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# Syntheses, characterization and reactivity of Lewis acid—base adducts based on B—N dative bonds



Sudeshna Saha<sup>a</sup>, Ravi Kumar Kottalanka<sup>b</sup>, Tarun K. Panda<sup>b</sup>, Klaus Harms<sup>c</sup>, Stefanie Dehnen<sup>c</sup>, Hari Pada Nayek<sup>a,\*</sup>

<sup>a</sup> Department of Applied Chemistry, Indian School of Mines, Dhanbad 826004, Jharkhand, India

<sup>b</sup> Department of Chemistry, Indian Institute of Technology, Hyderabad, Ordnance Factory Estate, Yeddumailaram 502205, Andhra Pradesh, India

<sup>c</sup> Fachbereich Chemie, Philipps Universität Marburg, Hans Meer-wein Strasse, Marburg, Germany

# A R T I C L E I N F O

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# ABSTRACT

Three Lewis acid—base adducts  $[(PhBO)_3 \cdot 2hmt]$  (1),  $[(PhBO)_3 - hmt - (PhBO)_3]$  (2) and  $[\{(F-Ph)BO\}_3 \cdot hmt]$ (3) (hmt = hexamethylenetetramine) were prepared by the treatment of phenylboronic acid  $[PhB(OH)_2]$ or 4-fluorophenylboroxine  $[\{(F-Ph)BO\}_3]$  with hexamethylenetetramine (hmt) in methanol or acetone. The solid state structures of all the compounds were established by single crystal X-ray diffraction analysis. Crystal structure determination indicates the formation of boroxine ring through ligandmediated dehydration of arylboronic acids. Triphenylboroxine acts as a bridge between two hmt molecules in 1, whereas hmt plays the role of a bridging ligand between two triphenylboroxine rings in 2. Compound 1 is rare 1:2 adduct of triphenylboroxine and hmt whereas compound 2 and 3 are 1:2 and 1:1 adducts of triphenylboroxine or 4-fluorophenylboroxine and hmt respectively. The lability of the B–N bond in solution was confirmed by NMR spectroscopy as well as by chemical reaction of 1 with  $[Co(H_2O)_6](ClO_4)_2$ , resulting in the formation of  $[Co(H_2O)_6](ClO_4)_2 \cdot (hmt)_2 \cdot 2H_2O$  (4), a boroxine free hydrogen bonded framework structure.

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# 1. Introduction

In recent years, boron compounds were extensively utilized as building blocks for the construction for macrocyclic two or three dimensional assemblies and frameworks [1-4]. In this context, the B–OH moieties of alkyl and arylboronic acids,  $RB(OH)_2$  (R = organic group) were condensed to B–O–B and B–OR functions, resulting in the formation of boroxines with six-membered B<sub>3</sub>O<sub>3</sub> ring structures or boronic esters on treatment with alcohols [5,6]. Boroxines are Lewis acidic compounds. It can be found from literature that boroxine can form adducts with N-donor ligands via formation of  $N \rightarrow B$  dative bonds extensively in 1:1 M ratio and adducts with 1:2 or 1:3 M ratio of boroxine and ligand are rare since they are thermodynamically unfavourable [7,8]. The boroxine-base adducts can be easily obtained by two different methods. One is a chemical dehydration process of boronic acids followed by derivatizations of the base and the other method is a ligand-mediated dehydration of boronic acids (Scheme 1). The latter method, ligand-mediated trimerization have been investigated for the construction of macromolecular architectures and frameworks featuring boroxines cores preferably [2]. For instance, very recently, the Fischer group reported the synthesis of covalent organic frameworks from 1,4benzenediboronic acid via an ammonia-assisted pathway [5]. A series of hetero-arylboroxines have also been reported [9]. A large number of macro cycles, 1D- and 2D polymers have been synthesized based on N  $\rightarrow$  B bonds. These were mainly synthesized by treatment of boronate esters with pyridyl based ligands [10–15]. Molecular cages, for example, have been obtained by condensation of a tetraboronic acid with a dicatechol linker or by condensation of triboronic acids with tetra-ols and hexaols [16].

One of our recent research interests is to synthesize supramolecular structures based on  $N \rightarrow B$  bonds using hexamethylenetetramine (hmt) as Lewis base. A recent review by Kirillov group on hmt clearly indicates the versatile nature of hmt ligand as it can adopt many coordination modes from monodentate-to-bridging-bi-, triand -tetradentate on treatment with transition metals. Thus, resulting coordination polymers possessing a large variety of topologies ranging from one-, two-, three-dimensional frameworks as well as honeycomb, diamondoid complex networks [17]. Inspired by flexible coordination mode of hmt, we report herein the synthesis of three Lewis acid—base adducts [(PhBO)<sub>3</sub>·2hmt] (1), [(PhBO)<sub>3</sub>—hmt— (PhBO)<sub>3</sub>] (2) and [{(F-Ph)BO}<sub>3</sub>·hmt] (3) exhibiting 1:2, 2:1 and 1:1 boroxine—hmt interactions. They can be prepared in good yields and

<sup>\*</sup> Corresponding author. E-mail address: hpnayek@yahoo.com (H.P. Nayek).

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Scheme 1. Adduct formation of boroxine with N-donor ligands, NRn'.

high purity from phenylboronic acid  $[PhB(OH)_2]$  (1 and 2) or 4-fluorophenylboroxine  $[(F-Ph)BO]_3$  (3) and hmt in presence (2) or absence (1, 3) of manganese perchlorate hexahydrate respectively. In solution, all the compounds show equivalent boron atoms in the boroxine rings, indicating according equilibria, and thus the labile nature of the B–N bonds in solution. The reaction of compound 1 with cobalt perchlorate hexahydrate leads to the formation of  $[Co(H_2O)_6](CIO_4)_2 \cdot (hmt)_2 \cdot 2H_2O$  (4). We present and discuss synthetic routes, spectroscopic studies and the solid state structures of 1–4.

#### 2. Experimental section

# 2.1. General consideration

All manipulations were performed under aerobic condition. Methanol, acetone were distilled prior to use.  $^{1}\text{H}$  NMR,  $^{13}\text{C}\{^{1}\text{H}\}$  and

<sup>11</sup>B{<sup>1</sup>H} NMR spectra were recorded on a BRUKER AVANCE III-400 spectrometer. IR spectra in KBr (4500–500 cm<sup>-1</sup>) were recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. Elemental analyses were performed on a Vario Micro cube for C, H, N, S Analyser by Elemental Analyser System GMBH. Phenylboronic acid, 4-fluorophenylboronic acid, cobalt carbonate, perchloric acid, hexamine were purchased from Spectrochem, India and used as such.  $[Co(H_2O)_6](ClO_4)_2$  was prepared by reacting cobalt carbonate with perchloric acid.  $[(F-Ph)BO]_3$  was synthesized by condensation of 4-fluorophenylboronic acid in toluene using dean stark apparatus. The NMR solvent CDCl<sub>3</sub> was purchased from Sigma Aldrich.

# 2.2. Syntheses

# 2.2.1. Preparation of $[(PhBO)_3 \cdot 2hmt]$ (1)

Phenylboronic acid (0.250 g, 2.05 mmol) was dissolved in 10 mL of methanol. Hexamethylenetetramine (0.144 g, 1.025 mmol) was added to the methanolic solution. The solution was warmed in water bath for 5 min, filtered and left in a conical for slow evaporation of the solvent. Colourless crystals were collected by filtration after 11 days. Yield: 0.350 g, 87%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 400 MHz):  $\delta$  4.52 (s, 24H, CH<sub>2</sub>), 7.28–7.37 (m, 9H, Ph), 7.89–7.96 (m, 6H, Ph) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C, 100 MHz):  $\delta$  73.6 (CH<sub>2</sub>), 127.4 (Ph), 129.7 (Ph), 134.2 (Ph), 137.0 (Ph) ppm; <sup>11</sup>B NMR (CDCl<sub>3</sub>, 25 °C, 128 MHz):  $\delta$  18.9 ppm. IR data (KBr, cm<sup>-1</sup>): 2975 (w), 2931 (w), 1596 (m), 1465 (m), 1444 (s), 1410 (m), 1376 (s), 1319 (s), 1251 (s), 1231 (s), 1189 (s), 1147 (m), 1069 (s), 996 (s), 908 (w), 827 (s), 738 (s), 655 (s), 621 (s), 592 (m). Anal. calcd for C<sub>30</sub>H<sub>39</sub>B<sub>3</sub>N<sub>8</sub>O<sub>3</sub>: Calc. C 60.85, H 6.64, N 18.92; found C 60.23, H 6.29, N 18.70.

## 2.2.2. Preparation of $[(PhBO)_3 - (\mu_2 - hmt) - (PhBO)_3]$ (2)

Phenylboronic acid (0.250 g, 2.05 mmol) and Mn(ClO<sub>4</sub>)·6H<sub>2</sub>O (0.370 g, 1.025 mmol) were dissolved in 10 mL of methanol. The solution was stirred for 10 min. Hexamethylenetetramine (0.144 g,



Scheme 2. Synthesis of 1 (top), 2 (centre) and 3 (bottom).



Fig. 1. <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of compound 1.

1.025 mmol) was added to the methanolic solution. The solution was refluxed for 1 h. Colourless crystals were appeared on slow evaporating of the solution. Yield: 0.200 g, 77%. IR data (KBr, cm<sup>-1</sup>): 3069 (w), 3021 (w), 1600 (s), 1494 (m), 1442 (s), 1380 (s), 1317 (s), 1252 (s), 1230 (m), 1195 (s), 1177 (m), 1127 (m), 1089 (w), 1064 (m), 1008 (m), 952 (w), 911 (m), 845 (m), 798 (w), 770 (m), 733 (s), 711 (s), 627 (m). Anal. calcd for  $C_{42}H_{42}B_6N_4O_6$ : Calc. C 66.06, H 5.54, N 7.34; found C 65.24, H 5.43, N 7.18.

# 2.2.3. Preparation of $[{(F-Ph)BO}_3 \cdot hmt]$ (3)

4-Fluorophenylboroxine (0.100 g, 0.273 mmol) was dissolved in 5 mL of acetone. Hexamethylenetetramine (0.077 g, 0.546 mmol) was added to the solution. The solution was stirred at room temperature for 14 h. filtered and left in a conical for slow evaporation of the solvent. Colourless crystals were obtained after 2 days. Yield: 0.100 g, 72%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 400 MHz): δ 4.66 (s, 12H, CH<sub>2</sub>), 7.06–7.11 (m, 6H, Ph), 7.93–7.97 (m, 6H, Ph) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C, 100 MHz):  $\delta$  74.0 (CH<sub>2</sub>), 114.4, 114.6 (d,  $J_{C-F} = 19.7$  Hz, Ph), 136.1, 136.2 (d,  $J_{C-F} = 7.7$  Hz, Ph), 163.2, 165.7 (d,  $J_{C-F} = 248.3$  Hz, Ph) ppm; <sup>11</sup>B NMR (CDCl<sub>3</sub>, 25 °C, 128 MHz): δ 19.5 ppm; <sup>19</sup>F NMR (CDCl<sub>3</sub>, 25 °C, 376 MHz):  $\delta$  –111.0 ppm. IR data (KBr, cm<sup>-1</sup>): 2975 (w), 2931 (w), 1590 (s), 1502 (w), 1428 (m), 1411 (s), 1379 (m), 1327 (s), 1288 (s), 1256 (m), 1211 (m), 1182 (w), 1154 (w), 1119 (w), 1084 (w), 1007 (s), 834 (m), 785 (w), 750 (s), Anal. calcd for C<sub>24</sub>H<sub>24</sub>B<sub>3</sub>N<sub>4</sub>O<sub>3</sub>F<sub>3</sub>: Calc. C 56.97, H 4.78, N 11.07; found C 56.81, H 4.64, N 10.92.

# 2.2.4. Preparation of $[Co(H_2O)_6](ClO_4)_2 \cdot (hmt)_2 \cdot 2H_2O$ (4)

Compound **1** (0.050 g, 0.08 mmol) was dissolved in 5 mL MeOH. A 5 mL of methanolic solution of  $Co(ClO_4)_2 \cdot 6H_2O$  (0.030 g, 0.08 mmol) was added to it and again 5 mL of MeOH was added to the solution. The solution was stirred for 1 h, kept in conical. After



**Fig. 2.** Solid state structure of compound **1** (top left), **2** (bottom) and **3** (top right) and selected bond lengths [Å] and bond angles [°]; **1**: B1–O1 1.4323(14), B1–O2 1.4564(16) B2–O2 1.3584(12), B1–N1 1.7196(16), B1–C1 1.6191(17), B2–C7 1.575(3), O1–B1–O2 115.70(10), B1–O2–B2 121.30(11), O2–B2–O2' 122.72(16), O1–B1–N1 104.49(9), C1–B1–N1 107.02(9); **2**: B1–O1 1.443(3), B1–O3 1.451(2), B2–O1 1.350(3), B2–O2 1.386(3), B3–O2 1.383(3), B3–O3 1.356(3), B4–O4 1.455(3), B4–O6 1.448(3), B5–O4 1.347(3), B5–O5 1.383(3), B6–O5 1.385(3), B6–O6 1.348(3) B1–N1 1.688(3), N3–B4 1.704(3), O1–B1–O2 115.70(10), B1–O2–B2 121.30(11), O2–B2–O2' 122.72(16), O1–B1–N1 104.49(9), C1–B1–N1 107.02(9); **3**: B1–O1 1.454(3), B1–O3 1.454(3) B2–O2 1.386(3), B1–N6 1.658(4), B1–C1 1.614(3), B2–C17 1.553(4), O1–B1–O3 113.61(19), B1–O1–B2 122.91(19), O2–B3–O3 121.28(2), O1–B1–N6 103.56(19), C11–B1–N6 110.5(19).

30 days pink coloured crystals were appeared. Yield: 0.035 g, 62.5%. IR data (KBr, cm<sup>-1</sup>): 3444 (br), 1643 (m), 1461 (w), 1236 (m), 1140 (s), 1107 (s), 1086 (s), 1011 (m), 690 (w), 623 (m). Anal. calcd for  $C_{12}H_{40}N_8O_{16}Cl_2Co$ : Calc. C 21.10, H 5.86, N 16.41; found C 20.86, H 5.76, N 16.09.

#### 2.3. X-ray crystallography

Single crystals of compounds 1 and 2 were mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in diffractometer at 298(2) K. Measurements of 1 and 2 were made on an Oxford Supernova Eos CCD detector with graphite-monochromatic Cu-Ka (1.54184 Å) radiation. The data of compound 3 and 4 were collected on a Bruker D8 Quest diffractometer equipped with a Photon 100 CMOS area detector system, using  $MoK_{\alpha}$  radiation with graphite monochromatization ( $\lambda = 0.71073$  Å) at T = 103 (2) K. The structures were solved by direct methods (SIR92) [24] and refined on  $F^2$  by full-matrix least-squares methods; using SHELXL-97 [25,26]. Nonhydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was  $\left[\sum w(Fo^2 - w)\right]$  $Fc^{2})^{2}$ ] ( $w = 1/[\sigma^{2} (Fo^{2}) + (aP)^{2} + bP]$ ), where  $P = (Max(Fo^{2}, 0) + bP)$  $2Fc^2$ )/3 with  $\sigma^2(Fo^2)$  from counting statistics. The function R1 and wR2 were  $(\Sigma ||Fo| - |Fc||)/\Sigma |Fo|$  and  $[\Sigma w (Fo^2 - Fc^2)^2 / \Sigma (wFo^4)]^{1/2}$ , respectively.

# 3. Results and discussions

# 3.1. Syntheses and characterizations

Compounds **1** and **2** were prepared by the treatment of phenylboronic acid  $[PhB(OH)_2]$  with hexamethylenetetramine (hmt) in methanol in absence or presence of manganese perchlorate hexahydrate respectively (Scheme 2). The synthesis of **2** was not possible in absence of manganese perchlorate hexahydrate under identical reaction condition. We assume it reacts with hmt and reduces the concentration of hmt in the reaction mixture, thus favouring the synthesis of **2**. Compound **3** was obtained by reacting

$$[(PhBO)_{3} \cdot 2hmt] (1) + [Co(H_{2}O)_{6}](ClO_{4})_{2}$$

$$\downarrow MeOH$$

$$[Co(H_{2}O)_{6}](ClO_{4})_{2}(hmt)_{2} \cdot 2 H_{2}O (4) + (PhBO)_{3}$$
Scheme 3. Synthesis of 4.

4-fluorophenylboroxine, [{(F-Ph)BO}<sub>3</sub>] with hmt in acetone (Scheme 2). Detailed synthesis procedures are provided in Experimental section. All the compounds were characterized by standard analytical/spectroscopic techniques and the solid-state structures were established by single crystal X-ray diffraction analysis.

The structures of  $[(PhBO)_3 \cdot 2hmt]$  (1),  $[(PhBO)_3 - hmt - (PhBO)_3]$ (2) and  $[{(F-Ph)BO}_{3} \cdot hmt]$  (3) reveal the existence of two of the three boron atoms in a chemically distinct environment. Consequently, different chemical shifts due to two types of phenyl groups and two types of methylene groups of hmt were anticipated for both <sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds **1**, **2** and **3** respectively. It is well established that  $N \rightarrow B$  bond dissociates in solution and the ligand undergoes fast exchange over the boron atoms. Therefore, compound **1** and **3** exhibit only one set of distinct signals in both <sup>1</sup>H and <sup>13</sup>C NMR spectra in solution at ambient temperature implying the magnetic equivalence of all three boron atoms [18]. This is further supported by <sup>11</sup>B NMR which shows only one signal at 18.3 ppm (1) or 19.5 ppm (3) respectively and by <sup>19</sup>F NMR which also shows one signal at -111.0 (**3**) [19,20]. Fig. 1 shows the <sup>11</sup>B NMR spectrum of 1. Compound 2 was not soluble in all common solvents at room temperature. Hence, its characterization by solution NMR measurements was not possible.

According to single crystal X-ray structure analyses, compound **1** and **2** crystallize in the monoclinic space group C2/c and  $P2_1/c$  respectively, with four formula units in the unit cell; compound **3** crystallizes in the triclinic space group *P*-1 with two formula units in the unit cell. Fig. 2 shows the molecular structures of **1**–**3**. Table 1 summarizes details of the X-ray analyses. The molecular structures of **1**, **2** and **3** confirm the formation of boroxine ring through condensation of phenylboronic acid or 4-fluorophenylboronic acid.

# Table 1

Crystal data and experimental details of the single-crystal X-ray analyses of compounds 1-4.

Compound	1	2	3	4
Empirical formula	C <sub>30</sub> H <sub>39</sub> B <sub>3</sub> N <sub>8</sub> O <sub>3</sub>	$C_{42}H_{42}B_6N_4O_6$	C <sub>24</sub> H <sub>24</sub> B <sub>3</sub> N <sub>4</sub> O <sub>3</sub> F <sub>3</sub>	C <sub>12</sub> H <sub>40</sub> Cl <sub>2</sub> N <sub>8</sub> O <sub>16</sub> Co
Formula weight/g mol $^{-1}$	592.12	763.66	505.90	682.35
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	C2/c	P 2 <sub>1</sub> /c	P-1	P-1
a/Å	17.0023(8)	12.5746(6)	10.910(4)	8.2075(10)
b/Å	10.8153(5)	19.6788(9)	11.238(4)	9.0886(13)
c/Å	16.3825(6)	20.2832(10)	11.295(4)	10.6609(14)
$\alpha/_{\circ}$			80.469(12)	93.679(4)
βl°	103.504(4)	127.970(3)	62.890(12)	104.312(3)
γ/°			72.457(12)	114.091(3)
V/Å <sup>3</sup>	2929.2(2)	3956.8(3)	1174.7(7)	691.05(16)
Ζ	4	4	2	1
$\rho_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.343	1.282	1.430	1.640
$\mu$ (Cu <sub>K<math>\alpha</math></sub> or Mo <sub>K<math>\alpha</math></sub> )/mm <sup>-1</sup>	0.702	0.664	0.109	0.898
$2\Theta$ range/°	8-142	8-142	5–51	5-51
Reflections measured	5663	11,322	12,636	7658
Independent reflections	2764	6603	4345	2566
R(int)	0.0195	0.0373	0.0946	0.0276
Ind. reflections $(I > 2\sigma(I))$	2447	5011	3004	2167
Parameters	201	503	430	228
$R_1 (I > 2\sigma(I))$	0.0388	0.0520	0.0600	0.0281
wR <sub>2</sub> (all data)	0.1106	0.1518	0.1853	0.0657
GooF (all data)	1.055	1.016	1.019	1.058
Max. peak/hole/e <sup>-</sup> 10 <sup>-6</sup> pm <sup>-3</sup>	0.254/-0.222	0.247/-0.233	0.391/-0.349	0.362/-0.313 e <sup>-</sup> Å <sup>-3</sup> .

The solid state structures also confirm that compound **1** is an adduct of triphenylboroxine-hmt in 1:2 M ratio, which was found to be rare. Triphenylboroxine acts as bridge between two hmt molecules in 1, whereas hmt plays the role of a bridging ligand between two triphenylboroxine rings in 2. A common feature of all compounds is the formation of planar or nearly planar B<sub>3</sub>O<sub>3</sub> rings. The sums of angles within the ring are 720°, 718° and 719.4° in **1**.2 and **3** respectively, confirming planarity (1) or near-planarity (2, 3)of the boroxine rings. In the structure of 1, two boron atoms, B1 and B1' reveal a tetrahedral environment as a result of the coordination by two hmt ligands. One boron atom B2 adopts a trigonal coordination geometry. In spite of the existence of two tetrahedrally coordinated boron atoms, the planarity of the boroxine ring in 1 is achieved due to the coordination of the two hmt's molecules from opposite site of the B<sub>3</sub>O<sub>3</sub> ring, thus balancing the effects of N  $\rightarrow$  B bond formation. The atoms B1 and B4 in 2 are in tetrahedral environment leaving other boron atoms in trigonal geometrical environment. In compound 3, B1 possesses a tetrahedral coordination geometry, whereas B2 and B3 have a trigonal ligand environment. The average B–O bond length, O–B–O and B–O–B angles were reported to be 1.382 Å and 119.3, 120.3° respectively for triphenylboroxine, [(PhBO)<sub>3</sub>] [21]. Compared to the latter, the corresponding O–B1–O bond angles decreases by 3.6° in 1, 5.17°, 5.49° in **2** and  $5.7^{\circ}$  in **3** at the tetrahedral boron atoms. The average O-B-O angle of the trigonal boron atoms increases by an average of  $2.5^{\circ}$ , 0.9° and 0.7° in **1**, **2** and **3** respectively.

# 3.2. Reactivity

Compound **1** was reacted with  $[Co(H_2O)_6](ClO_4)_2$  in methanol. It acts as a mild hmt-donating species at room temperature resulting in the formation of  $[Co(H_2O)_6](ClO_4)_2 \cdot (hmt)_2 \cdot 2H_2O$  (**4**) (Scheme 3).

Table 2

Distances (Å)	and angles	(°) within	the hydrogen	bonds of compound 4.	
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$D-H\cdots A$	D-H	$D \cdots  A$	Н…А	$\angle D - H \cdots A$
01-H1C…N1*	0.77(3)	2.854(3)	2.09(3)	175(3)
O4−H4B…N3	0.83(3)	2.773(2)	1.97(3)	165(3)
05−H4A…N4 <sup>\$</sup>	0.81(3)	2.827(3)	2.02(3)	174(2)
03-H11B…N2 <sup>#</sup>	0.87(3)	2.744(3)	1.88(3)	173(3)

Symmetry element \* = -1 - x, 1 - y, -z; \$ = x, -1 + y, z and # = 1 - x, 1 - y, 1 - z; D, donor; H, hydrogen; A, acceptor.

Compound **4** was obtained as pink crystals with colourless byproduct which was separated mechanically and identified by NMR spectroscopy to be triphenylboroxine. Compound **4** is isostructural with its manganese and nickel analogues, which were synthesized by reacting the corresponding metal perchlorate hexahydrate with hmt in water [22].

The solid state structure of compound **4** was established by single crystal X-ray analysis which shows that it crystallizes in the triclinic space group *P*-1 with one formula unit in the unit cell. The cobalt ion is located at the inversion centre and coordinated by six water molecules with Co–O distances of 2.0643(15)-2.1162(15) Å which is identical with the reported values [23]. It can be found from the structure that hmt and perchlorate anion are free from metal, remaining outside the coordination shell. Additionally, two non-coordinated water molecules were found in the structure. The six coordinated water molecules are further connected to the six free hmt molecules and each hmt is connected to three coordinating and one free water molecules through intermolecular hydrogen bonds. Fragments of the resulting hydrogen bonding framework is illustrated in Fig. 3 besides the unit cell of **4**. Details of the hydrogen bonding are given in Table 2.



**Fig. 3.** Fragments of the crystal structure of **4**: Unit cell (top left) O–H…N hydrogen bonds per formula unit (top right) and part of the hydrogen bonding framework (bottom). Large black spheres = Co, blue = N, red = O, green = Cl, grey = C, small black spheres = H). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

# 4. Conclusions

We have investigated the synthesis and characterization of three new Lewis acid–base adducts based on N  $\rightarrow$  B bonds in different boroxine–hmt molar ratio. Compound **1** exists as 1:2 adducts of triphenylboroxine and hmt in solid state, which is most interesting and exciting. NMR spectroscopic studies reveal fluctuation, hence reversible N  $\rightarrow$  B bond formation and bond break in solution. Further studies on the reactivity of **1** with cobalt perchlorate hexahydrate leads to the formation of **4**, which confirms that free hmt can be obtained from **1** in solution. This investigation sheds light on future work targeting at supramolecular structures based on N  $\rightarrow$  B bonds under employment of hmt as multi-dentate ligand.

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# Appendix A. Supplementary material

CCDC 943061–943064 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data\_request/cif.

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