Copper(2+) complexes of hydroxyoxidopolyborates: Synthesis and characterization of [Cu(MeNHCH2CH2NMeH)2(H2O)2][B5O6(OH)4]2.2B(OH)3.

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Copper(2+) complexes of hydroxyoxidopolyborates: Synthesis and characterization of $[Cu(MeNHCH_2CH_2NMeH)_2(H_2O)_2][B_5O_6(OH)_4]_2{\cdot}2B(OH)_3$.

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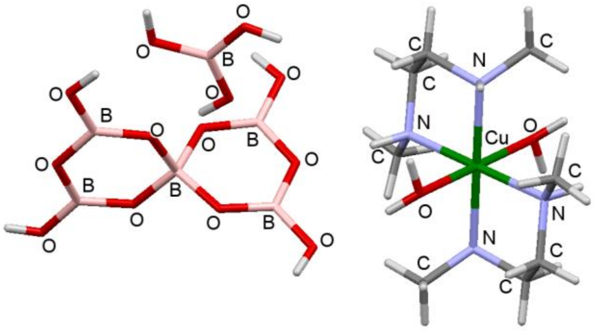
ABSTRACT *A The pentaborate(1-) salt, $[Cu(dmen)_2(H_2O)_2][B_5O_6(OH)_4]_2{\cdot}2B(OH)_3$(dmen = N,N'-dimethylethylenediamine, $MeHNCH_2CH_2NHMe$), has been synthesized in 48% yield as a crystalline product by reaction of $B(OH)_3$ with $[Cu(dmen)_2](OH)_2]_2$ (10:1 ratio) in aqueous solution. Single-crystal XRD analysis confirms its ionic structure with one interstitial $B(OH)_3$ per pentaborate(1-) unit. The pentaborate(1-) anions and $B(OH)_3$ molecules are involved in a supramolecular giant H-bonded lattice with $B(OH)_3$ units serving as 'spacers' to help accommodate the relatively large $[Cu(dmen)_2(H_2O)_2]^{2+}$ cations.*

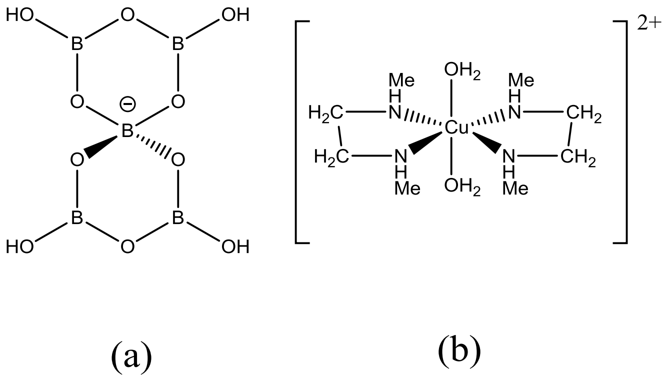
GRAPHICAL ABSTRACT



KEYWORDS Copper(2+) complexes; Boric acid; Oxidoborates; Pentaborate(1-); Polyborates; X-ray structure

INTRODUCTION

Hydroxyoxidopolyborate salts may be synthesized from the addition of $B(OH)_3$ to a basic aqueous solution containing templating cations or by solvothermal methods.[1] Hydroxyoxidopolyborate salts obtained from aqueous solution are usually comprised of discrete, insular anions, partnered by the templating cations. These salts are often pentaborate(1-) salts since the pentaborate(1-) anion is well adapted to forming a wide variety of crystalline lattices, held together by strong H-bond interactions.[2-5] In our search for novel hydroxyoxidopolyborate anions we have adopted a strategy of using transition-metal complexes as templating agents. We have recently reported the synthesis of several salts containing isolated polyborate anions partnered with transition-metal complexes and have described the synthesis and structures of two novel isolated polyborate salts containing the heptaborate(3-)[6] and octaborate(2-)[7] anions. We have also recently reported some novel species containing copper(2+)[8, 9] centers and this manuscript reports a new Cu(II) salt partnered by two pentaborate(1-) anions. The structure of a pentaborate(1-) anion, containing one tetrahedral and four trigonal-planar boron centres, is drawn schematically in Figure 1(a).

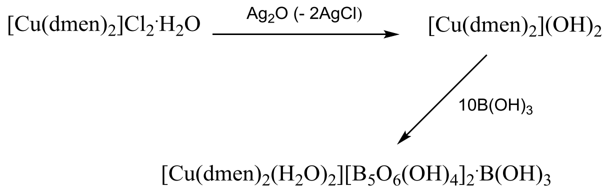


(a) (b)

Figure 1. Schematic structures of (a) the pentaborate(1-) anion, $[B_5O_6(OH)_4]^-$, and (b) the octahedral Cu(II) cation, $[Cu(dmen)_2(H_2O)_2]^{2+}$ found in **1**.

RESULTS AND DISCUSSION

The new Cu(II) polyborate $[Cu(dmen)_2(H_2O)_2][B_5O_6(OH)_4]_2 \cdot 2B(OH)_3$ (**1**) (dmen = *N*,*N'*-dimethylethylenediamine, $MeHNCH_2CH_2NHMe$) has been prepared according to Scheme 1 through a crystallization processes in basic aqueous solution involving a templating Cu(II) amine complex and $B(OH)_3$. The precursor Cu(II) complex, $[Cu(dmen)_2]Cl_2 \cdot H_2O$, was prepared by modifying a literature procedure in excellent yield.[10]



(**1**)

Scheme 1. Synthesis of the copper(II) pentaborate, $[Cu(dmen)_2(H_2O)_2][B_5O_6(OH)_4]_2{\cdot}2B(OH)_3$ (**1**) (dmen = *N*,*N'*-dimethylethylenediamine, $MeHNCH_2CH_2NHMe$).

The product **1** crystallized out from aqueous solution in moderate (48 %) yield after several days at room temperature. The product arises through alkaline hydrolysis/condensation of the $B(OH)_3$ and its subsequent crystallization from the solution. The reaction solution is a rich source of a variety of anions and cations[11, 12] since polyborate anions are in facile equilibrium in basic aqueous solution[13, 14] and Cu(II) amine complexes are also known[15] to be labile. Stoichiometery, pH, and energetics associated with crystal packing, steric congestion, hydrogen bonding, and coordination bond formation all have a role to play in many, and probably this, crystallization processes.[16, 17]

Compound **1** has been characterized by thermal studies (TGA/DSC), magnetic susceptibility measurements, elemental analyses, IR spectroscopy and single-crystal XRD studies.

The thermal TGA/DSC data obtained for **1** (see supplementary material) were consistent with the structure determined by single-crystal X-ray diffractions studies (see below) and were also consistent with thermal decomposition in air to the anhydrous copper borate with stoichiometry $CuB_{12}O_{19}$ (= $CuO{\cdot}6B_2O_3$). This product is formed *via* a stepwise process involving loss of coordinated H_2O, borate condensation, and finally ligand oxidation; such behavior has been previously observed for other metal complex polyborate salts.[6-9, 18-20]

Elemental analyses data were consistent with the single-crystal structures indicating that the bulk sample was homogeneous and that the crystal chosen for XRD studies was representative.

Compound **1** displays strong bands in the B-O stretching region (1450-750 cm^{-1}) which have been assigned to either symmetric or asymmetric B-O stretches to three or four-coordinate boron centres.[21] In particular, a strong band at 921 cm^{-1} (sym B_{trig}-O) is observed and this is reported to be diagnostic of the pentaborate(1-) anion.[22]

The ^{11}B NMR spectrum of **1** is also typical of that for a pentaborate(1-) salt[1, 4, 5] with signals associated with $B(OH)_3/[B(OH)_4]^-$ (17.5 ppm) and $[B_3O_3(OH)_4]^-$ (13.5 ppm) visible due to rapid borate exchange processess.[13,14]

^1H and ^{13}C spectra were not obtainable for **1**. This may be due to the proximity of the dmen ligand to the paramagnetic (d^9) Cu(II) centre. The magnetic susceptibility of **1** was in accord with other paramagnetic mono-copper(II) polyborate salts.[8]

Compound **1** is formulated as an ionic compound comprised of a copper(II) complex cation, $[Cu(MeNHCH_2CH_2N\text{-}MeH)_2(H_2O)_2]^{2+}$, with insular $[B_5O_6(OH)_4]^-$ anions. The crystal structure for **1** showing the asymmetric unit and indicating atomic numbering scheme is given in Figure 2. The cation is drawn schematically in Figure 1(b). The cation in **1** is centrosymmetric with the central Cu(II) in an elongated tetragonal octahedral geometry ($T^6 = 0.85$)[23] with the coordinated H_2O molecules axial and *trans* with Cu1-O21 at 2.4263(14) Å. The equatorial Cu1-N21, and Cu1-N22 distances are 2.0621(16) Å and 2.0430(16) Å, respectively. These data are unremarkable and similar to those observed in related copper(II) amine complexes.[8, 23]

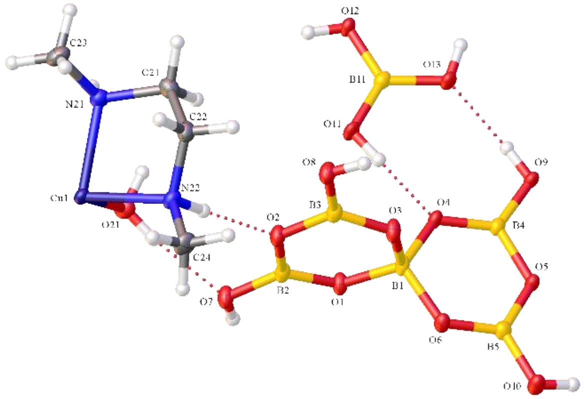


Figure 2. Asymmetric unit of **1** showing two different $R_2^2(8)$ H-bond intercations

Bond angles and distances for the $[B_5O_6(OH)_4]^-$ anions are unexceptional and are in accord with other known pentaborate structures.[1-5] There is a $B(OH)_3$ of crystallization for each pentaborate(1-) anion and these two structural units are hydrogen bonded together *via* $R_2^2(8)$ (Etter nomenclature[24]) motifs (Figure 2). In addition, H-bond donor sites on the coordinated $MeNHCH_2CH_2NMeH$ and H_2O ligands further stabilize the structure through interactions with acceptor sites on a pentaborate(1-) anion in a $R_2^2(8)$ motif (NH, OH donors; shown in Figure 2). The pentaborate(1-) anions and boric acid molecules link together to form a giant H-bond supramolecular network with the $B(OH)_3$ units acting as 'spacers' to help accommodate the large templating cation within the lattice (Figure 3).[25] Details of all these H-bond interactions are in the supplementary information.

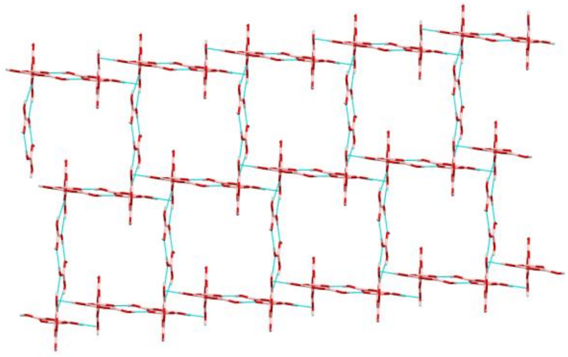


Figure 3. A view of a plane of pentaborate(1-) anions and spacer $B(OH)_3$ molecules. The copper(II) complex cations (not shown) are in the centres of the squares.

EXPERIMENTAL

General. All chemicals were obtained commercially. FTIR spectra were obtained (KBr pellets) on a Perkin-Elmer 100 FTIR spectrometer. NMR spectra were obtained on a Bruker Avance 400 spectrometer and reported in ppm with positive chemical shifts (δ) to high frequency (downfield) of TMS (^1H, ^{13}C) and $BF_3{\cdot}OEt_2$ (^{11}B). TGA/DSC analysis (in air) were 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}. Single-crystal X-ray crystallography was carried out at the EPSRC National Crystallography service at the University of Southampton. CHN analysis was obtained from OEA laboratories Ltd in Callington, Cornwall.

Synthesis of $[Cu(dmen)_2]Cl_2{\cdot}H_2O$: $CuCl_2{\cdot}2H_2O$ (4.1 g, 24 mmol) was dissolved in ethanol (40 mL) to give a clear green solution. *N*,*N'*-dimethylethylenediamine (5.2 mL, 47 mmol) in ethanol (10 mL) was added dropwise to the green solution which was left to stir for 10 minutes. The resulting dark blue solution was placed in an ice bath for 2 hours until a dark blue precipitate formed. The precipitate was collected by filtration and washed with Et_2O (2 × 5 mL) and dried for 30 min in desiccator. Yield: 7.5 g (95 %). M.p.: 209-211 ^{0}C. χ_m: 9.5×10^{-4} cm^3mol^{-1}. $C_8H_{26}CuN_4OCl_2$. Anal. Calc.: C = 29.2 %, H = 8.0 %, N = 17.0 %; Found: C = 29.5 %, H = 8.0 %, N = 17.0 %. FT-IR (KBr) (ν_{max}/cm^{-1}): 3495 (s), 3220 (s), 2921 (m), 1453 (s), 1421 (m), 1089 (m), 1065 (m), 1022 (s), 983 (m), 973 (s), 862 (m), 467 (m).

Synthesis, spectroscopic and analytical data for 1: $[Cu(dmen)_2]Cl_2 \cdot H_2O$ (1.00 g, 3 mmol), and Ag_2O (0.746 g, 3 mmol) were rapidly stirred in H_2O (25 mL) at room temperature for 30 minutes. The AgCl precipitate which formed was removed by filtration. $B(OH)_3$ (1.99 g, 32 mmol) was added to the dark blue filtrate which was left to stir for a further 30 minutes. The reaction mixture was again filtered and the filtrate placed in small vials and left for slow evaporation of the solvent to occur. After 7 days, blue crystals (1.2 g, 48 %) of **1**, $[Cu(MeNHCH_2CH_2NHMe)_2(H_2O)_2][B_5O_6(OH)_4]_2 \cdot 2B(OH)_3$, had formed. These were collected by filtration and dried in desiccator M.p. = > 300 ^{0}C. $\chi_m = 8.0 \times 10^{-4}$ cm^3mol^{-1}. $C_8H_{42}B_{12}CuN_4O_{28}$. *Anal.* Calc.: C = 11.5 %, H = 5.1 %, N = 6.7 %. Found: C = 11.3 %, H = 5.3 %, N = 6.6. NMR: ^{11}B/ppm 17.5 (90%), 13.5 (10%). IR (KBr/cm^{-1}): 3463(m), 3261(s), 1451(s), 1325(s), 1156(m), 1083(m), 1042(m), 1019(m), 921(s), 773(m), 706(m). TGA: 30-100 ^{0}C, loss of two coordinated H_2O, and three H_2O from $B(OH)_3$ condensation 10.1 % (10.7% calc.); 150-240 ^{0}C, condensation of polyborate which loss of four H_2O 18.2 % (19.3 % calc.); 280-450 ^{0}C, oxidation of organic content 41.6 % (40.5 % calc.); residual $CuB_{12}O_{19}$ 58.4 % (59.5 % calc.).

X-ray crystallography. A suitable crystal of **1** was selected and mounted on a MITIGEN holder in perfluoroether oil on a Rigaku FRE+ equipped with HF Varimax confocal mirrors an AFC12 goniometer and HG Saturn 724+ detector diffractometer. Crystals was kept at T = 100(2) K during data collection. Using Olex2,[26] the structure was solved with the ShelXT[27] structure solution program, using the Intrinsic Phasing solution method. The model were refined with version 2014/7 of ShelXL[28] using Least Squares minimisation.

Crystallographic data. 1: $C_8H_{42}B_{12}CuN_4O_{28}$, M_r = 835.71, triclinic, P-1 (No. 2), a = 8.5093(3) Å, b = 9.4281(3) Å, c = 10.5503(3) Å, α = 100.340(3)°, β = 90.409(2)°, γ = 101.096(3)°, V = 816.34(5) Å^3, T = 100(2) K, Z = 1, Z' = 0.5, $\mu(MoK_\alpha)$ = 0.780 mm^{-1}, 18141 reflections measured, 3732 unique (R_{int} = 0.0380) which were used in all calculations. The final wR_2 was 0.0989 (all data) and R_1 was 0.0362 ($I > 2\sigma(I)$).

CONCLUSIONS

A new Cu(II)/borate complex (**1**) has been crystallized from aqueous solution with a Cu:B ratio of 1:6. Compound **1** is a pentaborate(1-) salt with one interstitial $B(OH)_3$ per pentaborate(1-) unit. The role of the $B(OH)_3$ is to expand the H-bonded pentaborate(1-) lattice to accommodate the large octahedral $[Cu(dmen)_2(H_2O)_2]^{2+}$ cations.

Acknowledgements.

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Supplemental Materials.

^{11}B and IR spectra and a plot of the DSC analysis are available as supplementary information. Crystallographic data for the structural analysis of compound **1** is available as supplementary information and has also been deposited at the Cambridge Crystallographic Data Center (CCDC number 1881683). Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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