Borohydride-containing coordination polymers: synthesis, air stability and dehydrogenation†

Kentaro Kadota,a Nghia Tuan Duong, b Yusuke Nishiyama, c bc Easan Sivaniah, d ad Susumu Kitagawa d and Satoshi Horike efg

Control of the reactivity of hydride (H\textsuperscript{–}) in crystal structures has been a challenge because of its strong electron-donating ability and reactivity with protic species. For metal borohydrides, the dehydrogenation activity and air stability are in a trade-off, and control of the reactivity of BH\textsubscript{4}\textsuperscript{–} has been demanded. For this purpose, we synthesize a series of BH\textsubscript{4}\textsuperscript{–}-based coordination polymers/metal–organic frameworks. The reactivity of BH\textsubscript{4}\textsuperscript{–} in the structures is regulated by coordination geometry and neighboring ligands, and one of the compounds [Zn(BH\textsubscript{4})\textsubscript{2}(dipyridyl)/propane] exhibits both high dehydrogenation reactivity (1.4 wt% at 179 °C) and high air stability (50 RH% at 25 °C, 7 days). Single crystal X-ray diffraction analysis reveals that H\textsuperscript{+}⋯H\textsuperscript{–} dihydrogen interactions and close packing of hydrophobic ligands are the key for the reactivity and stability. The dehydrogenation mechanism is investigated by temperature-programmed desorption, in situ synchrotron PXRD and solid-state NMR.

Controlling the reactivity of hydride-based ions in the solid state is important for hydrogen-related functions such as hydrogen (H\textsubscript{2}) storage, heterogeneous hydrogenation catalysis and ion conduction.\textsuperscript{1–3} Hydride-based ions include hydride (H\textsuperscript{–}) and molecular ions such as borohydride (BH\textsubscript{4}\textsuperscript{–}) and alanate (AlH\textsubscript{4}\textsuperscript{–}), and they exhibit a strong electron-donating ability.\textsuperscript{4} The reactive character causes high sensitivity to moisture in the air, and it has been a challenge to design the dual properties of high reactivity of hydrides and air stability in the solid state. For example, the dehydrogenation reactivity and air stability are in a trade-off for BH\textsubscript{4}\textsuperscript{–} in metal borohydrides (MBHs). Air-stable NaBH\textsubscript{4} releases H\textsubscript{2} above 500 °C, whereas Al(BH\textsubscript{4})\textsubscript{2} is pyrophoric in contact with moisture in the air, and it releases H\textsubscript{2} at 60 °C.\textsuperscript{5,6} The properties of MBHs are affected by some parameters of metal ions – electronegativity and ionic radius.\textsuperscript{6} A number of studies to tune the properties of MBHs were made (e.g., mixed metal ion MBHs,\textsuperscript{7–9} hybridization with organic polymers,\textsuperscript{10} and nano-confinement in porous scaffolds\textsuperscript{11,12}). The reactivity of BH\textsubscript{4}\textsuperscript{–} in crystal structures depends on hydrogen–hydrogen interactions (e.g., hydrogen bonding and dihydrogen bonding).\textsuperscript{13,14} For the precise tuning of these interactions, we applied coordination polymers (CPs) and metal–organic frameworks (MOFs).\textsuperscript{15–19} Tuning the coordination geometry and reactivity of metal ions or bridging ligands can afford the precise configuration of ions/molecules in CP architectures. CP structures are thought to be constructed with BH\textsubscript{4}\textsuperscript{–}; however it has been unsuccessful because of the high reactivity of BH\textsubscript{4}\textsuperscript{–}.

The attempts to incorporate reactive BH\textsubscript{4}\textsuperscript{–} into CP structures readily lead to the reduction of metal ions or decomposition of organic ligands. There are many reports on polymeric crystal structures consisting of metal ions and bridging BH\textsubscript{4}\textsuperscript{–}.\textsuperscript{20} On the other hand, the extended BH\textsubscript{4}\textsuperscript{–}-based crystal structures constructed from metal ions and organic bridging ligands are limited: \{[Mg(BH\textsubscript{4})\textsubscript{2}(pyrazine)\textsubscript{2}] and [Th(OTer\textsubscript{Mes})\textsubscript{2}(BH\textsubscript{4})\textsubscript{2}(4,4′-bipyridyl)]\} were the only examples reported in the Cambridge Crystallographic Data Centre (CCDC) database.\textsuperscript{21,22} As shown in previous studies, neutral N-donor ligands are suitable to incorporate BH\textsubscript{4}\textsuperscript{–} as a counter anion in CP structures. We then used commercially available Mg(BH\textsubscript{4})\textsubscript{2} and Ca(BH\textsubscript{4})\textsubscript{2} for CP synthesis using neutral N-donor ligands under Ar. The solution reaction using Mg(BH\textsubscript{4})\textsubscript{2} and 4,4′-bipyridyl in acetonitrile (MeCN) afforded a polymeric structure. Ca(BH\textsubscript{4})\textsubscript{2} with poor solubility in organic solvents is not suitable for solution reactions. A solvent-free mechanochemical reaction of Ca(BH\textsubscript{4})\textsubscript{2} and...
Bases (HSAB) theory. The theory says that so... and octahedral, where BH$_4^-$ form stable coordination bonds with N-donor ligands. [PPh$_4$Zn(BH$_4$)$_3$] and [Mn(BH$_4$)$_2$·3THF] NaBH$_4$ were therefore prepared as starting materials. Bulk PPh$_4^+$ cations were incorporated to increase the solubility of the salt. Transition metal ion-based MBH precursors successfully form coordination bonds with pyridyl and imidazolate ligands, and 10 CP crystals were isolated as summarized in Fig. 1. In general, the structural analysis from a single crystal for MBH is difficult, and it is usually hard to determine the exact position of hydrogen atoms in BH$_4^-$.

As shown in Fig. 1, each product is classified according to the local coordination environments at the M$^{2+}$ center (tetrahedral, trigonal bi-pyramidal and octahedral, where BH$_4^-$ is assumed to occupy one site). As the coordination number of ligands increases, the M–B distance increases (tetrahedral: 2.339 Å, trigonal bi-pyramidal: 2.499 Å, and octahedral: 2.696 Å, Table S3†). Electron-donation from N-donor ligands to metal ions decreases the electronic interaction between M and BH$_4^-$.

The coordination mode of BH$_4^-$ to metal ions was clearly determined, and most of them were bidentate. In addition, BH$_4^-$ in the structures shows dihydrogen bonding with the hydrogen atoms of bridging ligands. A dihydrogen bond is an interaction between negatively charged hydrogen and positively charged hydrogen (e.g., B–H$^-$–H$^+$–C, normally <2.4 Å), and affects the crystal packing and physical properties. The number of dihydrogen bonds varies in the range of 0 to 3 as summarized in Table S3.† Four packing structures were observed, one-dimensional (1D) chain (1, 2, 3, 4), 1D ladder (5, 6, 7, 8), two-dimensional (2D) bilayer (9) and 2D sheet (10). The CPs with a higher coordination number of the ligands show higher structural dimensionality. 5, 6, 7 and 9 contain MeCN as guest molecules, and the permanent porosity of 5 and 6 was determined by N$_2$ and CO$_2$ adsorption (Fig. S27 and S28†).

Bulk powder samples were prepared under the same reaction conditions, and phase purity was confirmed by PXRD and infrared (IR) spectroscopy under Ar (Fig. S24 and S25†). The thermal properties were characterized by thermogravimetric analysis (TGA) under Ar (Fig. S26†). As various types of chemical environments of BH$_4^-$ were observed in 1–10, the dependence of the air stability on the local structure was examined. Each powder sample (30 mg) was exposed to humidified air (relative humidity (RH) 50% at 25 °C, Fig. S29†), and time-course IR spectra and PXRD patterns were recorded to monitor BH$_4^-$.

Reference MBHs, NaBH$_4$, and Mg(BH$_4$)$_2$ were also evaluated for comparison. After air exposure of Mg(BH$_4$)$_2$ for 3 hours, no peak is observed in the B–H region in the IR spectrum (Fig. 2A). The broad peak at 3500 cm$^{-1}$ indicates the hydrolysis of BH$_4^-$.

Although NaBH$_4$ is considered as an air-stable MBH, it showed deliquesce in 2 hours under the conditions and hydrolyzed to form Na$_2$[B$_4$O$_5$(OH)$_4$]·3H$_2$O.

Fig. 1 Crystal structures of BH$_4^-$-based CPs. Tetrahedral (1–3), trigonal bi-pyramidal (4–9) and octahedral (10) geometries, and constituent metal ions and ligands are represented, respectively.
after air exposure for 7 days (Fig. S30†). Humidified conditions are harsh enough to hydrolyze BH₄⁻ in most of the MBHs.

Some crystalline powder samples changed to amorphous in a few minutes (5, Mg²⁺ and 10, Ca²⁺) or 1 day (3–4, 6–9, Mn²⁺). Notably, among the BH₄⁻-CPs, Zn²⁺-based CPs (1 and 2) exhibited high air stability. In particular, 2 exhibits IR spectra identical before and after air exposure for 7 days in Fig. 2B. In addition, 2 retains highly crystalline peaks in PXRD (Fig. 2B, inset). The results demonstrate improved air stability of 2, and the mechanisms are discussed based on the crystal structure of 2. Although many structural parameters affect the air stability, we classify the main contributions to the high air stability of 2 as the (i) metal–ligand coordination bond (ii) dihydrogen bonding and (iii) packing structure. 2 shows higher air stability than the isostructural Mn²⁺-based 3. In general, a metal–ligand bond is an essential parameter to determine the air stability of CPs. The Zn–N bond in tetrahedral geometry is known to construct highly stable CPs. Meanwhile, limited examples of CPs with Mn–N in tetrahedral geometry have been reported, and most of them are sensitive to air. The tendency of air stability depending on metal ions is also suggested by a survey of the CCDC database. Fig. 3C displays the dihydrogen bond between BH₄⁻ and the neighboring dipyridylpropane (dpp) in the structure of 2. In addition to the X-ray diffraction analysis, the geometry optimization on 2 utilizing DFT calculation suggests that dihydrogen bonds form as well (Fig. S46†). In general, dihydrogen bonding stabilizes a crystal structure by the electrostatic interaction between oppositely charged hydrogen atoms, and the interaction lowers the electron donating ability of BH₄⁻. The intermolecular interaction and packing structure are also essential for air stability, because they affect the diffusion of H₂O molecules in the structure. BH₄⁻ is surrounded by the hydrophobic propyl group (2.545–3.010 Å) as shown in Fig. 2D, which avoids the attack of H₂O. In addition, the concentration of hydrophobic species around BH₄⁻ of 2 was compared with that of other CPs showing different air stability. The number of carbon atoms away from the boron atoms of BH₄⁻ within 5 Å was counted for 2, 9 and 10 (Fig. S47†). 2 shows a higher concentration of carbon atoms than 9 and 10 (the total number of carbon atoms within 5 Å, 2: 47, 9: 39, 10: 16), which also contributes to the high air stability of 2."
the higher air stability of 2 than NaBH$_4$. 2 exhibits a lower dehydrogenation temperature than NaBH$_4$ (170 vs. 505 °C). Note that dpp ligands decrease the amount of H$_2$ release per weight, and the 1.4 wt% of H$_2$ is smaller than that of the MBHs. The close contact of each BH$_4^-$ enables dehydrogenation at a lower temperature. The inset of Fig. 3A displays the closest distance between B–H⋯H–B (2.645 Å), which is comparable to that of Zn$^{2+}$-based MBHs ([LiZn$_2$(BH$_4$)$_5$]: 2.482 Å; [NaZn(BH$_4$)$_3$]: 2.291 Å). Tetrahedral geometry in 2 is suitable to arrange BH$_4^-$ in close proximity. The variable temperature synchrotron PXRD experiments indicate the structural expansion of 2 upon heating (25–226 °C, Fig. 3B and S39†). 2 does not exhibit an amorphous phase before dehydrogenation at 179 °C, and metallic Zn peaks are observed above 180 °C. The dehydrogenation of two BH$_4^-$ produces one molecule of H$_2$ and subsequently reduces Zn$^{2+}$ to metallic Zn.

The environment of BH$_4^-$ after the dehydrogenation was characterized by solid-state $^{11}$B magic angle spinning (MAS) nuclear magnetic resonance (NMR). The $^{11}$B NMR spectrum of pristine 2 shows two peaks at −45 and −47 ppm, and both peaks correspond to crystallographically independent BH$_4^-$ (Fig. 3B, inset). The dehydrogenized 2 displays $^{11}$B peaks at −8, 0, 15, and 30 ppm in Fig. 3B, and was further characterized by using the 2D multi-quantum (MQ) MAS NMR spectrum (Fig. S42†). To identify the resultant boron species, a 2D $^1$H/$^{11}$B through-bond heteronuclear multiple quantum coherence (HMQC) experiment was performed (Fig. S43†). The $^{11}$B peaks observed at −8 and 0 ppm correlate with the proton at 2 ppm, indicative of a B–H bond. These boron species are assigned to the [(BH$_3$)$_2$dpp] complexes.22 Meanwhile, the remaining two $^{11}$B peaks (15, 30 ppm) do not exhibit a clear correlation, indicating no direct bond between these boron species and hydrogen atoms. The $^{11}$B peak at 15 ppm corresponds to elemental boron and matches well with the simulated one (Fig. S44†), while the $^{11}$B peak at 30 ppm corresponds to B-3N species (e.g., [B(dpp)$_3$]).16–38 The 2D $^1$H/$^{13}$C heteronuclear correlation spectrum clearly exhibits the $^1$H and $^{13}$C peaks corresponding to the aromatic ring and aliphatic chain of dpp, indicating that dpp does not decompose during dehydrogenation (Fig. S45†).

The first peak of H$_2$ release at 179 °C in TPD corresponds to the dehydrogenation of BH$_4^-$ (eqn (1)). The release of toxic B$_2$H$_6$ is suppressed by the complexation with the N-donor dpp ligand to form [(BH$_3$)$_2$dpp] as revealed by solid-state NMR and IR spectra (Fig. S40†). The second peak of H$_2$ release at 203 °C in TPD corresponds to the further dehydrogenation of [(BH$_3$)$_2$dpp]. Solid-state NMR suggests that [(BH$_3$)$_2$dpp] partly forms elemental boron and B-3N species such as [B(dpp)$_3$] through the dehydrogenation (eqn (2)). 2 arranged BH$_4^-$ and nitrogen atoms of dpp close to each other in a 1 : 1 ratio (B⋯N distance: 3.450 and 3.462 Å, Fig. S35†), 2 maintains the crystal structure before dehydrogenation at 179 °C as observed by in situ PXRD. The results indicate that the pre-organized environment of BH$_4^-$ in 2 is preserved before the dehydrogenation, leading to the release of pure H$_2$ without B$_2$H$_6$.

Conclusions

By considering suitable combinations of metal ions and N-donor ligands, we have constructed 10 coordination polymer crystals involving reactive BH$_4^-$ with various coordination...
geometries. In particular, $[\text{Zn(BH}_4\text{)}_2(\text{dipyridylpropane})]$ (2) demonstrated both high dehydrogenation reactivity and high air stability. The crystal structure of 2 was intact under humidified conditions (50 RH% at 25 °C, 7 days) which indicates exceptionally high air stability as compared with conventional MBHs. This is due to the strong metal–ligand bond, the electrostatic stabilization by dihydrogen bonding, and close packing of the hydrophobic group with BH$_4^–$. In spite of the stabilization of BH$_4^–$, the dehydrogenation reactivity was maintained (pure H$_2$, 1.4 wt%, 179 °C). Tetrahedral geometry in 2 arranged two BH$_4^–$ closely, which accelerated the dehydrogenation. We demonstrated that crystal engineering of coordination polymers and metal–organic frameworks expands the library of hydride-based crystal structures and their properties.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank Dr Hiroyasu Sato from RIGAKU Corporation and Ms Nanae Shimanaka for their assistance in solving the crystal structure. The authors thank Dr Shogo Kagawuchi at the Super Photon Ring (SPring-8) for the synchrotron PXRD measurements. The work was supported by the Japan Society of the Promotion of Science (JSPS) for a Grant-in-Aid for Scientific Research (B) (JP18H02032) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and Strategic International Collaborative Research Program (SICORP) and Adaptable and Seamless Technology Transfer Program through Target-driven R&D (A-STEP) from the Japan Science and Technology, Japan.

References

1 T. He, P. Pachfule, H. Wu, Q. Xu and P. Chen, Nat. Rev. Mater., 2016, 1, 16059.
2 G. Kobayashi, Y. Hinuma, S. Matsuoka, A. Watanabe, M. Iqbal, M. Hirayama, M. Yonemura, T. Kamiyama, M. Iqbal, M. Hirayama, M. Yonemura, T. Kamiyama, 27 N. C. Burtch, H. Jasuja and K. S. Walton, Bull. Acad. Sci. USSR, 1987, 36, 1582–1586.
4 Y. Filinchuk, R. Černý and H. Hagemann, Chem. Mater., 2009, 21, 925–933.
26 N. V. Belkova, L. M. Epstein, O. A. Filippov and E. S. Shubina, Chem. Rev., 2016, 116, 8345–8587.
30 K. Müller-Buschbaum and F. Schönfeld, CSD Communication, 2014.
31 In CCDC database, the reported examples of $[\text{Zn(X)}_2(\text{pyridyl})_2]$ are greater than twice of the hydrated geometry, $[\text{Zn(X)}_2(\text{pyridyl})_2]\text{(H}_2\text{O})_2]$ (1306 vs. 814 hits). By contrast, Mn$^2+$ prefers the hydrated structure (unhydrated: 28 hits, hydrated: 375 hits).

32 J. Fanfrlik, M. Lepsik, D. Horinek, Z. Havlas and P. Hobza, *ChemPhysChem*, 2006, 7, 1100–1105.
33 I. V. Glukhov, K. A. Lyssenko, A. A. Korlyukov and M. Y. Antipin, *Russ. Chem. Bull.*, 2005, 54, 547–559.
34 X. Zhao, H. Yang, E. T. Nguyen, J. Padilla, X. Chen, P. Feng and X. Bu, *J. Am. Chem. Soc.*, 2018, 140, 13566–13569.
35 P. Veeraraghavan Ramachandran, A. S. Kulkarni, Y. Zhao and J. Mei, *Chem. Commun.*, 2016, 52, 11885–11888.
36 G. Xia, Q. Gu, Y. Guo and X. Yu, *J. Mater. Chem.*, 2012, 22, 7300–7307.
37 C. L. Turner, R. E. Taylor and R. B. Kaner, *J. Phys. Chem. C*, 2015, 119, 13807–13813.
38 P. M. I. Irene, A. C. Armando and C. Rosalinda, *Magn. Reson. Chem.*, 1993, 31, 189–193.