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# Macropolyhedral boron-containing cluster chemistry. Characterisation of rigid 77-atom $[Pt(B_{18}H_{20})_2]^{2-}$ dianion isomers and an unusual metallaborane homophilic interaction

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Reaction of $[Pt(cod)Cl_2]$ (cod = cycloocta-1,5-diene) with $[NEt_4]_2$[*anti*-$B_{18}H_{20}$] or with [*syn*-$B_{18}H_{22}$] and tmnda (tmnda = *N*,*N*,*N*′,*N*′-tetramethylnaphthalene-1,8-diamine) resulted in the generation of [Pt(*anti*-$B_{18}H_{20})_2]^{2-}$ or [Pt(*syn*-$B_{18}H_{20})_2]^{2-}$ dianions, for which intramolecular steric crowding imposes rigid slab structures, and which have unusual intimately packed anion-layer structures in their salts in the solid state.

In boron-containing cluster chemistry there appears, at first sight, to be a natural barrier to cluster size at the twelve-vertex icosahedron. This twelve-vertex barrier may be crossed by using cluster 'puncture and expansion' reactions, but at present this approach has an effective practical barrier at the fourteen-vertex 1:6:6:1 closed deltahedron.[1] Alternatively, the intimate fusion of one or more single clusters to generate 'macropolyhedral' extended contiguous multicluster assemblies can effectively shift the barrier to infinity. Here, the larger fused-cluster assemblies so generated offer possibilities of interesting cluster interactions, either (*a*) intramolecular, for example between subclusters bound in very closely adjacent positions in one molecule, or (*b*) intermolecular, for example between molecules that have large or complementary van der Waals surfaces or complementary polar domains. We here report that the new 77-atom platinaborane dianions [Pt(*anti*-$B_{18}H_{20})_2]^{2-}$ and [Pt(*syn*-$B_{18}H_{20})_2]^{2-}$ have interesting structural features resulting from both these structural effects. The parent 40-atom macropolyhedral binary borane precursors, *anti*-$B_{18}H_{22}$ and *syn*-$B_{18}H_{22}$, were structurally characterised some time ago.[2]

Typically, reaction between $[NEt_4]_2$[*anti*-$B_{18}H_{20}$] (240 μmol) and $[Pt(cod)Cl_2]$ (120 μmol) (cod = cycloocta-1,5-diene) in $CH_2Cl_2$ solution at room temperature for 18 h, followed by repeated chromatographic separation (TLC, silica gel, $CH_2Cl_2$–MeCN mixtures), afforded $[NEt_4]_2$[Pt(*anti*-$B_{18}H_{20})_2$] **1** as a mildly air- and temperature-sensitive orange solid (54%). A similar reaction between *syn*-$B_{18}H_{22}$ (240 μmol), *N*,*N*,*N*′,*N*′-tetramethylnaphthalene-1,8-diamine (tmnda) (480 μmol) and $[Pt(cod)Cl_2]$ (120 μmol), and similar work-up, similarly yielded the orange solid $[Htmnda]_2$[Pt(*syn*-$B_{18}H_{20})_2$] **2** (51%). Each of compounds **1** and **2** has been characterised by a single-crystal X-ray diffraction analysis (Fig. 1).* In each compound the anion has crystallographic inversion symmetry, the metal atoms being on the inversion centre. The *syn*-$B_{18}$ residue is chiral[7] and in compound **2** the anion is the (+)(−) diastereoisomer; other minor products that are revealed chromatographically may well include the (+)(+)/(−)(−) racemate, although it could be that the extreme steric intramolecular interactions in these species (see below) preferentially dictate the observed (+)(−) diastereoisomeric form.

Each of the isomeric $[PtB_{36}H_{40}]^{2-}$ dianions in compounds **1** and **2** can be viewed as two nineteen-vertex $\{PtB_{18}H_{20}\}$ subclusters joined *via* a common platinum vertex. In each case, each of these subclusters itself can be viewed as a *nido*-platinaundecaboranyl and a *nido*-decaboranyl subcluster unit fused with one boron–boron edge in common. The *nido*-platinadecaboranyl description implies an $\eta^4$ platinum-to-borane bonding mode, with similarities to that in the anions $[M(\eta^4\text{-}B_{10}H_{12})_2]^{2-}$ (where M is Ni, Pd or Pt)[8] and to that in the neutral species $[(PMe_2Ph)_2PtB_{10}H_{12}]$.[9] It is, however, much more similar to the bonding in the macropolyhedrals $[(PMe_2Ph)_2Pt(\eta^4$-*anti*-$B_{18}H_{20})]$ and $[(PMe_2Ph)_2Pt(\eta^4$-*syn*-$B_{18}H_{20})]$.[10] These last two compounds have, in addition to the $\eta^4$-$\{B_4\}$ boron-to-platinum bonding, close platinum–hydrogen approaches involving BH(*exo*) units from the otherwise non-co-ordinated second subcluster. These forced 'agostic' close approaches occur between the Pt(9) and H(2′) atoms, and take values of 3.08(3) Å in compound **1** and 2.92(3) Å in compound **2**.

Interestingly, in both compounds **1** and **2**, the intimate juxtapositioning of the two large $\{B_{18}H_{20}\}$ subclusters about the platinum atom results in very severe intramolecular steric crowding, with interhydrogen contacts between the two $\{PtB_{18}\}$ subclusters of H(2′)–H(5) 2.58(4), H(3′)–H(5) 2.06(4) and H(3′)–H(10) 2.65(5) Å in compound **1**, and H(2′)–H(5) 2.35(5), H(5′)–H(5) 2.40(5) and H(5′)–H(10) 2.66(5) Å in compound **2**, all comparable to or less than a two-hydrogen van der Waals radius sum of *ca.* 2.5 Å. This imposes a rigid slab-like structure on the anions, as in the lozenge-shaped anion of **1** (Fig. 2),

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* Crystals of compound **1** were grown by slow mutual diffusion of $C_6H_{14}$ into a MeCN–$Et_2O$ solution at −30 °C and those of compound **2** by slow mutual diffusion of $C_6H_{14}$ into a $Me_2CO$ solution at −30 °C. The data sets were collected at 150(2) K (compound **1**) and 160(2) K (compound **2**) on a Stoe STADI-4 diffractometer (Mo-Kα X-radiation, λ 0.710 73 Å), a semiempirical absorption correction (ψ scans) applied, and the structures solved by direct methods (SHELXS 86)[4] and refined (full-matrix least squares on $F^2$) using SHELXL 93.[5] Additional geometric calculations were performed using PARST 96.[6]

Compound **1**: (orange prism, 0.57 × 0.41 × 0.29 mm) $C_{16}H_{80}B_{36}N_2Pt$, $M = 885.1$, monoclinic, $P2_1/c$, $a = 10.5646(9)$, $b = 10.8128(9)$, $c = 20.3960(13)$ Å, $\beta = 104.232(6)°$, $U = 2258.4(3)$ Å$^3$, $Z = 2$, $D_c = 1.302$ Mg m$^{-3}$, $\mu = 3.127$ mm$^{-1}$, $F(000) = 896$. 5427 Data collected to $\theta_{max} = 25°$ ($-12 \leqslant h \leqslant 12$, $-11 \leqslant k \leqslant 12$, $-23 \leqslant l \leqslant 24$), of which 3977 were independent ($R_{int} = 0.0126$). Final $wR2 = 0.0527$, where $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$, and conventional $R1 = 0.0198$ for 3284 reflections with $F^2 > 2\sigma(F^2)$.

Compound **2**: (orange block, 0.40 × 0.35 × 0.30 mm) $C_{28}H_{78}B_{36}N_4Pt$, $M = 1055.2$, triclinic, $P1$, $a = 10.642(2)$, $b = 11.0560(14)$, $c = 12.2012(13)$ Å, $\alpha = 88.058(10)$, $\beta = 84.150(11)$, $\gamma = 85.995(10)°$, $U = 1424.0(3)$ Å$^3$, $Z = 1$, $D_c = 1.230$ Mg m$^{-3}$, $\mu = 2.492$ mm$^{-1}$, $F(000) = 532$. 5339 Data collected to $\theta_{max} = 25°$ ($-12 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 14$), of which 5034 were independent ($R_{int} = 0.0425$). Final $wR2 = 0.0652$ and $R1 = 0.0263$ for 5026 reflections with $F^2 > 2\sigma(F^2)$. CCDC reference number 186/607.

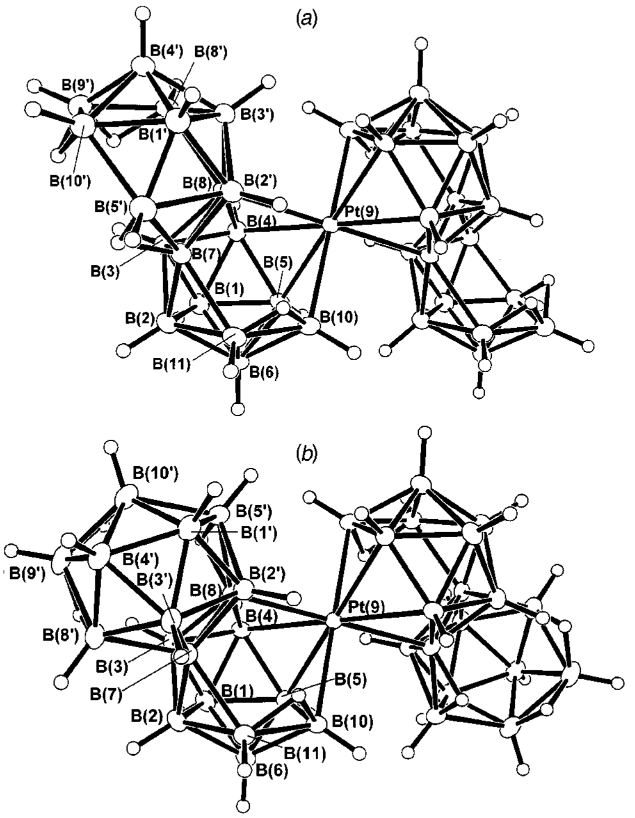

**Fig. 1** ORTEP-type[3] drawings of the crystallographically determined structures of (*a*) the $[Pt(anti\text{-}B_{18}H_{20})_2]^{2-}$ anion in $[NEt_4]_2[Pt(anti\text{-}B_{18}H_{20})_2]$ **1** and (*b*) the $[Pt(syn\text{-}B_{18}H_{20})_2]^{2-}$ anion in $[Htmnda]_2[Pt(syn\text{-}B_{18}H_{20})_2]$ **2**. Each anion has crystallographic inversion symmetry, the metal atoms being on the inversion centre. Selected interatomic distances (Å) are: for compound **1**; Pt(9)–B(4) 2.248(3), Pt(9)–B(5) 2.230(3), Pt(9)–B(8) 2.416(3), Pt(9)–B(10) 2.290(3), with interboron distances between 1.746(5) and 2.105(5) for the $\{PtB_{10}\}$ subcluster, and between 1.713(5) and 1.937(5) for the $\{B_{10}\}$ subcluster: for compound **2**; Pt(9)–B(4) 2.225(4), Pt(9)–B(5) 2.230(4), Pt(9)–B(8) 2.323(4) and Pt(9)–B(10) 2.302(4), with interboron distances between 1.715(6) and 1.980(5) Å for the $\{PtB_{10}\}$ subcluster and between 1.736(5) and 2.023(5) for the $\{B_{10}\}$ subcluster

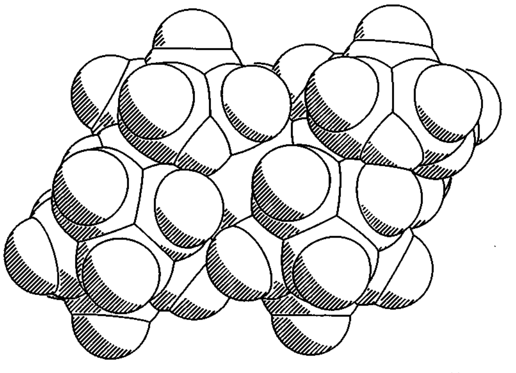

**Fig. 2** A van der Waals radius space-filling drawing[11] of the rigid lozenge-like structure of the $[Pt(anti\text{-}B_{18}H_{20})_2]^{2-}$ anion in its $[NEt_4]^+$ salt (compound **1**)

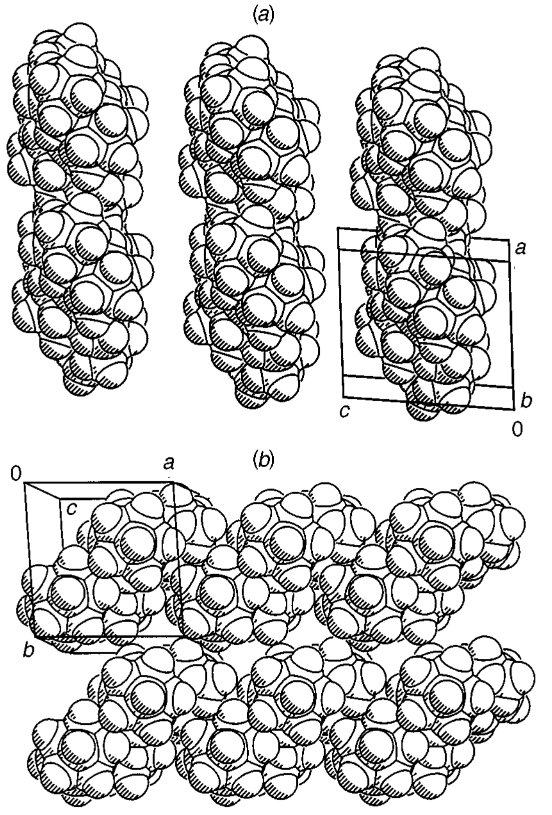

**Fig. 3** Two views[11] of the stacking of the $[Pt(syn\text{-}B_{18}H_{20})_2]^{2-}$ anion in its $[Htmnda]^+$ salt (compound **2**): (*a*) approximately normal to the *ac* plane showing three of the anionic layers, which have a *ca.* 2.5 Å spacing between them (*ca.* 5 Å between hydrogen atom centres); and (*b*) approximately normal to the *ab* plane, showing two of the van der Waals contact double sheets, and the steplike structure in each of these

which contrasts with the distinct non-rigidity of more open single-cluster analogues, such as $[(PMe_2Ph)_2Pt(B_{10}H_{12})]$,[9] which are fluxional in metal-to-borane bonding. This forced close approach engenders the possibility of intercluster condensation for more compact macropolyhedral generation *via* elimination of sterically squeezed hydrogen-atom pairs, which we plan to investigate.

A second interesting feature is that these rigid 77-atom anions stack together very intimately in the solid state. Thus, for example, the $[Pt(syn\text{-}B_{18}H_{20})_2]^{2-}$ anions in the salt **2** adopt an extended two-dimensional double-stack structure (Fig. 3). The dianions pack in layers parallel to the crystallographic *ab* plane [Fig. 3(*a*)], with the closest interlayer interhydrogen approach at *ca.* 5 Å. Within these strata, however, the dianions approach very closely indeed, to within 2.6 Å between hydrogen atom centres, comparable to the van der Waals radius sum [Fig. 3(*b*)]. Along the crystallographic *a* direction, they have a step-like arrangement with minimum interhydrogen distance H(9′)–H(10) of 2.59(6) Å, whereas along the $(a - b)$ diagonal they contact head-to-tail with H(4′)–H(8′) 2.74(5) Å, and along the $(a + b)$ diagonal they are in back-to-back contact with minimum distance H(11)–H(11) of 2.58(6) Å. In supramolecular chemistry, there is much current interest in the understanding and utilisation of molecular associations in condensed phases, such as the attractive sequences that engender $[PPh_4]^+$ cationic layering.[12] Intimate anionic layering is classically recognised in $AX_2$ structures such as that of $CdI_2$,[13] and for simpler complex anions such as the $[PtCl_4]^{2-}$ dianion in $K_2[PtCl_4]$,[14] but as far as we are aware it is not previously recognised in this type of larger metallaborane cluster. Here the closest investigated analogue is perhaps the $[TTF]^+$ [TTF = tetrathiafulvalene or 2-(1,3-dithiol-2-ylidene)-1,3-dithiole] salt of the 45-atom monoanion $[Cr(C_2B_{10}H_{10})_2]^-$, which has a solid-state structure that can be described in terms of alternating layers of cations and anions; but in which there are no close anion–anion contacts.[15] For the new, larger type of metallaborane anions reported here, alternative anionic stackings that may be induced by further variation of counter cation, and by the use of alternative types of macropolyhedral molecular assemblies, are currently subject to further investigation.

## Acknowledgements

Contribution number 64 from the Řež-Leeds Anglo-Czech Polyhedral Collaboration (ACPC). We thank the EPSRC (grant nos. GR/J/56929 and GR/K05818), the Grant Agency of the Czech Republic (grant no. 203/94/0362), the Grant Agency of the Czech Academy of Sciences (grant no. A4032701), the Royal Society and Borax Europe for support.

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*Received 7th May* 1997; *Communication* 7/03132G