

# Hydrotris(1,2,4-triazolyl)borato Complexes with the Main Group Elements Ca, Sr, and Pb – Unexpectedly Bent ML<sub>2</sub> Structures and a Stereochemically Inactive Lone Pair at Lead(II)

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*Dedicated to Professor Brigitte Sarry on the Occasion of her 80<sup>th</sup> Birthday*

**Abstract.** The coordination of the modified poly(azolyl)borato ligand hydrotris(1,2,4-triazolyl)borato (L) with main group metals leads to complexes with coordination numbers of eight and the formula [CaL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], [SrL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], and [PbL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]. The two L ligands coordinate in a “bent” arrangement to allow for the coordination of the two aqua ligands. This is in sharp contrast to six-coordinated, pseudo-octahedral CaTp<sub>2</sub> and PbTp<sub>2</sub> complexes [Tp = hydrotris(pyrazolyl)borato]. The calcium, strontium, and lead complexes are isostructural. No stereochemical lone pair activity is evident in [PbL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]. Two additional water molecules of crys-

tallization complete the crystal structure of [CaL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] · 2 H<sub>2</sub>O and [PbL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] · 2 H<sub>2</sub>O. In the synthesis of [PbL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] an intermediate of the form <sup>2</sup>[Pb(μ<sub>3</sub>-L)(NO<sub>3</sub>)H<sub>2</sub>O] could be isolated and structurally characterized. There, the lead(II) center is seven coordinated with a presumably stereochemically active lone pair. Long M–L bonds argue for a more ionic bonding to the modified tris(triazolyl)borato ligand when compared to analogous M–Tp complexes.

**Keywords:** Hydrotris(pyrazolyl)borato ligands; Main-group elements; Lone pair; Crystal structure

## Hydrotris(1,2,4-triazolyl)borato Komplexe mit den Hauptgruppenelementen Ca, Sr und Pb – unerwartet gewinkelte ML<sub>2</sub> Strukturen und ein stereochemisch inaktives freies Elektronenpaar an Blei(II)

**Inhaltsübersicht.** Die Koordination des modifizierten Poly(azolyl)borato-Liganden Hydrotris(1,2,4-triazolyl)borato (L) mit Hauptgruppenmetallen ergibt Komplexe mit der Koordinationszahl acht und der Formel [CaL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], [SrL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], and [PbL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]. Die beiden L-Liganden koordinieren in einer „gewinkelten“ Anordnung, um die Koordination der beiden Aqualiganden zu ermöglichen. Dies steht im Gegensatz zu den sechsfach-koordinierten, pseudo-oktaedrischen CaTp<sub>2</sub>- und PbTp<sub>2</sub>-Komplexen [Tp = hydrotris(pyrazolyl)borato]. Die Calcium-, Strontium- und Bleikomplexe sind isostrukturell. Es ist keine stereochemische

Aktivität des freien Elektronenpaares in [PbL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] zu erkennen. Zwei zusätzliche Kristallwasser-Moleküle vervollständigen die Kristallstruktur von [CaL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] · 2 H<sub>2</sub>O und [PbL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] · 2 H<sub>2</sub>O. Bei der Synthese von [PbL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] wurde eine Zwischenstufe mit der Formel <sup>2</sup>[Pb(μ<sub>3</sub>-L)(NO<sub>3</sub>)H<sub>2</sub>O] isoliert und strukturell charakterisiert. In dieser Zwischenstufe ist das Blei(II)-Atom siebenfach koordiniert mit einem vermutlich stereochemisch aktiven freien Elektronenpaar. Lange M–L Bindungen legen eine stärker ionische Anbindung des modifizierten Tris(triazolyl)borato-Liganden an das Metall nahe, im Vergleich zu den analogen M–Tp Komplexen.

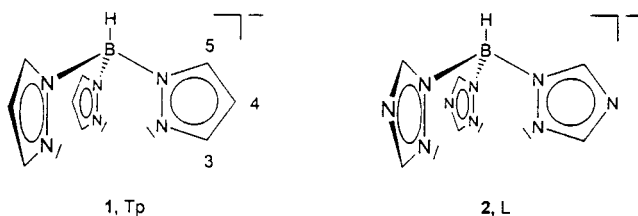
### Introduction

The tris(pyrazolyl)borato (Tp) ligand (**1**) together with various substituted forms has developed into one of the most versatile tripodal auxiliary ligand in metal coordination chemistry [1]. These ligands are mainly applied towards transition metals [2]. Yet, recently a surge in interest in main-group metal Tp complexes

can be noted [3–9]. Towards lead(II) this interest is closely related to the stereochemical activity or non-activity of the ‘lone pair’ of electrons on the metal atom [10]. For example, in PbTp<sub>2</sub> the lone pair was found to be stereochemically active, while with the more bulky ligand in PbTp<sub>2</sub><sup>Me<sub>2</sub></sup>, i. e. PbTp<sub>2</sub><sup>Me<sub>2</sub></sup> it is clearly inactive [11, 12].

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<sup>1</sup> According to a nomenclature suggested by Trofimenko (ref. [1]) the tris(pyrazolyl)borato ligand is abbreviated as Tp with the non-hydrogen substituents in the 3- and 5-positions on the pyrazolyl ring given as superscripts, e. g. [Tp<sup>Me<sub>3</sub></sup>] or [Tp<sup>Me<sub>2</sub></sup>] for tris(3,5-dimethylpyrazolyl)borato, for which the abbreviation Tp\* is also accepted.

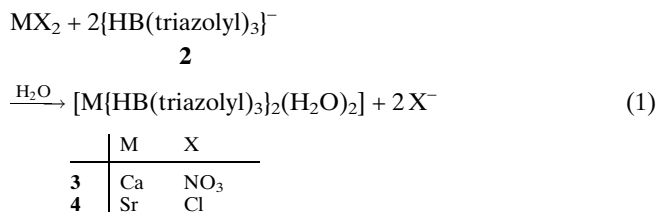


Particular attention is sometimes devoted to special azolyl rings, such as triazolyl [13–16], tetrazolyl [17], 3,5-bis(trifluoromethyl)pyrazolyl [18], and indazolyl [19, 20]. These ligands can exert quite different electronic and structural effects when compared with the Tp analog [15, 21]. We report here on the syntheses and structural investigations of main-group metal complexes with the hydrotris(1,2,4-triazolyl)borato ligand (**2**).

## Results and discussion

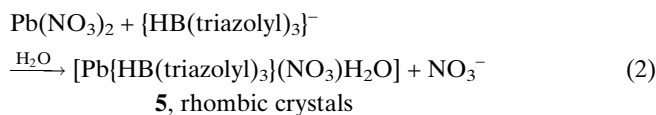
### Synthesis and Chemical Characterization

The hydrotris(triazolyl)borate anion  $\{\text{HB}(\text{triazolyl})_3\}^-$  (**2**) reacts with the main-group metal(II) salts in water with the formation of [bis{hydrotris(triazolyl)borato}-metal(II)] complexes (equation (1)). For  $M = \text{Ca}$  and  $\text{Sr}$ , the products were isolated upon slow solvent evaporation as crystalline solids. Yields were around 50%.



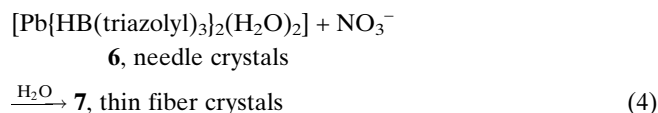
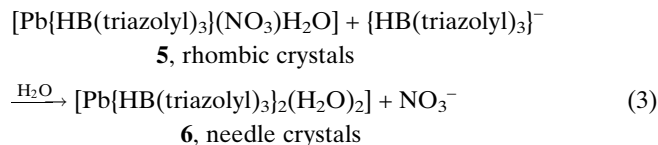
The results of the X-ray crystal structure investigation (see below) show that two aqua ligands complete the coordination sphere at the metal atom. Attempts to prepare the magnesium, barium or tin derivative under very similar conditions failed to give the desired product.

For lead, the reaction is more complicated. Appropriate mixing of the reactand solutions quickly (within a day) gives a rhombic crystalline product. This was identified as the 1:1 ligand-nitrato complex **5** (equation (2)), even when a 1:2 metal-to-ligand ratio was employed. According to X-ray crystallography an aqua ligand completes the coordination sphere in aqua-hydrotris(triazolyl)borato-nitratolead(II) (**5**).



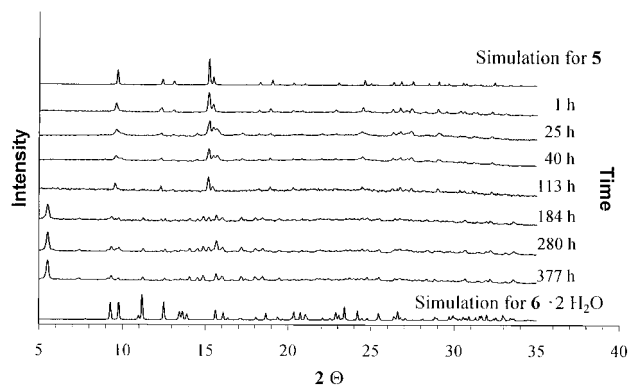
Upon remaining in the mother liquor, the rhombic crystals of **5** slowly (within days) transform into needle-shaped crystals. The latter represent the diaqua-

bis{hydrotris(triazolyl)borato}lead(II) complex **6** (equation (3)). Compound **5** may be described as the kinetic and **6** as a thermodynamic product in the reaction of  $\text{Pb}(\text{NO}_3)_2$  with **2** in water. The phase transition also takes place when complex **5** was prepared from a 1:1 reactand ratio and stored in the mother liquor, i. e. in the presence of unreacted ligand (and metal) ions. If compound **5** was stored on wet filter paper, no change was apparent. Storage in ion-free water still leads to the formation of needles of **6**. When  $\text{Pb}(\text{O}_2\text{CCH}_3)_2$  or  $\text{PbCl}_2$  were used instead of  $\text{Pb}(\text{NO}_3)_2$  very fine needle-shaped crystals which are intergrown to bushels formed within 3 days. After that time the thicker needles of **6** appear. A somewhat related slow transformation was observed earlier for a hydrotris(triazolyl)borato zinc complex going from the rapidly formed molecule  $[\text{Zn}\{\text{HB}(\text{triazolyl})_3\}_2]$  to the three-dimensional coordination polymer  ${}^3_{\infty}[\text{Zn}\{\mu_3\text{-HB}(\text{triazolyl})_3\}_2]$  [22].



With compound **6** the reaction is still not complete. When left in the mother liquor for over a week the needle-shaped crystals of **6** transform further into very thin, fiber-like crystals (**7**) (equation (4)). This also leads to a complete disappearance of any rhombic crystals which are otherwise still present for up to a week. Some needle crystals of **6** remain in a mixture with **7**. X-ray powder diffractometry shows the different nature of **7** versus **6** and **5**. From a strong X-ray powder peak at  $5.5^\circ$  a unit cell with at least one large axis ( $>15 \text{ \AA}$ ) is evident for **7**. Unfortunately, the crystal morphology of **7** did not allow for a single-crystal X-ray structure determination. Hence, the exact nature of **7** could not be determined. Elemental analysis suggests again the formation of a 1:1  $\{\text{HB}(\text{triazolyl})_3\}:\text{Pb}$  complex (with nitrate counterions). Possibly this complex is polymeric in nature with (triazolyl)borato ligands bridging through the exodentate nitrogen donor atoms (cf. the above example of the zinc complex [22]). The mass spectrum of **7** does not show any metal containing fragments. From a simulation of the powder spectra of  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{KNO}_3$ , and  $\text{K}\{\text{HB}(\text{triazolyl})_3\}$  it could be excluded that these salts give rise to the diffraction pattern of **7**.

The reaction rate for  $\text{5} \rightarrow \text{6} \rightarrow \text{7}$  depends strongly on the concentration of the reactand solution. At very low concentration only compound **5** is formed. With increasing concentration the time for the first appear-



**Fig. 1** X-ray powder diffractograms taken at different times to follow the transformation from the ligand-nitrato lead complex **5** to the bis-ligand lead compound **6** and to an unidentified lead complex **7**. Samples from the reaction of  $\text{Pb}(\text{NO}_3)_2$  (1.5 mmol) in water (5 ml) with  $\text{K}\{\text{HB}(\text{triazolyl})_3\}$  (3.0 mmol) in water (5 ml) by the overlaying technique. X-ray powder simulation from single-crystal X-ray data are included for **5** (top) and  $\mathbf{6} \cdot 2 \text{H}_2\text{O}$  (bottom). For comparison the intensity of the highest peak has been normalized to 1.

ance of **7** could be shortened to about 3 days. The transformation from **5** to **6** was followed by X-ray powder diffractometry. Fig. 1 shows a sequence of X-ray powder diffractograms starting from a freshly prepared sample of **5** up to a mixture of **6** and **7** after about 16 days (377 h). Simulated powder spectra from single-crystal X-ray data of **5** and **6** enable the assignment. Under the reaction conditions chosen here, the formation of **6** already together with **7** is evident after 184 h (7.7 days).

Once formed, the complexes **3** to **6** are only slightly soluble in water. The proton NMR spectra of all complexes are very similar to each other and also to the potassium salt in their chemical shifts [15, 23]. The BH signal could not be observed; possibly due to its broad resonance because of quadrupolar coupling and relaxation effects from the boron atom [24].

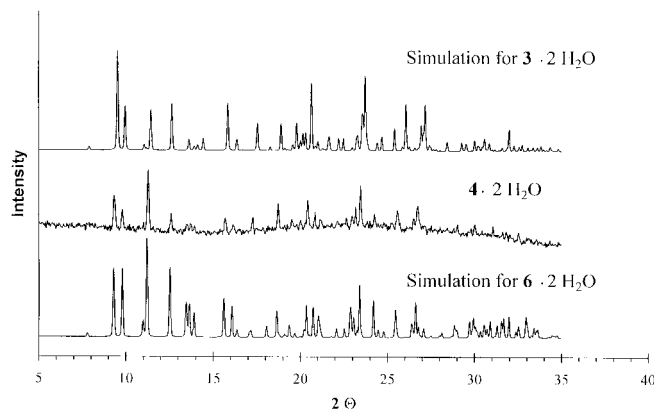
The mass spectrometric characterization shows the molecular ion  $\text{ML}_2$  (minus the aqua ligands) only for **3**. For **4** a hydrogen atom is lost from  $\text{ML}_2$  and for the lead compounds **5** and **6**  $\text{ML}_2$  minus a triazolyl ring is the highest mass fragment. The most likely fragmentation for the bis{hydrotris(triazolyl)borato}metall(II) complexes involves the loss of one and two triazolyl rings ( $\text{C}_2\text{H}_2\text{N}_3$ ) and the loss of one hydrotris(triazolyl)borato ligand. The lead complexes feature also the loss of HCN from their fragments. The very low abundance (below 1%) of the metal containing fragments in the bis-ligand lead complex **6** is noteworthy. This could support a certain instability of **6** which was apparent in the above reaction sequence to **7**. On the other hand, the mass spectrum of the ligand-nitrato lead complex **5** contains fragments which have to be derived from a bis-ligand complex  $\text{PbL}_2$ . The abundance of such fragments is much higher than for **6**, so

that they are likely to be formed under the thermal conditions in the mass spectrometer. This underscores a higher stability of **6** versus **5**.

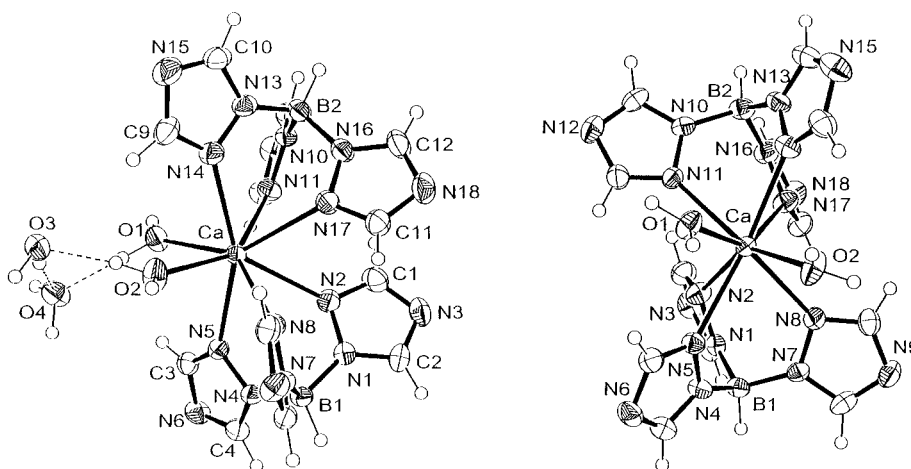
### Structures of Complexes $\mathbf{3} \cdot 2 \text{H}_2\text{O}$ , **5**, and $\mathbf{6} \cdot 2 \text{H}_2\text{O}$

These three complexes were investigated by single-crystal X-ray structure determination. From a comparison of X-ray powder data, the strontium compound **4** was shown to be isostructural to **3**. The calcium and lead dihydrate structures  $\mathbf{3} \cdot 2 \text{H}_2\text{O}$  and  $\mathbf{6} \cdot 2 \text{H}_2\text{O}$  are also isostructural (Fig. 2). Both structures consist of molecular metal complexes with the borato ligand functioning as a tridentate chelate through the endodentate nitrogen donor atoms. The additional exodentate nitrogen donors do not become involved in metal atom coordination. Fig. 3 and 4 depict the isostructural calcium and lead complex, respectively. Both metal atoms have coordination number eight, consisting of two oxygen atoms from aqua ligands and six nitrogen atoms from the two borato groups. The coordination motive is a rather distorted square antiprism. Metal ligand distances and angles are listed in Table 1. A search of the Cambridge Crystallographic Database revealed that a coordination number of eight or higher is not uncommon for calcium (over 130 entries) [25]. The aqua ligands are part of a hydrogen bonding framework which involves the two water molecules of crystallization and five out of six of the exodentate nitrogen donor atoms. The hydrogen bonding network is shown in Fig. 5, the distances and angles are listed in Table 2. The incorporation of water of crystallization into tris(triazolyl)borato metal complexes and hydrogen bonding to the nitrogen donor set of the tris(triazolyl)borato ligand which is not involved in metal coordination appears usual and has been observed before [13, 14, 17, 22, 26].

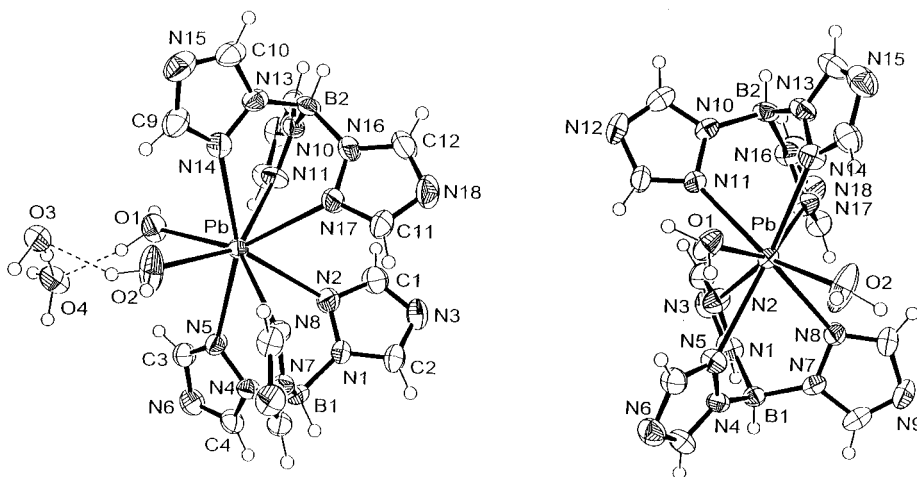
While the coordination number eight is not uncommon for calcium and lead complexes, at large, it is so



**Fig. 2** X-ray powder diffractograms for the bis{hydrotris(triazolyl)borato}calcium, -strontium, and -lead complex  $\mathbf{3} \cdot 2 \text{H}_2\text{O}$ ,  $\mathbf{4} \cdot 2 \text{H}_2\text{O}$ , and  $\mathbf{6} \cdot 2 \text{H}_2\text{O}$  to illustrate their isostructural nature.



**Fig. 3** Two views of the calcium complex in  $3 \cdot 2 \text{H}_2\text{O}$  showing the bent arrangement of the two borato ligands (left) and the distorted nature of the ligand assembly as a whole (right). The aqua ligands are part of a hydrogen bonding scheme with the water of crystallization as shown on the left. The water of crystallization is omitted in the “front view” on the right. For clarity not all triazolyl rings are fully labelled. Distances and angles are given in Table 1.



**Fig. 4** Two views of the lead complex in  $6 \cdot 2 \text{H}_2\text{O}$  showing the bent arrangement of the two borato ligands (left) and the distorted nature of the ligand assembly as a whole (right). The aqua ligands are part of a hydrogen bonding scheme with the water of crystallization as shown on the left. The water of crystallization is omitted in the “front view” on the right. For clarity not all triazolyl rings are fully labelled. Geometric parameters are given in Table 1.

for the poly(pyrazolyl)borato complexes of these ligands. Structures for comparison are available for  $\text{CaTp}_2$  [27],  $\text{CaTp}_2^*$  ( $\text{Tp}^* = \text{Tp}^{\text{Me}2}$ ) [28],  $\text{PbTp}_2$ ,  $\text{PbTp}_2^*$  [11], and  $\text{Tp}^*\text{Pb}(\text{3,5-Me}_2\text{pzH})_3\text{Cl}$  [29]. In all these structures, the metal centers have the coordination number six. Also, the larger strontium and barium ion have coordination number six in  $\text{SrTp}_2^*$  [28] and  $\text{BaTp}_2^*$  [30]. With the bulkier  $\text{Tp}^*$ -ligands a smaller coordination number can be understood on the basis of steric shielding by these encapsulating ligands. For  $\text{CaTp}_2$  and  $\text{PbTp}_2$  a bond length comparison with **3** and **6**, respectively, reveals a profound lengthening of the M–N bonds in the latter. Table 3 compares the minimum, maximum and average metal-nitrogen distances in  $\text{MTp}_2$  and **3** and **6**.

From Table 3 one recognizes that the the M–N dis-

tances in all three subsets are elongated for **3** and **6**. We view this as an indication of an increased ionic character in the metal-nitrogen interaction with the tris(triazolyl)borato ligand compared to the Tp analog. The electronic effect of triazolyl versus pyrazolyl, i.e. a third nitrogen atom in the azolyl ring, was earlier shown to lead to a decrease in ligand orbital energy. This, in turn, diminishes the (covalent) overlap with the metal orbitals.

Also, from Table 3 a wider variation between the minimum and maximum metal-nitrogen distances is evident for the calcium complex **3** than for its Tp and  $\text{Tp}^*$  analogs. Such a wide variation is also seen in **6** and in  $\text{PbTp}_2$ . This brings us to the arrangement of the two borato ligands or the complex symmetry. The compounds  $\text{CaTp}_2$ ,  $\text{CaTp}_2^*$  and  $\text{PbTp}_2^*$  are  $D_{3d}$ -sym-

**Table 1** Selected bond lengths/Å and angles/° in compounds **3** · 2H<sub>2</sub>O, **5**, and **6** · 2H<sub>2</sub>O

	<b>3</b> · 2H <sub>2</sub> O M = Ca	<b>5</b> M = Pb	<b>6</b> · 2H <sub>2</sub> O M = Pb
M–N2	2.701(3)	2.68(1)	2.821(5)
M–N5	2.617(3)	2.58(2)	2.791(4)
M–N8	2.542(3)		2.728(4)
M–N11	2.518(3)		2.641(4)
M–N14	2.553(3)		2.674(5)
M–N17	2.673(3)		2.757(4)
M–O1	2.435(3)	2.58(2)	2.634(4)
M–O2	2.398(3)	2.77(2)	2.605(4)
M–N3_4		2.71(2)	
N2–M–N5	67.06(9)	73.1(4)	64.8(1)
N2–M–N8	73.05(10)		70.3(1)
N5–M–N8	79.09(9)		75.8(1)
N11–M–N14	74.62(10)		71.9(1)
N11–M–N17	74.68(9)		72.0(2)
N14–M–N17	68.07(10)		66.6(1)
N2–M–N2_3		65.7(5)	
N2–M–N3_4		132.5(4)	
N2_3–M–N3_4		71.2(4)	
N5–M–N3_4		76.4(3)	
N3_4–M–N3_6		134.1(7)	
N2–M–O1	120.81(10)	139.5(5)	118.5(2)
N2–M–O2	141.01(10)	65.5(6)	140.8(2)
N5–M–O1	74.57(9)	85.0(8)	74.1(1)
N5–M–O2	87.45(10)	138.5(6)	88.2(2)
N8–M–O1	140.29(9)		139.3(1)
N8–M–O2	73.49(10)		75.9(1)
N11–M–O1	76.01(9)		77.1(1)
N11–M–O2	143.69(10)		142.3(2)
N14–M–O1	83.41(10)		85.1(2)
N14–M–O2	79.46(10)		79.6(2)
N17–M–O1	143.40(9)		143.1(1)
N17–M–O2	118.15(10)		118.4(2)
O1–M–O2	76.14(9)	128.3(7)	76.4(2)
N2_3–M–O1		139.5(5)	
N2_3–M–O2		88.5(4)	
N3_4–M–O1		70.7(4)	
N3_4–M–O2		132.8(6)	
M3_6–M–O1		70.7(4)	
N3_6–M–O2		91.1(6)	
B1···M···B2	131.0		131.5

symmetry relations:  $_{3}x, 0.5 - y, z; _4 0.5 + x, 0.5 - z; _6 0.5 + x, -y, 0.5 - z$

metrical complexes with a linear B···M···B axis. Both borato ligands are symmetry related. The metal center sits on a special position [11, 27, 28]. This is not so for PbTp<sub>2</sub> [11] and the compounds **3** and **6**. Here, we have a bent bis-borato ligand arrangement. The longer M–N distances together with the bis-borato ligand-bending then allow for the coordination of the aqua ligands in **3** and **6**. The crystals of PbTp<sub>2</sub> were grown from toluene and no solvent coordination was observed.

The structures of PbTp<sub>2</sub> and PbTp<sub>2</sub><sup>‡</sup> were investigated in a quest for a coordination complex with a stereochemically inactive lone pair. While the bending in PbTp<sub>2</sub> showed the active lone pair which is expected from valence shell electron pair repulsion (VSEPR) theory [31], this lone pair on lead is clearly stereochemically inactive in PbTp<sub>2</sub><sup>‡</sup> [10, 11]. The presence of a void in the coordination sphere is usually

**Table 2** Hydrogen bonding interactions **3** · 2H<sub>2</sub>O and **6** · 2H<sub>2</sub>O

<b>3</b> · 2H <sub>2</sub> O D–H···A	D–H	H···A	D···A	D–H···A
O1–H101···N12_3	0.97(2)	1.96(3)	2.932(5)	173(2)
O1–H102···O4	0.96(2)	1.85(4)	2.808(5)	176(3)
O2–H201···O3	0.96(2)	1.85(4)	2.798(5)	170(3)
O2–H202···N6_4	0.97(2)	1.93(3)	2.875(5)	165(2)
O3–H301···O4	0.97(2)	1.84(4)	2.802(5)	170(3)
O3–H302···N3_2	0.97(2)	1.91(3)	2.870(5)	174(2)
O4–H401···N9_4'	0.97(2)	1.88(3)	1.843(5)	179(2)
O4–H402···N18_2	0.96(2)	1.89(3)	2.827(5)	167(2)
D = Donor, A = acceptor. Symmetry transformations: $_{2} - y, -0.5 + y, 0.5 - z; _3 1 - x, 1 - y, 1 - z; _4 x, 0.5 + z; _4' 1 + x, 0.5 + z$				
<b>6</b> · 2H <sub>2</sub> O D–H···A	D–H	H···A	D···A	D–H···A
O1–H101···N12_3	1.00(2)	1.92(4)	2.885(9)	162(5)
O1–H102···O4	0.99(2)	1.83(4)	2.812(7)	169(4)
O2–H201···O3	0.99(2)	1.92(4)	2.782(7)	144(4)
O2–H202···N6_4	0.99(2)	1.85(4)	2.821(4)	166(5)
O3–H301···O4	0.98(2)	1.85(4)	2.824(7)	172(4)
O3–H302···N3_2	0.98(2)	1.91(4)	2.884(9)	173(5)
O4–H401···N9_4'	0.98(2)	1.90(4)	1.870(9)	171(5)
O4–H402···N18_2	1.00(2)	1.89(4)	2.833(9)	156(5)

D = Donor, A = acceptor. Symmetry transformations:  $_{2} - x, -0.5 + y, 0.5 - z; _3 1 - x, 1 - y, 1 - z; _4 x, 0.5 + z; _4' 1 + x, 0.5 + z$

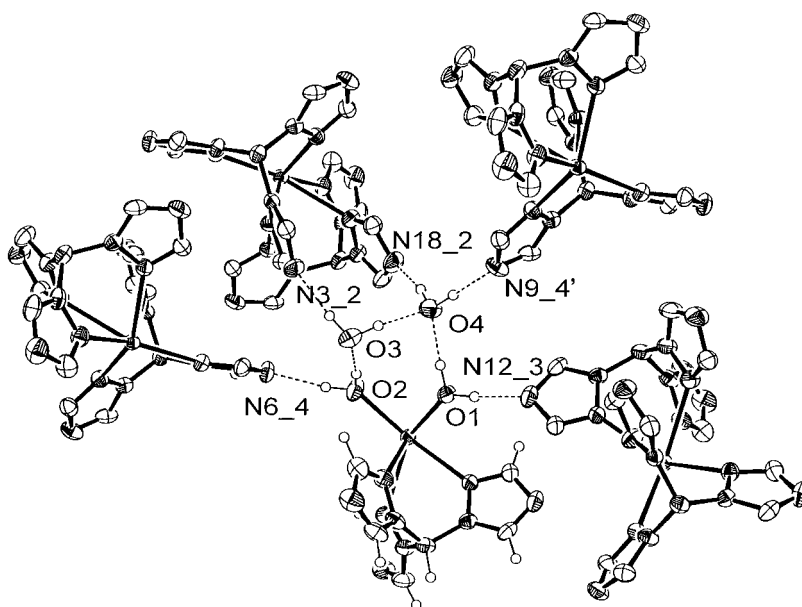
**Table 3** Comparison of metal–nitrogen distances (in Å) in various bis[hydrotris(azolyl)borato]metal compounds

Complex	M–N minimum	M–N average	M–N maximum
CaTp <sub>2</sub> [27]	2.407(4)	2.441	2.460(4)
CaTp <sub>2</sub> <sup>‡</sup> [28]	2.454(2) <sup>a)</sup>	2.454 <sup>a)</sup>	2.454(2) <sup>a)</sup>
[Ca{HB(triazolyl) <sub>3</sub> }] <sub>2</sub> · (H <sub>2</sub> O) <sub>2</sub> , <b>3</b>	2.518(3)	2.601	2.701(1)
PbTp <sub>2</sub> [11]	2.462(13)	2.607	2.806(13)
PbTp <sub>2</sub> <sup>‡</sup> [11]	2.610(5) <sup>a)</sup>	2.610 <sup>a)</sup>	2.610(5) <sup>a)</sup>
[Pb{HB(triazolyl) <sub>3</sub> }] <sub>2</sub> · (H <sub>2</sub> O) <sub>2</sub> , <b>6</b>	2.641(4)	2.735	2.821(5)

<sup>a)</sup> metal atom sits on a special position, only one independent pyrazolyl ring.

taken as evidence for a stereochemically active lone pair. For some time it was considered a synthetic challenge to design ligands that could render the lone pair on a main group metal stereochemically inert [32]. Earlier examples of molecules which defy VSEPR theory include N(SiH<sub>3</sub>)<sub>3</sub> in the gas phase [33], BrF<sub>6</sub><sup>−</sup> [34], (C<sub>5</sub>Ph<sub>5</sub>)<sub>2</sub>Sn [35], and one conformer of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Si [36] in the solid state.

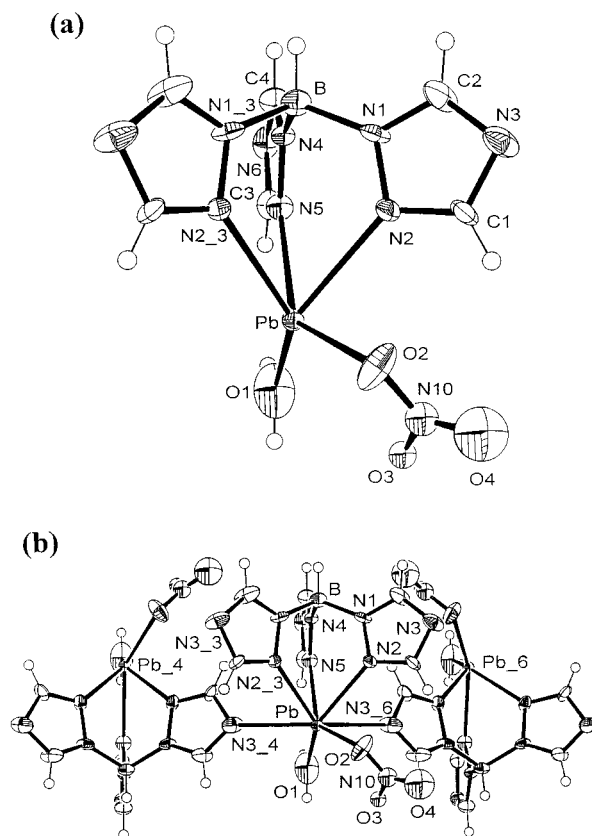
Compound **6** represents a bent PbL<sub>2</sub> structure. Yet, the coordination of two aqua ligands at the opening does not leave room for a lone pair. In **6** the bonds to the ligand atoms are distributed throughout the surface of an encompassing sphere. Such a ligand arrangement has recently been termed *holodirected*. A structure where the ligand atoms occupy only part of the encompassing globe surface, thus leaving a void, is called *hemidirected* [37]. A lone pair should favor a hemidirected geometry. A CSD structure search re-



**Fig. 5** Section of the crystal structure of  $3 \cdot 2\text{H}_2\text{O}$  (and isostructural  $6 \cdot 2\text{H}_2\text{O}$ ) to illustrate the hydrogen bonding of the water molecules to the exodentate nitrogen atoms of four complex molecules. One borato ligand of the central diaqua-containing complex molecule has been omitted for clarity. Distances and angles for the hydrogen bonded network are given in Table 2.

vealed that out of 26 lead(II) complexes with coordination number 8, 23 have holodirected ligands and only 3 have hemidirected ligands [37]. It should be pointed out that a holodirected structure does not necessarily exclude an active lone pair. There are homoleptic six-coordinate holodirected  $\text{Pb}^{\text{II}}$  complexes known which feature short and long bonds from Pb to the otherwise identical ligand atoms. Such repulsion could be attributed to a stereochemically active lone pair [38]. There is also an uneven distribution of long and short Pb–N bond lengths in **6**. From Table 1 it could be argued that one borato ligand in **6** shows the longer and the other one the shorter Pb–N bonds. Yet, the same distribution of bond lengths is also seen in the calcium complex **3**. This comparison with the fully isostructural calcium complex **3** clearly supports the notion of a stereochemically inactive lone pair at the lead(II) atom in **6**. Furthermore, in a correlation of lone pair activity on  $\text{Pb}^{\text{II}}$  with Pb–N bond lengths, from a data base of 10 compounds, it was suggested that when the lone pair is active, the Pb–N bond lengths fall in the range 2.37 to 2.56 Å. While for an inactive lone pair, the Pb–N bond lengths fall in the range 2.62 to 2.88 Å [39]. The data in Table 4 broadly agree with this correlation that a longer Pb–N bond is indicative of an inactive lone pair.

The structure of the borato-nitrato lead(II) compound **5** is shown in Fig. 6. Here we have a two-dimensional coordination polymer which is formed by the bridging action of the hydrotris(triazolyl)borato ligand. The borato ligand chelates a lead atom and bridges to two symmetry related lead atoms via two of its exodentate nitrogen donor atoms. The third exodentate nitrogen atom is not utilized for the metal co-



**Fig. 6** (a) Asymmetric unit of compound **5** and (b) section of the two-dimensional array through the bridging action of the borato ligand via N3. Geometric parameters are given in Table 1. A mirror plane passes through B, N4, N5, Pb, and O1. This mirror plane would also create a second position for the nitrato group, which is crystallographically disordered with half-occupancy on either side of the mirror plane.

ordination. For additional examples of exodentate nitrogen-metal coordination with the tris(triazolyl)borato ligand see ref. [13, 22]. The coordination number of seven for the lead atom in **5** is formed by three endodentate, chelating nitrogen atoms, two exodentate nitrogen donors, an aqua and a nitrate ligand. The coordination sphere is hemidirected leaving a void in ligand bond distribution. This open space may be assigned to the stereochemical activity of the lone pair. Interestingly, a CSD search revealed for seven coordinated lead(II) structures a majority with hemidirected ligands (21 out of 31) [37].

With respect to the aqua ligands in the structures of **5** and **6** we note that lead(II) bound water molecules are only found in about 10% of all lead(II) structures. Two thirds of these contain only a single aqua ligand and only one third possesses two lead-bound water molecules [37]. The high coordination numbers of seven and eight in the main group metal complexes with the tris(triazolyl)borato ligand **2** is also quite different from the coordination chemistry of this ligand towards transition metals [13, 14, 22, 23, 26].

## Conclusions

In summary, the bis{hydrotris(1,2,4-triazolyl)borato}-metal complexes,  $ML_2$ , of calcium, strontium, and lead have been synthesized and structurally characterized. In contrast to other bis{hydrotris(pyrazolyl)borato}-metal complexes,  $MTP_2$ , of these metals, the  $ML_2$  derivatives exhibit an unprecedented structure with the bending of the  $L_2$  moiety and the additional coordination of two aqua ligands to give a coordination number of eight in  $[ML_2(H_2O)_2]$ . The complex  $[PbL_2(H_2O)_2]$  shows no stereochemical activity of the lone pair. The differences can be traced to a more ionic metal-ligand bonding in  $ML_2$  versus  $MTP_2$ . Furthermore, the complex  $[PbL_2(H_2O)_2]$  is neither the initial nor the final product in the reaction of  $Pb(NO_3)_2$  with two one or two equivalents of KL. An isolable two-dimensional coordination polymer of the form  ${}^\infty [Pb(\mu_3-L)(NO_3)H_2O]$  presents an intermediate with a seven coordinate lead atom.

## Experimental

Doubly distilled or deionized water was used as a solvent. Instruments employed: CHN analysis, Perkin-Elmer Series II CHNS/O Analyzer 2400; IR spectroscopy, Nicolet Magna 750 as KBr disks; mass spectrometry, Varian MAT 311A/AMD in solid-probe EI mode at an ionization energy of 70 eV (the MS peaks listed refer to the most abundant isotope combination with  $^{40}Ca$ ,  $^{88}Sr$ ,  $^{208}Pb$ ,  $^{11}B$ ); X-ray powder diffractometry, Enraf-Nonius Inel, Cu-K $\alpha$  radiation, quartz monochromator, sample in 0.7 mm glass capillaries on rotating probe head; NMR spectroscopy, Bruker ARX200 (200.1 MHz for  $^1H$ , 50.3 MHz for  $^{13}C$ ) with calibration against the solvent signal ( $D_2O$   $^1H$ -NMR 4.87 ppm).

The salt  $K\{HB(triazolyl)_3\}$  was synthesized from  $KBH_4$  and triazole according to ref. [40].

### Diaqua-bis{hydrotris(triazolyl)borato}calcium-dihydrate (**3** · 2 $H_2O$ ).

A solution of calcium nitrate (160 mg, 0.98 mmol) and  $K\{HB(triazolyl)_3\}$  (510 mg, 2.00 mmol) in water (15 ml) was slowly narrowed in a test-tube through evaporation towards air at room temperature. After a month the colorless cubic crystals were collected. Yield 250 mg (47%), mp. >300 °C.

Calc. for  $C_{12}H_{22}N_{18}B_2CaO_4$  (544.12): C 26.49, H 4.08, N 46.34. Found C 26.56, H 3.66, N 44.19%.

$^1H$ -NMR ( $D_2O$ ):  $\delta$  7.90 (s, 1 H, H-3), 8.06 (s, 1 H, H-5). MS (300 °C),  $m/z$  472 (8,  $[M]^+$ ), 471 (21,  $[M-H]^+$ ), 404 (35,  $[M-C_2H_2N_3]^+$ ), 256 (78,  $[M-HB(C_2H_2N_3)_3]^+$ ),  $[Ca\{HB(C_2H_2N_3)_3\}]^+$ , 108 (91,  $[Ca(C_2H_2N_3)]^+$ ), 69 (20,  $[C_2H_2N_3]^+$ ),  $M = CaL_2$  without aqua ligands. IR (major peaks only): 3320 m, br (OH), 2497 w, 2468 w, 2425 w, sh ( $\nu_{BH}$ ), 1508 s, 1411 m, 1330 m, 1322 m, 1277 s, 1191 s, 1152 s, 1141 s, 1031 m, 1016 m, 1005 m, 972 m, 961 m, 890 m, 886 m, 872 sh, 771 sh, 730 m, 677 m  $cm^{-1}$ .

### Diaqua-bis{hydrotris(triazolyl)borato}strontium-dihydrate (**4** · 2 $H_2O$ ).

A solution of strontium chloride (480 mg, 3.03 mmol) and  $K\{HB(triazolyl)_3\}$  (1.53 g, 6.00 mmol) in water (10 ml) was slowly narrowed in a test-tube through evaporation towards air at room temperature. After a month the colorless cubic crystals were collected. Yield 900 mg (51%), mp. >300 °C.

Calc. for  $C_{12}H_{22}B_2N_{18}O_4Sr$  (591.66): C 24.36, H 3.75, N 42.61. Found C 24.30, H 3.25, N 41.36%.

$^1H$ -NMR ( $D_2O$ ):  $\delta$  7.92 (s, 1 H, H-3), 8.09 (s, 1 H, H-5). MS (384 °C):  $m/z$  519 (0.15,  $[M-H]^+$ ), 452 (3,  $[M-C_2H_2N_3]^+$ ), 304 (4,  $[M-HB(C_2H_2N_3)_3] = Sr\{HB(C_2H_2N_3)_3\}]^+$ ), 156 (3,  $[Sr(C_2H_2N_3)]^+$ ), 69 (39,  $[C_2H_2N_3]^+$ ),  $M = SrL_2$  without aqua ligands. IR (major peaks only): 3320 s, br ( $\nu_{OH}$ ), 2494 w, 2464 w ( $\nu_{BH}$ ), 1508 s, 1409 m, 1323 m, 1278 s, 1189 s, 1151 s, 1142 s, 1028 m, 1015 m, 1007 s, 971 s, 961 sh, 889 m, 884 m, 750 sh, 741 m, 729 s, 720 m, 678 s  $cm^{-1}$ .

### Aqua{hydrotris(triazolyl)borato}(nitrate)lead(II)-hydrate (**5**).

Reaction 1: Lead nitrate (330 mg, 1.00 mmol) dissolved in water (10 mL) was carefully overlaid in a test-tube with  $K\{HB(triazolyl)_3\}$  (260 mg, 1.02 mmol) dissolved in water (20 ml). Some amorphous precipitate was formed in the overlaying process and crystals started growing rapidly at the phase boundary. After 1 day a large amount of colorless rhombic crystals had formed in the metal-salt solution region. After a few additional days in the mother liquor, colorless needles started growing at the expense of the rhombic crystals.

Reaction 2: In order to produce exclusively the rhombic-shaped crystal phase, the reaction was repeated with a more dilute solution: Lead nitrate (170 mg, 0.51 mmol) dissolved in water (10 mL) was carefully overlaid in a test-tube with  $K\{HB(triazolyl)_3\}$  (either 130 mg, 0.51 mmol or 260 mg, 1.02 mmol) dissolved in water (20 ml). The solutions remained clear and no precipitate occurred. Crystals started to form at the boundary phase after 1 h. The rhombic crystals were collected after 1 day by filtration and stored on wet filter paper to avoid the loss of crystal water. Yield 120 mg (48%). During this storage no needle formation was observed and an X-ray powder diffractogram confirmed the single-phase character of the sample upon comparison with the simulated spectrum from the single-crystal X-ray data. mp. 290 °C (dec.).

Calc. for  $C_6H_9N_{10}BO_4Pb$  (503.21): C 14.32, H 1.80, N 27.84. Found C 14.96, H 1.83, N 27.82%.

<sup>1</sup>H-NMR (D<sub>2</sub>O):  $\delta$  7.97 (s, 1H, H-3), 8.25 (s, 1H, H-3). The MS shows signals which are derived for a bis-ligand complex  $\text{PbL}_2 = M$ . MS (330 °C):  $m/z$  570 (10,  $[\text{M}-(\text{C}_2\text{H}_2\text{N}_3)]^+$ ), 501 (4,  $[\text{M}-(\text{C}_2\text{H}_2\text{N}_3)_2]^+$ ), 423 (7,  $[\text{M}-\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3\}]^+$ ) =  $[\text{Pb}\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3\}]^+$ , 355 (7,  $[\text{Pb}\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_2\}]^+$ ), 328 (13,  $[\text{Pb}\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_2-\text{HCN}\}]^+$ ), 300 (25,  $[\text{Pb}\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_2-2\text{HCN}-\text{H}\}]^+$ ), 276 (14,  $[\text{Pb}(\text{C}_2\text{H}_2\text{N}_3)]^+$ ), 69 (100,  $[\text{C}_2\text{H}_2\text{N}_3]^+$ ),  $M = \text{PbL}_2$  without nitrate or aqua ligands;  $L = \{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3\}$ . IR (major peaks only): 3423 m, br ( $\nu\text{OH}$ ), 3115 m, 3111 m ( $\nu\text{CH}$ ), 2505 m, 2427 sh ( $\nu\text{BH}$ ), 1507 s, 1384 s, 1317 s, 1285 s, 1230 m, 1148 s, 1186 s, 1148 s, 1136 s, 1119 m, 1042 m, 1028 m, 1009 m, 981 m, 963 m, 904 m, 876 m, 730, 723 s, 672 s, 664 s, 651  $\text{cm}^{-1}$ .

#### Diaqua-bis[hydrotris(triazolyl)borato]lead(II)-dihydrate

**(6 · 2 H<sub>2</sub>O)**. Lead nitrate (330 mg, 1.00 mmol) dissolved in water (10 mL) was carefully overlaid in a test-tube with  $\text{K}\{\text{HB}(\text{triazolyl})_3\}$  (520 mg, 2.00 mmol) dissolved in water (20 ml). Some amorphous precipitate was formed in the overlaying process and rhombic crystals started growing rapidly at the phase boundary. After some days needles appeared at the expense of the initially formed rhombic crystals. After 7 days the colorless needle-shaped crystals were collected by filtration. They were manually separated from some remaining rhombic crystals under the microscope. An X-ray powder diffractogram then confirmed the single-phase character of the needles upon comparison with the simulated spectrum from the single-crystal X-ray data. Yield 280 mg (40%). mp. 290 °C (dec.).

Calc. for  $\text{C}_{12}\text{H}_{22}\text{N}_{18}\text{O}_4\text{B}_2\text{Pb}$  (711.24): C 20.26, H 3.12, N 35.45. Found C 20.68, H 2.99, N 35.20%.

<sup>1</sup>H-NMR (D<sub>2</sub>O):  $\delta$  7.96 (s, 1H, H-3), 8.22 (s, 1H, H-3). MS (280 °C):  $m/z$  570 (0.76,  $[\text{M}-\text{C}_2\text{H}_2\text{N}_3]^+$ ), 501 (0.29,  $[\text{M}-(\text{C}_2\text{H}_2\text{N}_3)_2]^+$ ), 474 (0.10,  $[\text{M}-(\text{C}_2\text{H}_2\text{N}_3)_2-\text{HCN}]^+$ ), 447 (0.03,  $[\text{M}-(\text{C}_2\text{H}_2\text{N}_3)_2-2\text{HCN}]^+$ ), 423 (0.38,  $[\text{M}-\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3\}]^+$ ) =  $[\text{Pb}\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_3\}]^+$ , 395 (0.24,  $[\text{Pb}\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_2\}]^+$ ), 355 (0.41,  $[\text{Pb}\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_2-\text{HCN}\}]^+$ ), 328 (0.56,  $[\text{Pb}\{\text{HB}(\text{C}_2\text{H}_2\text{N}_3)_2-2\text{HCN}\}]^+$ ), 276 (0.68,  $[\text{Pb}(\text{C}_2\text{H}_2\text{N}_3)]^+$ ), 69 (100,  $[\text{C}_2\text{H}_2\text{N}_3]^+$ ),  $M = \text{PbL}_2$  without aqua ligands. IR (major peaks only): 3368 m, br ( $\nu\text{OH}$ ), 3105 m ( $\nu\text{CH}$ ), 2494 w, 2465 w, 2427 w, sh ( $\nu\text{BH}$ ), 1505 s, 1498 sh, 1322 m, 1279 s, 1188 s, 1150 s, 1141 sh, 1028 m, 1024 m, 1014 m, 1006 m, 970 s, 959 m, 888 m, 882 m, 728 m, 675  $\text{cm}^{-1}$ .

The needle-shaped crystals of **6** have to be collected after 7 d. Shortly thereafter very thin, fiber-like crystals (**7**) appear

at the expense of the earlier crystalline forms. The microscopic investigation showed the complete disappearance of the rhombic crystals with some needles of **6** remaining. mp. 307 °C.

Elemental analysis, found C 13.85, H 1.36, N 25.38, Pb 33.85. Calc. for  $\text{C}_6\text{H}_7\text{BN}_9\text{Pb}(\text{NO}_3) \cdot (\text{H}_2\text{O})_2$  (521.23): C 13.83, H 2.13, N 26.87, Pb 39.75%.

IR: 3320 m, br ( $\nu\text{OH}$ ), 2504 w, 2427 w ( $\nu\text{BH}$ ), 1506 s, 1403 s, 1385 s, 1321 s, 1287 s, 1195 s, 1190 s, 1147 s, 1136 s, 1037 s, 1021 m, 1013 s, 981 m, 968 m, 961 m, 739 m, 733 m, 721 s, 679 m, 669 s  $\text{cm}^{-1}$ . The mass spectrum of **7** does not show any metal containing fragments.

#### Structure determinations

Data were collected by the  $\omega$ -2 $\theta$  scan method with Mo-K $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) and the use of a graphite monochromator on an Enraf-Nonius CAD4 (**3** · 2 H<sub>2</sub>O and **5**) and a Syntex P21 (**6** · 2 H<sub>2</sub>O) four-circle diffractometer. Structure solution was done by direct methods (SHELXS 97) [41]; refinement was done by full-matrix least-squares on  $F^2$  using the SHELXTL program package (Version 5.1, Bruker AXS). All non-hydrogen positions found and refined. The atoms were refined with anisotropic temperature factors except for the disordered nitrate anion in **5**. In the nitrate anion the atoms O3, O4 and N10 were refined isotropically with restrained geometry. In **3** · 2 H<sub>2</sub>O the hydrogen atoms were found and refined isotropically with free temperature factors. The O–H bond lengths were restrained to 1.0(1) Å. In **5** the hydrogen atoms were placed at calculated positions, using appropriate riding models and an isotropic temperature factor of  $B_{\text{eq}}(\text{H}) = 1.2 B_{\text{eq}}(\text{C or O})$ . In **6** · 2 H<sub>2</sub>O the hydrogen atoms were found and refined isotropically with free temperature factors but with bond lengths restrained to C/B–H = 0.93 Å and O–H = 1.0 Å. Crystal data are listed in Table 4. Graphics were obtained with ORTEP 3 for Windows [42]. Hydrogen bonding computations for the crystal structure discussions were carried out with PLATON for Windows [43]. The structural data has been deposited with

**Table 4** Crystal data for compounds **3** · 2 H<sub>2</sub>O, **5**, and **6** · 2 H<sub>2</sub>O

	<b>3</b> · 2 H <sub>2</sub> O	<b>5</b>	<b>6</b> · 2 H <sub>2</sub> O
Formula	$\text{C}_{12}\text{H}_{22}\text{B}_2\text{CaN}_{18}\text{O}_4$	$\text{C}_6\text{H}_9\text{BN}_{10}\text{O}_4\text{Pb}$	$\text{C}_{12}\text{H}_{22}\text{B}_2\text{N}_{18}\text{O}_4\text{Pb}$
<i>M</i>	544.18	503.23	711.29
<i>T/K</i>	298(2)	193(2)	298(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$Pcmm$	$P2_1/c$
<i>a</i> /Å	9.278(5)	7.273(2)	9.440(3)
<i>b</i> /Å	18.555(3)	11.449(3)	19.016(9)
<i>c</i> /Å	14.6553(14)	18.213(4)	14.781(10)
$\alpha$ /°	90	90	90
$\beta$ /°	107.04(3)	90	107.09(4)
$\gamma$ /°	90	90	90
<i>V</i> /Å <sup>3</sup>	2412(1)	1516.5(7)	2536(2)
<i>Z</i>	4	4	4
<i>D</i> /g cm <sup>-3</sup>	1.498	2.204	1.863
$\mu$ /cm <sup>-1</sup>	3.21	111.59	67.1
Measured reflections	4578	1822	4815
Unique reflections ( $R_{\text{int}}$ )	4198(0.015)	1822(0.085)	4468(0.058)
Observed reflections [ $I > 2\sigma(I)$ ]	2593	1555	3662
Parameters refined	422	115	422
Maximum, minimum $\Delta\rho/e \text{ \AA}^{-3}$	0.228; -0.224	5.331; -2.421 <sup>a)</sup>	0.971; -0.971 <sup>b)</sup>
<i>R1</i> ; <i>wR2</i> [ $I > \sigma(I)$ ]	0.0499; 0.0853	0.0566; 0.1536	0.0271; 0.0613
<i>R1</i> ; <i>wR2</i> all reflections	0.1051; 0.1017	0.0566; 0.1536	0.0401; 0.0667

<sup>a)</sup> residual electron density mostly near the poorly localized nitrate anion; <sup>b)</sup> residual electron density near lead



the Cambridge Crystallographic Data Center [No. CCDC-143947 ( $3 \cdot 2\text{H}_2\text{O}$ ), -143948 (**5**), and -143949 ( $6 \cdot 2\text{H}_2\text{O}$ )].

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