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Polyborate anions templated by cationic transition-metal complexes: $[\text{Co}(\text{diNOSar})]_2[\text{B}_3\text{O}_3(\text{OH})_4]\text{Cl}_5 \cdot 4.75 \text{H}_2\text{O}$

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GRAPHICAL ABSTRACT

Abstract The transition metal complexes $[\text{Co}(\text{diNOSar})]^{3+}$, $[\text{Co}(\text{en})_3]^{3+}$, $[\text{Co}(\text{dien})_2]^{3+}$ have been used to template unusual isolated polyborate anions by reaction of basic aqueous solutions containing the cations with $\text{B}(\text{OH})_3$ (1:10). The synthesis and characterization (TGA/DSC, IR, NMR, single-crystal XRD) of one such complex $[\text{Co}(\text{diNOSar})]_2[\text{B}_3\text{O}_3(\text{OH})_4]\text{Cl}_5 \cdot 4.75\text{H}_2\text{O}$ (**1**) is reported. Compound **1** is a rare example of a salt containing the isolated triborate(1-) anion, and its formation is engineered by the cation, which has extensive H-bond interactions with the anion in its secondary coordination sphere.

Keywords Triborate(1-); Self-assembly; H-bonds; $[\text{Co}(\text{diNOSar})]^{3+}$; X-ray Structure; Oxidoborate

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INTRODUCTION

Polyborate anions are conveniently classified¹ as either polymeric (2D or 3D chains, sheets or networks) or discrete ‘isolated’ anionic moieties. Isolated polyborate anions are readily synthesized by the addition of B(OH)₃ to a basic aqueous solution containing templating cations², or by solvothermic³ methods. Templated products arise since B(OH)₃ in basic aqueous solution exists as a dynamic combinatorial library of polyborate anions⁴. In general, pentaborate(1-) salts (containing the [B₅O₆(OH)₄]⁻ anion) are formed because these salts have a strong H-bonded anionic lattice, which is sufficiently flexible to accommodate many medium sized cations⁵. Salts containing polyborate anions other than pentaborate(1-) are relatively rare⁶. We are interested in the synthesis of structurally novel polyborate anions and have adopted a strategy of templating such species by the use of sterically demanding and/or highly charged cations^{7,8}. Herein, we report the synthesis of several salts containing isolated polyborate anions partnered with transition metal cations and describe in detail the synthesis and characterization of the salt [Co(diNOsar)]₂[B₃O₃(OH)₄]Cl₅·4.75 H₂O (**1**) which contains the isolated triborate(1-) anion.

RESULTS AND DISCUSSION

Synthesis

Halide salts of transition-metal complexes are readily transformed, provided they are stable in basic solution, into their hydroxide salts by use of a Dowex 550A hydroxide activated anion exchange resin. The resulting aqueous solutions, which are separated from the resin, were reacted with MeOH/H₂O solutions of B(OH)₃ (1:10) to afford polyborate anions salts of cationic transition-metal complexes. Several salts have been prepared *e.g.*

[Co(diNOsar)]₂[B₃O₃(OH)₄]Cl₅·4.75H₂O (**1**), [Co(en)₃][B₅O₆(OH)₄][B₈O₁₀(OH)₆]·5H₂O (**2**), *s-fac*-[Co(dien)₂][B₇O₉(OH)₆]·9H₂O (**3**). Compounds **2** and **3**, which contain previously unobserved octaborate(2-) and heptaborate(3-) anions, were prepared in reasonable yields (~40%) and details^{7,8} of their synthesis and full characterization can be found elsewhere. The starting complex [Co(diNOsar)]Cl₃ was prepared by a reported⁹ procedure for the synthesis of **1**. Compound **1** was isolated in low yield (10%) and its high chloride content would indicate that

the ion exchange was not completely successful in this case. Nevertheless, we were able to characterize¹⁰ the compound by elemental analysis, mpt, thermally (TGA/DSC) and by NMR (¹H, ¹³C, ¹¹B) and IR spectroscopy. Single-crystals were also suitable for a XRD study.

NMR spectra of **1** were obtained in D₂O. The ¹H NMR spectrum of **1** consists of AB doublets for the CH₂ groups of the capping units and a complex AA'BB' pattern¹¹ (looking like a doublet with $J = 9.2$ Hz) for the CH₂ protons of the ethylenediamine rings. The secondary amine protons are observed with the residual HOD signal at $\delta = 4.70$ ppm. The ¹³C{¹H} spectrum shows the expected 3 signals at $\delta = 51.4$ (ethylene diamine groups), $\delta = 55.1$ (CH₂ of capping groups) and $\delta = 87.8$ ppm (tertiary C-NO₂ cap). As a consequence of boron exchange associated with rapid B(OH)₃/[B(OH)₄]⁻/polyborate equilibria⁴ the ¹¹B spectrum shows just one signal at $\delta = +16.2$ ppm.

Thermal (TGA) analysis in air was consistent with a three step process involving low temperature (<125 °C) loss of water of crystallization, further dehydration to form an anhydrous polyborate (200-275 °C), and oxidation of organics (275-800 °C) to leave a glassy inorganic residue of composition Co₂B₃O₅Cl₅. Such thermal decomposition has been previously observed¹² for transition-metal polyborate salts.

X-ray structure of [Co(diNOsar)]₂[B₃O₃(OH)₄]Cl₅·4.75H₂O

Full crystallographic data for **1** are available in the supplementary information¹³ and crystallographic data are summarized in a footnote¹⁴. Compound **1** is an ionic compound and is a rare example of a salt containing the triborate(1-) anion. In addition to the [B₃O₃(OH)₄]⁻ anion, **1** contains 2 independent [Co(diNOsar)]³⁺ cations, 5 Cl⁻ anions and 4.75 H₂O molecules. There is a disordered water within the asymmetric unit. One area can exist as either one (25%) or two (75%) molecules of water, hence the fractional formula. Atomic labelling for the triborate(1-) anion is shown in Figure 1.

The [Co(diNOsar)]³⁺ cation comprises a central Co³⁺ ion surrounded by the 6 N donor atoms of the hexadentate neutral 'diNOsar' ligand in a distorted octahedral environment. *Cis* and *trans* N-Co-N angles range from 86.43(9) - 92.58(9)° (av. 90.06°) and 175.79(9) - 178.12(10)°

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(av. 176.62°) respectively. The Co-N bond lengths range from 1.963(2) - 1.975(2) Å, av. 1.969 Å. These data are not significantly different from previously reported data¹⁵ for this cation.

The $[\text{B}_3\text{O}_3(\text{OH})_4]^-$ ion of **1** possesses a B_3O_3 (boroxole) ring with one 4-coordinate and two 3-coordinate B centres. B-O bond lengths to 3-coordinate (B2 and B3) and 4-coordinate (B1) B centres range from 1.347(4) - 1.386(4) Å (av. 1.363 Å) and 1.466(4) - 1.471(4) Å (av. 1.488 Å), respectively. B2-O1 (1.351(3) Å) and B3-O3 (1.347(4) Å) are significantly shorter than the other B-O bonds within the boroxole rings. The boroxole ring is planar with ring angles ranging from 112.3(2) – 122.4(2)°. The smallest ring angle (O1B1O3) involves the 4-coordinate B centre, whereas ring angles at O1, O2, and O3 average 121.1° and those at the 3-coordinate B centres (B2 and B3) average 121.6°. This pattern of bond angles and bond lengths are in accord with previously reported data for this anion¹⁶ and mirror corresponding data observed¹⁷ in related isoelectronic systems such as $\text{Ar}_3\text{B}_3\text{O}_3\text{L}$ and $[\text{Ph}_3\text{B}_3\text{O}_3(\text{OH})]^-$.

Figure 1 Cation-triborate H-bond interactions in **1**. $d(\text{N13-H13})$ 1.00 Å, $d(\text{H13}\cdots\text{O4})$ 1.98 Å, $d(\text{N13}\cdots\text{O4})$ 2.935(3) Å, $\angle(\text{N13H13O4})$ 159.2°; $d(\text{N16-H16})$ 1.00 Å, $d(\text{H16}\cdots\text{O4})$ 1.73 Å, $d(\text{N16}\cdots\text{O4})$ 2.731(3) Å, $\angle(\text{N16H16O4})$ 177.4°; $d(\text{N32H32})$ 1.00 Å, $d(\text{H32}\cdots\text{O5})$ 1.81 Å, $d(\text{N32}\cdots\text{O5})$ 2.810(3) Å, $\angle(\text{N32H32O5})$ 175.8°; $d(\text{N35-H35})$ 1.00 Å, $d(\text{H35}\cdots\text{O5})$ 1.93 Å, $d(\text{N35}\cdots\text{O5})$ 2.898(3) Å, $\angle(\text{N35H35O5})$ 163.4°.

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There are multiple H-bond interactions within the solid-state structure of **1**. Full details can be found in the supplementary information. Polyborate anions usually display multiple anion-anion H-bond interactions and these are believed⁵ to be the driving force in the synthesis of non-metal cation pentaborate(1-) salts. Anion-anion interactions were found to be present in **2** and **3**. However, in **1**, triborate-triborate H-bond interactions are absent and each triborate(1-) anion is isolated from others by H₂O bridges, forming a sheet-like structure (Figure 2). This isolation implies that the crystal structure of **1** is engineered by interactions with other components within the system. The triborate(1-) anion is able to form 4 donor H-bonds and has 7 potential H-bond acceptor sites. The triborate(1-) anion in **1** does indeed form 4 donor interactions: three to H₂O molecules and one to a Cl⁻ anion (O6H6...Cl2). The triborate(1-) anion accepts 2 H-bonds at each hydroxyl group (O4 and O5) on the 4-coordinate B1, and also at O6 from H₂O (O54-H54...O6). The H-bonds directed at O4 and O5 originate from amine hydrogens on two [Co(diNOsar)]³⁺ cations in a chelating mode, as illustrated in Figure 1. These H-bond interactions are likely to be responsible for templating this salt and assembling the triborate(1-) anion. Secondary amine hydrogens of [Co(diNOsar)]³⁺ are known¹⁵ to form similar H-bond interactions *e.g.* [Co(diNOsar)][S₂CN(CH₂)₄]₃.

Figure 2 The triborate(1-) anions are arranged in planes linked together by H-bonds from H₂O molecules. The [Co(diNOsar)]³⁺ cations fill the cavities and H-bond to the triborate(1-) anions.

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Summary

[Co(diNOsar)]₂[B₃O₃(OH)₄]Cl₅·4.75H₂O is a rare example of a salt containing the isolated triborate(1-) anion. It has been obtained from a self-assembly reaction of (partially) OH⁻ exchanged aqueous solution of [Co(diNOsar)]Cl₃ with B(OH)₃ (1:10). The solid-state structure of **1** shows the anion in the secondary coordination sphere of the cation. There are strong cation-anion H-bond interactions, which help to engineer the formation of the triborate(1-) anion.

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10. Characterization data for **1**: C₂₈H_{73.50}B₃Cl₅Co₂N₁₆O_{19.75}. Elem. Anal Calc: C, 26.3; H 5.8; N, 17.5. Found: C, 25.6; H 6.5; N, 16.7%. Mp 285 °C. TGA: - 4.75 H₂O 7.8 % (6.7 % calc.), - 2H₂O 3.2 % (2.8% calc.), cation oxidation 57.7 % (58.6% calc.), residual Co₂B₃O₃Cl₅ 31.3% (31.9 % calc). IR (KBr/cm⁻¹): 3401(br,s), 3041(vs), 2871(vs), 1558(vs), 1432(m), 1345(s), 1077(m), 988(w), 849(w), 813(w). NMR (400 MHz, D₂O) δ¹H/ppm: 3.77 6H (d, 13.8 Hz), 3.41 6H (m), 3.24 6H (d, 13.8 Hz), 2.83 6H (m). δ¹¹B/ppm: 16.2. δ¹³C/ppm: 87.8, 55.1, 51.4.
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14. A Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of a FR-E+ SuperBright molybdenum rotating anode generator with VHF Varimax optics (70µm focus) was used. X-ray data for **1**: C₂₈H_{73.50}B₃Cl₅Co₂N₁₆O_{19.75}, M = 1278.06; triclinic space group *P*-1, *a* = 9.6900(4) Å, *b* = 10.0170(6) Å, *c* = 29.1374(7) Å, α = 85.079(3)°, β = 88.439(3)°, γ = 62.137(5)°; *U* = 2490.9(2) Å³; *Z* = 2; *T* = 100K; Wavelength = 0.71075 Å; density (calc) = 1.704 Mg/m³; Absorption coefficient 1.024 mm⁻¹; Crystal: orange lath, 0.180 x 0.030 x 0.010 mm³; *F*(000) 1331; θ range for data collection 2.420-29.944°; Index ranges -13 ≤ *h* ≤ 12, -13 ≤ *k* ≤ 13, -38 ≤ *l* ≤ 40; 36914 reflections collected with 12826 independent reflections [*R*_{int} = 0.0478]; Completeness to θ = 25.242°, 99.9%; absorption correction: semi-empirical from equivalents; refinement method: full-matrix least squares on *F*²; data/restraints/parameters 12826/0/668; goodness-of-fit on *F*², 1.023; Final *R* indices [*F*² > 2σ(*F*²)] *RI* = 0.0485, *wR*2 = 0.0976; *R* indices (all data) *RI* = 0.0740, *wR*2 = 0.1072; extinction coefficient n/a; largest diff. peak and hole 0.881 and -0.662 e Å⁻³.
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