement stable. The crystals were enantiomeric twins (0.69 : 0.31).

[Gd(NO₃)₂]₂(L³)] · 2.4(dmF) [5 · 2.4(dmF)]: C₄₈H₃₆B₂Gd₂N₂₂O₁₂ · 2.4(C₃H₇NO), *M* = 1624.6; crystal size 0.05 × 0.1 × 0.15 mm³, tetragonal, space group *P*4₂/n, *a* = 16.622(6), *b* = 16.622(4), *c* = 24.19(5) Å, *U* = 6682(5) Å³, *Z* = 4, *D*_c = 1.628 g cm⁻³, *F*(000) = 3262, μ(Mo-Kα) = 2.050 mm⁻¹. Data were collected on a Siemens SMART diffractometer to 2θ_{max} = 40° at -100 °C. Refinement of 3059 unique data (600 parameters, 477 restraints) using the SHELXTL 5.03 package¹¹ converged at *R*₁ = 0.1072, *wR*₂ = 0.2559. The two ends of the molecule are crystallographically equivalent, with a *C*₂ axis through the B—B bond and perpendicular to it. These crystals diffracted very weakly due to a combination of their small size and substantial disorder: one of the bidentate pyridyl/pyrazolyl arms, one of the nitrate ligands, and a dmF molecule are all disordered over two orientations (site occupancies 0.60/0.40). Another dmF molecule is disordered about a *C*₂ axis. Thus, over one third of the atoms in the structure are disordered over two sites, and numerous restraints on the thermal parameters and geometries of the disordered components were required to keep the refinement stable. Only the major component of the disorder is shown in Fig. 2.

CCDC reference number 440/035.

[†] We use the notation of Trofimenko (ref. 2) in which Tp^{A,B} means that all three pyrazolyl rings have a substituent A at C³ and B at C⁵.

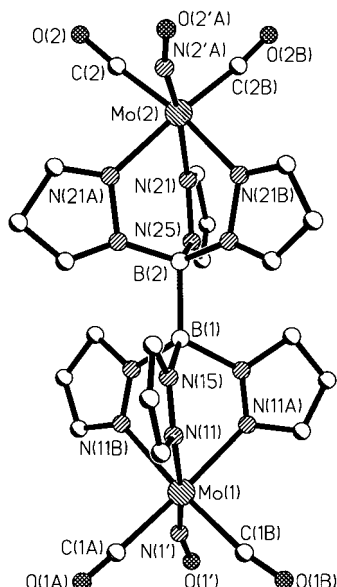


Fig. 1 Crystal structure of complex **1**. Selected bond distances (Å): Mo(1)—N(11) 2.216(13), Mo(1)—C(1A) 2.05(2), Mo(1)—N(1) 1.81(3), Mo(2)—N(21), 2.185(12); Mo(2)—C(2), 1.95(2); Mo(2)—N(2'A), 1.75(3); B(1)—B(2), 1.749(13). The poor precision of the Mo—carbonyl and Mo—nitrosyl distances is a consequence of the NO/CO disorder

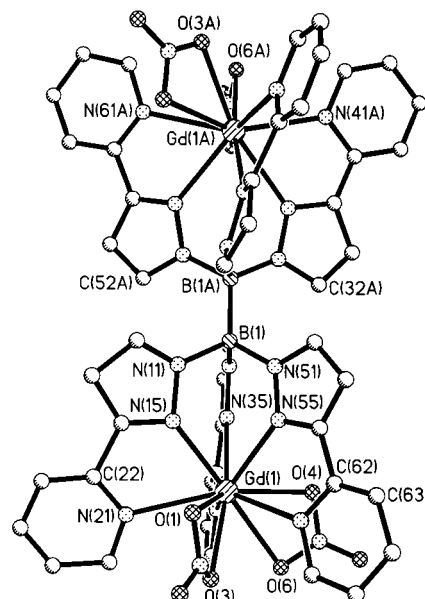


Fig. 2 Crystal structure of complex **5**. Given the relatively poor level of the refinement, arising from the small crystal size and extensive disorder, metric parameters are not given. We note however that the bond lengths and angles are comparable with those of the mononuclear lanthanide analogues $[M(Tp^{2-Py,H})(NO_3)_2]$ (ref. 12)

$[Mo(CO)_2(NO)]_2(L^2)$ (**2**). Further functionalisation of the two Mo fragments of **2** proved to be straightforward, using the same conditions as have been established for reactions of mononuclear $[Mo(CO)_2(NO)(Tp^{Me,Me})]$.^{9,10} Thus, reaction of **2** with NOCl afforded $[MoCl_2(NO)]_2(L^2)$ (**3**) which reacted further with 4-(*tert*-butyl)pyridine and Et₃N to give $[MoCl(NO)(Bu^t-py)]_2(L^2)$ (**4**). Complex **4** contains two 17-electron (paramagnetic) metal centres which are also electrochemically active, undergoing both 17e–16e and 17e–18e (e = valence electrons) couples.¹⁰ Cyclic voltammetry of **4** in thf showed that the two one-electron oxidations are coincident at $E_{1/2} = +0.16$ V *vs.* Fc/Fc⁺, but the two one-electron reductions are separated by 90 mV ($E_{1/2} = -2.11$ and -2.20 V *vs.* Fc/Fc⁺), indicating a weak Coulombic interaction across the B—B bond. The room-temperature EPR

spectrum of **4** revealed a signal at $g = 1.979$, consisting of superimposed singlet, sextet and undecet components with a hyperfine coupling A_{Mo} of 2.5 mT, *i.e.* exactly consistent with an exchange interaction between the two unpaired spins such that $|J| \gg A_{Mo}$ (where J is the exchange coupling constant and A_{Mo} is the hyperfine coupling).¹⁰ At 77 K a half-field $\Delta m_s = 2$ signal was also observed. These observations all suggest that **4** will be able to act as a versatile precursor for the preparation of higher-nuclearity species with interesting magnetic and electrochemical properties: for example use of a bridging ligand such as 4,4'-bipyridine in place of monodentate pyridine could give oligomeric chains with alternating 4,4'-bipyridyl and B—B bridges.

Our second target was the preparation of the 'superpodand', $[3-(2-py)pz]_3B-B[3-(2-py)pz]_3]^{2-}$ (L^3 ; py = pyridyl), prepared using the same general method used for L^1 and L^2 , *i.e.* by direct reaction of 3-(2-pyridyl)pyrazole with $B_2(NMe_2)_4$.⁹ We have previously shown that the hexadentate cavity of $Tp^{2-Py,H}$ is ideal for lanthanide ions and have prepared a range of complexes $[Ln(Tp^{2-Py,H})(NO_3)_2]$.¹² Accordingly reaction of K_2L^3 with $Gd(NO_3)_3 \cdot 6H_2O$ afforded X-ray quality crystals of $[Gd(NO_3)_2]_2(L^3)$ (**5**) (Fig. 2).[†] The structure confirms the bis-hexadentate nature of the ligand, and the coordination environment about each metal ion is similar to those observed for the mononuclear analogues $[Ln(Tp^{H,Py})(NO_3)_2]$. Again the two sets of three pyrazolyl groups are staggered about the B—B bond.

Complexes of lanthanides have potential medical applications such as luminescent probes for bioimmunoassays (Eu, Tb) and contrast reagents for magnetic resonance imaging (Gd), not to mention their use as components of magnetic materials because of their high magnetic moments. The binucleating ligand L^3 therefore offers considerable scope for the preparation of multinuclear lanthanide complexes with interesting applications.

Acknowledgements

We are grateful to the EPSRC Chemistry Programme for studentships which have supported this work.

Syntheses. The new compounds K_2L^2 and K_2L^3 were prepared by the same route used for K_2L^1 , *i.e.* reaction of the appropriate pyrazole (4 equiv.), the potassium salt of the same pyrazole (2 equiv.) and $(Me_2N)_2B-B(NMe_2)_2$ (1 equiv.) in toluene at reflux for 20 h.⁷ The solid products were filtered off, washed with diethyl ether, and dried. As noted in ref. 7 these products are difficult to purify for solubility reasons, and so were used crude. However the presence of the correct product was established by negative-ion FAB mass spectrometry in each case.

Complexes **1** and **2** were prepared from K_2L^1 and K_2L^2 by the same sequence of reactions used to prepare their mononuclear counterparts from KTp and $KTp^{Me,Me}$ (ref. 8); purification was by column chromatography (silica, CH_2Cl_2), the main dark yellow band being collected in each case to give yields of *ca.* 60% for both complexes. Conversion of **2** to **3** by reaction with NOCl in CH_2Cl_2 also followed the published method (ref. 9). Recrystallisation of the crude product from CH_2Cl_2 –hexane gave **3** as a yellow-green solid in 63% yield. Reaction of **3** with 4-(*tert*-butyl)pyridine to give **4** followed the method of ref. 10; purification by column chromatography [silica, CH_2Cl_2 –thf (98 : 2)] gave the green product in 28% yield. Correct elemental analyses ($\pm 0.4\%$) for C, H and N were obtained in every case and correct molecular ions were observed in the FAB mass spectra.

Complex **5** was prepared by reaction of K_2L^3 (0.25 g, 0.28 mmol) with $Gd(NO_3)_3 \cdot 6H_2O$ (0.23 g, 0.51 mmol) in MeOH for 3 h. The resulting white precipitate was filtered off, dried, and recrystallised by diffusion of diethyl ether vapour into a concentrated dmf solution to give X-ray quality crystals of **5** (0.085 g, 23%). A correct elemental analysis (C, H, N) was obtained.

References

- 1 S. Trofimenko, *J. Am. Chem. Soc.*, 1967, **89**, 3170; *Inorg. Chem.*, 1970, **1**, 99.
- 2 S. Trofimenko, *Chem. Rev.*, 1993, **93**, 942.
- 3 N. Kitajima and Y. Moro-oka, *J. Chem. Soc., Dalton Trans.*, 1993, 2665; N. Kitajima, K. Fujisawa, M. Tanaka and Y. Moro-oka, *J. Am. Chem. Soc.*, 1992, **114**, 9232; S. Hikichi, T. Ogihara, K. Fujisawa, N. Kitajima, M. Akita and Y. Moro-oka, *Inorg. Chem.*, 1997, **36**, 4539; A. Kremer-Aach, W. Klaui, R. Bell, A. Strerath, H. Wunderlich and D. Mootz, *Inorg. Chem.*, 1997, **36**, 1552.
- 4 B. J. Coe, T. A. Hamor, C. J. Jones, J. A. McCleverty, D. Bloor, G. H. Cross and T. L. Axon, *J. Chem. Soc., Dalton Trans.*, 1995, 673; V. A. Ung, A. M. W. Cargill Thompson, D. A. Bardwell, D. Gatteschi, J. C. Jeffery, J. A. McCleverty, F. Totti and M. D. Ward, *Inorg. Chem.*, 1997, **36**, 3447.
- 5 V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759; M. D. Ward, *Chem. Soc. Rev.*, 1995, 121.
- 6 F. F. de Biani, F. Jäckle, M. Spiegler, M. Wagner and P. Zanello, *Inorg. Chem.*, 1997, **36**, 2103.
- 7 C. P. Brock, M. K. Das, R. P. Minton and K. Niedenzu, *J. Am. Chem. Soc.*, 1988, **110**, 817.
- 8 J. A. McCleverty, D. Seddon, N. A. Bailey and N. W. Walker, *J. Chem. Soc., Dalton Trans.*, 1976, 898.
- 9 M. Cano, J. V. Heras, A. Monge, E. Gutierrez, C. J. Jones, S. L. W. McWhinnie and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1992, 2435.
- 10 A. Das, J. C. Jeffery, J. P. Maher, J. A. McCleverty, E. Schatz, M. D. Ward and G. Wollermann, *Inorg. Chem.*, 1993, **32**, 2145; A. J. Amoroso, A. M. W. Cargill Thompson, J. P. Maher, J. A. McCleverty and M. D. Ward, *Inorg. Chem.*, 1995, **34**, 4828.
- 11 SHELXTL 5.03 program system, Siemens Analytical X-Ray Instruments, Madison, WI, USA, 1995.
- 12 P. L. Jones, A. J. Amoroso, J. C. Jeffery, J. A. McCleverty, E. Psilakis, L. H. Rees and M. D. Ward, *Inorg. Chem.*, 1997, **36**, 10.

*Received in Basel, Switzerland, 24th February 1998;
Letter 8/03034K*