

**Oxidopolyborate chemistry: The self-assembled, templated, synthesis, and an XRD study of a 1-D coordination polymer, [Cu(en){B6O7(OH)(6)}](.)3H(2)O (en=1,2-diaminoethane)**

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Oxidopolyborate chemistry: the self-assembled, templated, synthesis and an XRD study of a 1-D coordination polymer, $[\text{Cu}(\text{en})\{\text{B}_6\text{O}_7(\text{OH})_6\}] \cdot 3\text{H}_2\text{O}$ (en = 1,2-diaminoethane).

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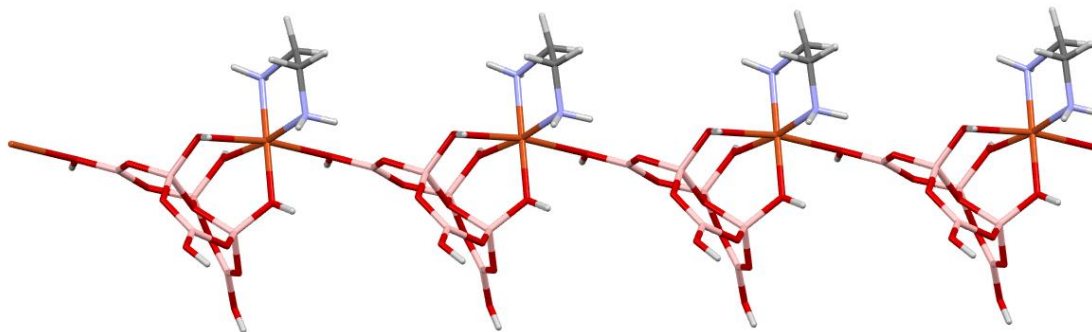
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Dedicated to Professor Alan Welch on the occasion of his retirement at Heriot-Watt University.

ABSTRACT

$[\text{Cu}(\text{en})\{\text{B}_6\text{O}_7(\text{OH})_6\}] \cdot 3\text{H}_2\text{O}$ (**1**) (en = 1,2-diaminoethane), obtained as a crystalline solid in low yield (31%) after prolonged standing of an aqueous solution initially containing $[\text{Cu}(\text{en})_2](\text{OH})_2$ and $\text{B}(\text{OH})_3$ (1:7 ratio), was characterized by thermal analysis (TGA/DSC), ¹¹B NMR and IR spectroscopy, powder XRD and single-crystal XRD studies, and magnetic susceptibility measurements. The single-crystal X-ray diffraction revealed that the oxidoborate complex is a 1-D coordination polymer with the hexaborate(2-) ligand bridging two hexacoordinate Cu(II) centres, in an alternating a *fac*-tridentate ($\kappa^3\text{-O}$) and monodentate ($\kappa^1\text{-O}$) arrangement. Cu-O coordination bonds and extensive H-bonding networks promote and stabilize the self-assembly of $[\text{Cu}(\text{en})\{\text{B}_6\text{O}_7(\text{OH})_6\}] \cdot 3\text{H}_2\text{O}$ from the Dynamic Combinatorial Libraries of available reactants. $[\text{Cu}(\text{en})\{\text{B}_6\text{O}_7(\text{OH})_6\}] \cdot 3\text{H}_2\text{O}$ is thermally decomposed to $\text{CuB}_6\text{O}_{10}$ in air at 700 °C.

GRAPHICAL ABSTRACT



KEYWORDS Copper(2+) complex; 1-D coordination polymer; Hexaborate(2-); Oxidoborate; Polyborate.

INTRODUCTION

There are many known naturally occurring and synthetic salts containing insular or polymeric polyborate (oxidopolyborate) anions.^[1-3] Polyborates have found applications as bulk industrial products^[4-5] (*e.g.* ceramics, fire-retardant materials, agricultural uses) and also as specialized fine chemicals (*e.g.* NLO^[6] materials). Oxidopolyborates are easily prepared from aqueous solution, or solvothermally, from an appropriate cation and B(OH)₃.^[7] At moderate to high pH, B(OH)₃ exists as a Dynamic Combinatorial Library (DCL)^[8] of hydroxyoxidopolyborate (oxidopolyborate) anions,^[9-10] and the cations present template the crystallization of oxidopolyborate salts^[11] through self-assembly processes. Labile cationic transition-metal complexes^[12] may introduce a DCL of potential cations into reaction medium, allowing the oxidopolyborate to enter the primary coordination shell (as oxygen donor ligands) of the metal with the formation of templated transition-metal complexes. We have recently investigated the reactions of labile Zn^(II)^[13-15] and Cu^(II)^[16-18] complexes and prepared species containing the following anionic hydroxyoxidopolyborate ligands:

[B₂O₃(OH)₂]²⁻,^[17] [B₅O₆(OH)₄]⁻,^[16] [B₆O₇(OH)₆]²⁻,^[14-16,18] [B₁₂O₁₈(OH)₆]⁶⁻^[13-15] and [B₂₀O₃₂(OH)₈]¹²⁻.^[17] The [B₆O₇(OH)₆]²⁻ dianion (Figure 1) is relatively uncommon but is known to occur in a few minerals such as *mascallisterite* and *aksaitite*^[2] and there are also some synthetic examples.^[7] This dianion also has interesting ligand properties and has been shown to coordinate to metal centres through up to four of its hydroxyl oxygen atoms in tridentate,^[2, 14-16, 18-20] bidentate,^[15] or monodentate modes.^[14,15] The monodentate mode has only been observed in 1-D coordination polymers^[14,15] and we herein report the synthesis and characterization of a further example of such a system, [Cu(en){B₆O₇(OH)₆}]·3H₂O.

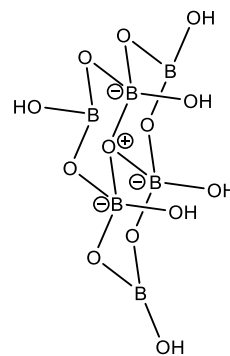
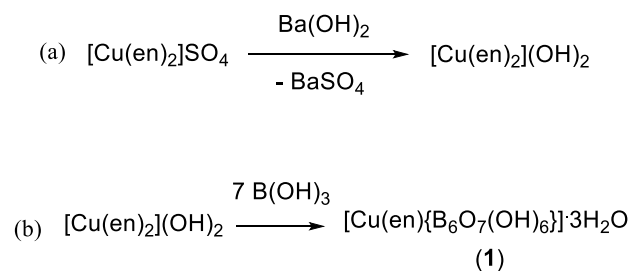


Figure 1. Schematic drawing of the hexaborate(2-) as found in [Cu(en){B₆O₇(OH)₆}]·3H₂O (**1**). The three 4-

coordinate B atoms have formal negative charges and the 3-coordinate O atom has a formal positive charge.

RESULTS AND DISCUSSION

The new 1-D coordination polymer $[\text{Cu}(\text{en})\{\text{B}_6\text{O}_7(\text{OH})_6\}]\cdot 3\text{H}_2\text{O}$ (**1**) was prepared in low yield (31%) as a crystalline blue solid from an aqueous solution originally charged with $[\text{Cu}(\text{en})_2](\text{OH})_2$ (prepared in situ) and $\text{B}(\text{OH})_3$ (1:7 ratio) (Scheme 1). Crystallization of the product developed over a period of several weeks.



Scheme 1. Preparation of $[\text{Cu}(\text{en})\{\text{B}_6\text{O}_7(\text{OH})_6\}]\cdot 3\text{H}_2\text{O}$ (**1**).

The formation of **1** arises through self-assembly and solid-state stabilization of a preferred $\text{Cu}^{\text{(II)}}$ /polyborate complex from the DCLs of polyborate anions and $\text{Cu}^{\text{(II)}}$ species present in the original reactant solution.^[7,11] These solid-state interactions,

including the formation of Cu-O (borate) coordination bonds and strong H-bond interactions, are discussed later. Compound **1** was characterized by thermal analysis (TGA/DSC), spectroscopy (^{11}B NMR and IR), XRD studies (powder and single-crystal), and a magnetic susceptibility measurement. Compound **1** was analytically pure and its experimental powder XRD spectrum had peaks consistent with data calculated from the single-crystal XRD analysis, indicating that it was a pure crystalline material. Compound **1** is thermally decomposed in air to an amorphous blue glassy solid and TGA (20-800 °C) gave data consistent with a multistep process involving dehydration (100-180 °C) and further dehydration and oxidation (180-700 °C) of the en ligand to afford a blue the anhydrous copper(II) borate, $\text{CuB}_6\text{O}_{10}$. Such thermal behaviour has been observed previously in other copper(II) complex oxidopolyborate species^[16-18] and in related metal-complex oxidopolyborate salts.^[21-23] The IR spectrum of **1** shows several strong peaks 1500-600 cm^{-1} which can be attributed to B-O stretches with peaks at 955 cm^{-1} and 808 cm^{-1} diagnostic of the hexaborate(2-) dianion.^[24] A magnetic susceptibility

measurement on **1** demonstrated that it was paramagnetic ($\chi_m = 1917 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$) in agreement with the presence of a $d^9 \text{ Cu}^{\text{II}}$ ion.^[16] Compound **1** was insoluble in organic solvents, including CDCl_3 but dissolved in aqueous solution. However, this process caused decomposition to an equilibrium mixture of its component parts. Ligand ^1H and ^{13}C NMR were not obtainable for **1** in this decomposition solution, probably as a consequence of the proximity of the paramagnetic Cu^{II} centre, but the ^{11}B NMR spectrum of this decomposition solution showed 1 peak at 17.7 ppm, associated with isolated exchanging $\text{B}(\text{OH})_3/[\text{B}(\text{OH})_4^-]$ species.^[9,25]

The single-crystal XRD analysis of **1** confirms its empirical formula of $\text{C}_2\text{H}_{20}\text{B}_6\text{CuN}_2\text{O}_{16}$ and demonstrated that it is a 1-D coordination polymer with three H_2O of crystallization. Two of these water molecules (containing O22/O23 and O24/O25) are disordered. The monomeric repeating unit, a neutral complex is shown in Figure 3, together with the crystallographic atomic numbering for non H-atoms. The en ligand also exhibits disorder about the ‘ CH_2CH_2 ’ moiety over 2 positions and the

two carbons positions with highest s.o.f., 0.862(5), are shown.

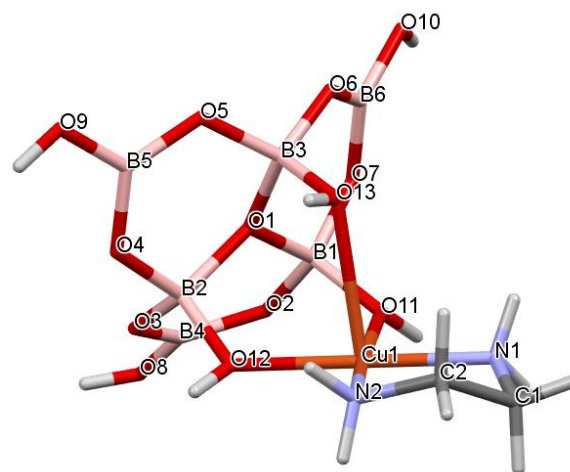


Figure 2. Drawing of ‘monomeric’ repeating unit in **1**, showing atomic numbering scheme for the non-hydrogen atoms. The three H_2O of crystallization are omitted for clarity. The 6th coordination site of the Cu^{II} (not shown, but *trans* to O13) is from O10* of a neighbouring monomeric complex (see Figure 3).

Thus, **1** is comprised of a 6-coordinate Cu^{II} ion coordinated by a bidentate en ligand and a tridentate *fac*-hexaborate(2-) ligand through three hydroxyl O atoms (O11, O12, O13) of the hexaborate(2-) ligand. Tridentate *fac*-coordination of hexaborate(2-) ligands through these hydroxyl borate O atoms is not uncommon.^[14-16,18-20] The primary coordination sphere around Cu(1) is completed from another borate hydroxyl O atom (O10*) from an adjacent ‘monomer’

leading to an infinite chain (see Graphical Abstract and a schematic representation in Figure 3). The geometry about the Cu^(II) ion is a tetragonally distorted octahedron ($T = 0.79$ [26]) with O13 and O10* *trans* and at significantly longer distances to Cu(1) (av. 2.5202(18) Å) than Cu(1)-O11 and Cu(1)-O12 distances (av. 1.9620 (17) Å). Cu(1)-N bond lengths are 2.010(2) and 1.998(2) Å. These O-Cu(1) and N-Cu(1) bonds lengths and interligand angles in accord with similar copper amine [26] and copper(II) borate [16-18] structures. Likewise, B-O bond lengths and interatomic angles within the hexaborate(2-) ligands are in accord with those observed in other hexaborate ligands [14-16, 18-20] and are similar to these standard parameters found in other related oxidopolyborate systems. [25,27-31]

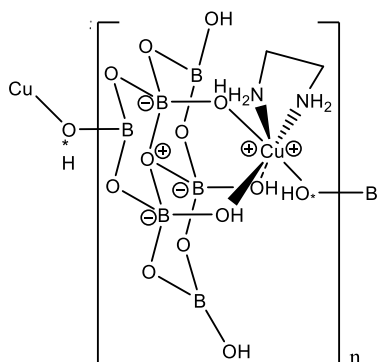


Figure 3. Schematic drawing of the 1-D polymeric structure of $[\text{Cu}(\text{en})\{\text{B}_6\text{O}_7(\text{OH})_6\}]\cdot 3\text{H}_2\text{O}$ (H_2O of crystallization omitted for clarity). O* is O10 in Figure 2.

In dynamic systems found for the self-assembly of **1**, where the product is crystallized from solution, there are usually multiple H-bonding interactions stabilizing the solid-state structure. [7,25,32] Therefore, unsurprisingly, all six hydroxyl functions of the hexaborate(2-) ligand and all four amino-hydrogens of the en ligand (in the conformation of highest sof) are involved in donor H-bond interactions. Three of the hexaborate(2-) H-bond donor interactions (those arising from O9H9, O10H10, and O11H11) may be described [33] as reciprocal $\text{R}_2^2(8)$ interactions. The $\text{R}_2^2(8)$ motif that involves O11 is unusual in that it includes tetrahedral B-centres (B1) within a non-planar ‘chair-like’ ring rather than trigonal B-centres within a planar ring. [25] Two borate H-bond donors (O12H12 and O13H13) are involved with H-bonding to the waters of crystallization. The final borate H-bond interaction is novel and an unusual $\text{R}_2^2(6)$ interaction arising from O8H8. This involves Cu(1)* within the ring and the acceptor in this interaction is O13*, which is also coordinated to this Cu(1)* in a parallel polymer chain (Figure 4). This six-membered $\text{R}_2^2(6)$ ring is completed with an amino hydrogen (H1AB*) of the en ligand on

Cu(1)* acting as an H-bond donor to O8. The other three amino-hydrogen en H-bond donation interactions are to neighbouring hexaborates, $N1HAA \rightarrow O8^*$, $N2H2AB \rightarrow O6^*$, and a water of crystallization ($N2H2BC \rightarrow O21$). Previously, we have shown that $[Cu(L_2)(\text{hexaborate})]$ (L = amino ligand) complexes contain either a square-based pyramidal $Cu^{(II)}$ centre (in an isolated molecular complex) or a tetragonally distorted octahedral structure (in a 1-D polymeric chain) and that in the absence of destabilizing steric effects the polymeric structure with the additional Cu-O (borate) bond is preferred.^{16,18} Thus, a 1-D coordination polymer is formed with $L_2 = (NH_3)_2$ ^[18] but isolated species are formed with $L_2 = NH_2CH_2CH_2NR_2$ ($R = Me$,^[16] Et^[18]) or $Me_2NCH_2CH_2NMe_2$.^[16] En therefore appears to be small enough not to inhibit formation of the this energetically favourable and additional coordinate bond to $Cu^{(II)}$ by formation of the 1-D coordination polymer. In related $[Zn(L_2)(\text{hexaborate})]$ chemistry 1-D coordination polymer chains are also formed when $L = en$ and 1,2-pn.^[14]

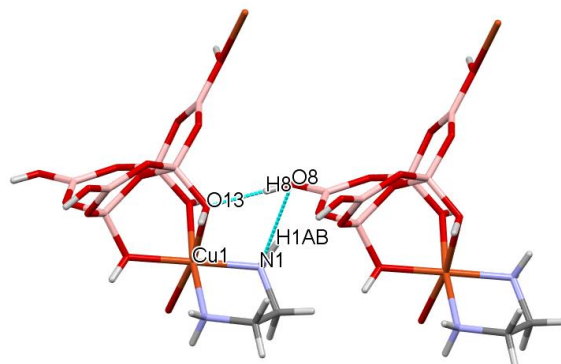


Figure 4. The unusual $R_2^2(6)$ interaction involving the amino hydrogen of the en ligand in a neighbouring polymer chain.

EXPERIMENTAL

General. ^{11}B NMR spectra were obtained on a Bruker Avance 400 spectrometer and data are reported in ppm with positive chemical shifts (δ) to high frequency (downfield) of $BF_3 \cdot OEt_2$. TGA/DSC analysis (in air) was performed on an SDT Q600 V4.1 Build 59 instrument using Al_2O_3 crucibles, between 10-800 °C with a ramp temperature rate of 10 °C min^{-1} . The FTIR spectrum was obtained on a Perkin-Elmer 100 FTIR spectrometer as KBr pellets. Single-crystal X-ray crystallographic analysis was performed at the EPSRC National Crystallography service at the University of Southampton. Magnetic susceptibility measurements were performed on a Johnson-Matthey magnetic

susceptibility balance. CHN analysis was obtained from OEA laboratories Ltd in Callington, Cornwall.

Synthesis, spectroscopic, and analytical data for [Cu(en){B₆O₇(OH)₆}]·3H₂O (1).

[Cu(en)₂]SO₄ (1.00 g, 3.57 mmol)^[34] and Ba(OH)₂·8H₂O (1.13 g, 3.56 mmol) were dissolved in H₂O (20 mL). The solution was stirred at room temperature for 20 mins and the precipitate, BaSO₄, was removed by filtration. B(OH)₃ (1.43 g, 24.9 mmol) was added to the filtrate which was then stirred for 40 mins. The resulting solution was left in several small vials to crystallize. After standing for 35 days the product, [Cu(en){B₆O₇(OH)₆}]·3H₂O (1) (0.5 g, 31 %), was harvested by filtration as blue crystals. M.p. = 288-291 °C. $\chi_m = 1917 \times 10^{-6}$ cm³ mol⁻¹. C₂H₂₀CuB₆N₂O₁₆. Anal. Calc.: C = 5.3 %, H = 4.4 %, N = 6.1 %. Found: C = 5.4 %, H = 4.5 %, N = 6.1 %. ¹¹B/ppm: 17.7. IR (KBr/cm⁻¹): 3350(s), 2924(m), 2854(w), 1600(m), 1405(m), 1450(s), 1360(s), 1133(s), 1090(s), 1044(s), 955(m), 908(m), 851(m), 809(s), 696(m), 537(m). p-XRD d-spacing/Å (% rel. int.): 13.9 (51), 12.9 (38), 7.0 (50), 6.5 (100), 5.7 (37), 4.6 (59), 4.3 (53), 2.0 (36), 1.2 (20). TGA: 100-180 °C, loss of three interstitial H₂O: 10.5% (11.8%

calc.); 180-700 °C, condensation of polyborate and oxidation of en to afford a residue, CuB₆O₁₀: 62.6% (63.1% calc.).

X-ray crystallography. A suitable crystal of **1** (0.190×0.140×0.020) mm³ was selected and mounted on a MITIGEN holder in oil on a Rigaku FRE+ equipped with HF Varimax confocal mirrors and an AFC12 goniometer and HG Saturn 724+ detector diffractometer. The crystal was kept at $T = 100(2)$ K during data collection. Using Olex2^[35] the structure was solved with the ShelXT^[36] structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2014/7 of ShelXL^[37] using Least Squares minimisation.

Crystal Data. C₂H₂₀B₆CuN₂O₁₆, $M_r = 456.60$, triclinic, P-1 (No. 2), $a = 7.68855(13)$ Å, $b = 8.01077(15)$ Å, $c = 14.0029(3)$ Å, $\alpha = 94.2162(16)^\circ$, $\beta = 92.0190(15)^\circ$, $\gamma = 105.3103(16)^\circ$, $V = 828.25(3)$ Å³, $T = 100(2)$ K, $Z = 2$, $Z' = 1$, $\mu(\text{MoK}\alpha) = 1.404$ mm⁻¹, 19125 reflections measured, 3795 unique ($R_{int} = 0.0221$) which were used in all calculations. The final wR_2 was 0.1010 (all data) and R_1 was 0.0388 ($I > 2\sigma(I)$).

CONCLUSIONS

A new Cu^(II)/hexaborate complex, [Cu(en){B₆O₇(OH)₆}]·3H₂O (**1**), has been crystallized in a self-assembly process from aqueous solution. This self-assembly is facilitated and templated by solid-state H-bonded networks to neighbouring complexes. In addition, the preference of the Cu^(II) centre to form an additional coordinate bond (by the formation of a 1-D polymer) with the sterically ‘small’ en spectator ligand is noted.

Acknowledgements.

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Supplemental Materials

Crystallographic data for the structural analysis of compound **1** has been deposited at the Cambridge Crystallographic Data Center (CCDC number 1990215). Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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TEMPLATED Cu(II) OXIDOBORATE CHEMISTRY