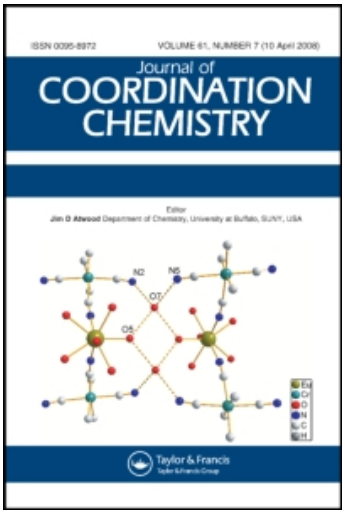

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Synthesis, characterization, and coordination chemistry of the dihydrobis(5-aminotetrazol-1-yl)borate anion

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Synthesis, characterization, and coordination chemistry of the dihydrobis(5-aminotetrazol-1-yl)borate anion

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The new anionic dihydrobis(5-aminotetrazol-1-yl)borate ligand was synthesized in high yield and structurally characterized. Electron donating effects of the amino substituent on the tetrazole ring are discussed comparing the basicity and coordination chemistry to the previously reported unsubstituted dihydrobistetrazol-1-ylborate anion. Both mono- and diprotonated ligand species were isolated and structurally characterized. Increased σ-electron donating strength of the aminotetrazole compound provides more than one tetrazolyl nitrogen position capable of metal coordination. One-dimensional coordination polymers of $\{H_2B(H_2NCN_4)_2\}_2Cu(NH_3)_2$ and $\{H_2B(H_2NCN_4)_2\}Zn(NH_3)Cl$ are structurally characterized demonstrating both a symmetrically bridging and a new unsymmetrically bridging motif involving more than one of the tetrazolyl ring positions of the ligand.

Keywords: Coordination polymers; Bridging ligands; Tetrazolylborate; 5-Aminotetrazole; Boronium ion

1. Introduction

Self-assembly of coordination polymers comprised of metal centers with ligands that bond exclusively in a bridging mode provides a convenient method for the design and synthesis of functional materials. For that purpose, new bridging ligands contribute to the ability of the chemists to adjust the structure and properties of materials for a particular application. As a modification of the extensively studied poly(pyrazolyl) borate ligand chemistry [1], Janiak [2] synthesized the first dihydrobistetrazol-1-ylborate ligand and established its coordination chemistry as exclusively symmetrically bridging through the exocyclic nitrogens neighboring the C–H positions to form 2-D frameworks [3]. Although the dihydridobistetrazol-1-ylborate ligand possesses the additional ring nitrogens that are available for metal coordination, only the C–H neighboring nitrogens act as donors in the complexes characterized to date, consistent with the tetrazolylborate charge distribution predicted by AM-1 calculations [4]. Additional tetrazole nitrogens have, however, been shown to participate as donors in extensive hydrogen bonding which strongly influences the lattice structure and properties of tetrazolylborate coordination complexes [5].

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This study expands the tetrazolylborate chemistry to include synthesis and chemical properties of the anionic dihydrobis(5-aminotetrazol-1-yl)borate σ-donor ligand and explicates the importance of pH control in the synthesis of metal complexes using tetrazolylborate ligands. The ligand synthesis herein uses the more readily available 5-aminotetrazole which, unlike 1H-tetrazole, can be safely shipped in a solid hydrated form. The electron donating influence of the amino group reduces the acidity of 5-aminotetrazole (pKa = 5.93) [6] *versus* 1H-tetrazole (pKa = 4.89) [7]. The electron-donating ability of the 5-aminotetrazole ring nitrogens is similarly enhanced in the dihydrobis(5-aminotetrazol-1-yl)borate anion over the unsubstituted anion resulting in increased basicity and metal–ligand bond strengths, thus providing more than one ring nitrogen position with sufficient σ-donor strength for metal coordination.

2. Experimental

2.1. *General remarks*

Sodium borohydride and potassium borohydride as well as anhydrous acetonitrile were purchased from Aldrich chemicals and used as received. While no special precautions were taken to exclude air from the apparatus, the 5-aminotetrazole with metal borohydride reactions were carried out under a blanket of nitrogen to exclude water. 5-Aminotetrazole was obtained as the monohydrate and the water of hydration was removed prior to use by drying overnight in a vacuum oven at 100°C. Caution! Anhydrous 5-aminotetrazole as well as many of the other high-nitrogen compounds described in this article are energetic and the deflagration reactions are rapid and highly exothermic producing large quantities of gaseous products and should be treated accordingly. In particular, the reactions of dihydrobis(5-aminotetrazol-1-yl)borate compounds with transition metal salts or oxidizing acids produce energetic compounds that are friction and impact sensitive.

2.2. *Synthesis of tetrazolylborate compounds*

2.2.1. Potassium dihydridobis(5-aminotetrazol-1-yl)borate (1a). Potassium borohydride, KBH_4 10.79 g (200 mmol) was added with stirring to 100 mL of anhydrous acetonitrile in a 250 mL round-bottom flask fitted with a magnetic stir bar. While rapidly stirring the mixture, 34.027 g (400 mmol) of anhydrous 5-aminotetrazole was added slowly in small portions. The suspension was warmed and rapid gas evolution occurred during the addition. The flask was fitted with a reflux condenser and the slurry was refluxed for 4 days under a dry nitrogen atmosphere with continuous rapid stirring. The solution was cooled and the solid was collected on filter paper and then dried *in vacuo* to yield 41.83 g (190.1 mmol) of crude product (95.0% yield). Anal. Calcd for $C_2H_6N_{10}BK$ (%): C, 10.92; H, 2.75; and N, 63.65. Found (%): C, 11.42; H, 3.11; and N, 63.07. ^{1}H-NMR (DMSO-d_6): δ 5.64 (s, NH_2, 4H); and 3.28 (b, BH_2, 2H). $^{13}C\{^1H\}$ 159.19 (s, CNH_2, 1C). ^{11}B −13.66 (b, BH_2, 1B).

2.2.2. Sodium dihydridobis(5-aminotetrazol-1-yl)borate (1b). Sodium borohydride, $NaBH_4$, was substituted in the reaction described for **1a** without any significant changes in the procedure, thus the reaction of 7.567 g (200 mmol) $NaBH_4$ with 34.027 g (400 mmol) of anhydrous 5-aminotetrazole provided 38.46 g (188.6 mmol) of **1b** (94.3% yield).

2.2.3. (5-Amino-1-H-tetrazole)dihydro(5-aminotetrazol-1-yl)borane hemihydrate (2). Glacial acetic acid (10 mL) was slowly added to a solution of 5.00 g (22.7 mmol) **1a** in 10 mL of water with stirring. The solution was left undisturbed without stirring for 30 min as the product crystallized. The solid was collected on a glass frit and washed three times with 10 mL of water and then air-dried. Yield: 3.558 g (17.78 mmol) 78.3%. Anal. Calcd for $C_4H_{16}N_{20}B_2O$ (%): C, 12.58; H, 4.22; and N, 73.35. Found (%): C, 12.82; H, 4.31; and N, 72.87. ^{1}H-NMR (DMSO-d_6): δ 8.5 (b, NH, OH, 2H); 7.15 (b, NH_2, 4H); and 3.30 (b, BH_2, 2H). $^{13}C\{^1H\}$155.50 (s, CNH_2, 1C). ^{11}B −13.30 (b, BH_2, 1B).

2.2.4. (1-H-tetrazole)tetrazol-1-ylborane (3). A sample of $KH_2B(HCN_4)_2$ 370 mg (1.95 mmol) was dissolved in 5 mL H_2O. Trifluoroacetic acid (TFA) 870 mg (7.63 mmol) was slowly added with stirring. After the addition was complete, stirring was stopped and the solution was left undisturbed for 5 min while the product crystallized. The product was collected on a frit and washed with 1 mL of cold 1.5 mol L^{-1} TFA. The solid was dried *in vacuo* providing 201 mg colorless crystalline solid (68% yield). Anal. Calcd for $C_2H_5N_8B$ (%): C, 15.81; H, 3.32; and N, 73.76. Found (%): C, 15.92; H, 3.18; and N, 73.11. ^{1}H-NMR (DMSO-d_6): δ 14.30 (s, NH, 1H); 8.94 (s, CH, 2H); and 3.75 (bd, BH_2, 2H). $^{13}C\{^1H\}$ 147.11 (s, CH, 1C). ^{11}B −1.10 (t, BH_2, 1B; $J = 100$ Hz).

2.2.5. Bis(5-amino-1-H-tetrazole)boronium nitrate (4). A suspension of **2**, 1.59 g (7.78 mmol) in 75 mL anhydrous methanol was stirred and a solution of 10 mL anhydrous methanol with 0.687 g of 70% HNO_3 (7.78 mmol HNO_3) was slowly added. The mixture was stirred for 30 min to produce a colorless solution with a small amount of solid that was removed by filtration. The solution was reduced to a solid with about 10 mL mother liquor. Chloroform 25 mL was added to the mixture and the solid collected on filter paper and washed twice with 5 mL chloroform and dried *in vacuo*. Yield: 1.792 g (7.37 mmol) 94.7%. Anal. Calcd for $C_2H_8N_{11}BO_3$ (%): C, 9.81; H, 3.29; and N, 62.90. Found (%): C, 10.22; H, 3.46; and N, 63.18. ^{1}H-NMR (DMSO-d_6): δ 14.7 (b, NH, 2H); 8.03 (b, NH_2, 4H); and 3.32 (b, BH_2, 2H). $^{13}C\{^1H\}$ 152.75 (s, CNH_2, 1C). ^{11}B −12.42 (b, BH_2, 1B). Safety sensitivity test results [8]: Impact 50% Pt = 10 CM; impact low fire Pt = 6 CM; ABL friction 50% Pt: 269 LBS, ABL friction low fire Pt: 251 LBS; electrostatic 50% Pt: 10/10 No Fires @ 0.25 J.

2.2.6. Bis(dihydridobis(5-aminotetrazol-1-yl)borate)bisammoniacopper(II) (5). Cupric chloride (176 mg, 1.31 mmol) was dissolved in 1 mL water and then 3 mL of concentrated ammonium hydroxide solution was added. A second solution containing **2** (500 mg, 2.16 mmol) in 5 mL concentrated ammonium hydroxide was added with stirring. The dark blue solution was left undisturbed for a period of 5 days to allow

excess ammonia to escape. The dark blue crystals were washed thoroughly four times with 10 mL water and collected on a glass frit and dried *in vacuo*. Yield: 559 mg (92.9%). Anal. Calcd for $C_4H_{18}N_{22}B_2Cu$ (%): C, 10.46; H, 3.95; and N, 67.06. Found (%): C, 10.54; H, 3.98; and N, 66.81.

2.2.7. (Dihydrobis(5-aminotetrazol-1-yl)borate)(ammonia)zinc(II)chloride, 6. Anhydrous zinc chloride, 294 mg (2.16 mmol) was dissolved in 3 mL of water and added to a solution of **2** (500 mg, 2.16 mmol) in 5 mL concentrated ammonium hydroxide. The solution was left undisturbed for 1 week and then evaporated to dryness. The colorless crystalline solid was washed thoroughly three times with 10 mL water, collected on a glass frit, and then air dried. Yield: 455 mg (1.44 mmol) 67%. Anal. Calcd for $C_2H_{11}BClN_{11}OZn$ (%): C, 7.58; H, 3.50; and N, 48.63. Found (%): C, 7.34; H, 3.68; and N, 48.32.

2.3. *Single-crystal X-ray structure analysis*

X-ray quality single crystal specimens of the compounds were grown using the crystallization methods and the solvent systems are given in table 1. X-ray intensity data were collected for omega scans at 296 K on a Bruker SMART APEX II diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Frames were integrated using SAINT software, data were corrected for absorption using the empirical multi-scan method (SADABS), and the structures solved by direct methods using SHELXTL and refined by full-matrix least squares refinement on F^2.

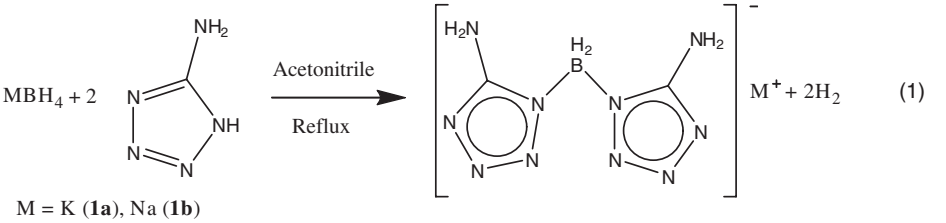
3. Results and discussion

Synthesis of bis(5-aminotetrazolyl)borate salts using a procedure analogous to the "dry method" previously reported for dihydrobistetrazol-1-ylborate [2] wherein an intimate dry mixture of the borohydride and tetrazole are heated was considered, but not attempted due to the potential for a thermal runaway reaction without the heat sinking effect of a solvent. Instead, various solvents were investigated to find a suitable reaction medium. For high-boiling solvents in which the reagents and product are highly soluble such as dimethylformamide (DMF) and dimethylacetamide (DMAC), the products were of low purity and included significant solvent that could not be removed [9]. An immediate reaction occurred in acetonitrile, a solvent that was easily and completely removed under vacuum; however, since the reagents and product have very limited solubility in acetonitrile, it was necessary to run the reaction at elevated temperature. When the reaction was run as a slurry in refluxing acetonitrile with vigorous mixing and for an extended period, excellent conversion to the desired product was achieved (equation 1). Nearly all of the hydrogen evolution occurred upon the addition of the 5-aminotetrazole to the borohydride suspension. An unidentified intermediate phase initially formed that required continuous mixing and extended heating to generate the final product in a pure form. The tetrazolyl borate product was conveniently isolated by filtering the solvent from the solid reaction product and drying. In experiments where stirring was inadequate, the mixture caked into a solid mass and the intermediate was not fully converted to the final product leaving some water

Table 1. Crystallographic and structure refinement parameters for **1–6**.

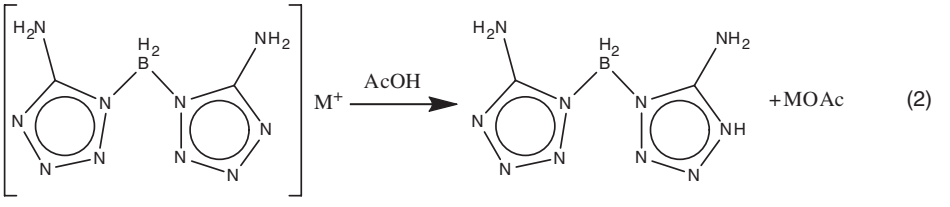
	1a	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_2H_6BKN_{10}$	$C_4H_{16}B_2N_{20}O$	$C_2H_5BN_8$	$C_2H_8BN_{11}O_3$	$C_4H_{18}B_2CuN_{22}$	$C_2H_{11}BClN_{11}OZn$
Formula weight	220.08	381.99	151.95	245.00	459.56	316.85
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group (no.)	$P\,21/c$ (14)	$C\,2/c$ (15)	$P\,21$ (4)	$P\,21/n$ (14)	$P\bar{1}$ (2)	$P\,mc21$ (26)
Crystal color, shape	Colorless, rod	Colorless, plate	Colorless, plate	Colorless, plate	Blue, cube	Colorless, rod
Unit cell dimensions (Å, °)						
a	10.6215(5)	19.373(5)	4.7917(10)	10.319(2)	6.58547(7)	9.4283(5)
b	11.9583(5)	8.711(2)	15.506(3)	8.2903(17)	7.26151(7)	5.0074(2)
c	6.8367(2)	12.495(3)	8.9904(18)	12.562(3)	9.68964(10)	12.3291(5)
α	90	90	90	90	74.7310(4)	90
β	97.842(1)	126.652(2)	95.901(2)	114.027(2)	82.7281(4)	90
γ	90	90	90	90	79.1780(4)	90
Volume (Å^3), Z	860.24(7), 4	1691.7(8), 4	664.4(2), 4	981.5(3), 4	437.560(10), 1	582.07(5), 2
Calculated density (Mg m^{-3})	1.699	1.500	1.519	1.658	1.744	1.808
Absorption coefficient (mm^{-1})	0.595	0.117	0.114	0.142	1.298	2.344
Crystal size (mm^3)	$0.08 \times 0.08 \times 0.24$	$0.08 \times 0.15 \times 0.17$	$0.02 \times 0.45 \times 0.61$	$0.09 \times 0.21 \times 0.36$	$0.27 \times 0.42 \times 0.47$	$0.07 \times 0.09 \times 0.30$
θ range for data collection (°)	1.94–27.53	2.62–25.49	2.28–27.51	2.17–27.21	2.19–33.15	2.16–27.55
Reflections collected	9770	8360	7715	10,853	13,313	6328
Independent reflections	1974	1580	1579	2185	3296	1405
R_{int} (%)	2.11	2.57	2.22	2.09	1.40	2.18
Goodness-of-fit on F^2	1.043	1.006	0.992	0.973	1.066	1.009
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0265$, $wR_2 = 0.0699$	$R_1 = 0.0318$, $wR_2 = 0.0732$	$R_1 = 0.0269$, $wR_2 = 0.0626$	$R_1 = 0.0295$, $wR_2 = 0.0714$	$R_1 = 0.0243$, $wR_2 = 0.0738$	$R_1 = 0.0168$, $wR_2 = 0.0400$
R indices (all data)	$R_1 = 0.0320$, $wR_2 = 0.0735$	$R_1 = 0.0403$, $wR_2 = 0.0788$	$R_1 = 0.0293$, $wR_2 = 0.0642$	$R_1 = 0.0364$, $wR_2 = 0.0758$	$R_1 = 0.0245$, $wR_2 = 0.0740$	$R_1 = 0.0178$, $wR_2 = 0.0405$
Crystallization method, solvent	Cooling, isopropanol	Evaporation, methanol	Reaction mix, TFA/water	Evaporation, methanol	Evaporation, ammonia/water	Evaporation, ammonia/water
CCDC reference number	769644	769645	769646	769647	769648	769649

sensitive material. Near quantitative conversion was obtained using either sodium or potassium borohydride reagents. The colorless compounds **1a** and **1b** are thermally stable to above 150°C, air and moisture insensitive, and very soluble and stable in aqueous or alcoholic solutions. As with the previously reported 1H-tetrazole reaction, there was no evidence of further substitution on the boron center beyond two equivalents of 5-aminotetrazole.



M = K (**1a**), Na (**1b**)

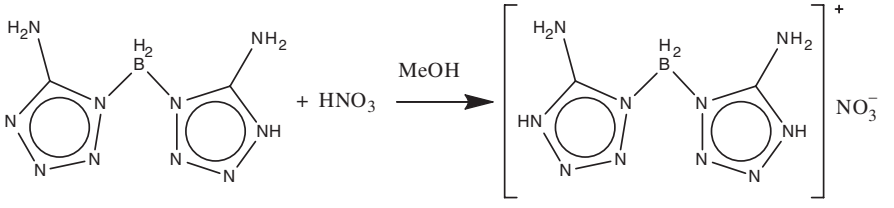
The strong electron withdrawing effect of the 5-aminotetrazolyl groups on the two remaining boron hydrogens is dramatically demonstrated by their inert behavior toward even very strong acids. The BH_2 fragment without any hydridic character is reminiscent of the ligand stabilized boronium complexes $L_2BH_2^+$ described by Muetterties [10]. Rather than the electrophilic abstraction of a hydride in acetic acid solutions ($pK_a = 4.76$), the tetrazolyl rings of **1a** or **1b** are protonated to form **2** (equation 2). This behavior prompted us to investigate the behavior of the previously reported potassium dihydrobistetrazol-1-ylborate [1] in acidic solutions, which revealed that a stronger acid such as TFA ($pK_a = 0.3$) was required to protonate solutions of the anion to form the neutral compound **3**. Compounds **2** and **3** were indefinitely stable in the solid state, however, solutions of the compounds, for example in dimethyl sulfoxide (DMSO), slowly decompose with **2** being much more stable than **3**.



M = K (**1a**), Na (**1b**) **2**

The second tetrazolyl ring of **2** was subsequently protonated by strong acids to form the diprotonated cationic complex **4,** according to equation (3). Addition of even a large excess of concentrated hydrochloric acid did not produce any hydrogen from **2** and resulted in near quantitative conversion to the hydrochloride salt that was isolated and characterized as a hydrate using single crystal X-ray diffraction (XRD) methods. For strong oxidizing acids such as nitric or perchloric acid, it was necessary to conduct the reaction stoichiometrically in methanol to avoid the oxidation of the compound. Addition of excess oxidizing acid resulted in unstable products that decomposed on workup. The nitrate salt **4** is an explosive compound that is both impact and friction sensitive, and therefore safety precautions should be taken during its synthesis and handling. The perchlorate acid salt product formation was confirmed by single crystal

XRD but was only prepared on a few milligram scale and qualitatively classified as a primary explosive too sensitive to handle safely. Attempts to isolate the corresponding acid salts from strong acid solutions of **3** failed to provide analytically pure products. The diprotonated product from reactions of hydrochloric acid and **3** was contaminated with a significant amount of the unsubstituted parent tetrazolate salt, indicating that the target diprotonated species of **2** is unstable to reaction with the loss of tetrazole in strong acid solutions. This is likely due to a consequence of the poorer σ-donating ability of the 1H-tetrazole to the boronium (BH_2^+) center. As stated in earlier studies on boronium complexes, the stability is dependent on the size and Lewis base strength of the stabilizing ligands [10]. The protonated 5-aminotetrazole moiety is apparently a sufficiently strong σ-donor to stabilize the boronium complex, whereas the 1H-tetrazole complex dissociates in the solution.



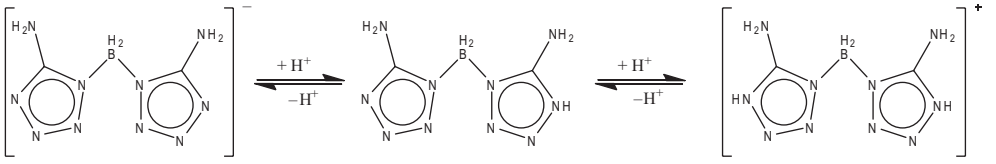
2 **4**

Acidification of the crude product from the reaction of 5-aminotetrazole and borohydride with acetic acid was used as a convenient purification method. Samples of the sodium or potassium salt (**1a**, **1b**) were dissolved in a minimum of water, filtered, and added to 2 volume equivalents of glacial acetic acid. Compound **2,** which has very limited solubility in weakly acidic solutions, crystallizes to proide greater than 90% isolated conversion to the neutral compound that may subsequently be transformed back to a salt by reaction with either a base or strong acid.

The dibasic nature of the dihydrobis(5-aminotetrazolyl)borate and unusual stability of the protonated species illustrated in scheme 1 allows the capability to easily alter or eliminate the counterion to the ligand selecting from an assortment of cations, to no counterion, to a variety of anions including oxidizers.

Unequivocal characterization of the 5-aminotetrazolyl compounds using nuclear magnetic resonance (NMR) spectroscopic methods was not possible. The proton spectra are generally very broad and the shifts were highly dependent on the trace amounts of water in the sample. The structures of the compounds were therefore unambiguously identified by single crystal XRD methods. Representative single crystal structure ORTEP diagrams for all three unprotonated, monoprotonated, and diprotonated species of the dihydrobis(5-aminotetrazolyl)borate as well as the monoprotonated dihydrobistetrazo-1-lylborate compound are shown in figure 1. Examination of the crystal data revealed no significant structural changes in the bond distances with only a minor decrease ($\sim$0.03 Å total) in the C–NH_2 bond length as the ligand is sequentially protonated. The unit cell of **3**, the monoprotonated dihydrobis(5-aminotetrazol-1-yl)borate, contains two crystallographically independent molecules due to a rotation of one tetrazole ring about the B–N bond.

Reactions of the sodium or potassium salts (**1a** or **1b**) with transition metal chlorides were investigated to compare the coordination chemistry of



Scheme 1. Sequential and reversible protonation of the tetrazolyl rings of the dihydrobis(5-aminotetrazol-1-yl)borate ligand.

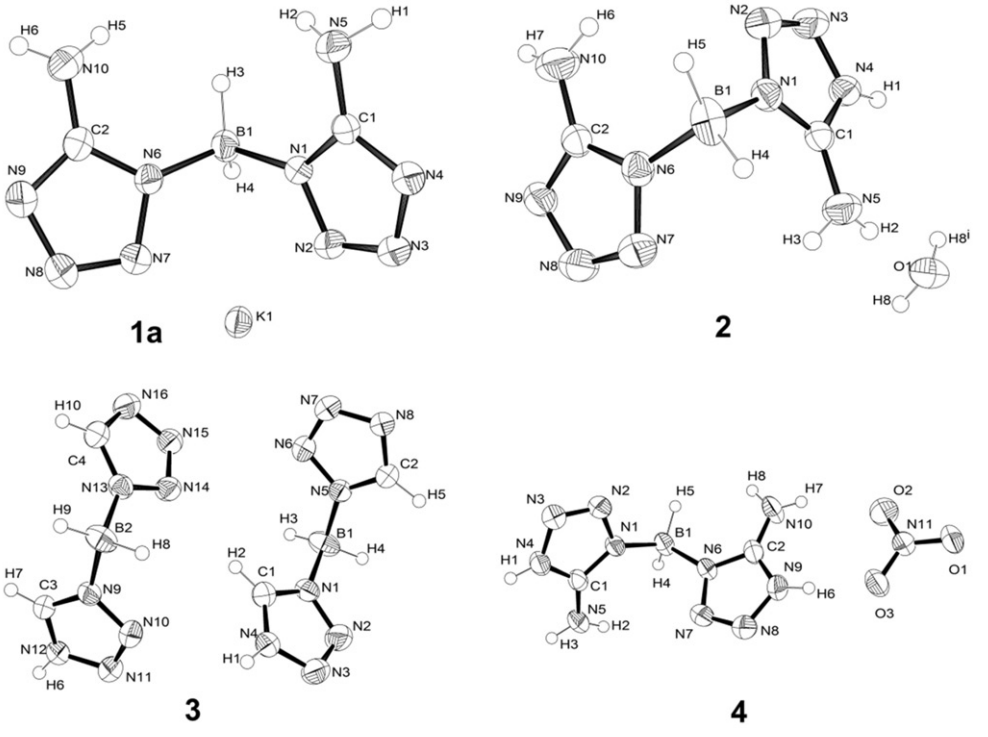


Figure 1. Crystal structures of **1–4** showing atom labeling schemes. ORTEP plots drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

the dihydrobis(5-aminotetrazol-1-yl)borate to the previously reported dihydrobistetrazol-1-ylborate metal complexes. The transition metal dihydrobis(5-aminotetrazol-1-yl)borate complexes are of interest as potential propellant ingredients containing both metal and boron centers might act as burn rate modifiers [11]. In all cases, upon mixing an aqueous solution of **1a** or **1b** with a metal chloride solution, a precipitate was immediately produced. The Cu, Co, and Ni products were fine powders of blue, pink, and green colours, respectively, that were insoluble in all common solvents. In the case of iron chloride, it was determined that the product was primarily the neutral compound **2** contaminated with a small amount of an unidentified brown solid. This can be explained by the low pH of ~2 for 1% $FeCl_3$ solutions [12]. Slower metathesis reactions were conducted in attempts to grow single crystals by layering separate solutions of **1a** or **1b** and the transition metal chloride solution. These aqueous solution studies also failed to produce any X-ray quality crystals.

Thermal decomposition of the resulting high-nitrogen transition metal complex powders was both rapid and exothermic. The compounds are impact sensitive and therefore appropriate precautions should be taken when preparing or handling them. Initiation of the tetrazolylborates or their metal complexes produced heat, a large amount of gas, and a voluminous porous residual ash. For the copper compound, the amorphous white solid residue was produced together with a low-density copper foam whose identity was confirmed by its characteristic powder XRD pattern. Similar low-density metal foams were also reported to be produced from the thermal decomposition of bistetrazoleamine (BTA) metal compounds [13].

Reactions of dihydrobis(5-aminotetrazol-1-yl)borate with cupric chloride or zinc chloride in a 2 : 1 or 1 : 1 mole ratio, respectively, in aqueous ammonia solution produced the 1-D coordination polymers **5** and **6**. The same zinc product was isolated from the reaction of a 2 : 1 mole ratio of ligand to zinc(II) chloride. An analogous reaction of excess potassium dihydridobis(3-nitro-1,2,4-triazolyl)borate with zinc(II) chloride also formed a 1 : 1 complex exclusively [14]. Both **5** and **6** are insoluble in water but soluble in ammonia solution. X-ray quality single crystals were grown by the slow evaporation of ammonia solutions of the complexes. Thermal decomposition of **6** also produced a copper foam as one of the products.

In **5**, the copper(II) center is coordinated to two *trans* ammonia ligands and four tetrazole nitrogens in an octahedral arrangement with a typical strong Jahn–Teller distortion. The bond lengths are within the expected range and close to the previously published structure for the $Cu(NH_3)_2\{\mu\text{-}H_2B(CHN_4)_2\}$ analog [15] with a slight decrease in the shortest Cu-tetrazolyl bonds and increased Jahn–Teller distortion. It is not appropriate, however, to compare the coordination too closely in the two complexes since the dihydrobistetrazol-1-ylborate forms a 2-D framework with symmetrically bridging ligands, while **5** crystallizes as a 1-D coordination polymer with unsymmetrically bridging ligands. Adjacent coppers in **5** share two dihydrobis(5-aminotetrazol-1-yl)borate ligands in which the C–NH_2 neighboring nitrogens on one tetrazole ring form the short Cu–N bonds (Cu1–N4 at 2.0277(8) Å) and the nitrogens adjacent to the C–NH_2 neighboring nitrogen on the second tetrazole ring form the other set of Cu–N bonds (Cu1–N8 at 2.564(1) Å). The result is a 1-D chain-like structure, as shown in figure 2, with the lattice packing dictated by extensive inter-chain hydrogen bonding of the amino and ammonia hydrogens to tetrazole nitrogens. The Cu–Cu intrachain distance of 8.840 Å is longer than the published 2-D dihydrobistetrazol-1-ylborate copper structure (7.653(3) or 8.170(3) Å); however, the close packing of the chain structure of **5** provides somewhat shorter interchain Cu–Cu distances (7.261 or 6.585 Å).

Complex **6** crystallizes as a 1-D coordination polymer (figure 3) with adjacent distorted tetrahedral zinc centers linked by a single symmetrically bridging dihydrobis(5-aminotetrazol-1-yl)borate ligand *via* the C–NH_2 neighboring nitrogens (Zn–N4 bond). Extensive hydrogen bonding involving the water, amino, ammonia, and tetrazole acceptor donor pairs link adjacent strands in the lattice.

4. Conclusions

A convenient, low-cost, high-yield synthesis of a new dihydrobis(5-aminotetrazol-1-yl)-borate anionic ligand from the reaction of 5-aminotetrazole with potassium or sodium

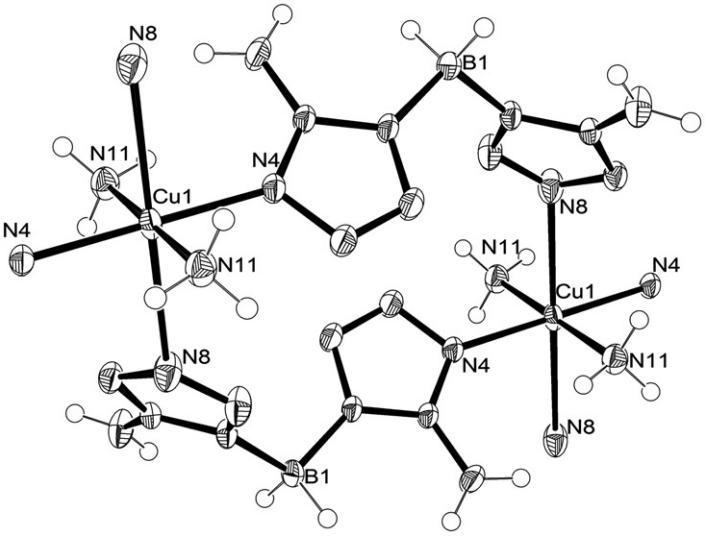


Figure 2. Crystal structure of **5** with atom labeling scheme for atoms coordinated to copper depicting the repeating link of the 1-D chain construction with unsymmetrical bridging ligand. ORTEP plots are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

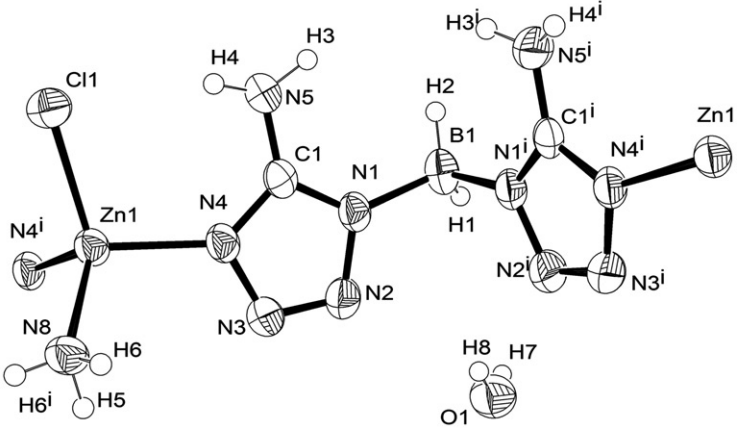


Figure 3. Structure and atom labeling scheme of the repeating unit in the 1-D coordination polymer **6** with a symmetrical bridging ligand. ORTEP plots are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

borohydride has been demonstrated. The dibasic properties of the ligand can be exploited to produce stable mono- or diprotonated forms. While this expands the available chemistry of the compound for other purposes, metal complexation acidic conditions must be avoided where stable protonated species are produced that are not capable of binding to a metal center. Electron donation from the amino substituent on the tetrazole rings increases the basicity of dihydridobis(5-aminotetrazol-1-yl)borate relative to the previously reported dihydrobistetrazol-1-ylborate and increases the σ-donating

ability of the tetrazole ring nitrogens toward metal centers. As a result, two bridging motifs are demonstrated in the metal complexes described in this article, wherein dihydrobis(5-aminotetrazol-1-yl)borate provides multiple nitrogens for coordination to metal centers. First, an unusual asymmetric bridging mode in which the C–NH_2 neighboring nitrogen (the 4 position) on one tetrazole ring and the nitrogen adjacent to the C–NH_2 neighboring nitrogen (the 3′ position) on the second tetrazole ring bridge two copper centers. Second, a symmetrical bridging mode in which the C–NH_2 neighboring nitrogens (the 4, 4′ positions) of both tetrazole rings bridge Zn centers. The new dihydrobis(5-aminotetrazol-1-yl)borate anion ligand offers stronger σ-donor strength and more diverse metal coordination chemistry than the previously reported dihydrobis(1H-tetrazol-1-yl)borate compound.

Supplementary material

Crystallographic data for the structures **1a**–**6** in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC nos 769644–769649, respectively. 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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