Direct solution-based synthesis of the $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$ solid electrolyte

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Abstract: All-solid-state batteries (ASSBs) promise higher power and energy density compared to batteries based on liquid electrolytes. Recently, a stable 3V ASSB based on the super ionic conductor (1mS cm^{-1} near RT) $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$ has demonstrated excellent cycling stability. Herein we developed a 5 steps, scalable and solution-based synthesis of $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$. The use of the wet chemistry approach allows solution processing with high throughput and addresses the main drawbacks for this technology, specifically, the limited electrodes-electrolyte contact and high cost. Moreover, through the same process, we achieved a cost efficient synthesis for the expensive precursors $\text{Na}_2\text{B}_{10}\text{H}_{10}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$. We investigated the mechanism of the reactions and highlighted two key parameters to tune the kinetics and selectivity: the choice of the counter cation, herein tetraethylammonium ($(\text{C}_2\text{H}_5)_4\text{N}^+$, TEA^+), and the solvent.

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We developed a facile solution based synthesis of the superionic conductor $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$, starting from the low cost and safe hydroborate NaBH_4 , without toxic boranes. Our synthesis method is a step forward to design novel all-solid-state battery using impregnation techniques with high throughput.

KEYWORDS. All-solid-state batteries, boron chemistry, closo-hydroborate, energy storage, solid electrolyte.

1. Introduction

All-solid-state batteries (ASSBs) are considered as promising novel electrochemical energy storage devices with increased energy and power density with improved safety.^[1] The development of ASSBs requires to simultaneously addressing challenges related to the solid electrolyte (SE) properties, notably, ionic conductivity and stability, as well as its integration into devices, including in particular the chemo-mechanical stability of electrode-electrolyte interfaces upon cycling.^[2] Cost effective synthesis and processing methods are also required in view of a future large-scale production of ASSBs.^[3] Significant efforts have already been made to develop materials with high ionic conductivity,^[4] such aspects related to device integration are becoming increasingly important.

Recently, an emerging class of materials, namely *closo*-hydroborates,^[5] has demonstrated excellent performances in this regard. $\text{Na}_2(\text{CB}_{11}\text{H}_{12})(\text{CB}_9\text{H}_{10})$ exhibits one of the highest ionic conductivity recorded with 70 mS cm^{-1} at RT,^[4b] while Duchêne et al. have reported an operational all-solid-state 3V stable battery based on the $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$ SE which possesses an ionic conductivity of about 1 mS cm^{-1} at 20°C and compatibility with a metallic sodium anode,^[5c, 6] where most of other SEs are unstable toward metallic Na.^[7] The peculiar anion dynamic within $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$ was identified as being responsible of the high cation diffusion.^[8] In addition, Moury et al. studied the behavior of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ under pressure and demonstrated its high compressibility with a bulk modulus as low as 14 GPa.^[9] This result highlights that this class of materials could be suitable to accommodate volume changes of the electrodes during cycles. For the aforementioned reasons *closo*-hydroborates based electrolyte are promising candidates for the developments of ASSBs technology. Although *closo*-hydroborates are solution processable,^[4b, 6, 10] they are often synthesized through toxic and expensive boranes (BH_3 , B_2H_6 or $\text{B}_{10}\text{H}_{14}$),^[11] hindering their development for any practical applications, some syntheses starting from NaBH_4 carried out in diglyme and using iodine to oxidize NaBH_4 into NaB_3H_8 were developed, however purity and solvent removal are issues for the performance of the solid-state conductor.^[12]

Herein develop a novel strategy to simultaneously address the cost effectiveness and processing challenges for *closo*-hydroborate SEs. We demonstrate a straightforward and selective wet chemistry approach to synthesize the superionic conductor and highly stable electrolyte $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$. Specifically, we present a five steps scalable synthesis starting from inexpensive, readily available and non toxic precursors, reacting in mild conditions. The use of solvothermal synthesis compared to the ceramic routes usually used enable designing more sustainable batteries.^[13] The process involves two intermediates of interest for hydroborate chemistry namely B_2H_7^- and B_3H_8^- .^[14] The final product is obtained by drying an isopropanol solution. Impedance spectroscopy of the as-prepared SE confirms its high conductivity which is independent from the synthesis route (ball milling vs wet chemistry).

Finally, we discuss the mechanism of the reaction pathways and show the possibility to obtain deuterium labeled samples in mild conditions.

2. Results and discussion

2.1. Synthesis process

Due to the greater control on the reaction steps, solution based method is often superior to gas-solid or solid-state approaches that are often used for *closo*-hydroborates synthesis.^[11, 15] This strategy allows high throughput, facilitating scale-up to enhance productivity. To keep the process safe and to maximize cost competitiveness, sodium tetrahydroborate (NaBH_4) was used as starting reagent. As NaBH_4 is barely soluble in organic solvents and readily reacts with protic ones such as alcohols, the first step is to exchange the inorganic cation (Na^+) with an organic one, in this case to form tetraethylammonium tetrahydroborate ($((\text{C}_2\text{H}_5)_4\text{NBH}_4$, TEABH_4). The metathesis was achieved mechano-chemically using a planetary ball-mill. The successful quantitative exchange is evidenced by FTIR spectroscopy as displayed in Figure 1 where no more B-H stretching modes characteristic for NaBH_4 ($2000\text{--}2600\text{ cm}^{-1}$) were detected. Instead, a new signal in this region characteristic for TEABH_4 was recorded and it is in agreement with previous report.^[16]

Figure 1. Comparison of the FTIR spectra of the NaBH_4 precursor (blue line), the TEABH_4 intermediate (red line) and the TEAB_3H_8 product (black line). The letters “b” and “t” on the figure stand for bridging and terminal B-H stretching modes respectively.

For the second step towards larger boron clusters, tetraethylammonium octahydrotriborate ($((\text{C}_2\text{H}_5)_4\text{NB}_3\text{H}_8$, TEAB_3H_8) was synthesized as an intermediate, following the strategy developed in reference.^[10b] TEABH_4 was dissolved in dichloromethane (CH_2Cl_2 , DCM) and allowed to react with

DCM by heating the mixture at 70°C during 36h in an autoclave. Figure 1 shows the typical terminal (2250-2500 cm⁻¹) and bridging (2000-2200cm⁻¹) B-H stretching modes,^[10b, 16-17] confirming the formation of TEAB₃H₈.

Inspired by older studies,^[18] and following strategies developed in our previous work,^[10b] we discovered that thermal dehydrocoupling of TEAB₃H₈ in toluene at 185°C in a closed system (step 3) leads to the selective formation of an equimolar mixture of TEA₂B₁₀H₁₀ and TEA₂B₁₂H₁₂ (Figure 2). The as-obtained products can be processed in two different ways. The first approach was aimed to target the direct synthesis of Na₄(B₁₂H₁₂)(B₁₀H₁₀) SE. In order to exchange the organic TEA cation back to sodium, we exploit the low solubility of tetraethylammonium tetraphenylborate ((C₂H₅)₄NB(C₆H₅)₄, TEABPh₄) as reaction product in alcohol or water, by adding sodium tetraphenylborate (NaB(C₆H₅)₄, NaBPh₄) in the equimolar mixture. This enables the fast precipitation of TEABPh₄ which can be easily filtered out.^[19] The metathesis was performed in boiling water, where both starting compounds are soluble, allowing the precipitation of TEABPh₄ as described by Eq. 1.

Figure 2. ¹¹B NMR spectrum recorded in DMSO-d₆ on the solid obtained phase after 16h thermolysis of TEAB₃H₈ at 185°C.

Drying the solution of Na₂B₁₀H₁₀ and Na₂B₁₂H₁₂ did not lead to the formation of the mixed-anion compound Na₄(B₁₂H₁₂)(B₁₀H₁₀) but rather to a mixture of the two individual materials Na₂B₁₀H₁₀ and Na₂B₁₂H₁₂ (step 4). We attribute this to hydrate formation, preventing the crystallization of the desired composition of Na₄(B₁₂H₁₂)(B₁₀H₁₀). To circumvent hydrate formation, we dissolved the dried mixture of Na₂B₁₀H₁₀ and Na₂B₁₂H₁₂ (ratio 1:1) in isopropanol (IPA), which is less coordinating than water.

After solvent removal, we obtained the electrolyte with the right defined composition (Eq. 2) and the conductive *fcc* packing as shown in Figure 3a (step 5).

The conductivity of the solution processed electrolyte was found to be on the order of 1 mS cm^{-1} near RT (Figure 3b and Figure S1), comparable to the one previously reported for the same phase prepared *via* solid-state mechanical milling followed by heat treatment.^[5c] Our synthesis method is thus particularly interesting in view of the scalable fabrication of ASSBs using solution processing methods.

Figure 3. (a) Comparison of XRD diffraction patterns for the wet synthesis approach (black line) and the mechano-chemical route (red line). (b) Temperature dependent Na^+ ion conductivity upon heating of the solution processed electrolyte $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$ compared with previously mechano-chemically processed reported literature data.^[5a]

The second approach was aimed to separate the equimolar mixture $\text{TEA}_2\text{B}_{12}\text{H}_{12} + \text{TEA}_2\text{B}_{10}\text{H}_{10}$ (obtained in step 3) to obtain the individual *closo*-hydroborates $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{10}\text{H}_{10}$. This was achieved in reflux of methanol followed by fractional re-crystallization of the liquid phase ($\text{TEA}_2\text{B}_{12}\text{H}_{12}$ being less soluble in methanol than $\text{TEA}_2\text{B}_{10}\text{H}_{10}$) (step 4', Figure S2). Finally, we used the same aforementioned method for the salt metathesis in boiling water and obtained both sodium salts, $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{10}\text{H}_{10}$, separately (step 5', Figure S3). Both salts are also valuable for basic research on this class of materials.

The whole process can be summarized as describe in Scheme 1, starting with NaBH_4 we directly obtained the SE $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$ through a 5 steps process and we have demonstrated the possibility to separate both *closo*-hydroborates. It is worth noting that except for the use of DCM, the solvents used in this process are alcohol, water and toluene; the latter can be produced from bioethanol,^[20] which adheres to a sustainable development approach. Moreover, we believe that the

used of DCM can be reduced to the role of reactant using stoichiometric quantities or even exchanged by another electrophile agent.

Scheme 1. Summary of the 5 steps process starting from NaBH_4 to 1st: the highly conductive electrolyte $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$ and 2nd $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{10}\text{H}_{10}$ separately.

2.2. Mechanism

2.2.1. TEAB_3H_8

In order to monitor the second reaction step, different reaction times (1h, 3h, 8h, 12h, 16h, 24h, and 36h) were chosen and the progress of this solvothermal synthesis was monitored by *ex-situ* ^{11}B NMR spectroscopy (Figure 4). The complete conversion of BH_4^- into B_3H_8^- was achieved within 36h at 70°C . The signal corresponding to B_2H_7^- confirms the mechanisms proposed by Büchner et al. and Moury et al. for the formation of tetrabutylammonium octahydrotriborate (TBAB_3H_8).^[10b, 16, 21] In this experiment, the conversion of BH_4^- into B_2H_7^- is more obvious than in previous studies revealing that the reaction involves two steps, i.e. $\text{BH}_4^- \rightarrow \text{B}_2\text{H}_7^- \rightarrow \text{B}_3\text{H}_8^-$. In fact, between 8 and 12h only B_2H_7^- is formed. It starts to convert after 12h into B_3H_8^- and is completely converted after 36h. These observations differ from the ones made in the previous studies for the synthesis of TBAB_3H_8 in two points. First, for TBAB_3H_8 , the formation of a borane adduct (tributylborane TrBu-BH_3) was reported and proposed to be involved in the mechanism and secondly, the signal corresponding to the formation of TBAB_2H_7 had very low intensity compared to the signal of TEAB_2H_7 recorded herein. From these observations, we conclude that the adduct triethylamine borane (TrEA-BH_3) is more reactive than TrBA-BH_3 which reacts readily with TEABH_4 to give TEAB_2H_7 (Eq. 3) whereas, TEAB_2H_7 is more stable than TBAB_2H_7 lowering the kinetic of the conversion into TEAB_3H_8 (Eq. 4).

From this conclusion, we highlighted that the choice of the counter cation is a crucial parameter to selectively obtain the desired product, confirming that solution-based routes allow tuning of the reaction mechanism. Finally we would like to stress that this procedure can be scaled up to at least 10 g scale (see syntheses details in SI and Figure S4).

Figure 4. ^{11}B NMR spectra recorded on the liquid phase during the solvothermal synthesis of TEAB_3H_8 at different reaction times. NMR experiments were made in CD_2Cl_2 .

To gain insight the role of the B-H bond reactivity, we performed the synthesis starting from the deuterated precursor, NaBD_4 . After 36h, a majority of B_2D_7^- was formed and increasing the temperature to 90°C was necessary to convert B_2D_7^- into B_3D_8^- (Figure S5). This result demonstrates that the B-H bond breaking to form hydrogen described in Eq. 4 is the rate limiting step. Moreover, through this experiment, we demonstrate that the procedure can be adapted to synthesize deuterated B_3D_8^- and $\text{B}_2\text{D}_7^{2-}$ salts in liquid phase starting from NaBD_4 , which is of high interest for neutron diffraction studies.

2.2.2. $\text{TEA}_2\text{B}_{10}\text{H}_{10}$ and $\text{TEA}_2\text{B}_{12}\text{H}_{12}$

To identify the different by-products after dehydrocoupling of TEAB_3H_8 , we performed 1D ^1H (Figure S6) and ^{11}B (Figure S7) NMR on the liquid and the solid obtained after 16 h at 185°C and 2D ^1H - ^{13}C HSQC NMR on the liquid phase (Figure S8). This allowed to identify (see experimental section for NMR assignments) the selective formation of $\text{TEA}_2\text{B}_{10}\text{H}_{10}$ and $\text{TEA}_2\text{B}_{12}\text{H}_{12}$ with a ratio 1:1 (obtained by integration of ^{11}B NMR spectrum) and $\text{TEA}_2\text{B}_{11}\text{H}_{11}$ as minor impurity in the solid phase as shown in the Figure 5.

With regards to the liquid phase, we identified triethylamine borane ($(\text{C}_2\text{H}_5)_3\text{NBH}_3$, TEA-BH_3) (Figure S5, S6 and S7) and triethylamine ($(\text{C}_2\text{H}_5)_3\text{N}$, TEA) formation (Figure S6 and S7).^[22] Based on these observations, we propose the following equation for the reaction (Eq 5):

Makhoulf et al. performed a similar study on the thermolysis of TEAB₃H₈ in dry conditions at 185°C, yet they did not observe the formation of TrEA-BH₃ and TEA₂B₁₂H₁₂. They also found that dry thermolysis at 185°C starting with tetramethylamine octahydrotriborate ((CH₃)₄B₃H₈, TMAB₃H₈), leads to the formation of similar products as describe by Eq.5, though no TrEA was detected.^[18] Furthermore, despite our efforts, the thermal treatment of TBAB₃H₈ in toluene did not lead to the formation of any *closo*-hydroborates. Consequently, the cation, as previously noticed, and the solvent influence the reaction mechanism by stabilizing intermediates during addition of boron in the growing of the *closo*-hydroborates cluster. As a result, TrMA-BH₃, TrEA-BH₃ and TrBA-BH₃ have different reactivity leading to different kinetics and selectivity, and finally different products are obtained. In other words, we identified two parameters to tune the reaction, which are the cation and the solvent.

Reaction 5 implies that the formation of B₁₀H₁₀²⁻ and B₁₂H₁₂²⁻ is entropy-driven due to the release of 16 hydrogen molecules. We recently calculated the formation enthalpies of neutral and charged tetrahydroborates in the gas phase by density functional theory (DFT),^[23] as well as their temperature-dependent thermodynamical properties from anharmonic DFT calculations.^[24] Using these data in conjunction with thermodynamic data for H⁻ and H₂, we can compute the free energy of the following reactions in the gas phase as a function of temperature:

Reactions 6 and 7 describe together the simplified reaction of 8 B₃H₈⁻ of Eq 5. Both reactions become spontaneous at 500 K, in line with the experimental observations and explain qualitatively the formation of both B₁₀H₁₀²⁻ and B₁₂H₁₂²⁻, without considering however the contribution of the counterions which are experimentally very important. Interestingly, reaction 8 (which is in principle also possible) is spontaneous even at 300 K with Δ_rG° = -228.6 kJ/mol. In this case, the progress of the reaction must be thus kinetically controlled, as no reaction is seen at 300K

3. Conclusion

In this work, we addressed two significant challenges regarding the development of ASSBs technology that are the processing of SEs and their expensive synthesis. We demonstrated the feasibility of selectively obtaining from solution the Na₄(B₁₂H₁₂)(B₁₀H₁₀) *closo*-hydroborate based SE with the right composition without loss of conductivity. This also allows the use of conventional slurry coating technique to obtain sheet like electrodes with high electrodes/electrolyte ionic contacts.^[6, 25] Further, the inherent recrystallization with IPA allows to keep a constant purity of the electrolyte which is not guaranteed when ball-milling solids of different origin.

Regarding the cost effectiveness, we developed a process starting with the inexpensive and safest hydroborate source available: NaBH₄. We used a solution-based approach allowing an easy scale-up of the process. Moreover, most of the solvents used during the synthesis, especially water and IPA

are environmentally friendly, cost effective and easily available in laboratories. While toluene can be obtained from biomass, owing to its toxicity it would be better to use another solvent as limonene for instance. DCM could be used as reactant in stoichiometric quantities, then decreasing notably the amount. We studied the reaction mechanism for the different steps and highlighted the importance of the solvent and the nature of the organic cation in tuning the kinetics and selectivity. The solvothermal method described herein enables to screen more solvents at temperature above their boiling point in order to improve the sustainability and the cost effectiveness of the process. Moreover, the potential emission of toxic boranes like diborane B_2H_6 is confined in the autoclave preventing safety issues and loss of boron source which would be detrimental for the yield of the synthesis. Therefore, we strongly believe that this process would pave the way of development in a large scale synthesis for further studies and the design of novel all-solid-state sodium batteries.

4. Experimental section

4.1. Characterizations

- FTIR experiments were performed with a Biorad Excalibur Instrument equipped with a portable Specac Golden Gate heatable ATR setup allowing to prepare samples in the glovebox. IR spectra were recorded with a spectral resolution of 1 cm^{-1} , with 30 scans in the range $600 - 4000\text{ cm}^{-1}$.

- ^1H and HSQC NMR experiments were carried out at 298K using a Bruker Avance III 500 MHz spectrometer with a 5-mm DCH ^{13}C - ^1H /D helium-cooled cryogenic probe equipped with a z-gradient coil. 2D HSQC experiments (Bruker pulse program "hsqcetgpsisp2.2") were recorded in 5 minutes (for commercial samples) and in 40 min (for experimental samples) with a 17 ppm spectral width in the ^1H dimension and a 200 ppm spectral width in the ^{13}C dimension. Each of the 256 increments in t_1 was acquired with 1 scan (for commercial samples) and with 8 scans (for experimental samples), a 1.0 s recycle delay between scans and 2048 points in the direct dimension.

For ^{11}B NMR spectra, two spectrometers were used: $\text{TEA}_2\text{B}_{12}\text{H}_{12}$ and $\text{TEA}_2\text{B}_{10}\text{H}_{10}$ spectra were recorded at 298K on a Bruker ADVANCE III HD-NanoBay 400 MHz spectrometer, equipped with a 5 mm CryoProbe Prodigy (CPPBBO BB-1H/19F/D), at a frequency of 400.13 MHz. TEAB_3H_8 experiments were performed at RT on a Bruker ADVANCE III HD-NanoBay 300 MHz spectrometer, equipped with a 5 mm BB(F)-H-D probe, at a frequency of 300.13 MHz.

- Powder XRD data were collected in a Debye-Scherrer geometry (0.5 mm diameter sealed capillary) on a STOE diffractometer STADI-P with a 1D plate IP-PSD detector and a $\text{Cu-K}_{\alpha 1}$ radiation ($\lambda = 1.5406\text{ \AA}$) with a germanium monochromator.

- Ionic conductivity was measured by electrochemical impedance spectroscopy using a BioLogic VMP3 multi-channel potentiostat in a frequency range from 1 MHz to 1 Hz with a voltage amplitude of 10 mV. The powder samples were pressed under a pressure of 500 MPa into a 10 mm diameter pellet with a thickness of 0.85mm. The pellet was loaded in a custom made air tight cell and contacted between two spring loaded electrodes. Indium foils were mechanically pressed on the pellet surfaces to

improve the contact between the sample and the molybdenum electrodes. Ionic conductivity was measured in steps of 20 °C between -40 °C and 80 °C. The temperature was controlled by a climatic chamber and equilibrating the cell for 2 h at each temperature.

4.2. NMR Assignments

¹H

NMR characterization of the liquid phase after thermolysis of TEAB₃H₈ at 185 °C du 16h: TrEA-BH₃: δ (ppm): 0.84 (t, $J = 7.3$ Hz, -CH₃) and δ (ppm): 2.32 (q, $J = 7.3$ Hz, -CH₂-), TrEA: δ (ppm): 1.00 and δ (ppm): 2.41 ppm, signal too broad to distinguish coupling.

NMR characterization of commercial samples: TrEA-BH₃: δ (ppm): 0.88 (t, $J = 7.3$ Hz, -CH₃), δ (ppm): 2.37 (q, $J = 7.3$ Hz, -CH₂-). TEA: δ (ppm): 2.42 (q, $J = 7.20$ Hz, -CH₂-), δ (ppm): 1.00 (t, $J = 7.20$ Hz, -CH₃).

¹¹B

BH₄⁻: δ_{11B} (ppm): -39 (q, $^1J_{B,H} = 82$ Hz), B₂H₇⁻: δ_{11B} (ppm): -25.3 (quartet of doublets), B₃H₈⁻: δ_{11B} (ppm): -30.1, (n, $^1J_{B,H} = 33$ Hz), B₁₂H₁₂²⁻: δ_{11B} (ppm): -15.5 (d, $^1J_{B,H} = 125$ Hz), B₁₀H₁₀²⁻: δ_{11B} (ppm): -28.8 (d, $^1J_{B,H} = 125$ Hz, 8B, 2 to 9) and -0.6 (d, $^1J_{B,H} = 141$ Hz, 2B, 1 and 10, see Fig. S8 for numbering), B₁₁H₁₁²⁻: δ_{11B} (ppm): -17.2 doublet overlapped with B₁₂H₁₂²⁻, TrEA-BH₃: δ_{11B} (ppm): -12.3 ppm (q, $^1J_{B,H} = 97$ Hz).

HSQC

TrEA: -CH₂- signal at 2.41/46.5 ppm, -CH₃- signal at 1.00/12.4 ppm, TrEA-BH₃: -CH₂- signal at 2.32/52.0 ppm, -CH₃- signal at 0.84/8.1 ppm.

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Conflicts of interest

There are no conflicts to declare.

Supporting informations

The SI contains all syntheses details, Nyquist plots, thermochemical data, additional NMR, FTIR and XRD, and picture of autoclaves.

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