Carbaborane salts of $[ZnCl(Hpz^{tBu})_3]^+$, a host for inorganic anions (Hpz^{tBu} = 5-*tert*-butylpyrazole)

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The cations in $[ZnCl(Hpz^{tBu})_3]Y$ ($Y^- = [Co(C_2B_9H_{11})_2]^-$ or [1-Ph-*closo*-1-$CB_9H_9]^-$) associate into dimers in the crystal, presenting a bowl-shaped face into which the carbaborane anions can pack. In contrast, the cations in $[ZnCl(Hpz^{tBu})_3][6,7,8,9,10\text{-}Br_5\text{-}closo\text{-}1\text{-}CB_9H_5]\cdot H_2O$ associate with each other into a 1-D hydrogen-bonded polymer.

We have recently described the series of complexes $[ZnX(Hpz^{tBu})_3]X$ ($X^- = Cl^-$, Br^-, I^-)[1,2] and $[ZnCl(Hpz^{tBu})_3]Y$ ($Y^- = BF_4^-$, ClO_4^-, NO_3^-, $CF_3SO_3^-$, PF_6^-; Hpz^{tBu} = 5-*tert*-butylpyrazole).[2] These compounds all contain a distorted tetrahedral $[ZnX(Hpz^{tBu})_3]^+$ cation, whose Hpz^{tBu} ligands are oriented so as to form a bowl-shaped pocket on one face of the molecule. The charge-balancing X^- or Y^- anion lies within this cavity, forming hydrogen bonds to the three pyrazole N–H groups. These supramolecular structures are retained in $CDCl_3$ solution, so that the $[ZnCl(Hpz^{tBu})_3]^+$ moiety can be considered as a receptor for a variety of anion guests.[2] While the coordination chemistry of anions is a rapidly emerging field,[3] we are aware of only one other C_{3v}-symmetric anion host that is structurally comparable with our system.[4] The single crystal structure of $[ZnCl(Hpz^{tBu})_3]PF_6$ showed some structural distortion of the complex cation, owing to steric interactions between the Hpz^{tBu} ligands and the PF_6^- anion.[2] This suggested that anions larger than PF_6^- might not interact with the zinc complex in the same way. We have now investigated this, by preparing salts of $[ZnCl(Hpz^{tBu})_3]^+$ with a series of globular, carbaborane anions. We have successfully crystallised three of these products, and now present their structures.

The Ag(I) salts of $[Co(C_2B_9H_{11})_2]^-$, [1-Ph-*closo*-1-$CB_9H_9]^-$ and [6,7,8,9,10-Br_5-*closo*-1-$CB_9H_5]^-$ were prepared by metathesis of the Na^+ or NEt_4^+ salts of these anions[5,6] with $AgNO_3$ in water.[6] Treatment of $[ZnCl(Hpz^{tBu})_3]Cl$ with these silver salts cleanly afforded $[ZnCl(Hpz^{tBu})_3]Y$ ($Y^- = [Co(C_2B_9H_{11})_2]^-$, **1**; Y^- = [1-Ph-*closo*-1-$CB_9H_9]^-$, **2**; Y^- = [6,7,8,9,10-Br_5-*closo*-1-$CB_9H_5]^-$, **3**) as sparingly soluble orange (**1**) or white (**2** and **3**) solids. IR spectroscopy of all three compounds established the presence of Hpz^{tBu} and the appropriate carbaborane anion, while electrospray mass spectrometry showed in each case a strong peak at $m/z = 471$ from $[^{64}Zn^{35}Cl(Hpz^{tBu})_3]^+$. ^1H NMR spectroscopy of **1**–**3** in $CDCl_3$ showed a single Hpz^{tBu} environment, together with peaks from C-bound H atoms of the anions. Variable concentration studies of **1**–**3**, to determine the degree of cation:anion association in solution,[2] were not possible because of their limited solubility.

Single crystal X-ray analyses were obtained from crystals of formula **1**, **2**·$0.2C_5H_{12}$ and **3**·H_2O. As in salts of $[ZnCl(Hpz^{tBu})_3]^+$ with small inorganic anions,[1,2] the cations in all three compounds have a distorted tetrahedral geometry and interact with the carbaborane anions *via* the Hpz^{tBu} ligands. However, there are important differences between the structures of **1**–**3** and these other compounds. In $[ZnCl(Hpz^{tBu})_3]Y$ ($Y^- = Cl^-$, BF_4^-, ClO_4^-, NO_3^-, $CF_3SO_3^-$) the three Hpz^{tBu} ligands are oriented so that their N–H and *tert*-butyl groups all lie on the same face of the tetrahedron, forming a pocket that is occupied by the guest 'Y^-' anion.[2] However, in **1** and **2** two of the three pyrazole ligands are rotated away from the carbaborane anions, so that these form hydrogen bonds to the Cl^- ligand of a neighbouring complex cation, related by a crystallographic inversion centre. Thus, the cations in **1** and **2** all associate into hydrogen-bonded dimers in the crystal (Fig. 1). Either as a result of this hydrogen-bonding, or because of steric contacts with the carbaborane anions, the N–Zn–N angles relating the two pyrazole moieties involved in this hydrogen bonding [*e.g.* N(12)–Zn(1)–N(21) and N(57)–Zn(46)–N(66) in Fig. 2] are very obtuse, ranging between 126.26(6)–132.99(7)° for the two structures. The plane of the third pyrazole ligand is oriented approximately parallel to the Zn···carbaborane vector (Fig. 1). The Cl–Zn–N angle to this Hpz^{tBu} ligand [*e.g.* Cl(2)–Zn(1)–N(3) and Cl(47)–Zn(46)–N(48) in Fig. 2] is slightly compressed, at 98.21(5)–104.58(5)°. All other bond lengths and angles in **1** and **2** lie in the usual ranges.

The structures of **1** and **2** each contain two crystallographically independent cations and anions per asymmetric unit. In both structures, each carbaborane anion lies within the concave surface afforded by the Hpz^{tBu} ligands from one complex cation (Fig. 1). In one molecule of **1**, the 'parallel' pyrazole is oriented so that its N–H group points towards the associated anion (Fig. 1). In contrast, for the other molecule the corresponding Hpz^{tBu} ligand has rotated by approximately 180° about the Zn–N bond. As a result, it is now the C–H group at the 3-position of this pyrazole ring that points towards the adjacent anion, while its N–H group forms a weak intramolecular N–H···Cl hydrogen bond. The two $[Co(C_2B_9H_{11})_2]^-$ anions also adopt different orientations in the pockets formed by the two non-equivalent cations. The closest intermolecular N–H···H–B or C–H···H–B contacts for both molecules in **1** are 2.5–2.6 Å, which is close to the sum of the van der Waals radii of two H atoms, of 2.4 Å.[7]

The unique complex cations in **2** adopt essentially the same conformation, with their 'parallel' pyrazole ligand oriented such that its N–H group is directed towards the included anion (Fig. 2). This N–H group makes very close contact with one B–H group from each [1-Ph-*closo*-1-$CB_9H_9]^-$ anion. The

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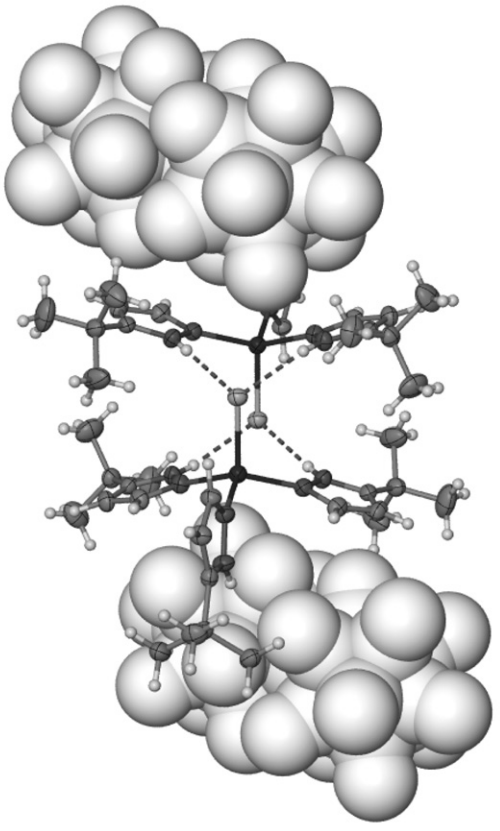

Fig. 1 View of one of the two independent molecules in the crystal of **1**, and its symmetry equivalent generated by inversion through $1-x$, $-y$, $-z$. The $\{[ZnCl(Hpz^{tBu}{}_3)_3]_2\}^{2+}$ dimers are presented as ball-and-stick models with 50% probability ellipsoids, while the $[Co(C_2B_9H_{11})_2]^-$ anions are space-filling.

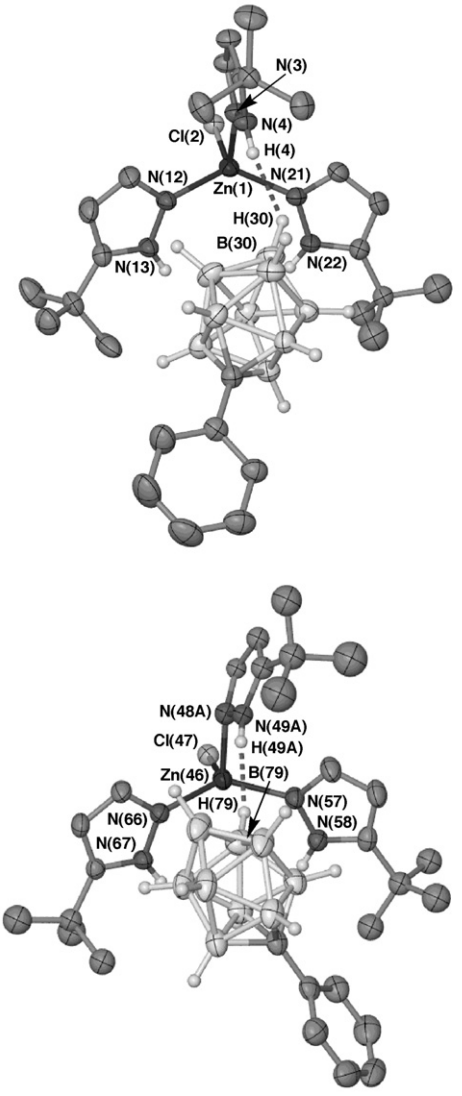

Fig. 2 Views of the two individual molecules in the structure of **2**$0.2C_5H_{12}$. For clarity, only one orientation of the disordered Hpz^{tBu} ligand [which includes N(48A) and N(49A)], and the disordered *tert*-butyl groups, are shown. Thermal ellipsoids are at the 50% probability level.

cation containing Zn(1) exhibits a contact to the 10-B–H position of the cluster anion, with uncorrected parameters of H(4)···H(30) = 1.95 Å, N(4)–H(4)···H(30) = 145.8° and H(4)···H(30)–B(30) = 120.7° (Fig. 2). In contrast, the anion associated with the cation at Zn(46) adopts a different orientation, so that it is H(49) that makes a similar contact to the B–H group at the 6-position of the cluster, B(79)–H(79). Unfortunately, disorder in this Hpz^{tBu} ligand means that accurate metric parameters for this second interaction cannot be derived.

As in **1** and **2**, two of the three Hpz^{tBu} ligands in **3**·H_2O take part in hydrogen-bonding to the Cl ligand of a neighbouring complex cation. However, in this case these cations associate into a 1-D chain, parallel to the crystallographic *b* direction (Fig. 3). As in **1** and **2**, this hydrogen bonding results in a large N(12)–Zn(1)–N(21) angle of 119.76(10)° (Fig. 4). The third Hpz^{tBu} ligand on each cation hydrogen bonds, *via* the water molecule, to the Br atom at the 10-position of the [6,7,8,9,10-Br_5-*closo*-1-CB_9H_5]$^-$ cage [Br(41)] (Fig. 4). We suggest that this different structure arises because of the larger cone angle of the anion in **3**·H_2O compared to those in **1** and **2**, which would prevent it from packing effectively into the bowl-shaped surface of the $\{[ZnCl(Hpz^{tBu}{}_3)_3]_2\}^{2+}$ dimer.

These structures provide important insight into how the $[ZnCl(Hpz^{tBu}{}_3)_3]^+$ receptor is likely to aggregate in non-polar solvents, in the absence of strongly interacting anions. This will have important implications for our goal to produce an anion sensor based on the $[ZnCl(pyrazole)_3]^+$ framework. In addition, the $\{[ZnCl(Hpz^{tBu}{}_3)_3]_2\}^{2+}$ dimer (Fig. 1), which from this work and that in ref. 2 appears to form readily in the presence of moderately sized globular anions, represents a new addition to the range of known bowl-shaped acceptors for three-dimensional cage guests.[8] This could therefore be a useful tecton for crystal engineering; we are currently investigating that possibility.

Experimental

Unless stated otherwise, all manipulations were performed in air using commercial grade solvents. Hpz^{tBu},[9] NEt_4[1-Ph-*closo*-1-CB_9H_9][5] and NEt_4[6,7,8,9,10-Br_5-*closo*-1-CB_9H_5][6] were prepared according to the published methods, while $AgNO_3$ and $Na[Co(C_2B_9H_{11})_2]$ were used as supplied.

Syntheses of 1–3

The syntheses of all of these complexes followed the same basic procedure, as described here for **1**. Filtered solutions of $Na[Co(C_2B_9H_{11})_2]$ (1.00 g, 2.9 mmol) and $AgNO_3$ (0.49 g, 2.9 mmol) in water (25 cm^3 each) were mixed, and the resultant solution concentrated *in vacuo* until an orange precipitate began to form. Storage at 0 °C yielded $Ag[Co(C_2B_9H_{11})_2]$[6] as an orange powder, which was filtered, dried and used without further purification. A mixture of $ZnCl_2$ (0.18 g, 1.3 mmol) and Hpz^{tBu} (0.50 g, 4.0 mmol) in MeOH (50 cm^3) was stirred until all the solid had dissolved. A solution of $Ag[Co(C_2B_9H_{11})_2]$

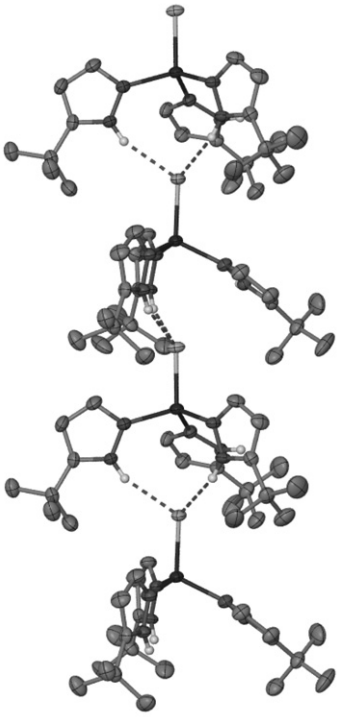

Fig. 3 Partial packing diagram of $3{\cdot}H_2O$, showing the association of the $[ZnCl(Hpz^{tBu})_3]^+$ cations into a hydrogen-bonded 1-D polymer.

(0.56 g, 1.3 mmol) in MeOH (10 cm^3) was then added, and the mixture stirred for 30 min. The mixture was filtered, and the filtrate evaporated to dryness. The orange residue was redissolved in a minimum volume of CH_2Cl_2, and a large excess of pentane added to the solution. Storage at −30 °C gave orange crystals of the product. Similar reactions beginning with equivalent amounts of NEt_4[1-Ph-*closo*-1-CB_9H_9] or NEt_4[6,7,8,9,10-Br_5-*closo*-1-CB_9H_5] afforded **2** and **3** as white solids. Final crystalline yields were *ca.* 40%.

For $[ZnCl(Hpz^{tBu})_3][Co(C_2B_9H_{11})_2]$ (**1**): found C, 37.6; H, 7.2; N, 10.7%. Calcd. for $C_{25}H_{58}B_{18}ClCoN_6Zn$ C, 37.7; H, 7.3; N, 10.5%. Electrospray mass spectrum: $m/z = 471$ $[^{64}Zn^{35}Cl(Hpz^{tBu})_3]^+$. ^{1}H NMR spectrum ($CDCl_3$): δ 9.2 (br s, 3H, N*H*), 7.90 (d, 2.3 Hz, 3H, pz H^3), 6.41 (d, 2.3 Hz, 3H, pz H^4), 3.87 (br s, 4H, anion C*H*), 1.37 (s, 18H, CCH_3).

For $[ZnCl(Hpz^{tBu})_3]$[1-Ph-*closo*-1-CB_9H_9] (**2**): found C, 49.7; H, 7.3; N, 12.6%. Calcd. for $C_{28}H_{49}B_9ClN_6Zn$ C, 50.3; H, 7.4; N, 12.6%. Electrospray mass spectrum: $m/z = 471$ $[^{64}Zn^{35}Cl(Hpz^{tBu})_3]^+$. ^{1}H NMR spectrum ($CDCl_3$): δ 8.03 (d, 2.3 Hz, 3H, pz H^3), 7.63 (m, 5H, anion C_6H_5), 6.31 (d, 2.3 Hz, 3H, pz H^4), 1.39 (s, 18H, CCH_3).

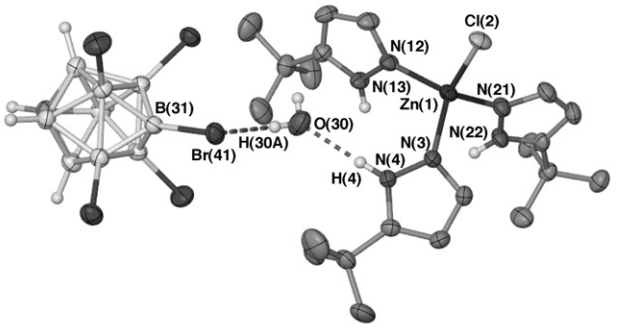

Fig. 4 View of the asymmetric unit in the structure of $3{\cdot}H_2O$. All C-bound H atoms have been omitted for clarity. Thermal ellipsoids are at the 50% probability level.

For $[ZnCl(Hpz^{tBu})_3]$[6,7,8,9,10-Br_5-*closo*-1-CB_9H_5]·H_2O ($3{\cdot}H_2O$): found C, 26.4; H, 4.3; N, 8.4%. Calcd. for $C_{22}H_{43}B_9Br_5ClN_6OZn$ C, 26.3; H, 4.3; N, 8.4%. Electrospray mass spectrum: $m/z = 471$ $[^{64}Zn^{35}Cl(Hpz^{tBu})_3]^+$. ^{1}H NMR spectrum ($CDCl_3$): δ 7.91 (d, 2.2 Hz, 3H, pz H^3), 6.35 (d, 2.2 Hz, 3H, pz H^4), 5.20 (br s, 1H, anion C*H*), 1.38 (s, 18H, CCH_3).

Single crystal X-ray structure determinations

All crystals were grown by storage of solutions of the compounds at −30 °C in hexanes (**1**), diethyl ether/pentane ($2{\cdot}0.2C_5H_{12}$) and CH_2Cl_2/pentane ($3{\cdot}H_2O$). The structure of **1** was solved by a Patterson synthesis, while $2{\cdot}0.2C_5H_{12}$ and $3{\cdot}H_2O$ were solved by direct methods (SHELXS 86).[10] All three structures were refined by full matrix least-squares on F^2 (SHELXL 97).[11] H atoms were placed in calculated positions and refined using a riding model, unless otherwise stated.

CCDC reference numbers 192037–192039. See http://www.rsc.org/suppdata/nj/b2/b207966f/ for crystallographic data in CIF or other electronic format.

For 1. $C_{25}H_{58}B_{18}ClCoN_6Zn$, $M_r = 797.10$, triclinic, $P\bar{1}$, $a = 15.0060(1)$, $b = 17.6110(2)$, $c = 17.9379(2)$ Å, $\alpha = 84.1973(3)$, $\beta = 65.6599(4)$, $\gamma = 82.3658(5)°$, $V = 4275.19(7)$ Å^3, $Z = 4$, μ(Mo-Kα) = 1.039 mm^{-1}, $T = 150(2)$ K; 106 482 measured reflections, 19 588 independent, $R_{int} = 0.066$; $R(F) = 0.037$, $wR(F^2) = 0.104$. No disorder was detected during refinement of this structure, and no restraints were applied. All non-H atoms were refined anisotropically.

For $2{\cdot}0.2C_5H_{12}$. $C_{29}H_{52.4}B_9ClN_6Zn$, $M_r = 683.28$, triclinic, $P\bar{1}$, $a = 10.8007(1)$, $b = 15.4087(1)$, $c = 24.7967(3)$ Å, $\alpha = 100.3662(4)$, $\beta = 97.0776(4)$, $\gamma = 100.9195(6)°$, $V = 3932.70(7)$ Å^3, $Z = 4$, μ(Mo-Kα) = 0.720 mm^{-1}, T = 150(2) K; 81 059 measured reflections, 18 005 independent, $R_{int} = 0.074$; $R(F) = 0.044$, w$R(F^2) = 0.128$. The asymmetric unit contains two crystallographically independent complex cations and two anions, all lying on general positions; and, a badly disordered region of solvent lying across a crystallographic inversion centre. This solvent was modelled using two partial environments of pentane, each with occupancy 0.2. One Hpz^{tBu} ligand in the model was badly disordered, and was modelled over three orientations with occupancies of 0.45, 0.35 and 0.20. The *tert*-butyl groups on three other Hpz^{tBu} moieties were also disordered, and were modelled over two or three different subsites. The following restraints were applied to the disordered residues in the final model: N–N = 1.36(1), N=C = 1.32(1), N–C = 1.35(1), C=C = 1.36(1), intrapyrazole C–C = 1.39(1), *tert*-butyl and pentane C–C = 1.52(2), *tert*-butyl and pentane 1,3–C···C = 2.48(2) Å. All crystallographically ordered non-H atoms were refined anisotropically.

For $3{\cdot}H_2O$. $C_{22}H_{43}B_9Br_5ClN_6OZn$, $M_r = 1005.28$, orthorhombic, *Pbca*, $a = 24.0110(2)$, $b = 12.3005(1)$, $c = 27.2856(3)$ Å, $V = 8058.73(13)$ Å^3, $Z = 8$, μ(Mo-Kα) = 5.661 mm^{-1}, $T = 150(2)$ K; 99 938 measured reflections, 9218 independent, $R_{int} = 0.105$; $R(F) = 0.032$, w$R(F^2) = 0.078$. No disorder was detected during refinement of this structure, and no restraints were applied. All non-H atoms were refined anisotropically. The water H atoms were located in the difference map and allowed to refine freely.

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