

Superprotonic conduction of $\{\text{NBu}_{4-n}(\text{enOH})_n\}[\text{MnCr}(\text{ox})_3]$ (Bu = *n*-butyl; enOH = 2-hydroxyethyl; *n* = 1–3) in successive multiplication of hydroxyl proton-carrier in the cation

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Hisashi Ōkawa

Hisashi Ōkawa received Ph.D. (1969) from Kyusyu University and was promoted to Professor of Kyusyu University in 1991. His researches related to bi- and polynuclear metal complexes and molecular-based magnets. He received Daiwa Award (1996) and the Chemical Society of Japan Award (2000). After retired in 2004, he worked as CREST Research Fellow in Kyoto University (Prof. Hiroshi Kitagawa).



Yukihiro Yoshida

Yukihiro Yoshida earned his Ph.D. degree in 2001 from Kyoto University under the direction of Prof. Gunzi Saito. After postdoctoral research at Kyoto University and Université de Rennes 1, he moved to Meijo University as an assistant professor. In 2017, he moved back to Kyoto University and is currently an associate professor at the same university. His research interest has been the development of new electronic/protonic materials such as charge-transfer complexes and metal complexes including coordination polymers. He has authored or co-authored more than 150 peer-reviewed publications.



Hiroshi Kitagawa

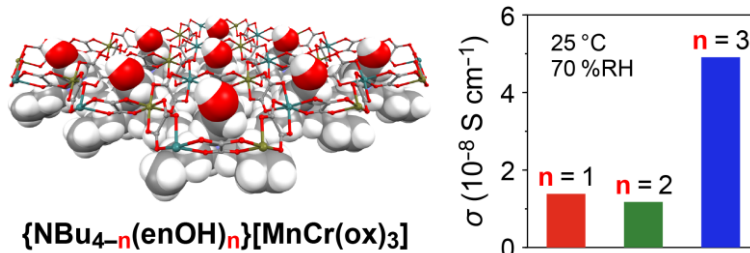
Hiroshi Kitagawa, born in 1961, received his Ph.D. from Kyoto University in 1992 and, after working as an assistant professor at the Institute for Molecular Science and the Japan Advanced Institute of Science and Technology, was appointed associate professor at the University of Tsukuba in 2000. He became a professor at Kyushu University in 2003 and returned to Kyoto University in 2009. He is now employed at JST as Director of "Exploring Innovative Materials in Unknown Search Space". He has published more than 550 original research papers on solid-state chemistry, coordination chemistry, nanoscience, low-dimensional electron systems and molecule-based conductors.

Abstract

Proton conduction in a new series of two-dimensional metal-organic frameworks, $\{\text{NBu}_{4-n}(\text{enOH})_n\}[\text{MnCr}(\text{ox})_3]$ (*n* = 1: $(\text{B}_3\text{O})\text{MnCr}$; *n* = 2: $(\text{B}_2\text{O}_2)\text{MnCr}$; *n* = 3: $(\text{BO}_3)\text{MnCr}$), was studied with respect to their molecular and network structures. Crystallographic studies revealed that $(\text{B}_3\text{O})\text{MnCr}$ consisted of honeycomb-based oxalate-bridged bimetallic $[\text{MnCr}(\text{ox})_3]^-$ sheets with $\{\text{NBu}_3(\text{enOH})\}^+$ ions intercalated in between. The enOH group was inserted into the cavity of the honeycomb sheet and the hydroxy group protruded out of the cavity to form a *hydroxyl-face* on the sheet, which played a pivotal role in proton conduction via the vehicle mechanism under low relative humidity (RH). Under high RH conditions, water adsorption modified the *hydroxyl-face* such that a hydrogen-bonding network was formed, which mediated proton transfer via the Grotthuss mechanism. The proton conductivities (σ) of $(\text{B}_3\text{O})\text{MnCr}$ and $(\text{B}_2\text{O}_2)\text{MnCr}$ at 25 °C under 95% RH were 6.2×10^{-5} and 6.7×10^{-4} S cm⁻¹, respectively, which increase to 1.7×10^{-4} and 2.0×10^{-3} S cm⁻¹, respectively, with increasing the temperature to 50 °C. $(\text{BO}_3)\text{MnCr}$ deliquesces under the same conditions; however, the σ value under 70% RH was higher than those of $(\text{B}_3\text{O})\text{MnCr}$ and $(\text{B}_2\text{O}_2)\text{MnCr}$, primarily because of the further introduction of the enOH group in the cation.

Keywords: bimetallic oxalate sheet, metal-organic framework, proton conductor

Graphical abstract

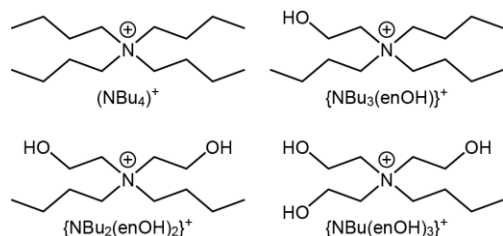


A new series of two-dimensional layered metal-organic frameworks, $\{NBu_{4-n}(enOH)_n\}[MnCr(ox)_3]$ ($n = 1$: $(B_3O)MnCr$; $n = 2$: $(B_2O_2)MnCr$; $n = 3$: $(BO_3)MnCr$), was synthesized and characterized. The hydroxy group of an enOH part protrudes out of the cavity of the $[MnCr(ox)_3]^-$ sheet to form the *hydroxyl-face*, which plays a pivotal role in the proton conduction. The vehicle/Grotthuss interconversion of proton transfer mechanism was observed by varying the relative humidity.

1. Introduction

Proton conduction is a prime concern in the study of functional metal-organic frameworks (MOFs).¹⁻³ A variety of proton conductive MOFs have been produced by different methods^{4,5} and nowadays MOFs with a proton conductivity (σ) on the order of $10^{-1} S cm^{-1}$ have been reported.⁶⁻¹⁴ Our approach to the synthesis of proton conductive materials relates to two-dimensional (2D) layered MOFs, $(A)[M_b^{II}M_a^{III}(ox)_3]$ (A^+ : quaternary ammonium or phosphonium ions), which were initially developed as molecular magnets.¹⁵⁻¹⁷ They involve the 2D constitution of the honeycomb-based bimetallic sheets with an alternating array of M_a^{III} and M_b^{II} ions extended by oxalate groups and A^+ ions intercalated between the sheets.^{18,19} A proton conducting pathway is formed between the sheets when a proton carrier is introduced into the A^+ ion.²⁰⁻²⁴ For example, $(NBu_4)[MnCr(ox)_3]$ with innocent NBu_4 ions is inherently non-conductive, whereas $\{NBu_3(CH_2COOH)\}[MnCr(ox)_3]$ decorated with carboxy group in a cation shows an appreciable proton conductivity ($5.2 \times 10^{-7} S cm^{-1}$ at 90% RH)²² and $\{NBu_2(CH_2COOH)_2\}[MnCr(ox)_3]$ further decorated with carboxy group shows a higher proton conductivity ($1.8 \times 10^{-3} S cm^{-1}$ at 95% RH).²⁴ Our approach has the advantage of controlling the proton conduction by manipulating the cation incorporated in the MOFs while maintaining the 2D framework.

In this paper, we report the proton conductivity of a series of new $MnCr(ox)_3$ -based MOFs derived from $\{NBu_{4-n}(enOH)_n\}^+$ ($enOH = 2$ -hydroxyethyl; $n = 1-3$; Scheme 1)



Scheme 1. Molecular structures of $(NBu_4)^+$ and $\{NBu_{4-n}(enOH)_n\}^+$ ($n = 1-3$) ions.

with different numbers of enOH moieties. Proton conduction was assessed when the alcoholic proton source incorporated onto the cation was increased successively.

2. Experimental

2.1 Preparation of $\{NBu_{4-n}(enOH)_n\}Br$ ($n = 1, 2$, or 3)

$\{NBu_3(enOH)\}Br$, $\{NBu_2(enOH)_2\}Br$, and $\{NBu(enOH)_3\}Br$ were prepared according to the literature method.²⁵

2.2 Preparation of $\{NBu_{4-n}(enOH)_n\}[MnCr(ox)_3]$ ($n = 1, 2$, or 3)

To a mixture of $(NH_4)_3[Cr(ox)_3] \cdot 3H_2O$ (215 mg, 0.5 mmol) and $MnCl_2 \cdot 4H_2O$ (100 mg, 0.5 mmol) in methanol (12 cm³) was dropwise added a solution of $\{NBu_{4-n}(enOH)_n\}Br$ ($n = 1, 2$, or 3 ; 0.6 mmol) in a minimum amount of methanol. Resulting bluish-purple microcrystals were separated, washed with methanol and dried in air.

$\{NBu_3(enOH)\}[MnCr(ox)_3] \cdot 2H_2O$ (**(B₃O)MnCr**): Yield 195 mg (0.31 mmol, 61%). Anal. Calcd (%): C, 37.69; H, 5.69; N, 2.20. Found (%): C, 37.83; H, 5.21; N, 2.29. Mn/Cr = 0.95 by X-ray fluorescence spectrometry (XRFS). Selected FT-IR (ATR): 1619 and 1431 cm⁻¹.

$\{NBu_2(enOH)_2\}[MnCr(ox)_3] \cdot 2H_2O$ (**(B₂O₂)MnCr**): Yield 210 mg (0.34 mmol, 67%). Anal. Calcd (%): C, 34.57; H, 5.16; N, 2.24. Found (%): C, 34.78; H, 4.93; N, 2.34. Mn/Cr = 0.94 by XRFS. Selected FT-IR (ATR): 1619 and 1432 cm⁻¹.

$\{NBu(enOH)_3\}[MnCr(ox)_3] \cdot 2H_2O$ (**(B₃O)MnCr**): Yield 170 mg (0.28 mmol, 55%). Anal. Calcd (%): C, 31.32; H, 4.60; N, 2.28. Found (%): C, 31.19; H, 4.48; N, 2.29. Mn/Cr = 0.95 by XRFS. Selected FT-IR (ATR): 1619 and 1429 cm⁻¹.

2.3 Characterizations

The X-ray fluorescence spectroscopy (XRFS) was conducted using a Rigaku ZSX Primus IV spectrometer with rhodium anode X-ray tube generator. Fourier transform infrared (FT-IR) spectra were measured using a Perkin Elmer Spectrum 100 spectrometer equipped with a single-reflection platinum attenuated total reflection (ATR) accessory. Thermal gravimetric (TG) measurements were conducted on a Bruker TG-DTA2000SA at a heating rate of 5 K min⁻¹ under a nitrogen atmosphere with open aluminum pans. Powder X-ray diffraction (PXRD) measurements were

1 performed with a Bruker D8 ADVANCE using CuK α
 2 radiation ($\lambda = 1.5418 \text{ \AA}$) in a 2θ range of $5\text{--}50^\circ$. Single-
 3 crystal X-ray diffraction (SCXRD) measurements were
 4 performed on a Rigaku XtaLAB P200 diffractometer with a
 5 graphite monochromatized MoK α radiation ($\lambda = 0.71069 \text{ \AA}$)
 6 at 100 K. The crystal structure was solved by the direct
 7 method using the SHELXS-2014 program²⁶ and refined by a
 8 full-matrix least-squares method on F^2 using the SHELXL-
 9 2014 program.²⁷ Crystallographic data reported in this
 10 manuscript have been deposited with Cambridge
 11 Crystallographic Data Centre (CCDC), reference numbers
 12 2359992. Water adsorption and desorption isotherms were
 13 measured at 298 K with a BELSORP-max volumetric
 14 adsorption system. Proton conductivities of the pellets (2.5
 15 mm in diameter) were measured by the ac impedance
 16 technique with an applied voltage of 100 mV using a
 17 Solartron SI 1260 Impedance/Gain-Phase Analyzer and
 18 1296 Dielectric Interface in the frequency range from 0.1
 19 Hz to 1 MHz. Measurements were performed in a
 20 temperature- and humidity-controlled chamber ESPEC SH-
 21 221.

23 3. Results and discussion

24 The 2D MOFs, $\{\text{NBu}_3(\text{enOH})\}[\text{MnCr}(\text{ox})_3]\cdot 2\text{H}_2\text{O}$
 25 $(\text{B}_3\text{O})\text{MnCr}$, $\{\text{NBu}_2(\text{enOH})_2\}[\text{MnCr}(\text{ox})_3]\cdot 2\text{H}_2\text{O}$
 26 $(\text{B}_2\text{O}_2)\text{MnCr}$, and $\{\text{NBu}(\text{enOH})_3\}[\text{MnCr}(\text{ox})_3]\cdot 2\text{H}_2\text{O}$
 27 $(\text{BO}_3)\text{MnCr}$, have been produced in polycrystalline form
 28 (see Experimental section in detail). Our attempts to prepare
 29 an analogous MOF with $\{\text{N}(\text{enOH})_4\}^+$ ion were in vain
 30 because the cation decomposed into $\{\text{NH}(\text{enOH})_3\}^+$ during
 31 preparative operations.²⁸ The three MOFs were formulated
 32 as dihydrates according to elemental analysis, although the
 33 water content was somewhat variable in repeated syntheses.
 34 The TG profiles of the compounds show a continuous

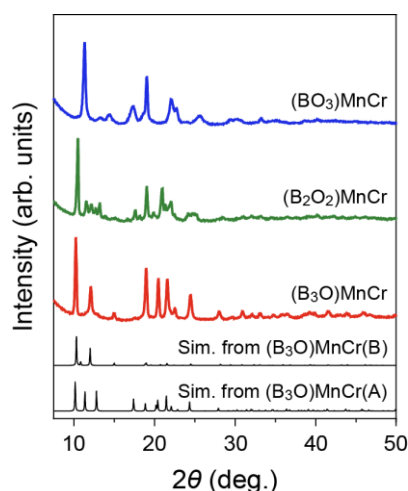


Fig. 1. Powder X-ray diffraction patterns of $(\text{B}_3\text{O})\text{MnCr}$ (red), $(\text{B}_2\text{O}_2)\text{MnCr}$ (green), and $(\text{BO}_3)\text{MnCr}$ (blue). Black lines show patterns simulated from the single-crystal diffraction data of $(\text{B}_3\text{O})\text{MnCr}(\text{A})$ and $(\text{B}_3\text{O})\text{MnCr}(\text{B})$ (see text), where the pattern of $(\text{B}_3\text{O})\text{MnCr}(\text{B})$ was simulated using only the refined $[\text{MnCr}(\text{ox})_3]^-$ sheets.

35 weight loss of 2–3% up to 100 °C (Supplementary Fig. S1),
 36 suggesting that two water molecules (ca. 2.9 wt%) are
 37 weakly adsorbed in the crystals.

38 The target compounds were difficult to crystallize due to
 39 the high degree of flexibility within the cations. After much
 40 effort, two types of single-crystalline $(\text{B}_3\text{O})\text{MnCr}$ solids
 41 were obtained in small portions when an aqueous methanol
 42 solution of the microcrystalline sample was slowly
 43 dehydrated by the diffusion of 2,2-dimethoxypropane. One
 44 form (hereafter, $(\text{B}_3\text{O})\text{MnCr}(\text{A})$) with trigonal crystal
 45 system (space group: $R3c$) contains six $[\text{MnCr}(\text{ox})_3]^-$ sheets
 46 within the unit cell, whereas another form (hereafter,
 47 $(\text{B}_3\text{O})\text{MnCr}(\text{B})$) with hexagonal crystal system (space
 48 group: $P6_322$) contains two $[\text{MnCr}(\text{ox})_3]^-$ sheets within the
 49 unit cell. At present, we could refine the crystal structure of
 50 $(\text{B}_3\text{O})\text{MnCr}(\text{A})$ as described below, although PXRD
 51 measurements indicate that the majority of polycrystalline
 52 $(\text{B}_3\text{O})\text{MnCr}$ has a structure identical to that of
 53 $(\text{B}_3\text{O})\text{MnCr}(\text{B})$ (Fig. 1 and Supplementary Fig. S2).
 54 However, because the two forms have a comparable
 55 intersheet distance (8.50 Å for $(\text{B}_3\text{O})\text{MnCr}(\text{A})$ vs. 8.54 Å
 56 for $(\text{B}_3\text{O})\text{MnCr}(\text{B})$) despite having different stacking
 57 arrangements (Supplementary Fig. S3), it is most likely that
 58 $\{\text{NBu}_3(\text{enOH})\}^+$ ions are accommodated between sheets
 59 with similar packing motifs in both forms. Thus, the crystal
 60 structure of the minor phase, $(\text{B}_3\text{O})\text{MnCr}(\text{A})$, can provide
 61 useful information about the molecular and network
 62 structures of polycrystalline $(\text{B}_3\text{O})\text{MnCr}$ which was used to
 63 evaluate proton conductivity by electrochemical impedance
 64 spectroscopy. Notably, $(\text{B}_2\text{O}_2)\text{MnCr}$ and $(\text{BO}_3)\text{MnCr}$ show
 65 similar PXRD patterns to that of $(\text{B}_3\text{O})\text{MnCr}$ (Fig. 1), in
 66 which the most intense peak at $2\theta \sim 10^\circ$ is assigned to the
 67 (002) reflection (as $(\text{B}_3\text{O})\text{MnCr}(\text{B})$). Thus, it is apparent
 68 that the three MOFs exhibit isomorphous layered structures
 69 consisting of $[\text{MnCr}(\text{ox})_3]^-$ sheets. Furthermore, the
 70 antisymmetric and symmetric $\nu(\text{CO})$ stretching bands at
 71 1619 and 1429–1431 cm^{-1} , respectively, in the infrared
 72 spectra is additional evidence of the formation of oxalate-
 73 bridged bimetallic sheets (Supplementary Fig. S4). The
 74 different intersheet distances, i.e., 8.51 Å for $(\text{B}_3\text{O})\text{MnCr}$,
 75 8.42 Å for $(\text{B}_2\text{O}_2)\text{MnCr}$, and 8.03 Å for $(\text{BO}_3)\text{MnCr}$,
 76 estimated from the 2θ position of the (002) reflection must
 77 be manifested due to the existence of intersheet $\{\text{NBu}_4\text{--}$
 78 $\text{n}(\text{enOH})\text{n}\}^+$ ions with different sizes. We note that the three
 79 MOFs remained intact even after being placed under wet
 80 conditions (at 25 °C for 3 hours; Supplementary Fig. S5).

81 SCXRD study revealed that anhydrous $(\text{B}_3\text{O})\text{MnCr}(\text{A})$
 82 belongs to a noncentrosymmetric trigonal system with space
 83 group $R3c$ at 100 K (Supplementary Table S1). One-third of
 84 the $\{\text{NBu}_3(\text{enOH})\}^+$ ions and one-third of the $[\text{MnCr}(\text{ox})_3]^-$
 85 units are crystallographically independent. In the crystal,
 86 there are oxalate-bridged bimetallic sheets situated in the ab
 87 plane, and the unit cell contains six sheets aligned along the
 88 c axis. The two metal centers are distinguished by their long
 89 $\text{Mn}^{\text{II}}\text{--O}$ bonds (av. 2.181 Å) and short $\text{Cr}^{\text{III}}\text{--O}$ bonds (av.
 90 1.989 Å). In the intersheet space, the $\{\text{NBu}_3(\text{enOH})\}^+$ ions
 91 are positioned such that the enOH group are located on the
 92 3-fold axis and oriented toward the honeycomb cavity (Fig.
 93 2a). Notably, the disordered hydroxy group has no O–

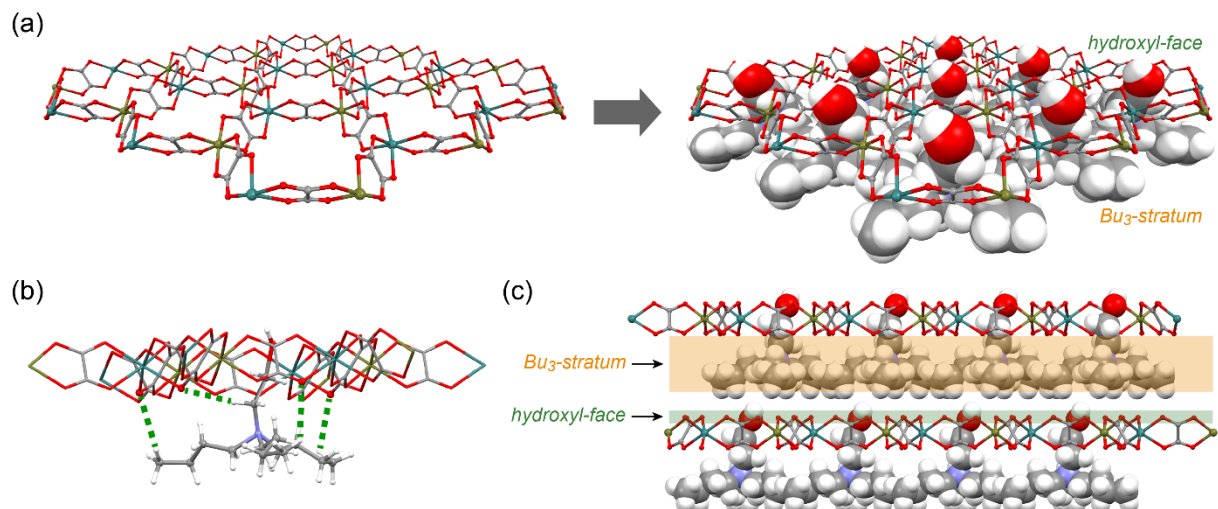


Fig. 2. (a) (left) Oxalate-bridged honeycomb [MnCr(ox)₃]⁻ sheet and (right) dissymmetric sheet with the *hydroxyl-face* and *Bu₃-stratum* labelled in **(B₃O)MnCr(A)**. (b) C-H...O(ox) hydrogen bonds between the (NBu₃(enOH))⁺ ion and [MnCr(ox)₃]⁻ sheet (green dotted line), where oxygen atoms participating in hydrogen bonds are depicted as red spheres. (c) Formation of the *hydroxyl-face* and *Bu₃-stratum* in the intersheet space, viewed along the *a* axis (gray, C; white, H; green, Cr; yellow, Mn; blue, N; red, O). The crystal structure was determined by SCXRD, where only one orientation of the disordered {NBu₃(enOH)}⁺ ions is shown.

1 H...O(ox) contacts shorter than the sum of van der Waals
 2 radii (2.72 Å²⁹), whereas the ethylene moiety of the enOH
 3 group has a C-H...O(ox) hydrogen bond with an H...O
 4 distance of 2.81 Å (vs. sum of the van der Waals radii: 2.90
 5 Å;²⁹ Fig. 2b). The C-H...O(ox) hydrogen-bonding
 6 interaction was also found between the *n*-butyl groups of the
 7 {NBu₃(enOH)}⁺ ion and the [MnCr(ox)₃]⁻ sheet (H...O
 8 distance: 2.80 Å). To the best of our knowledge, this is the
 9 first crystallographically characterized example of
 10 hydrogen-bonding interactions between the [MnCr(ox)₃]⁻
 11 sheets and the alkyl residues of the cation in the MOF. The
 12 hydroxy terminus protruded slightly out of the cavity to
 13 form a hydrophilic *hydroxyl-face* on one side of the
 14 [MnCr(ox)₃]⁻ sheet (Fig. 2c), whereas the other side is
 15 covered by a stratum of hydrophobic *n*-butyl groups (*Bu₃-*
 16 *stratum*). It is apparent that proton transfer occurs through

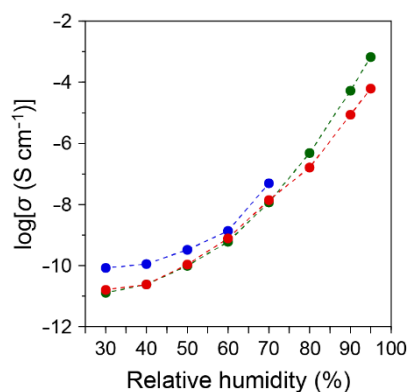


Fig. 3. Relative humidity dependence of proton conductivity (σ) at 25 °C of **(B₃O)MnCr** (red), **(B₂O₂)MnCr** (green), and **(B₃O)MnCr** (blue).

17 the interspace between the *hydroxyl-face* of one sheet and
 18 the *Bu₃-stratum* of an adjacent sheet. The packing structure
 19 of **(B₃O)MnCr(A)** is comparable to that of
 20 {NBu₃(CH₂COOH)}[MnCr(ox)₃]^{22,24} where the carboxy
 21 groups form a *carboxyl-face* on one side of the
 22 [MnCr(ox)₃]⁻ sheet, enabling a proton to migrate through
 23 the interspace between the *carboxyl-face* and the *Bu₃-*
 24 *stratum*. The enOH part group must also insert into the
 25 honeycomb cavity in **(B₂O₂)MnCr** and **(B₃O)MnCr** as
 26 hydrogen-bonding interaction between the enOH moiety
 27 and its surrounding cavity must stabilize the packing
 28 structure. Therefore, it is possible that the enOH-containing
 29 strata, *Bu₂(enOH)-stratum* and *Bu(enOH)₂-stratum*, form in
 30 the intersheet spaces in **(B₂O₂)MnCr** and **(B₃O)MnCr**,
 31 respectively.

32 Relative humidity (RH) dependence of proton
 33 conductivity (σ) at 25 °C for the three MOFs are shown in
 34 Fig. 3. The profile of **(B₃O)MnCr** was drawn up to 70% RH,
 35 above which it exhibited distinct deliquescence. Apart from
 36 sensitivity to moisture, the σ values of all three compounds
 37 show similar RH-dependence; namely, a steady increase in
 38 σ with increasing RH. The σ value of **(B₃O)MnCr** and
 39 **(B₂O₂)MnCr** reached 6.2×10^{-5} and 6.7×10^{-4} S cm⁻¹ at
 40 95% RH, respectively. As will be shown below, the σ
 41 values increased with increasing temperature to 50 °C; $1.7 \times$
 42 10^{-4} S cm⁻¹ for **(B₃O)MnCr** and 2.0×10^{-3} S cm⁻¹ for
 43 **(B₂O₂)MnCr**. The σ value of **(B₃O)MnCr** was estimated to
 44 be 4.9×10^{-8} S cm⁻¹ at 70% RH, which is apparently higher
 45 than those of **(B₃O)MnCr** (1.4×10^{-8} S cm⁻¹) and
 46 **(B₂O₂)MnCr** (1.2×10^{-8} S cm⁻¹) under the same conditions
 47 (i.e., 70% RH). It is noticed that reported alcohol-based
 48 MOFs show comparable proton conductivity under
 49 humidification ($10^{-6} - 10^{-4}$ S cm⁻¹).^{20,23,30-34}

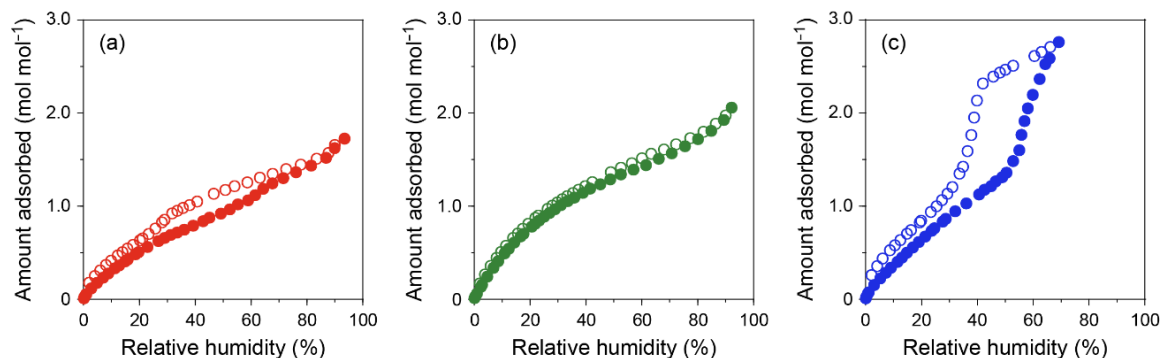


Fig. 4. Water adsorption (closed circles) and desorption (open circles) isotherms of (a) $(\text{B}_3\text{O})\text{MnCr}$, (b) $(\text{B}_2\text{O}_2)\text{MnCr}$, and (c) $(\text{BO}_3)\text{MnCr}$ (blue) at 25°C.

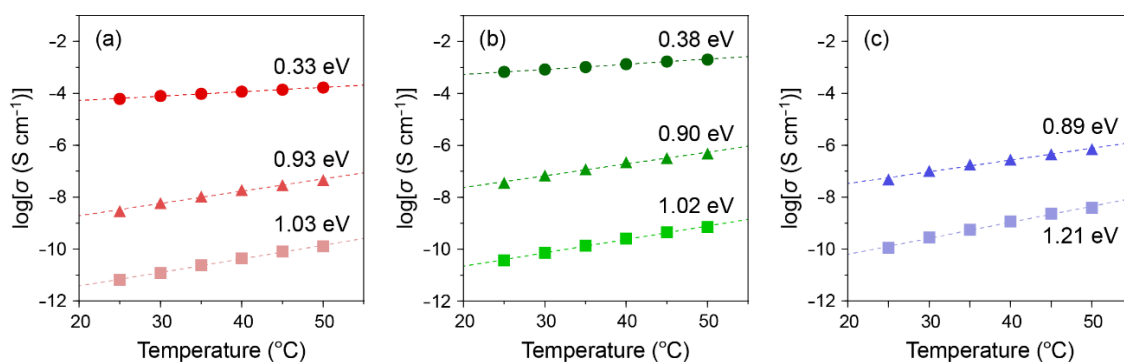


Fig. 5. Temperature dependence of proton conductivity (σ) of (a) $(\text{B}_3\text{O})\text{MnCr}$, (b) $(\text{B}_2\text{O}_2)\text{MnCr}$, and (c) $(\text{BO}_3)\text{MnCr}$ under different relative humidities (40% RH: square symbols, 70% RH: triangle symbols, 95% RH: circle symbols). The values indicated in the figures are the activation energies estimated from the Arrhenius equation.

To gain insight into the proton conduction mechanism, water vapor adsorption isotherms were measured at 25 °C (Fig. 4). In the case of $(\text{B}_3\text{O})\text{MnCr}$ and $(\text{B}_2\text{O}_2)\text{MnCr}$, water adsorption gradually increased with increasing RH and approached two equivalents of water at 95% RH; no noticeable hysteresis was observed during desorption. However, the isotherm of $(\text{BO}_3)\text{MnCr}$ shows a gradual uptake of water up to ca. 55% RH followed by a sharp uptake approaching approximately three equivalents of water at 70% RH. The highest water adsorption capacity in $(\text{BO}_3)\text{MnCr}$ is possibly related to the presence of hydrophilic cations in the intersheet space. The steady increase in adsorbed water in all compounds was manifested in the RH-dependent proton conductivity, which increased with the formation of hydrogen-bonding networks involving the adsorbed water molecules. The clear hysteresis observed in $(\text{BO}_3)\text{MnCr}$ is potentially a reflection of the hydrogen-bonding interactions of adsorbed water molecules with the $\{\text{NBu}_3(\text{enOH})\}^+$ ions in the intersheet space.

Vehicle^{35,36} and Grotthuss^{37,38} mechanisms have been proposed to describe proton transfer in solid compounds. The vehicle mechanism involves the transfer of a protonated species (e.g., H_3O^+ and NH_4^+) through space, whereas the Grotthuss mechanism involves proton migration through an

infinite hydrogen-bonding network. The two mechanisms are commonly distinguished by the activation energy for proton transfer (E_a); $E_a > 0.5$ eV for the vehicle mechanism whereas $E_a < 0.5$ eV for the Grotthuss mechanism.^{5,39} The E_a values of the present compounds were evaluated at different RHs by constructing Arrhenius plots for proton conductivity using the equation, $\sigma T = A \exp(-E_a/k_B T)$ (A : pre-exponential factor, k_B : Boltzmann constant; Fig. 5). When evaluated at 40 and 70% RHs, all compounds had E_a values higher than 0.5 eV. Therefore, the vehicle mechanism is responsible for proton transfer below 70% RH in all compounds. On the contrary, the E_a values of $(\text{B}_3\text{O})\text{MnCr}$ and $(\text{B}_2\text{O}_2)\text{MnCr}$ at 95% RH are less than 0.5 eV, indicating that proton transfer is governed by the Grotthuss mechanism. The highest σ value, $2.0 \times 10^{-3} \text{ S cm}^{-1}$, was achieved by $(\text{B}_2\text{O}_2)\text{MnCr}$ at 50 °C and 95% RH, which lies in the range for superprotonic level despite using the less acidic hydroxy groups as proton sources. The interconversion between vehicle and Grotthuss proton transfer mechanisms has been recognized in $\{\text{NBu}_2(\text{CH}_2\text{COOH})_2\}[\text{MnCr}(\text{ox})_3]$,²⁴ where the E_a value is 0.98 eV at 70% RH (vehicle mechanism) and 0.31 eV at 95% RH (Grotthuss mechanism). In this compound, the *carboxyl-face* and the *AcBu₂-stratum* act together to construct an intersheet hydrogen-bonding

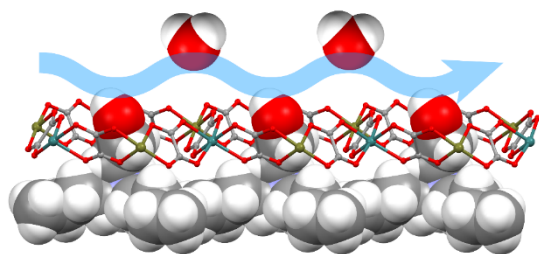


Fig. 6. Schematic of Grotthuss-type proton conduction on the *hydroxyl-face* facilitated by adsorbed water molecules (blue wavy arrow).

network at 95% RH. However, such intersheet hydrogen bond was ruled out in $(\text{B}_3\text{O})\text{MnCr}$ because of the hydrophobic nature of the *Bu*₃-stratum. Instead, the adsorbed water molecules can modify the *hydroxyl-face* to construct a hydrogen-bonding network (Fig. 6), which explains the interconversion of the proton transfer process from the vehicle mechanism below 70% RH to the Grotthuss mechanism at 95% RH. The same applies to $(\text{B}_2\text{O}_2)\text{MnCr}$, which shows a water vapor sorption isotherm and RH-dependent proton conductivity similar to those of $(\text{B}_3\text{O})\text{MnCr}$ (Fig. 4 and 5). It should be noted that the *Bu*₂(*enOH*)-stratum in $(\text{B}_2\text{O}_2)\text{MnCr}$ is not sufficient to prompt proton conduction, because proton transfer between the hydroxy groups of the *Bu*₂(*enOH*)-strata is potentially interrupted by the adjacent *n*-butyl groups. Although similar intervention is operative in the *Bu*(*enOH*)₂-stratum in $(\text{B}_3\text{O})\text{MnCr}$ under low RH conditions, the *enOH*-rich stratum facilitates the formation of an intersheet hydrogen-bonding network, even under relatively low RH conditions. The second water uptake process above 55% RH (Fig. 4) is assigned as the initiation of intersheet hydrogen bonding between the *hydroxyl-face* and the *Bu*(*enOH*)₂-stratum.

4. Conclusion

In summary, proton conductivity of a series of new 2D MOFs, $\{\text{NBu}_{4-n}(\text{enOH})_n\}[\text{MnCr}(\text{ox})_3]$, was governed by the *hydroxyl-face* that mediates proton transfer mainly based on the vehicle mechanism under low RH conditions. Under high RH conditions, the Grotthuss mechanism is operative whereby the *hydroxyl-face* is modified to favor increased proton conductivity along the hydrogen-bonding network. Adsorbed water molecules apparently facilitate superprotonic conductivity yielding the value of $2.0 \times 10^{-3} \text{ S cm}^{-1}$ for $(\text{B}_2\text{O}_2)\text{MnCr}$ at 50 °C and 95% RH, in which the less acidic hydroxy groups serve as proton sources. Increasing the number of *enOH* groups successively in the cation has a small but significant effect on proton conduction in $\{\text{NBu}_{4-n}(\text{enOH})_n\}[\text{MnCr}(\text{ox})_3]$, thereby indicating the importance of *enOH* groups in strata for increasing proton conductivity. The synthesis of analogous MOFs, $\{\text{NR}_{4-n}(\text{enOH})_n\}[\text{MnCr}(\text{ox})_3]$ (R: alkyl groups), is under way to investigate proton conducting behavior in light of intersheet hydrogen-bonding interactions.

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Supplementary data

Supplementary material is available at *Bulletin of the Chemical Society of Japan*.

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Finding

This work was supported by JSPS KAKENHI (Grant No. 20H02708 and 20H05623).

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Conflict of interest statement. None declared.

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Data availability

The data supporting this article have been included as part of the Supplementary material.

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