Synthesis and characterization of polyborates templated by cationic copper(II) complexes: structural (XRD), spectroscopic, thermal (TGA/DSC) and magnetic properties.

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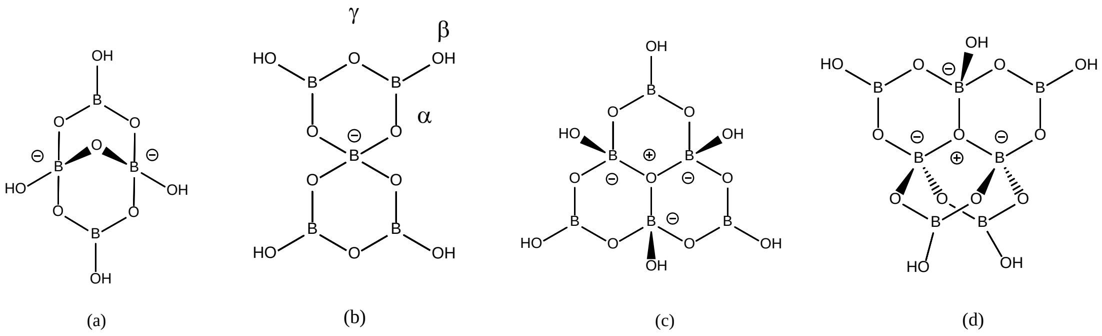
ABSTRACT

Several polyborate containing species templated by cationic copper(II) coordination compounds have been synthesized. The ionic species $[Cu(en)_2][B_5O_6(OH)_4]_2{\cdot}2H_2O$ (en = 1,2-diaminoethane) (**1**), $[Cu(dmen)_2(H_2O)][B_5O_6(OH)_4]_2{\cdot}3H_2O$ (dmen = *N*,*N*-dimethyl-1,2-diaminoethane) (**2**), $[Cu(pn)_2\{B_5O_6(OH)_4\}][B_5O_6(OH)_4]{\cdot}4H_2O$ (pn = 1,2-diaminopropane) (**3**), $[Cu(dach)_2(H_2O)_2][Cu(dach)_2][B_7O_9(OH)_5]_2{\cdot}4H_2O$ (dach = 1,2-diaminocyclohexane) (**4**), and the neutral species $[Cu(dmen)\{B_6O_7(OH)_6\}]{\cdot}4H_2O$ (**5**) and $[Cu(tmeda)\{B_6O_7(OH)_6\}]{\cdot}6H_2O$ (tmeda = *N*,*N*,*N'*,*N'*-tetramethyl-1,2-diaminoethane) (**6**) have been synthesized in aqueous solution and characterized by spectroscopic and thermal (TGA/DSC) methods. The previously prepared compound $[Cu(en)_2][B_4O_5(OH)_4]_2{\cdot}2B(OH)_3$ (**7**) has also been prepared by an alternative route. Compounds **1**-**6** have been further characterized by single-crystal XRD studies. The new compounds show extensive H-bond interactions and display a range of structural features: **1**-**3** have isolated pentaborate(1-) anions whilst **4** possesses an isolated heptaborate(2-) anion. In addition, **3** has a pentaborate(1-) and **5** and **6** have hexaborate(2-) anions directly coordinated to their copper(II) centers, in mondentate and tridentate manners, respectively. The copper(II) centers show a variety of coordination numbers and geometries: square-planar (**1**, **7**), octahedral (**4**) and square-based pyramidal (**2**, **3**, **5**, **6**). Thermal studies (TGA/DSC) and magnetic susceptibility measurements have been undertaken on all compounds.

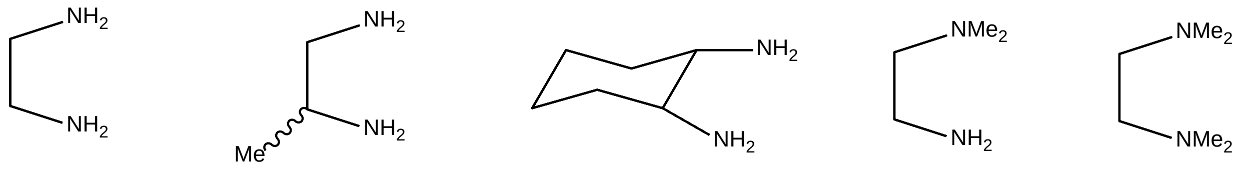
1. Introduction

Borate minerals and chemicals are of great industrial importance as bulk chemicals [1] and polyborates, both natural and synthetic, are also finding more specialized applications *e.g.* wide band-gap semi-conductors [2], fluorescent [3], piezoelectric [4] or SHG [5] optical materials. There are over 200 borate minerals known and more than 100 of these have been characterized by single-crystal X-ray diffraction studies [6]. Borate minerals show great structural diversity [6] and, with the exception of two ammonium salts, all contain Lewis acidic cationic metal centres with either condensed (chains, sheets or networks) or isolated (insular) polyborate anions. In recent years many synthetic polyborate compounds have been prepared containing either Lewis acidic metals, organic cations or transition-metal cations to counterbalance the charge [7]. One synthetic approach is to crystallize polyborate salts from aqueous solution. Solvothermal, hydrothermal or solid-state synthesis are alternative approaches [7]. Borate speciation is aqueous solution is pH and concentration dependent [8], but in general a dynamic combinatorial library (DCL) [9] of polyborate anions co-exist in facile equilibrium. Pentaborate(1-) salts (See Figure 1(b) for structure of this anion) often crystallize out of such solutions, particularly if the cation has a charge of +1, since the $[B_5O_6(OH)_4]^-$ anion is ideally shaped to form multiple, strong anion-anion H-bonded interactions and these interactions lead to giant structures, with the cations occupying the lattice ‘cavities’ [10]. On rare occasions isolated polyborate anions other than pentaborate have been observed [7a] *e.g.* triborate(1-), heptaborate(2-) (2 isomers), heptaborate(3-), octaborate(2-) (2 isomers), nonaborate(3-), tetradecaborate(4-), pentadecaborate(3-), and these anions have been structure directed by the cations which are present. Solvothermal methods often lead to more condensed polyborate structures [7]. We are interested in expanding the structural diversity of isolated polyborate chemistry and have developed a strategy of incorporating relatively highly charged cations [11] with the potential of forming multiple H-bond interactions into the aqueous DCL of borate anions so that they can template and crystal-engineer new structures. At present, copper(II) polyborate systems containing isolated anions are restricted to $[Cu(C_{12}N_2H_8)_2(C_2H_3O_2)][B_5O_6(OH)_4]\cdot C_4H_9NO$ [12], $[Cu(en)_2(C_5H_9NO)][B_5O_6(OH)_4]_2\cdot C_5H_9NO$ [13], $[Cu(en)_2][B_4O_5(OH)_4]\cdot 2B(OH)_3$ [14] and $[Cu(en)_2B(OH)_3(H_2O)][B_4O_5(OH)_4]\cdot 1/2H_2O$ [14]. In this article we report on the use coordination complexes of copper(II) containing 1,2-diaminoethane (en), *rac*-1,2-diaminopropane (pn), *rac*-1,2-diaminocyclohexane (dach), *N*,*N*-dimethyl-1,2-diaminoethane (dmen) and *N*,*N*,*N'*,*N'*-tetramethyl-1,2-diaminoethane (tmeda) ligands (Figure 2) to synthesize new polyborate compounds.



(a) (b) (c) (d)

Figure 1. Schematic structures of polyborate anions found in **1**-**7**: (a) tetraborate(2-) as in **7**, (b) pentaborate(1-) as in **1**, **2** and **3** (oxygen atoms labelled α, β or γ [18,19]), (c) hexaborate(2-) as in **5** and **6**, (d) heptaborate(2-) as in **4**.



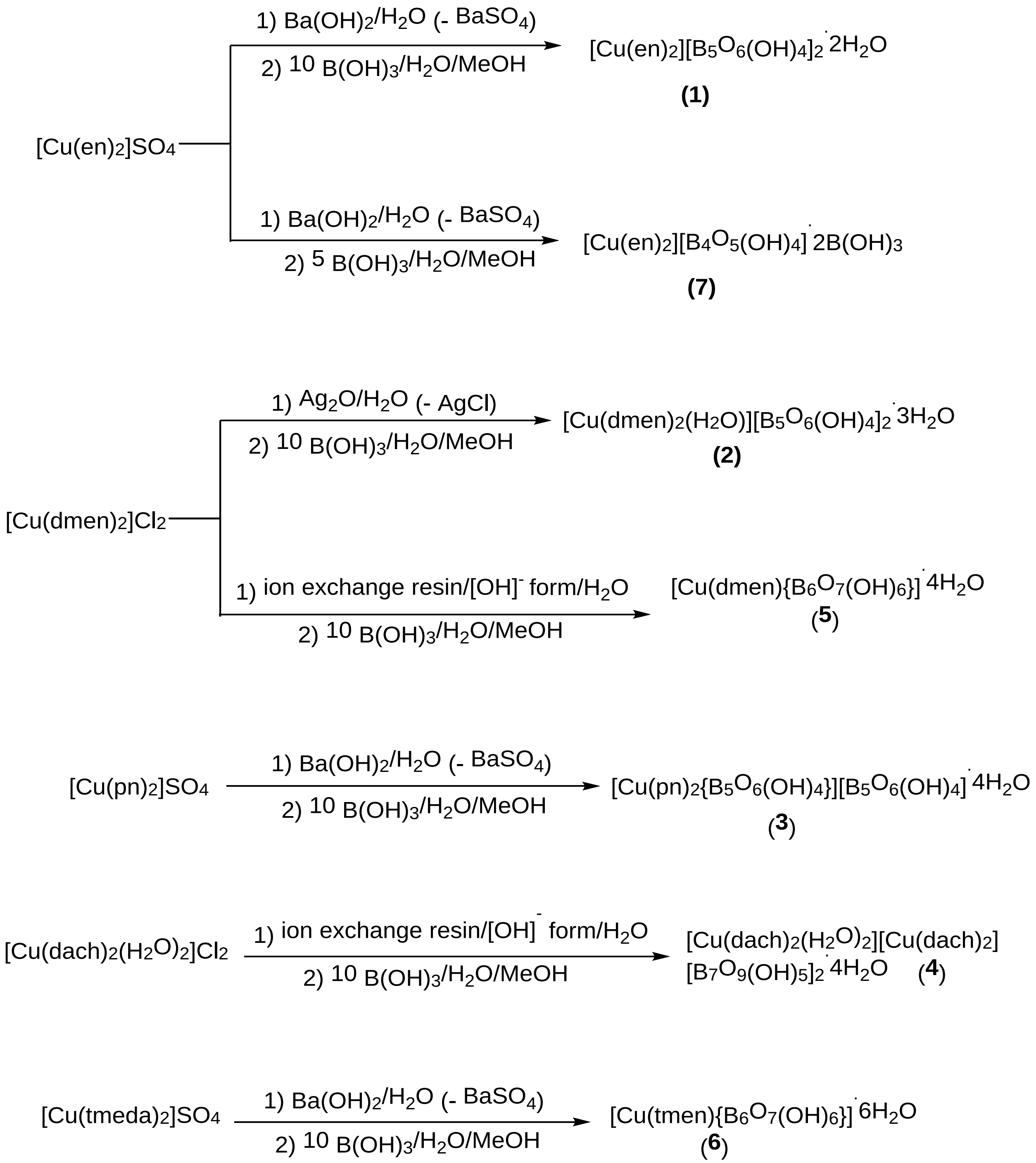
(a) (b) (c) (d) (e)

Figure 2. Schematic line drawings of the diamino ligands found in structures **1**-**7**. (a) 1,2-diaminoethane (en), (b) (+/-)-1,2-diaminopropane (pn) , (c) 1,2-diaminocyclohexane (dach), (d) *N,N*-dimethyl-1,2-diaminoethane (dmen), (e) *N,N,N',N'*-tetramethyl-1,2-diaminoethane (tmeda).

2. Results and discussion

2.1 Synthesis and general discussion

Copper(II) complex polyborate compounds **1-7** were prepared as crystalline solids from the reaction of copper(II) complex cation hydroxides with boric acid in a ratio of 1:10 or 1:5. The copper(II) complex cation hydroxides were obtained *in situ* from the corresponding salts with chloride or sulfate anions by anion exchange or Ag_2O, or by reaction with $Ba(OH)_2{\cdot}8H_2O$, respectively (Scheme 1). The new compounds were identified as $[Cu(en)_2][B_5O_6(OH)_4]_2{\cdot}2H_2O$ (en = 1,2-diaminoethane) (**1**), $[Cu(dmen)_2(H_2O)][B_5O_6(OH)_4]_2{\cdot}3H_2O$ (dmen = *N,N*-dimethyl-1,2-diaminoethane) (**2**), $[Cu(pn)_2\{B_5O_6(OH)_4\}][B_5O_6(OH)_4]{\cdot}4H_2O$ (pn = 1,2-diaminopropane) (**3**), $[Cu(dach)_2(H_2O)_2][Cu(dach)_2][B_7O_9(OH)_5]_2{\cdot}4H_2O$ (dach = 1,2-diaminocyclohexane) (**4**), $[Cu(dmen)\{B_6O_7(OH)_6\}]{\cdot}4H_2O$ (**5**), $[Cu(tmeda)\{B_6O_7(OH)_6\}]{\cdot}6H_2O$ (tmeda = *N,N,N'N'*-tetramethyl-1,2-diaminoethane) (**6**) and $[Cu(en)_2][B_4O_5(OH)_4]_2{\cdot}2B(OH)_3$ (**7**) on the basis of XRD



Scheme 1. Reagents and stoichiometry of reactants involved in self-assembly of copper(II) polyborates from copper(II) complexes with $B(OH)_3$ in methanolic aqueous solution.

(single-crystal and powder) studies, thermal decomposition studies (TGA and DSC) and spectroscopic (NMR and IR) analysis. The products arise through self-assembly processes associated with H-bonded structure directing effects induced by the cations present [15]. The tetraborate(2-), pentaborate(1-), hexaborate(2-), and heptaborate(2-) anions present in structures **1**-**7** are shown schematically in Figure 1.

A single-crystal X-ray study of tetraborate **7** has been previously reported and unit cell measurements on single-crystals of **7** were in accord with published data [14]. Our procedure for the synthesis of **7** is not reported elsewhere and we now report additional data (^{11}B NMR, p-XRD, magnetic properties, and thermal analyses). All compounds were prepared in moderate to yields (41-59 %) and had satisfactory elemental analysis data.

2.2 Structural studies

Compounds **1**-**3** are ionic compounds containing cations comprised of copper(II) complexes, pentaborate(1-) anions and either two, three, or four waters of crystallization. The stoichiometry is such that they have two pentaborate(1-) anions per copper(II) complex cation and in **1** the anions are symmetry related whereas in **2** and **3** they are crystallographically independent. Compounds **1**-**3** contain a 'core' square-planar $[Cu(L\text{-}L)_2]^{2+}$ (L-L = bidentate N_2 donor diamine ligand) motif within their cations but have additional axially bound oxygen donors at various distances. Compound **1** has Cu-N distances ranging from to 2.0035(14) - 2.0188(14) Å (av. 2.012 Å) and two pentaborate(1-) anions hydroxyl oxygen atoms (O7) at axial positions at 2.839 Å. The tetragonality (T^n) approach of Hathaway and Hodgson [16] yields a T value of 0.7. This T value is at the low end of the range for elongated tetragonal octahedral geometry and at the high end of the range for square planar geometry. However, the axial Cu-O interactions are presumably weak (see **3** below, for an example of a stronger interaction), and we have formulated the cation in **1** as square planar, $[Cu(en)_2]^{2+}$. The two 5-membered chelate rings of **1** are non-planar with one en fragment adopting a λ conformation and the other a δ conformation.

The $[Cu(dmen)_2(H_2O)]^{2+}$ cation in **2** has Cu-N distances ranging from 1.9937(11) - 2.0781(11) Å (av. 2.0353 Å) with a fifth ligand (H_2O) at a distance of 2.3368(10) Å. This Cu-O distance is significantly shorter than that found in **1** and since the nearest potential oxygen donor on the other axial site is at 3.55 Å the complex is best considered as a 5-coordinate square-based pyramid. This is confirmed by a T^5 value of 0.87. A τ-index [17] of 0.12 for this cation supports a square-based pyramidal rather than a trigonal bipyramidal 5-coordinate geometry. The dmen ligands are arranged so that the methyl substituents are mutually *trans* with both substituted diaminoethane chelates adopting δ conformations.

The cation in **3** is also best formulated as a square-based pyramid (T^5 = 0.80, τ-index = 0.0013), $[Cu(pn)_2\{B_5O_6(OH)_4\}]^+$, with Cu-N distances of 1.9714(11) - 2.0115(12) Å (av. 1.9936 Å) and an axial Cu-O (hydroxyl group from borate) distance of 2.490 Å. There is also a sixth axially weakly coordinated H_2O 'ligand' at 2.785 Å. The core $[Cu(pn)_2]^{2+}$ motif has pn ligands in both *R* and *S* configurations with their associated chelate rings adopting λ and δ conformations and with the methyl groups equatorial and *transoid*. The Cu-N in complexes **1**-**3** distances are typical of those found in $[Cu(L\text{-}L)_2]^{2+}$ cations [16] *e.g.* $[Cu(en)_2]Cl_2{\cdot}H_2O$ (2.00 Å), $[Cu(en)_2]Br_2{\cdot}H_2O$ (1.98 Å) [23], $[Cu(pn)_2](NO_3)_2$ (2.05 Å) and $[Cu(dach)_2](NO_3)]NO_3$ (2.015 Å).

Insular pentaborate(1-) anions are well-represented in the literature [7a], and the structural parameters for the anions found for **1**-**3** are not notably different to those reported previously [10, 18]. Pentaborate(1-)-pentaborate(1-) H-bond interactions are usually influential in determining the overall crystal structure of many non-metal cation pentaborates salts [10d]. This appears to be partially the case for **1**-**3**, but there are numerous additional cation-anion, cation-H_2O, and H_2O-pentaborate(1-) interactions which also help to crystal-engineer the structure. In particular, all eight possible donor amino hydrogens in **1** (cutoff distance 3.13 Å) are involved in H-bonding interactions to pentaborate(1-) oxygen centres, and all four amino hydrogens in **2** are H-bonded to either pentaborate(1-) anions or water molecules. The coordinated H_2O molecule in **2** is H-bonded to a pentaborate(1-) anion and a further H_2O molecule. The oxygen atoms of the pentaborate(1-) anions have been labelled as α, β, or γ sites (Figure 1b)[18,19] according to their distance from the 4-coordinate boron centre. Similarly, oxygen acceptor sites in H_2O molecules have been labelled ω sites [20]. Using these labels each pentaborate(1-) anion in **1** and **2** forms four H-bond donor interactions to neighbouring $\alpha\alpha\alpha\omega$ (**1**) and $\alpha\alpha\beta\gamma$ and $\alpha\alpha\alpha\alpha$ (**2**) sites. The pentaborate(1-) interactions to α-centres are reciprocated (Figure 3) and two interactions in **1** and all five of these interactions in **2** are well known eight-membered rings, $R_2^2(8)$ (Etter nomenclature [21]). The third reciprocal-α interaction for **1** is novel and has not been observed before. This may be designated as $R_2^2(12)$ with the H-bond perpendicular to a boroxole ring (at O3) of a neighbouring pentaborate(1-) anion (Figure 3). The direction of the H-bond interactions at O3 in **1** clearly supports sp^2 hydridization for this oxygen atom [22], with acceptor pairs in sp^2 and a *p* orbitals.

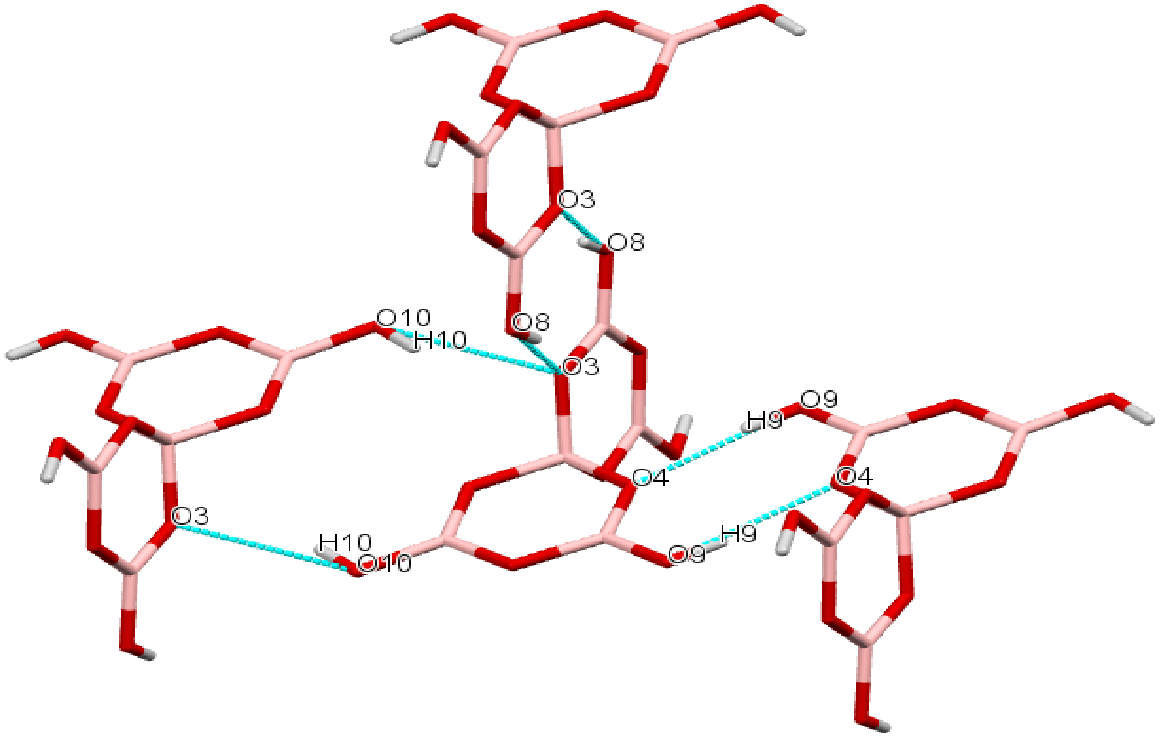


Figure 3. Pentaborate(1-)-pentaborate(1-) H-bond interactions displayed in **1** arranged *d*(H…A)/Å , *d*(D…A)/Å, <(DHA)/°. $R_2^2(8)$: O8*H*8…O3, 1.92, 2.7434(16), 166.77; $R_2^2(8)$: O9**H9**…O4, 1.93, 2.7596(16), 171.7; $R_2^2(12)$: O10***H10***…O3, 2.17, 2.9007(15), 145.3.

Compound **3** contains two pentaborate(1-) anions and one of which is isolated (as in **1** and **2**), and the other one is coordinated to the copper(II) centre, as illustrated in Figure 3. The donor coordination site of the pentaborate(1-) anion is a β hydroxyl oxygen atom rather than a bridging α or γ oxygen centre. Coordination of a pentaborate(1-) to a transition-metal centre has not been observed previously. The related deprotonated dianion, $[OB_5O_6(OH)_3]^{2-}$, has been as found coordinated to a transition-metal centres in $[Co(tren)\{OB_5O_6(OH)_3\}]$ [23] (tren = *tris*(2-aminoethyl)amine) and $[Zn(tren)\{OB_5O_6(OH)_3\}]$ [24]. The isolated and the coordinated pentaborate(1-) anions form H-bond donor interactions to αααω and ααβω sites, respectively, with the coordinated hydroxy group of the pentaborate(1-) anion (O9) linking to a β-site (O18) of a neighbouring isolated pentaborate(1-) anion. The bond angles and bond lengths associated with the coordinated oxygen atom (O9) and its adjacent boron atom (B4) are not significantly different from non-coordinated hydroxyl sites within the anion, and other reported pentaborate(1-) structures [10,18]. The cation in **3**, $[Cu(pn)_2\{B_5O_6(OH)_4\}]^+$, has eight amino H-atoms and which form 8 donor H-bonds: four to water molecules, three to neighboring βγγ pentaborate(1-) sites and one intramolecular H-bond to the coordinated pentaborate(1-) α-site (N11H11A…O4) and details of which can be found in the legend to Figure 4.

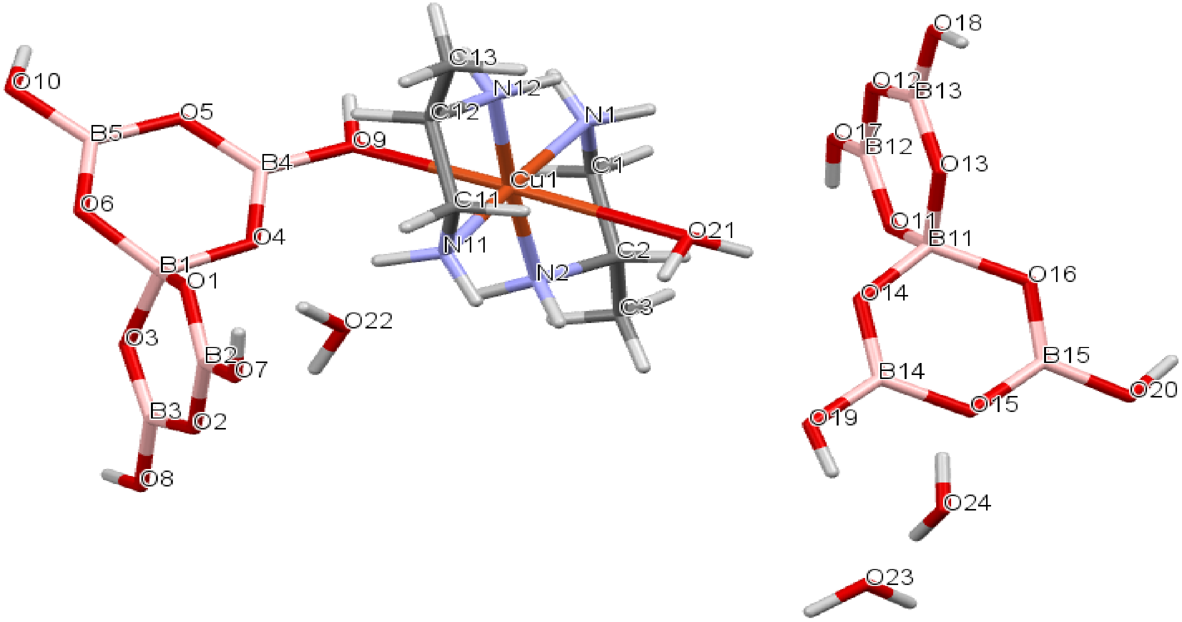


Figure 4. Drawing of compound **3**, showing atomic numbering scheme. The intramolecular H-bond between N11H11…O4 has *d*(H11A…O4) 2.23 Å, *d*(N11…O4) 3.0360(14) Å, < (N11H11O4) 147.5º.

Compound **4** is a salt and comprised of two cationic copper(II) complexes, two heptaborate(2-) anions, and four waters of crystallization. The dach ligands in both complexes are disordered and bond length data summarized below relate to the highest site occupancy. The 'core' square-planar $[Cu(dach)_2]^{2+}$ motif, containing (1*S*,2*S*)-1,2-diaminocyclohexane and (1*R*,2*R*)-1,2-diaminocyclohexane, is present within both cations: one cation is designated square-planar {*T* = 0.70, Cu-N distances range from 1.963(7) - 2.013(8) Å (av. 1.988 Å); Cu-O ($2H_2O$), 2.836 Å} and the other is an axially elongated octahedron {*T* = 0.80, Cu-N distances range from 1.910(13) - 1.923(11) Å (av. 1.917 Å); Cu-O ($2H_2O$), 2.381(3) Å}. These 'short' and 'long' axial Cu-O distances are similar to those found in **1**-**3**.

The heptaborate(2-) anion, $[B_7O_9(OH)_5]^{2-}$, is known to exist in two isomeric forms [25] and the 'O+' isomer, which is found in **4**, is shown schematically in Figure 1(d). This anion has been previously observed in the following three compounds $[H_3N(CH_2)_7NH_3][B_7O_9(OH)_5].H_2O$ [26], [*cyclo*-$C_6H_{11}NH_3]_2[B_7O_9(OH)_5]^{\cdot}3H_2O^{\cdot}B(OH)_3$ [20] and [*cyclo*-$C_7H_{13}NH_3]_2[B_7O_9(OH)_5]^{\cdot}2H_2O^{\cdot}2B(OH)_3$ [20]. This anion has not been previously observed with transition-metal complex cations. A drawing of this anion, together with atomic labelling is shown in Figure 5. The anion has a 3-coordinate oxygen atom (O1, with a formal positive charge) and two 4-coordinate boron atoms (B1 B2, and B3, with formal negative charges). QTAIM analysis on this anion [25a] has shown that the 'real' charges on these atoms are very different: the oxygen centre carries a charge of -1.53 and the three 4-coordinate boron centres have a charge of +2.30. The 3-coordinate oxygen atom is pyramidal with ΣB-O-B angles at 349.25°, with O1 sitting 0.288 Å out of the plane containing B1, B2 and B3. Bond lengths to O1 are given in the legend to Figure 5 and average 1.509 Å; these long single bonds have been noted before in the related compounds [20,26]. B_{trig}-O bond-lengths range in **4** from 1.355(4) - 1.376(2) Å and are also significantly shorter than B_{tet}-O bond-lengths which range from 1.436(3) - 1.468(3) Å (excluding bonds from O1 which as noted above are significantly longer).

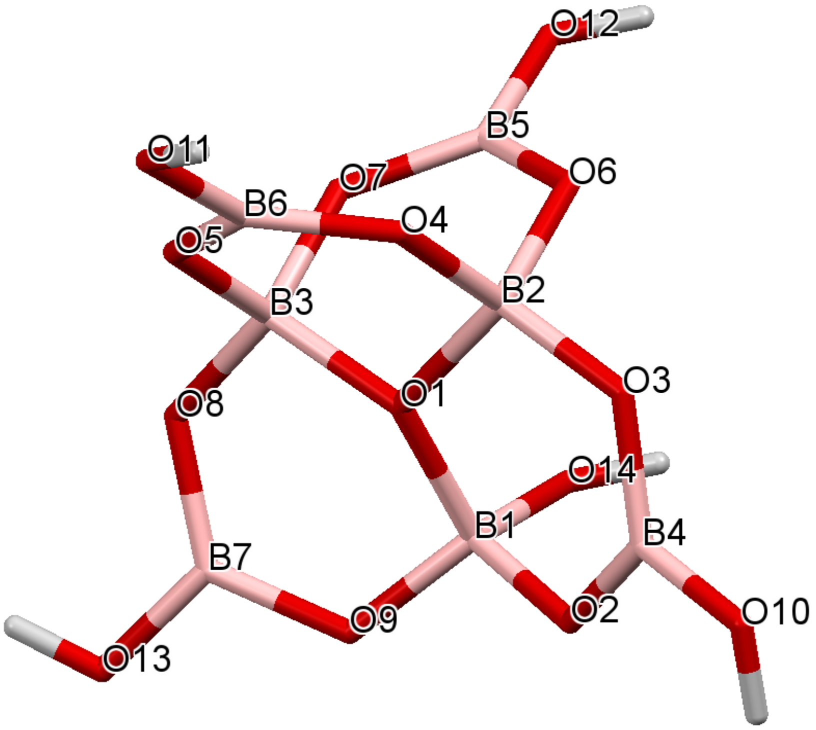


Figure 5. the Heptaborate(2-) anion as found in compound **4**. Selected bond distances (Å) and angles (^{o}): O1-B1, 1.511(3); O1-B2, 1.505(3); O1-B3, 1.512(3); B1-O14, 1.461(4); B1-O1-B2, 119.42(19); B1-O1-B3, 119.13(19); B2-O1-B3, 110.7(2).

The heptaborate(2-) anion has the opportunity to form many H-bonds with five donor sites and fifteen potential acceptor sites. Four out of the five donor sites in **4** are involved in H-bonding to four different heptaborate(2-) anions involving a reciprocal $R_2^2(8)$ interaction {O10H10…O2*} and a reciprocal $R_2^2(12)$ {O13H13…O5*} and two non-reciprocal $R_2^2(8)$ interactions {O11H11...O6*, O12*H12*…O4 and O11*H11*...O6, O12H12…O4*} forming a giant repeating H-bonded anion-anion structure (Figure 6). The unique hydroxyl group (O14H14) on the four coordinate boron centre (B1) is *transoid* to O1 and is not involved in H-bonding. The heptaborate(2-) ions are further held within the second coordination spheres of both the $[Cu(dach)_2(H_2O)_2]^{2+}$ and $[Cu(dach)_2]^{2+}$ cations by H-bonds involving the amino hydrogen atoms. The $[Cu(dach)_2(H_2O)_2]^{2+}$ cation forms two five-point H-bond contacts with its neighbouring heptaborate(2-) anions {N2-H2A…O8, N1-H1A…O14, O21-H21B…O14, N1-H1B…O12, O21-H21B…O9} and this is likely to be strongly involved in structure directing the formation of the compound. Likewise a $R_2^2(8)$ interaction where the heptaborate(2-) is a double acceptor, is present for the square planar $[Cu(dach)_2]^{2+}$ centre (Figure 7).

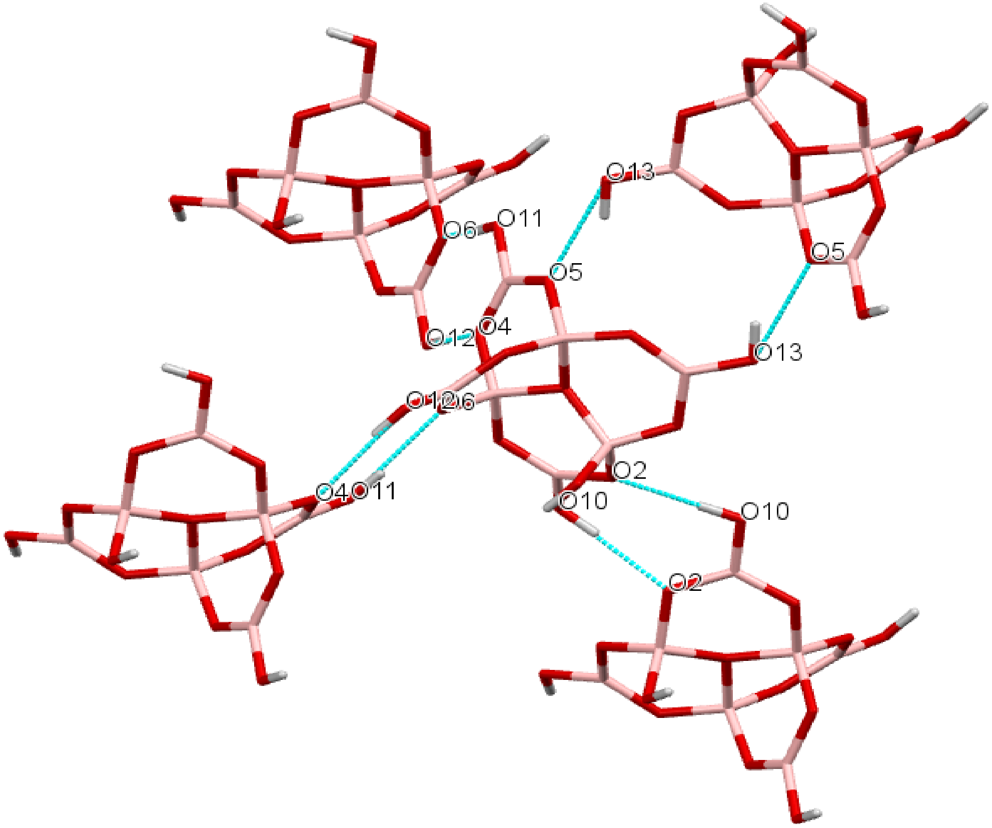


Figure 6. The three $R_2^2(8)$ and one $R_2^2(12)$ connections between heptaborate(2-) anions in **4**. The data are arranged *d*(H…A)/Å , *d*(D…A)/Å, < (DHA)/°. $R_2^2(8)$: O10-H10…O2, 1.89 2.724(3) 176.2. $R_2^2(8)$: O11-H11F…O6, 1.89 2.717(3) 169.9; O12-H12F…O4, 1.91 2.740(3) 170.6. $R_2^2(12)$: O13-H13…O5, 1.94 2.693(3) 149.0

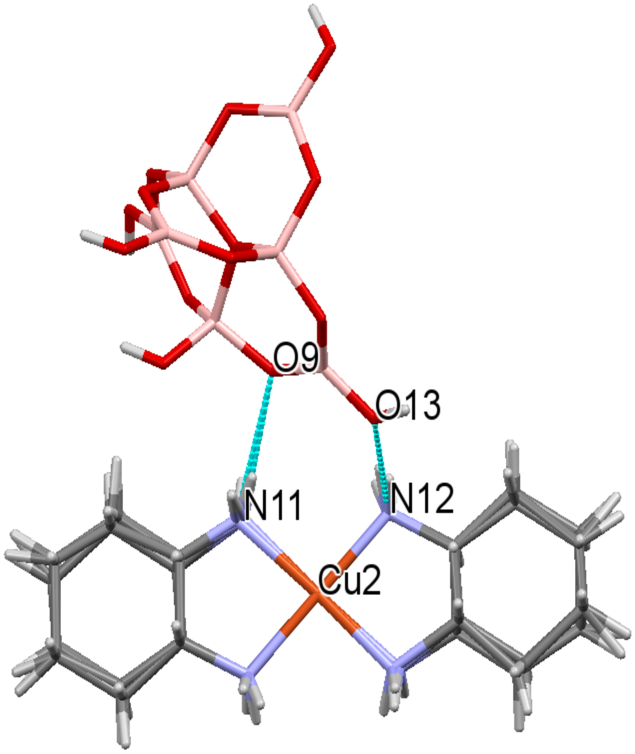


Figure 7. The $R_2^2(8)$ interaction in **4**. The H-bond data are arranged *d*(H…A)/Å , *d*(D…A)/Å, < (DHA)/º. N11-H2A…O9, 2.10,3.002(9), 169.5; N12-H12B…O13, 2.07, 2.869(15), 146.6.

Compounds **5** and **6** are structurally very similar and a drawing of the structure of **5** is shown in Figure 8. Within this paragraph the atomic labels refer to compound **5** and Figure 8. The diamine ligands of compound **6** are disordered over two sites and the data summarized below relates to the species with highest site occupancy (0.63). Both compounds **5** and **6** are neutral complexes arising from the coordination of tridentate hexaborate(2-), $[B_6O_7(OH)_6]^{2-}$, ligands to $[Cu(L\text{-}L)]^{2+}$ centres {L-L = dmen (**5**) or tmeda (**6**)}. The 5-coordinate copper(II) centres in **5** and **6** have τ-indices of 0.19 and 0.02 respectively, demonstrating that they are both best represented as square-based pyramidal structures [17]. The copper(II) centres have their bidentate diamine ligands within the square plane and the tridentate hexaborate(2-) anions complete the two remaining coordination sites of the square plane and coordinates at one axial site (O9 in **5**); the geometry of **5** is slightly more distorted. Compounds **5** and **6** have Cu-N distances of 2.0011(11) Å (N1) and 2.0478(11) Å (N2) (av. 2.025 Å), and 2.035(6) Å and 2.069(10) Å, (av. 2.052 Å), respectively. The square plane Cu-O distances for **5** and **6** are 2.0052(9) Å (O8) and 1.9566(9) Å (O10) (av. 1.9809 Å), and 1.9802(16) Å and 1.9934(16) Å (av. 1.9868 Å), whilst the Cu-O axial distances are 2.2481(9) Å (O9) and 2.1871(16) Å respectively.

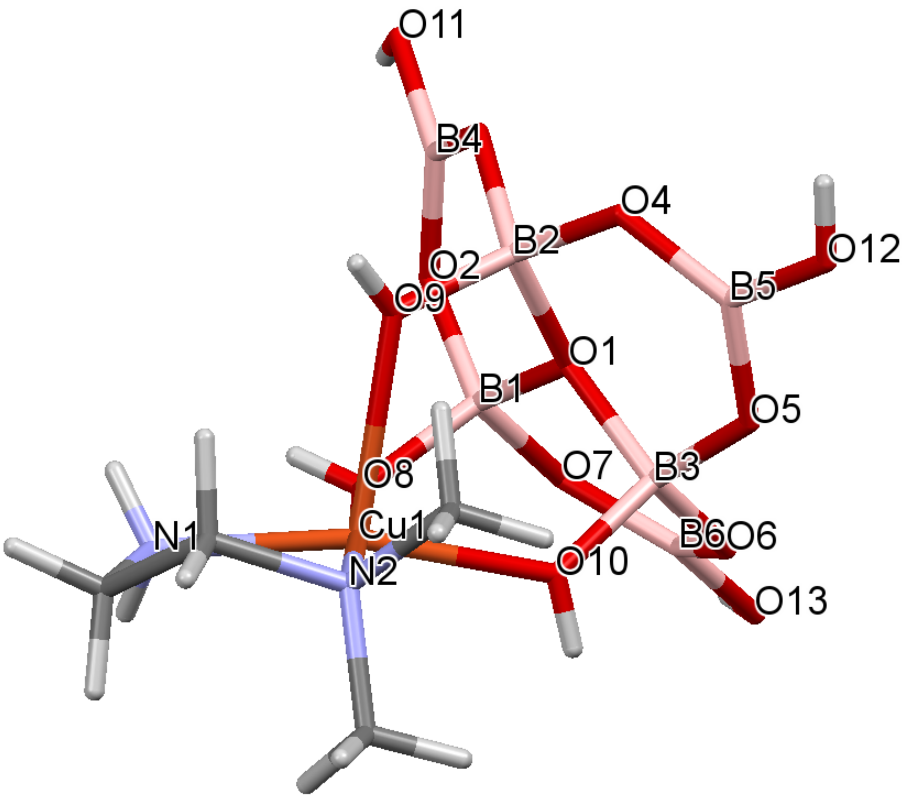


Figure 8. Drawing of the structure of **5** showing the atomic numbering scheme. Four water molecules of crystallization (containing O21, O22, O23, and O24) are omitted from the diagram for clarity.

There are relatively few examples of structures containing the isolated hexaborate(2-) anion although it is represented by the minerals *aksaite* [6a], $Mg[B_6O_7(OH)_6]\cdot 2H_2O$ and *macallisterite* [6a], $Mg_2[B_6O_7(OH)_6]_2\cdot 9H_2O$. Synthetic compounds include $[Ni(H_2O)_4\{B_6O_7(OH)_6\}].H_2O$ [6a], $[Co(H_2O)_6][Co\{B_6O_7(OH)_6\}_2].2H_2O$ [6a], $[Me_2NHCH_2CH_2NHMe_2][Zn\{B_6O_7(OH)_6\}_2].2H_2O$ [27] and $[C_4N_2H_{12}][Co\{B_6O_7(OH)_6\}_2]\cdot 6H_2O$ [28] with the latter two containing non-metal cations.

Compounds **5** and **6** are unusual in that they are neutral coordination complexes, and these neutral molecules strongly interact with their neighbours in the solid-state through numerous H-bond interactions. All six potential H-bond donor sites in the hexaborate(2-) anion in **5** are involved in donor interactions: the three coordinated hydroxyl groups H-bond to one hexaborate(2-) (from O10) and two H_2O molecules, whilst the three uncoordinated hydroxyl groups H-bond to two hexaborate(2-) anions and one H_2O molecule. Therefore, each $[Cu(dmen)\{B_6O_7(OH)_6\}]$ unit has three other such units in its secondary coordination sphere, facilitated through these H-bond interactions. The hexaborate(2-)-hexaborate(2-) interactions (O13H13…O7*, O13*H13*…O7) in **5** can be designated as reciprocal $R_2^2(8)$. The two amino hydrogens on the coordinated nitrogen of the dmen ligand in **5** are also both involved in H-bonding to neighboring hexaborate(2-) anions. This results in a reciprocal $R_2^2(16)$ {N1…O11*, N1*…O11} motif and an unusual $R_2^2(10)$ motif in which a neighbouring hexaborate(2-) is a double acceptor from donor hydrogen atoms on coordinated O10 and N1 atoms; both motifs includes the copper(II) centre within their rings (Figure 9). In **6** all six potential H-bond donor sites of the hexaborate(2-) anion partake in H-bond interaction: three coordinated hydroxyl groups are H-bonded to H_2O molecules and the three uncoordinated hydroxyl groups are H-bonded to one H_2O and two hexaborates. However, **6** does not possess any amino hydrogen atoms in the tmeda ligand, and this leads to only hexaborate(2-)-

hexaborate(2-) interactions between neighbouring [Cu(tmeda){$B_6O_7(OH)_6$}] units linked into infinite chains through two-reciprocal $R_2^2(8)$ interactions.

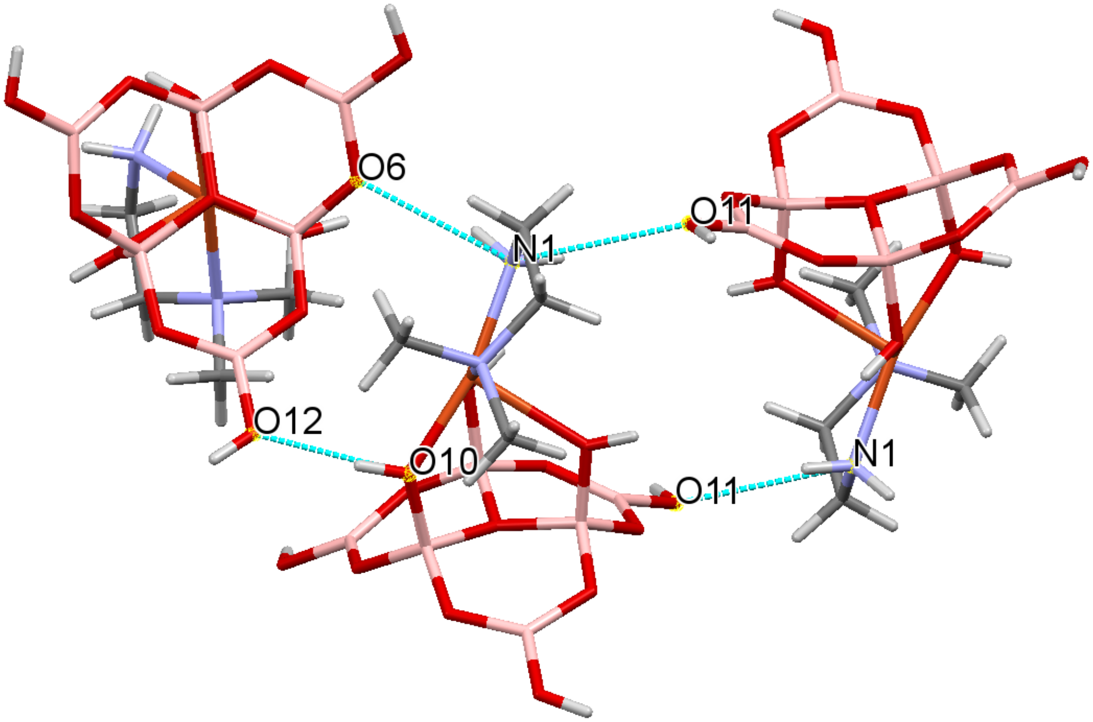


Figure 9. The $R_2^2(16)$ and the unusual $R_2^2(10)$ interactions in **5**. The H-bond data are arranged *d*(H…A)/Å , *d*(D…A)/Å, < (DHA)/°. $R_2^2(10)$: N1-H1A…O6*, 2.153(19), 2.9064(14), 142.6(16). $R_2^2(16)$: N1-H1B…O11*, 2.25(2), 3.0385(15), 151.6(16); O10-H10…O12*, 1.853(10), 2.6839(13), 172(2).

2.3 Magnetic and spectroscopic properties

All compounds contain copper(II) ions. The molar magnetic susceptibilities of compounds **1**-**7** are included in the experimental section and χ_m varies from 820 x 10^{-6} to 1364 x 10^{-6} cm^3 mol^{-1}. These values were very similar to those obtained for the copper(II) starting reagents and correspond to μ_{eff} of 1.40 - 2.02BM. Using the spin-only formula this equates to 0.72 - 1.25 unpaired electron per copper(II) atom consistent with their d^9 electronic configurations. Attempts were made to obtain ^{1}H, ^{13}C and ^{11}B spectra of compounds **1**-**7** in D_2O solution, but we were unable to obtain any ^{1}H and ^{13}C NMR spectra. This may be attributed to paramagnetic effects of the copper(II) ion broadening the signals associated with the organic ligands which are within the primary coordination sphere of the metal. However, ^{11}B NMR spectra were obtainable since the polyborates in **1**-**4** and **7** are discrete insular anions, which are less influenced by the copper(II) ions. Compounds **2**, **5** and **6** contain coordinated polyborates but the observation of ^{11}B signals for these compounds would indicate that the borate ligands are labile, and undergo the expected equilibria reactions once dissociation to the aqueous solution has taken place [8]. The neutral hexaborate(2-) complexes (**5** and **6**) were insoluble in organic solvents including $CDCl_3$. The ^{11}B spectra of compounds **1** and **3** were typical of those previously observed for pentaborate(1-) compounds [7a] whereas all other samples gave just a single signal between 16.9 and 13.9 ppm. The calculated chemical shift values (based on the B_{total}/B^- ratio) [10d] for **4** and **7** were in good agreement with observed values, but chemical shifts to higher frequency than calculated were observed for **2**, **5** and **6**.

IR spectra of **1**-**3** all show a band at 918-927 cm^{-1}, attributable to a symmetric B_{trig}-O stretch, and diagnostic of pentaborate(1-) anions [29]. Compound **4** contains the heptaborate(2-) anion and strong IR absorption bands at 905 and 863 cm^{-1} have been tentatively assigned [20] to this anion in the *cyclo*-alkylammonium heptaborates, [*cyclo*-$C_6H_{11}NH_3]_2[B_7O_9(OH)_5]\cdot 3H_2O\cdot B(OH)_3$ and [*cyclo*-$C_7H_{13}NH_3]2\cdot H_2O\cdot 2B(OH)_3$. However, **4** displays only one of these two strong bands (at 854 cm^{-1}) and it must now be assumed that the bands at 905 cm^{-1} in the *cyclo*-ammonium heptaborates are organic related. Compounds **5** and **6** both contain the hexaborate(2-) anion and IR literature data on compounds containing this anion are sparse. However, Li *et al.* [30] have noted that a strong IR band is observed at 808-813 cm^{-1} (symmetric B_{tet}-O) in magnesium hexaborates and calcium hexaborates, and a medium-strong band is at 958 cm^{-1} (symmetric B_{trig}-O). Consistent with this, compounds **5** and **6** display these diagnostic bands at 958 and 808, and 953 and 809 cm^{-1}, respectively.

2.4 Thermal properties

The thermal properties of **1**-**7** have been investigated under atmospheric conditions by TGA/DSC analysis. All compounds thermally decompose to coloured glassy solids with the residual material consistent (by mass) with the formation of anhydrous copper(II) borates with Cu:B stoichiometries consistent with that of the initial compound. The TGA/DSC traces indicate multi-step processes which involve initial dehydration with subsequent oxidation of the organics present. Thus, for example compound **6**, $[Cu(tmeda)\{B_6O_7(OH)_6\}]\cdot 6H_2O$, decomposes to CuB_6O_{10} (= $CuO\cdot 3B_2O_3$) upon heating to 650°C. The TGA plot shows 3 distinct steps which we attribute to (i) loss of four waters of crystallization, 70-180 °C; (ii) further loss of three waters from the dehydration of the hexaborate, 180-250 °C; and (iii) oxidation of the organics, 250-650 °C. This is consistent with previous observations for thermal (in air) decomposition of other transition-metal complex polyborates [11, 13, 31]. Full details for compounds **1**-**7** are given in the experimental section and DSC/TGA traces are available as Electronic Supplementary Information.

3. Conclusion

$B(OH)_3$ in basic aqueous solution exists as a Dynamic Combinatorial Library of polyborate anions and from which it is possible to crystallize self-assembled compounds. These self-assembled compounds are templated by the copper(II) complex cations present. By this method we have prepared ionic compounds containing isolated tetraborate(2-), pentaborate(1-) or heptaborate(2-) anions and neutral complexes containing coordinated tridentate hexaborate(2-) anions. In all cases it appears that that H-bonding interactions (anion-anion and/or cation-anion) contribute to the crystal-engineering process with unusual ring motifs, *e.g.* $R_2^2(8)$ and $R_2^2(10)$, involving the copper(II) centres. $[Cu(pn)_2\{B_5O_6(OH)_4\}][B_5O_6(OH)_4]\cdot 4H_2O$ (**3**) is the first reported example of a transition-metal complex with a coordinated pentaborate(1-) anion and $[Cu(dach)_2(H_2O)_2][Cu(dach)_2][B_7O_9(OH)_5]_2\cdot 4H_2O$ (**4**) is the first example of a compound containing a heptaborate(2-) partnered with a transition-metal complex cation. We are currently employing this current synthetic strategy to other transition-metal systems, with the aim of discovering new self-assembled polyborate architectures.

4. Experimental

4.1 General

Copper(II) complexes $[Cu(en)_2]SO_4$ [32], $[Cu(pn)_2]SO_4$ [33], $[Cu(dach)_2(H_2O)_2]Cl_2$ [34] and $[Cu(dmen)_2]Cl_2$ [35] were prepared by literature methods. NMR spectra were obtained on a Bruker Avance-400 spectrometer. ^{11}B NMR spectra were obtained on samples dissolved in D_2O at 128 MHz. FTIR spectra were obtained as KBr pellets on a Perkin-Elmer 100FTIR spectrometer. TGA and DSC were performed on an SDT Q600 instrument using Al_2O_3 crucibles with a ramp rate of 10 ^{o}C per minute (RT to 1000 ^{o}C in air). Powder X-ray diffraction was carried out on a Phillips X'Pert 2040/60 XRD diffractometer with spectra obtained using the Phillips X'Pert Data Collector software. X-ray crystallography was performed at the EPSRC national crystallography service centre at Southampton University. Magnetic susceptibility measurements were performed on a Johnson-Matthey magnetic susceptibility balance. CHN analyses were obtained from OEA Laboratories (Callingham, Cornwall).

4.2 *X-ray crystallography*

Crystallographic data for **1**-**6** are given in Table 1. The crystallographic data collection of compounds were performed on Rigaku AFC12 goniometer equipped with an enhanced sensitivity HG Saturn 724+ detector mounted at the window on an FR-E+ SuperBright molybdenum rotating anode generator with either HF Varimax optics (**1**, **2, 3**, **5**, and **6**) or VHF Varimax optics (**4**) at 100(2) K [36a]. Cell determinations and data collections were carried out using CrystalClear [36b]. Data reduction, cell refinement and absorption correction used either CrystalClear (**1**) or CrysAlisPro [36c] (**2 - 6**). Structures were solved using using Olex2 [36d] and either Superflip [36e] (**1**, **2**, **3**, **4**, **6**) or SHELXT (**5**) and models refined with SHELXL [36f]. Structure refinement details are given in Table 1, and in the supplementary material.

4.3 *Preparation of* $[Cu(en)_2][B_5O_6(OH)_4]_2{\cdot}2H_2O$ (***1***)

$[Cu(en)_2]SO_4$ (1.00 g, 3.57 mmol) and $Ba(OH)_2{\cdot}8H_2O$ (1.13 g, 3.57 mmol) were dissolved in distilled water (25 mL). The mixture was stirred at room temperature for 10 minutes and the white precipitate which had formed ($BaSO_4$) was removed by filtration. $B(OH)_3$ (2.20 g, 35.7 mmol) was added to the filtrate and the solution was stirred for 30 mins. The volume of the reaction solution was then reduced to 5 mL by gentle evaporation on a warm water bath. The crude product was collected by filtration and recrystallized using a water/ethanol mixture (1:1) to afford purple crystals (1.20 g, 52 %). M.p. = 283-285 °C (dec.). $\chi_m = 1134 \times 10^{-6}$ cm^3 mol^{-1}. $C_4H_{28}CuB_{10}N_4O_{22}$. *Anal.* Calc.: C = 7.5 %, H = 4.1 %, N = 8.8 %. Found: C = 7.4 %, H = 4.4 %, N = 8.6 %. ^{11}B/ppm 1.3 (3 %), 13.4 (25 %), 17.3 (72 %). IR (KBr/cm^{-1}): 3459 (s), 3328 (s), 3282 (s), 1614 (m), 1416 (s), 1314 (s), 1139 (s), 1094 (s), 1041 (s), 927 (s), 776 (s), 708 (s), 549 (m), 464 (m). p-XRD d-spacing/Å (% rel. int.): 7.20 (62), 6.33 (64), 5.65 (66), 5.26 (75), 3.92 (100), 3.23 (41). TGA: 70-180 °C, loss of two interstitial H_2O 6.0 % (5.5 % calc.); 180-280 °C, condensation of polyborate with loss of four further H_2O 16.0% (16.5 % calc.); 280-600 °C, oxidation of organic content 32.9 % (34.9 % calc.); residual $CuB_{10}O_{16}$ 67.1 % (65.1 % calc.).

*4.4 Preparation of $[Cu(dmen)_2(H_2O)][B_5O_6(OH)_4]_2{\cdot}3H_2O$ (**2**)*

$[Cu(dmen)_2]Cl_2$ (1.00 g, 3 mmol), and Ag_2O (0.746 g, 3 mmol) were rapidly stirred in H_2O (25 mL) at room temperature for 30 minutes and the precipitate which had formed (AgCl) was removed by filtration. $B(OH)_3$ (1.99 g, 32 mmol) was added to the dark blue filtrate and left to stir for a further 30 mins. The reaction mixture was filtered again and the filtrate was placed in small vials and left to allow for slow evaporation of solvent. After 12 h , purple crystals had formed and these were collected by filtration and dried in desiccator (1.19 g, 53 %). M.p. = > 300 ^{0}C. χ_m = 820

× 10^{-6} cm^3 mol^{-1}. $C_8H_{40}CuN_4B_{10}O_{24}$. *Anal.* Calc.: C = 12.8 %, H = 5.4 %, N = 7.5 %. Found: C = 13.0 %, H = 5.3 %, N = 7.3. ^{11}B/ppm: 16.5. IR (KBr/cm^{-1}): 3587 (m), 3336 (m), 3271 (m), 1421 (s), 1308 (s), 1158 (m), 1125 (m), 1065 (m), 1017 (m), 918 (m), 776 (m), 708 (m). p-XRD: d-spacing/Å (% rel. int.): 6.67 (16), 5.71 (100), 5.51 (12), 4.54 (25), 3.73 (40), 3.34 (12), 2.03 (13). TGA: 30-90 ^{0}C, loss of three interstitial and one coordinated H_2O 9.8% (9.6% calc.); 90-250 ^{0}C, condensation of polyborate with loss of four further H_2O 11.5 % (9.6 % calc.); 250-630 ^{0}C, oxidation of organic content 23.8 % (23.5 % calc.); residual $CuB_{10}O_{16}$ 54.9 % (57.3 % calc.).

*4.5 Preparation of $[Cu(pn)_2\{B_5O_6(OH)_4\}][B_5O_6(OH)_4]\cdot 4H_2O$ (**3**)*

The preparation of a $[Cu(pn)_2](OH)_2$ solution was carried out from $[Cu(pn)_2]SO_4$ (1.00 g, 3.24 mmol) and $Ba(OH)_2\cdot 8H_2O$ (1.02 g, 3.24 mmol). using the method described in the preparation of **1**. $B(OH)_3$ (2.00 g, 32.4 mmol) was added to the solution. After stirring for 30 minutes the solution's volume was concentrated to 5 mL by gentle evaporation on a warm water bath. The crude product was collected by filtration, and recrystallized by using water/ethanol. The product was carefully washed with ethanol and then acetone and then dried at 40 ^{o}C for 5 hours to yield purple crystals (1.30 g, 56 %). M.p. = 296-298 $^\circ$C (dec.). χ_m = 1094 × 10^{-6} cm^3 mol^{-1}. $C_6H_{36}B_{10}CuN_4O_{24}$. *Anal.* Calc.: C = 10.0 %, H = 5.0 %, N = 7.8 %. Found: C = 10.1 %, H = 5.4 %, N = 7.6 %. ^{11}B/ppm: 1.5 (2 %), 13.2 (24 %), 16.9 (74 %). IR (KBr/cm^{-1}): 3405 (s), 3305 (s), 2974 (s), 1423 (s), 1380 (s), 1336 (s), 1305 (s), 1121 (m), 1061 (s), 1019 (s), 921 (s), 778 (s), 708 (s). p-XRD d-spacing/Å (% rel. int.): 7.57 (33), 6.21 (17), 5.39 (18), 4.69 (100), 3.39 (51), 2.03 (20). TGA: 70-180 °C, loss of four interstitial H_2O 9.1 % (10 % calc.); 180-250 °C, condensation of polyborate with loss of four further H_2O 18.2 % (20 % calc.); 250-650 °C, oxidation of organic content 38.1 % (40.6 % calc.); residual $CuB_{10}O_{16}$ 61.9 % (59.4 % calc.).

*4.6 Preparation of $[Cu(dach)_2(H_2O)_2][Cu(dach)_2][B_7O_9(OH)_5]_2{\cdot}4H_2O$ (**4**)*

$[Cu(dach)_2(H_2O)_2]Cl_2$ (1.0 g, 2.5 mmol.) was added to an aqueous (40 mL) suspension of excess activated Dowex 550A (30 g) mesosphere ion exchange resin (OH^- form). The suspension was stirred overnight, the ion exchange resin was removed by filtration and washed with water (4 × 5mL). The filtrate, containing $[Cu(dach)_2(H_2O)_2](OH)_2$, was reduced in volume by using rotary evaporator to ~15mL and then diluted with methanol (15 mL). $B(OH)_3$ (1.55 g, 25 mmol) was added to the H_2O/MeOH solution which was gently warmed with stirring for 3 hours. The solution volume was reduced to 5 mL using a rotary evaporator. The product was collected by filtration and allowed to dry overnight in an oven at 40 °C to yield purple crystals of **4** (0.84 g, 52 %). M.p. = 263-265 °C (dec.). $\chi_m = 1145{\times}10^{-6}$ cm^3 mol^{-1}. $C_{12}H_{39}B_7CuN_4O_{17}$. *Anal.* Calc.: C = 22.2 %, H = 6.0 %, N = 8.6 %. Found: C = 22.0 %, H = 6.1 %, N = 8.5 %. ^{11}B/ppm 14.7. IR (KBr/cm^{-1}): 3480(s), 3304(s), 3245(s), 2931(s), 2863(m), 1603(w), 1468(m), 1454(s), 1350(s), 1183(s), 1134(s), 1059(s), 987(w), 949(w), 919(w), 854(s), 815(s), 686(w). p-XRD d-spacing/Å (% rel. int.): 10.80 (71), 9.76 (100), 6.27 (45), 5.95 (36), 5.31 (36), 4.25 (40), 3.77 (41). TGA: 70-190 °C, loss of six interstitial H_2O 9.0 % (8.3 % calc.); 190-250 °C, condensation of polyborate with loss of five further H_2O 16.0 % (15.2 % calc.); 250-650 °C, oxidation of organic content 51.0 % (50.4 % calc.); residual $CuB_7O_{11.5}$ 49.0 % (49.6 % calc.).

*4.7 Preparation of $[Cu(dmen)\{B_6O_7(OH)_6\}]\cdot 4H_2O$ (**5**)*

$[Cu(dmen)_2]Cl_2$ (1.00 g, 3 mmol) was dissolved in H_2O (40 mL) to give a dark blue solution. DOWEX® Monosphere 550A Ion Exchange Resin (60 g) was added to the solution which was left to stir for 24 hours. The ion exchange resin was removed by filtration and $B(OH)_3$ (1.99 g, 30 mmol) was added to the filtrate which was then left to stir for 30 minutes. The dark blue reaction mixture was filtered into vials and left to allow for slow evaporation of H_2O to occur. After 1 week, the blue crystals of **6** which had formed were collected filtration (0.61 g, 41%). M.p.: > 300 ^{0}C. χ_m: 880×10^{-6} cm^3 mol^{-1}. $C_4H_{26}CuN_4B_6O_{17}$. *Anal.* Calc.: C = 9.5 %, H = 5.2 %, N = 5.6 %. Found: C = 9.7 %, H = 5.2 %, N = 5.5 %. ^{11}B/ppm: 16.9. IR (KBr/cm^{-1}): 3340 (b), 3254 (b), 2931 (w), 2859 (w), 2814 (w), 1641 (w), 1586 (w), 1467 (sh), 1423 (s), 1366 (s), 1269 (s), 1137 (s), 1091 (s), 1052 (s), 1007 (m), 958 (m), 892 (m), 859 (m), 808 (s), 784 (m), 694 (m), 574 (w). p-XRD d-spacing/Å (% rel. int.): 10.87 (100), 8.64 (25), 7.30 (28), 3.65 (23). TGA: 30-120 ^{0}C, loss of four interstitial H_2O 14.2 % (14.3 % calc.); 120-250 ^{0}C, condensation of polyborate with loss of three further H_2O 11.8 % (10.7 % calc.); 250-650 ^{0}C, oxidation of organic content 18.3 % (17.5 % calc.); residual CuB_6O_{10} 55.7 % (57.5 % calc.).

*4.8 Preparation of $[Cu(tmeda)\{B_6O_7(OH)_6\}]\cdot 6H_2O$ (**6**).*

A solution of *N*,*N*,*N'*,*N'*-tetramethylethylendiamine (tmeda) (3.72 g, 32.04 mmol) in water (3 mL) was added to an aqueous solution of $CuSO_4\cdot 5H_2O$ (4.00 g, 16.02 mmol) in water (10 mL). The reaction mixture was stirred at room temperature for 60 minutes, and then a solution of barium $Ba(OH)_2\cdot 8H_2O$ (5.05 g, 16.02 mmol) in water (15 mL) was added. The reaction mixture was stirred for a further 30 minutes and then filtered to remove $BaSO_4$. A solution of $B(OH)_3$ (9.90 g, 160.2

mmol) in water (10 mL) was added to the filtrate and the reaction mixture was stirred at room temperature for 3 hours. The volume of the solution was reduced to 20 mL by using a rotary evaporator. The solution was distributed over a number of small vials and left for 10 days to yield bright blue crystals of **5** (4.80 g, 53 %). M.p. = 243-245 °C (dec.). χ_m = 1320×10^{-6} cm^3 mol^{-1}. $C_6H_{34}B_6CuN_2O_{19}$. *Anal.* Calc.: C = 12.7 %, H = 6.1 %, N = 4.9 %. Found: C = 12.8 %, H = 6.2 %, N = 5.0 %. ^{11}B/ppm: 15.3. IR (KBr/cm^{-1}): 3399(s), 2926(w), 1638(w), 1470(m), 1419(s), 1366(s), 1133(s), 1086(s), 1037(s), 953(s), 902(m), 852(m), 809(s), 694(w). p-XRD d-spacing/Å (% rel. int.): 8.57 (100), 7.75 (66), 7.04 (28), 5.75 (75), 4.29 (28), 2.03 (48), 1.22 (30)**.** TGA: 70-180 °C, loss of six interstitial H_2O 19.4 % (19.1 % calc.); 180-250 °C, condensation of polyborate with loss of three further H_2O 28.6 % (28.6 % calc.); 250-650 °C, oxidation of organic content 48.1 % (49.2 % calc.); residual CuB_6O_{10} 51.9 % (50.8 % calc.).

*4.9 Preparation of [Cu(en)$_2$][B$_4$O$_5$(OH)$_4$]·2H$_3$BO$_3$ (**7**).*

The preparation of complex hydroxide solution was carried out in the same method as described previously in the preparation of **1** from $[Cu(en)_2]SO_4$ (1.00 g, 3.57 mmol) and $Ba(OH)_2 \cdot 8H_2O$ (1.12 g, 3.57 mmol). $B(OH)_3$ (1.10 g, 17.85 mmol) was directly added to the filtrate. After stirring for 30 minutes the solution volume was reduced to 5 mL using a rotary evaporator. The crude product was collected by filtration and recrystallized using a H_2O/EtOH mixture (1:1) to yield navy crystals of **2** (1.05 g, 59 %). M.p. = 275-276 °C (dec.). χ_m = 1007×10^{-6} cm^3 mol^{-1}. $C_4H_{26}CuB_6N_4O_{15}$. *Anal.* Calc.: C = 9.6 %, H = 5.2 %, N = 11.2 %. Found: C = 9.7 %, H = 5.4 %, N = 11.4 %. ^{11}B/ppm: 13.9. IR (KBr/cm^{-1}): 3513(s), 3346(s), 3252(s), 2960(s), 2920(m), 1612(w), 1466(s), 1432(s), 1363(s), 1219(m), 1147(m), 1042(s), 1005(s), 943(m), 882(m), 806(m), 707(m), 681(m), 524(m), 494(m), 461(m). p-XRD d-spacing/Å (% rel. int.): 7.26 (76), 6.37 (81), 5.67 (73), 5.28 (93), 4.21 (54), 3.92 (100). TGA: 100-200 °C, condensation of polyborate with loss of five H_2O 18.9 % (18.1 % calc.); 200-550 °C, oxidation of organic content 41.2 % (42.2 % calc.); residual CuB_6O_{10} 58.8 % (57.8 % calc.).

Table 1. X-ray crystallographic data and structure refinement for **1-6**.

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_4H_{28}B_{10}CuN_4O_{22}$	$C_8H_{40}B_{10}CuN_4O_{24}$	$C_6H_{36}B_{10}CuN_4O_{24}$	$C_{12}H_{39}B_7CuN_4O_{17}$	$C_4H_{26}B_6CuN_2O_{17}$	$C_6H_{34}B_6CuN_2O_{19}$
Formula weight	655.94	748.08	720.03	650.68	502.67	566.75
Temperature	100(2) K	100(2) K	100(2) K	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*–1	p-1	*P*–1	*C*2/*c*	$P2_1/n$	$P2_1/c$
Unit cell dimensions Å	*a* = 8.0286(5), *b* = 8.6193(5), *c* = 9.6553(7)	*a* = 11.7189(4), *b* = 11.7226(4), *c* = 12.9108(4)	*a* = 11.1860(5), *b* = 11.4551(8), *c* = 12.2830(6)	*a* = 22.4696(9), *b* = 10.8711(3), *c* = 23.0016(7)	*a*=12.75604(17), *b* = 9.86582(12), *c* = 15.7331(2)	*a* = 15.4209(3), *b* = 17.0706(3), *c* = 8.88230(10)
Volume	636.97(7) Å^3	1582.49(9)Å^3	1420.35(15) Å^3	5335.4(3) Å^3	1927.41(5) Å^3	2337.95(7) Å^3
Z	1	2	2	8	4	4
Density (calculated)	1.710 Mg / m^3	1.57 Mg / m^3	1.684 Mg / m^3	1.620 Mg / m^3	1.732 g / cm^3	1.610 Mg / m^3
Absorption coefficient	0.958 mm^{-1}	0.786 mm^{-1}	0.872 mm^{-1}	0.903 mm^{-1}	1.219 mm^{-1}	1.021 mm^{-1}
F(000)	335	774	742	2712	1036	1180
Crystal	Blade; Purple	Prism; purple	Block; Purple	Blade; Purple	Prism; deep blue	Hexagonal Prism; Blue
Crystal size	0.180 × 0.090 × 0.030 mm^3	0.210 × 0.150 × 0.110 mm^3	0.230 × 0.110 × 0.050 mm^3	0.090 × 0.050 × 0.020 mm^3	0.110 × 0.100 × 0.050 mm^3	0.130 × 0.080 × 0.060 mm^3
θ range for data collection	2.399 – 27.477°	2.366 – 27.484°	1.966 – 27.776°	2.175 – 27.483°	2.456 - 27.480°	1.780 – 27.633°
Index ranges	–10 ≤ *h* ≤ 10, –10 ≤ *k* ≤ 11, –12 ≤ *l* ≤ 11	–15 ≤ *h* ≤ 14, –15 ≤ *k* ≤ 13, –16 ≤ *l* ≤ 16	–14 ≤ *h* ≤ 14, –14 ≤ *k* ≤ 13, –15 ≤ *l* ≤ 15	–28 ≤ *h* ≤ 27, –13 ≤ *k* ≤ 14, –29 ≤ *l* ≤ 29	–16 ≤ *h* ≤ 16, –12 ≤ *k* ≤ 12, –20 ≤ *l* ≤ 20	–19 ≤ *h* ≤ 20, –22 ≤ *k* ≤ 22, –11 ≤ *l* ≤ 11

Reflections collected	9270	26183	24265	26756	24614	9533
Independent reflections	2915 [R_{int} = 0.0341]	7230 [R_{int} = 0.0230]	6574 [R_{int} = 0.0178]	6106 [R_{int} = 0.0378]	4397 [R_{int} = 0.0195]	9533 [R_{int} = -*]
Completeness to $\theta = 25.242°$	99.6 %	99.5%	99.7 %	99.9 %	99.5 %	99.8 %
Absorption correction	Semi–empirical from equivalents	Semi–empirical from equivalents	Semi–empirical from equivalents	Semi–empirical from equivalents	Semi–empirical from equivalents	Semi–empirical from equivalents
Max. and min. transmission	1.000 and 0.808	1.00000 and 0.86808	1.00000 and 0.94563	1.00000 and 0.79858	1.00000 and 0.84361	1.00000 and 0.87243
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2915 / 0 / 194	7230/ 0/ 509	6574 / 24 / 438	6106 / 940 / 525	4397 / 12 / 337	9533 / 147 / 380
Goodness-of-fit on F^2	1.071	1.068	1.028	1.045	1.066	1.109
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1$ = 0.0299, $wR2$ = 0.0795	$R1$ = 0.0248, $wR2$ = 0.0657	$R1$ = 0.0243, $wR2$ = 0.0665	$R1$ = 0.0522, $wR2$ = 0.1330	$R1$ = 0.0221, $wR2$ = 0.0597	$R1$ = 0.0354, $wR2$ = 0.1326
R indices (all data)	$R1$ = 0.0333, $wR2$ = 0.0811	$R1$ = 0.0258, $wR2$ = 0.0664	$R1$ = 0.0252, $wR2$ = 0.0669	$R1$ = 0.0656, $wR2$ = 0.1404	$R1$ = 0.0231, $wR2$ = 0.0604	$R1$ = 0.0381, $wR2$ = 0.1405
Extinction coefficient	n/a	n/a	n/a	n/a	n/a	n/a
Largest diff. peak and hole molecules structure	0.392 and –0.327 e Å^{-3}	0.336 and –0.521 e Å^{-3}	0.397 and –0.402 e Å^{-3}	1.516 and –0.557 e Å^{-3}	0.348 and -0.404 e Å^{-3}	0.621 and –0.650 e Å^{-3}

*No R_{int} for **6** as the crystal was a non-merohedral twin and all data merged

Appendix A. Supplementary data.

CCDC1534199-1534204 contains the supplementary crystallographic data for **1-6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ (fax +44 1223 336033) or email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk. Electronic Supplementary Information (crystallographic and TGA/DSC data) associated with this article can also be found in the online version at http//……..

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