

PAPER

[View Article Online](#)
[View Journal](#) | [View Issue](#)Cite this: *Dalton Trans.*, 2025, **54**, 13929A simple and efficient method to synthesize metal salts of $M_2[trans-B_{20}H_{18}]$ ($M = Li, Na, K$, and Cu)Xin-Ru Yin,^a Zhi-Wei Lu,^b Xi-Meng Chen,^b Li-Qing He^{*c} and Xuenian Chen^{id} ^{*a,b}

The synthesis of $[trans-B_{20}H_{18}]^{2-}$ from $[closo-B_{10}H_{10}]^{2-}$ based on redox principles has been developed but is still limited. Using different oxidants often leads to various by-products and affects yields. This paper presents a facile and efficient method for synthesizing $[trans-B_{20}H_{18}]^{2-}$ by directly using the alkali metal salt of $[closo-B_{10}H_{10}]^{2-}$ as the precursor. This approach enables the synthesis of the metal salts of $[trans-B_{20}H_{18}]^{2-}$. When $Cu(OTf)_2$ is used as the oxidant, $Cu_2[trans-B_{20}H_{18}]$ is formed with a yield exceeding 94%. On the other hand, when $H_3P(Mo_3O_{10})_4 \cdot xH_2O$ is used as the oxidant, alkali metal salts of $[trans-B_{20}H_{18}]^{2-}$ ($M = Li, Na$, and K) are obtained with a yield of up to 85%. All synthesized compounds were characterized by IR, TGA-DSC, and NMR spectroscopy, and $M_2[trans-B_{20}H_{18}]$ ($M = K, Cu$) was characterized by X-ray single crystal diffraction. Both methods allow for the rapid completion of the reaction in a short time. This synthesis method offers promising potential for further applications, particularly as an all-solid-state electrolyte in battery technology.

Received 21st July 2025,
Accepted 19th August 2025
DOI: 10.1039/d5dt01718arsc.li/dalton

Polyhedral borane anions, with a general formula of $[B_nH_n]^{2-}$ ($n = 6-12$), are a type of typical boron/hydrogen compound,¹⁻³ and have been widely applied in materials, medicine, and catalysis fields because their *closo*-structural features, resulting in their σ -aromaticity and high stability, compared with the small borane Lewis base adducts.⁴⁻⁷ Among the polyhedral borane compounds, the $[closo-B_{10}H_{10}]^{2-}$ anion derivatives have relatively low stability, low symmetry, and higher reactivity. The B-H of the $[closo-B_{10}H_{10}]^{2-}$ anions could be substituted with various functional groups, leading to a wide range of derivatives. Due to the presence of highly reactive “cap” B atoms and low stability in the double-capped square antiprism structure, the conjuncto-hydroborate anion, $[B_{20}H_{18}]^{2-}$,⁸⁻¹⁰ could be synthesized by performing oxidative dehydrogenation coupling of the $[closo-B_{10}H_{10}]^{2-}$ anion derivatives. The high symmetry and stability of the icosahedral structure of $B_{12}H_{12}^{2-}$ prevent it from undergoing dimerization reactions.

The synthesis of polyhedral borane polymers centers on utilizing the active sites of boron clusters (such as B-H bonds and heteroatom substituents) to react with oxidants, bridging agents, and metal ions, thereby achieving inter-cluster linkages through covalent or coordination bonds. These methods are potentially applicable to the expansion of highly reactive boron

cages, and provide a reference pathway for the design of functionalized borane materials (e.g., ion conductors and catalyst supports).

In particular, the conjuncto-hydroborate anion, $[B_{20}H_{18}]^{2-}$, exists as various isomers:¹¹⁻¹⁸ $[trans-B_{20}H_{18}]^{2-}$, $[cis-B_{20}H_{18}]^{2-}$, $[iso-B_{20}H_{18}]^{2-}$, and $[cross-B_{20}H_{18}]^{2-}$, in which $[trans-B_{20}H_{18}]^{2-}$ is the most easily obtained and stable conformer (Fig. 1). Compared to the parent ten-boron $[closo-B_{10}H_{10}]^{2-}$ anion, each $[B_{20}H_{18}]^{2-}$ molecular formula unit contains twice the number of boron atoms. Such a $\{B_{20}\}$ family, as a high-boron content and tumor-targeting agent, is particularly important in boron neutron capture therapy. On the other hand, the aromatic behavior in such species should be noted, as it is due to the formation of the fused $\{B_{20}\}$ core. However, the inherent spherical

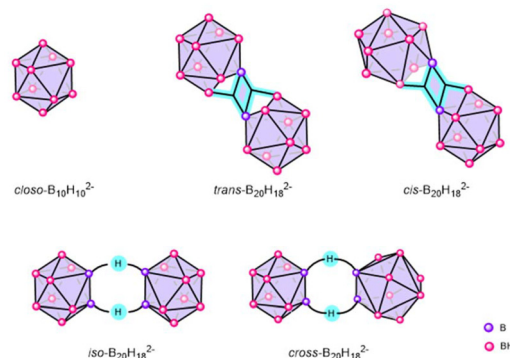


Fig. 1 Structure of $[B_{10}H_{10}]^{2-}$ and four types of $[B_{20}H_{18}]^{2-}$ anions.

^aCollege of Chemistry, Zhengzhou University, Zhengzhou, Henan 450001, China^bSchool of Chemistry and Chemical Engineering, Henan Key Laboratory of Boron Chemistry and Advanced Materials, Henan Normal University, Xinxiang, Henan 453007, China. E-mail: xuenian_chen@zzu.edu.cn, chenximeng@htu.edu.cn^cHefei General Machinery Research Institute Co., Ltd, Hefei 230031, China.E-mail: heli_limao@163.com

aromatic characteristics of the parent $closo-[B_{10}H_{10}]^{2-}$ cluster is persistent in both *iso*- and *trans*- $[B_{20}H_{18}]^{2-}$ isomers as an interplay between the spherical aromatic properties from both B₁₀ motifs, leading to an overlap of the shielding regions from shielding cone properties, ascribed to a dual spherical-spherical aromatic cluster.¹⁹ The variation of the B₁₀–B₁₀ backbone provided by the intercluster B-interaction, thus, results in a more effective aggregation connecting such building units, towards boron-based cluster materials.^{20–23}

Although the synthesis of the $[trans-B_{20}H_{18}]^{2-}$ anion derivatives has been extensively studied based on oxidative dehydrogenation coupling of the $[closo-B_{10}H_{10}]^{2-}$ anion derivatives since the 1960s, the synthetic methods are still limited. The most examined starting materials are organic ammonium salts of the $[closo-B_{10}H_{10}]^{2-}$ anion. In 1962, the first ammonium salt, $[Et_3NH]_2[trans-B_{20}H_{18}]$, was synthesized by reacting Fe^{3+} with $[Et_3NH]_2[closo-B_{10}H_{10}]$ under high-temperature conditions.¹⁰ However, this method only worked for the ammonium salt and did not apply to alkali metal salts such as $M_2[trans-B_{20}H_{18}]$ ($M = Li, Na, \text{ and } K$). Therefore, the various salts of the $[trans-B_{20}H_{18}]^{2-}$ anions with different counteractions and organic ligands synthesized by metathesis reactions and their coordination chemistry have been widely explored. Several silver(I) salts with PPh_3 ligands were isolated and reported.²⁴ The lead(II) salts with Bipy ligands of $[B_{20}H_{18}]^{2-}$ were synthesized and characterized by IR spectroscopy and X-ray diffraction.²⁵ A tris-chelate manganese(II) complex with a Bipy ligand $[Mn(Bipy)_3][B_{20}H_{18}]^{2-}$ ²⁶ and an iron(II) complex with a cyclopentadienyl ligand $[CpFe(Cp-CH_2-NMe_2Et_2)][B_{20}H_{18}]^{2-}$ ²⁷ were isolated and characterized. In addition, iron(II), cobalt(II), and nickel(II) complexes with 1,10-phenanthroline and 2,2'-bipyridyl in the presence of $[B_{20}H_{18}]^{2-}$, with varying reagent ratios and solvents, were obtained. Several tris-chelate and binuclear complexes were isolated and studied by IR spectroscopy, elemental analysis, and X-ray diffraction.²⁸ The gold(III) salts of a $[B_{20}H_{18}]^{2-}$ anion, $[Au(L)Cl_2]_2[B_{20}H_{18}]$ ($L = \text{bipy, phen}$), were isolated and characterized.²⁹ Moreover, the synthesis of a nickel(II) complex $[Ni(Phen)_3][B_{20}H_{18}]$ was briefly reported, indicating Ni(II) complexes with $[B_{20}H_{18}]^{2-}$ formed by the oxidation of the complex $[Ni(Phen)_3][B_{10}H_{10}]$ with cerium(IV).²⁵

The oxidative dehydrogenation coupling of the $[closo-B_{10}H_{10}]^{2-}$ anion derivatives was generally carried out in an aqueous solution with Fe^{3+} or Ce^{4+} as an oxidizer (Fig. 2). Only

one attempt was made to use acetonitrile as a solvent⁸ and an electrochemical method used CH_2Cl_2 , THF, or CH_3CN .³⁰ Another approach involved the high-temperature pyrolysis of $[NMe_4][N_2B_{10}H_9]$ to obtain $[NMe_4]_2[trans-B_{20}H_{18}]$, but it suffered from low yield, long reaction time, and the need for high temperature.³¹

To solve the limitations of these methods, especially for synthesizing alkali metal-based advanced polyhedral boron cluster compounds, we found that by using $H_3P(Mo_3O_{10})_4 \cdot xH_2O$ as the oxidant, alkali metal salts of the $[trans-B_{20}H_{18}]^{2-}$ anion could be directly synthesized in non-aqueous solvent, based on our group's work on the synthesis of polyhedral boranes and functionalization of carborane.^{32–35} $M_2[trans-B_{20}H_{18}]$ ($M = Na, K$) can be obtained as solvent-free salts, while $Li_2[trans-B_{20}H_{18}] \cdot 0.23CH_3CN$ is formed with a small amount of acetonitrile solvent. The yield ranges from 83% to 86%. Interestingly, when $Cu(OTf)_2$ is used as the oxidant, oxidative dehydrogenation coupling of $M_2[closo-B_{10}H_{10}]$ ($M = Li, Na, \text{ and } K$) leads to the formation of $Cu_2[trans-B_{20}H_{18}] \cdot 1.2CH_3CN$, different from the reaction carried out in aqueous solution.¹⁰ Both methods achieve rapid reactions under simple and mild conditions.

The primary synthetic methods of $[trans-B_{20}H_{18}]^{2-}$ anions³⁶ reported so far are shown in eqn (1)–(3). Using Fe^{3+} as an oxidant, at 100 °C, $[Et_3NH]_2[closo-B_{10}H_{10}]$ could convert a salt of $[Et_3NH]_2[trans-B_{20}H_{18}]$ (eqn (1)) with a yield of up to 95%.¹⁰ Using Ce^{4+} as the oxidizing agent, $[NiL_3][closo-B_{10}H_{10}]$ was converted to $[NiL_3][trans-B_{20}H_{18}]$ at room temperature with a yield of 80% (eqn (2)).³⁷ By the electrochemical synthesis, the $[trans-B_{20}H_{18}]^{2-}$ anion was obtained with a reaction time of 4 hours and a yield of 85%.³⁰ Another method involves the pyrolysis of $[N_2B_{10}H_9]^-$, which was discovered accidentally (eqn (3)), with a lower yield, a longer reaction time, and high temperatures.³¹ As reported in the literature, the direct synthesis of the alkali metal salts of $[trans-B_{20}H_{18}]^{2-}$ remained unexplored.³⁸

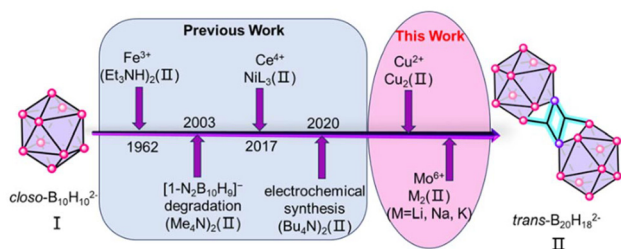
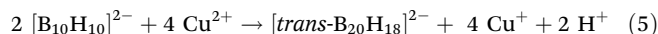
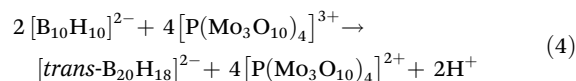
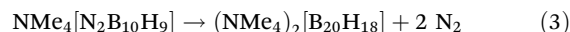
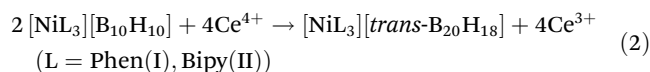
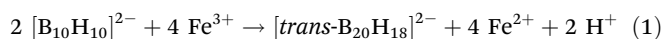
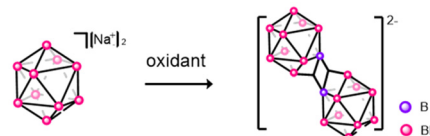


Fig. 2 Methods for the synthesis of $[trans-B_{20}H_{18}]^{2-}$ anions.

We have developed an efficient one-step direct synthesis method of $M_2[trans-B_{20}H_{18}]$ under mild conditions using $M_2[closo-B_{10}H_{10}]$ ($M = Li, Na, \text{ and } K$) as the starting material. Yields of $M_2[trans-B_{20}H_{18}]$ can reach an impressive 83–86%. The mechanism of the reaction is similar to that of the ammonium salt of $[trans-B_{20}H_{18}]^{2-}$, in which an appropriate oxidant was used to induce oxidative dehydrogenation coupling of $M_2B_{10}H_{10}$ to form $M_2[trans-B_{20}H_{18}]$. We initially used $Na_2B_{10}H_{10}$ as the substrate and employed the established

Table 1 Reaction of Na₂B₁₀H₁₀ with different types of oxidants at 30 °C^a


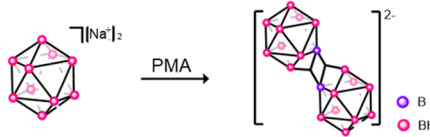
Entry	Oxidant	t/h	Yield ^b (%)
1	PMA	1.5	83
2	Cu(OTf) ₂	1.5	91
3	Al(OTf) ₃	2	Trace
4	FeCl ₃	2	43
5	Fe(OTf) ₃	2	46
6	Ni(OTf) ₂	2	Trace
7	Ce(OTf) ₃	2	Trace
8	Ce(OTf) ₄	2	38
9	Ce(NH ₃) ₂ (NO ₃) ₆	2	41
10	CF ₃ COOCu	2	32

^a Reaction conditions: Na₂B₁₀H₁₀ (5 mmol) and different oxidants (10 mmol) in CH₃CN (25 mL) at 30 °C. ^b Isolated yield as Na⁺ salts.

method reported in the literature to screen various Lewis acid oxidants (Table 1). The experimental results show that [trans-B₂₀H₁₈]²⁻ can be obtained from both H₃P(Mo₃O₁₀)₄·xH₂O and Cu(OTf)₂. Both [P(Mo₃O₁₀)₄]³⁺ (eqn (4)) and Cu²⁺ (eqn (5)) could act as oxidizers and exhibit high compatibility with the polyhedral borane [closo-B₁₀H₁₀]²⁻. When Cu(OTf)₂ is used as the oxidant, Cu₂[trans-B₂₀H₁₈] is produced with a yield exceeding 94%. It is worth noting that the solvents play a crucial role in these reactions. Cu²⁺ does not play an oxidant role to initiate such oxidative dehydrogenation coupling of M₂[closo-B₁₀H₁₀] under similar conditions in aqueous solution, where only a CuB₁₀H₁₀ precipitate was formed.¹⁰ On the other hand, when H₃P(Mo₃O₁₀)₄·xH₂O is used as the oxidant, alkali metal salts of [trans-B₂₀H₁₈]²⁻ (M = Li, Na, and K) are obtained, with a yield of up to 85%.

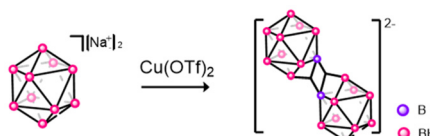
We then examined the effects of different molar ratios of Na₂B₁₀H₁₀ to H₃P(Mo₃O₁₀)₄·xH₂O or Cu(OTf)₂ and found that the optimized molar ratio for the reaction was different when the oxidants were H₃P(Mo₃O₁₀)₄·xH₂O or Cu(OTf)₂. The ideal ratio of Na₂B₁₀H₁₀ to H₃P(Mo₃O₁₀)₄·xH₂O is 3 : 1 (Table 2). The optimal ratio of Na₂B₁₀H₁₀ to Cu(OTf)₂ is 1 : 3 (Table 3). The excess usage of H₃P(Mo₃O₁₀)₄·xH₂O might have been due to every Mo⁶⁺ in PMA being an efficient oxidant.

It is worth noting that when H₃P(Mo₃O₁₀)₄·xH₂O is used as the oxidant and M₂[closo-B₁₀H₁₀] (M = Li, Na, and K) as the substrate, the corresponding alkali metal advanced polyhedral boranes M₂[trans-B₂₀H₁₈] (M = Li, Na, and K) are obtained, with yields ranging from 83% to 86%. Alkali metal salts, Na₂[trans-B₂₀H₁₈] and K₂[trans-B₂₀H₁₈], can be obtained without acetonitrile coordination, while Li₂[trans-B₂₀H₁₈]·0.23CH₃CN is obtained with a small amount of solvent coordination because of the stronger coordination ability of Li⁺. What is more interesting is that when Cu(OTf)₂ is used as the oxidant and M₂[closo-B₁₀H₁₀] (M = Li, Na, and K) as the

Table 2 Reaction of Na₂B₁₀H₁₀ with PMA in CH₃CN (25 mL) at 30 °C^a


Entry	PMA/Na ₂ B ₁₀ H ₁₀	t/h	Yield ^b (%)
1	1 : 2	2	83
2	1 : 3	2	83
3	1 : 4	2	62
4	1 : 5	2	38
5	1 : 10	2	27

^a Reaction conditions: Na₂B₁₀H₁₀ (5 mmol) and PMA (x mmol) in CH₃CN (25 mL) at 30 °C. ^b Isolated yield as Na⁺ salts.

Table 3 Reaction of Na₂B₁₀H₁₀ with Cu(OTf)₂ in CH₃CN (25 mL) at 30 °C^a


Entry	Cu(OTf) ₂ /Na ₂ B ₁₀ H ₁₀	t/h	Yield ^b (%)
1	1 : 1	2	48
2	2 : 1	2	84
3	3 : 1	2	91
4	4 : 1	2	82
5	5 : 1	2	75

^a Reaction conditions: Na₂B₁₀H₁₀ (5 mmol) and Cu(OTf)₂ (x mmol) in CH₃CN (25 mL) at 30 °C. ^b Isolated yield as Cu⁺ salts.

substrate, the final product is Cu₂[trans-B₂₀H₁₈]·1.2CH₃CN, with a yield as high as 91–94%, rather than the alkali metal salts. This result indicates that the formed Cu⁺ cations after reaction have a stronger interaction ability with the [B₂₀H₁₈]²⁻ anions in the presence of acetonitrile solvent.

These M₂[trans-B₂₀H₁₈] (M = Cu, Li, and K) complexes were fully characterized by NMR spectroscopy (¹H, ¹H{¹¹B}, ¹¹B, and ¹¹B{¹H} NMR) (Fig. S1–S24), XRD, XPS, and TGA (Fig. S25–S29). To further prove the role of Mo⁶⁺ as an oxidizer in reactions, the valence state of Mo in H₃P(Mo₃O₁₀)₄·xH₂O was detected by XPS before and after reactions. After the reactions, the valence state of a part of Mo in H₃P(Mo₃O₁₀)₄·xH₂O was transformed from +6 to +5 (Fig. S29).

These M₂[trans-B₂₀H₁₈] (M = Cu, Li, and K) complexes were fully characterized using XRD patterns and infrared spectra (Fig. S25–S27). Thermogravimetric analysis (TGA) results reveal the temperatures at which the remaining solvent molecules are removed from the samples: for Li₂B₂₀H₁₈·1.5CH₃CN (Fig. S27), K₂B₂₀H₁₈·0.3CH₃CN (Fig. S28), and hydrous Cu₂B₂₀H₁₈·1.2CH₃CN (Fig. S29) the temperatures are approximately 200, 290, and 190 °C, respectively. This viewpoint has been verified through computational analysis.

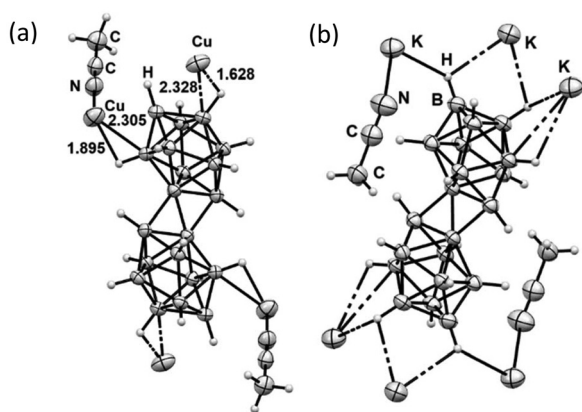


Fig. 3 Molecular structures of $[\text{Cu} \cdot \text{CH}_3\text{CN}]_2[\text{trans-B}_{20}\text{H}_{18}]$ (a) and $[\text{K} \cdot \text{CH}_3\text{CN}]_2[\text{trans-B}_{20}\text{H}_{18}]$ (b) both showing 50% probability thermal ellipsoids.

The single-crystal structures of the salts $[\text{Cu} \cdot \text{CH}_3\text{CN}]_2[\text{trans-B}_{20}\text{H}_{18}]$ and $[\text{K} \cdot \text{CH}_3\text{CN}]_2[\text{trans-B}_{20}\text{H}_{18}]$ were successfully determined (Fig. 3). While the structure of the octadecahydroeicosa-borate anion is similar to those reported in the literature, the interactions between the cation and anion are different.^{23–29} In the structure of $[\text{Cu} \cdot \text{CH}_3\text{CN}]_2[\text{trans-B}_{20}\text{H}_{18}]$, each Cu(I) cation is coordinated to one CH_3CN molecule with the Cu–N distance of 1.933 Å, in which CH_3CN acts as a monodentate ligand. Each Cu(I) also coordinated to two B–H bonds with the distances of 2.305 and 2.328 Å for Cu–B and 1.890 and 1.628 Å for Cu–H, in which Cu adopts a three-coordination, based on which the interactions between Cu(I) and the B–H bond are partly covalent. Moreover, each $\text{B}_{20}\text{H}_{18}^{2-}$ anion also interacts with four Cu(I) cations *via* two $\text{Cu} \cdots \text{H} \cdots \text{B}$ interactions. A similar interaction between cations and H atoms also exists in the compound $[\text{Au}(\text{L})\text{Cl}_2][\text{trans-B}_{20}\text{H}_{18}]$ (L = bipy, phen).²⁹ In contrast, $[\text{K} \cdot \text{CH}_3\text{CN}]_2[\text{trans-B}_{20}\text{H}_{18}]$ seems to be an ion pair structure, which is different from $[\text{Cu} \cdot \text{CH}_3\text{CN}]_2[\text{trans-B}_{20}\text{H}_{18}]$. Each CH_3CN , as a η^2 -ligand, bonds with two K cations with K–N distances of 2.872 and 3.029 Å, similar to the coordination geometry of $\text{K}_2[\text{B}_{20}\text{H}_{18}] \cdot 4\text{CH}_3\text{CN}$ ³⁹ and $\text{K}[\text{B}(\text{CN})_4] \cdot \text{CH}_3\text{CN}$, resulting in the formation of an extended cation chain with the alternating linkages of K^+ ions and CH_3CN molecules. Each K cation interacts with 5 B–H bonds in its other half sphere with distances of 2.868–3.014 Å, indicating an electrostatic attraction. A similar behavior was observed for $[\text{Fe}(\text{Bipy})_3][\text{B}_{20}\text{H}_{18}] \cdot \text{Bipy} \cdot 2\text{CH}_3\text{CN}$, $[\text{Ni}(\text{Phen})_3][\text{B}_{20}\text{H}_{18}] \cdot 2\text{DMF}$, and $[\text{Co}(\text{Phen})_3][\text{B}_{20}\text{H}_{18}] \cdot 4\text{CH}_3\text{CN}$ complexes.²⁸ Each $[\text{B}_{20}\text{H}_{18}]^{2-}$ anion is surrounded by eight K, with the K–B distances of 3.417–4.513 Å, consisting of a rectangular prism. Such weak interactions between K and B–H may be why Cu(I) could replace the alkali metals, Li, Na, and K, in the reaction to afford the u(i) salt.

In conclusion, we have developed facile methods for directly synthesizing $\text{M}_2[\text{trans-B}_{20}\text{H}_{18}]$ (M = Li, Na, K, and Cu) by the reactions of $\text{M}_2[\text{B}_{10}\text{H}_{10}]$ (M = Li, Na, and K) with an oxidizer, such as $\text{H}_3\text{P}(\text{Mo}_3\text{O}_{10})_4 \cdot x\text{H}_2\text{O}$ or $\text{Cu}(\text{OTf})_2$. It was found

that when $\text{H}_3\text{P}(\text{Mo}_3\text{O}_{10})_4 \cdot x\text{H}_2\text{O}$ was used as an oxidizer with its molar ratio to $\text{M}_2[\text{B}_{10}\text{H}_{10}]$ (M = Li, Na, and K) of 1 : 3, $\text{M}_2[\text{trans-B}_{20}\text{H}_{18}]$ (M = Li, Na, and K) was obtained with yields of 83–86%. When $\text{Cu}(\text{OTf})_2$ was used as an oxidizer with its molar ratio to $\text{M}_2[\text{B}_{10}\text{H}_{10}]$ of 3 : 1, $\text{Cu}_2[\text{trans-B}_{20}\text{H}_{18}]$ was obtained with yields of 91–94%. This work not only provides an efficient synthetic method for $[\text{trans-B}_{20}\text{H}_{18}]^{2-}$ but also paves the way for the practical application of $\text{M}_2[\text{trans-B}_{20}\text{H}_{18}]$ (M = Li, Na, and K) derivatives in various fields, including solid ionic conductors.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the SI: experimental procedure, supplementary figures and NMR spectra. See DOI: <https://doi.org/10.1039/d5dt01718a>.

CCDC 2449540 and 2415748 contain the supplementary crystallographic data for this paper.^{40a,b}

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 22171246, U23A2078, and 22479039).

References

- 1 E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth and H. C. Miller, *Inorg. Chem.*, 1964, **3**, 444–451.
- 2 M. F. Hawthorne, E. L. Muetterties and W. H. Knoth, *Science*, 1968, **161**, 153.
- 3 K. Y. Zhizhin, A. P. Zhdanov and N. T. Kuznetsov, *Russ. J. Inorg. Chem.*, 2010, **55**, 2089–2127.
- 4 J. R. Plešek, *Chem. Rev.*, 1992, **92**, 269–278.
- 5 F. Teixidor, C. Viñas, A. Demonceau and R. Nuñez, *Pure Appl. Chem.*, 2003, **75**, 1305–1313.
- 6 I. B. Sivaev and V. V. Bregadze, *Eur. J. Inorg. Chem.*, 2009, **11**, 1433–1450.
- 7 M. F. Hawthorne, K. Shelly and F. Li, *Chem. Commun.*, 2002, **6**, 547–554.
- 8 R. A. Watson-Clark and M. F. Hawthorne, *Inorg. Chem.*, 1997, **36**, 5419–5420.
- 9 A. R. Pitochelli, W. N. Lipscomb and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1962, **84**, 3026–3027.
- 10 A. Kaczmarczyk, R. D. Dobrott and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S. A.*, 1962, **48**, 729–733.
- 11 V. V. Avdeeva, M. I. Buzin, A. O. Dmitrienko, P. V. Dorovatovskii, E. A. Malinina, N. T. Kuznetsov,

- E. D. Voronova, Y. V. Zubavichus and A. V. Vologzhanina, *Chem. – Eur. J.*, 2017, **23**, 16819–16828.
- 12 Z. B. Curtis, C. Young, R. Dickerson, K. K. Lai and A. Kaczmarczyk, *Inorg. Chem.*, 1974, **13**, 1760–1763.
 - 13 J. Zhang, M. Zhang, Y. Zhao, B. Chen and C. C. Sun, *J. Comput. Chem.*, 2006, **27**, 1817–1821.
 - 14 F. Li, K. Shelly, C. B. Knobler and M. F. Hawthorne, *Angew. Chem., Int. Ed.*, 1998, **110**, 1969–1972.
 - 15 M. F. Hawthorne, R. L. Pilling and P. F. Stokely, *J. Am. Chem. Soc.*, 1965, **87**, 1893–1899.
 - 16 M. F. Hawthorne and R. L. Pilling, *J. Am. Chem. Soc.*, 1966, **88**, 3873–3874.
 - 17 R. S. Shamsiev, V. V. Avdeeva, A. S. Kubasov, E. Y. Matveev, E. A. Eshtukova-Shcheglova, A. V. Golubev, V. I. Privalov, E. A. Malinina, K. Y. Zhizhin and N. T. Kuznetsov, *Inorg. Chem. Commun.*, 2025, **173**, 113911.
 - 18 P. L. Rodríguez-Kessler and A. Muñoz-Castro, *Dalton Trans.*, 2024, **53**, 13960.
 - 19 A. Muñoz-Castro, *Phys. Chem. Chem. Phys.*, 2025, **27**(10), 5249–5255.
 - 20 P. L. Rodríguez-Kessler and A. Muñoz-Castro, *Phys. Chem. Chem. Phys.*, 2025, **27**(21), 11112–11118.
 - 21 P. L. Rodríguez-Kessler and A. Muñoz-Castro, *Phys. Chem. Chem. Phys.*, 2025, **27**(13), 6744–6750.
 - 22 P. L. Rodríguez-Kessler and A. Muñoz-Castro, *Dalton Trans.*, 2025, **54**, 9679–9688.
 - 23 V. V. Avdeeva, M. I. Buzin, E. A. Malinina, N. T. Kuznetsov and A. V. Vologzhanina, *CrystEngComm*, 2015, **17**, 8870–8875.
 - 24 V. V. Avdeeva, M. I. Buzin, A. O. Dmitrienko, P. V. Dorovatovskii, E. A. Malinina, N. T. Kuznetsov, E. D. Voronova, Y. V. Zubavichus and A. V. Vologzhanina, *Chem. – Eur. J.*, 2017, **23**, 16819–16828.
 - 25 E. A. Il'inchik, T. M. Polyanskaya, M. K. Drozdova, K. G. Myakishev, V. N. Ikorskii and V. V. Volkov, *Russ. J. Gen. Chem.*, 2005, **75**, 1545–1552.
 - 26 U. Siriwardane, S. S. C. Chu, N. S. Hosmane, H. Zhu and G. Zhang, *Cryst. Struct. Commun.*, 1989, **45**, 333–336.
 - 27 V. V. Avdeeva, A. S. Kubasov, S. E. Korolenko, V. I. Privalov, E. A. Malinina and N. T. Kuznetsov, *Polyhedron*, 2022, **217**, 115740.
 - 28 V. V. Avdeeva, A. V. Vologzhanina, A. S. Kubasov, N. S. Akhmadullina, O. N. Shishilov, E. A. Malinina and N. T. Kuznetsov, *Inorganics*, 2022, **10**, 99.
 - 29 V. V. Avdeeva, A. V. Vologzhanina, A. S. Kubasov, N. S. Akhmadullina, O. N. Shishilov, E. A. Malinina and N. T. Kuznetsov, *Dokl. Chem.*, 2019, **487**, 180–183.
 - 30 D. Naoufal, B. Bonnetot and H. Mongeot, *Appl. Organomet. Chem.*, 2003, **17**, 244–246.
 - 31 Y. Jing, X.-R. Liu, X. Wang, H. Han, S.-S. Liang, X.-M. Chen and X. Chen, *Sci. China: Chem.*, 2025, **68**, 1355–1361.
 - 32 Y. Jing, X. Wang, H. Han, X.-R. Liu, X.-C. Yu, X.-M. Chen, D. Wei, L.-S. Wang and X. Chen, *Sci. China: Chem.*, 2024, **67**, 876–881.
 - 33 X. Li, K. Wang, Y.-G. Li, Q. Zhao, Y.-N. Ma and X. Chen, *J. Am. Chem. Soc.*, 2025, **147**, 1893–1902.
 - 34 Y. Wang, Y.-G. Li, M.-M. Wang, L.-X. Li, X. Chen and Y.-N. Ma, *ACS Catal.*, 2025, **15**, 7646–7652.
 - 35 E. O. Firsova, V. V. Avdeeva, V. I. Privalov, N. A. Votnova, E. A. Malinina and N. T. Kuznetsov, *Dokl. Chem.*, 2015, **465**, 291–294.
 - 36 Z. Yang, M. Jin, S. Cheng, X. Ma, Z. Qin, J. Zhang, Y. Yang and Y. Guo, *J. Mater. Chem.*, 2022, **10**, 7186–7194.
 - 37 V. V. Voinova, I. N. Klyukin, A. S. Novikov, A. Y. Koz'menkova, A. P. Zhdanov, K. Y. Zhizhin and N. T. Kuznetsov, *Russ. J. Inorg. Chem.*, 2021, **66**, 295–304.
 - 38 E. Bernhardt, D. J. Brauer, M. Finze and H. Willner, *Angew. Chem., Int. Ed.*, 2007, **46**, 2927–2930.
 - 39 T. Küppers, M. Köckerling and H. Willner, *Z. Anorg. Allg. Chem.*, 2007, **633**, 280–284.
 - 40 (a) X.-R. Yin, Z.-W. Lu, X.-M. Chen, L.-Q. He and X. Chen, CCDC 2449540: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2n6yf8](https://doi.org/10.5517/ccdc.csd.cc2n6yf8); (b) X.-R. Yin, Z.-W. Lu, X.-M. Chen, L.-Q. He and X. Chen, CCDC 2415748: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2m2scw](https://doi.org/10.5517/ccdc.csd.cc2m2scw).