



Rapid Communication

A new 3D nickel(II) framework composed of large rings: Ionothermal synthesis and crystal structure

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ABSTRACT

Ionothermal reaction between Ni²⁺ and 1,3,5-benzentricarboxylic acid (H₃BTC) with [AMI]Cl (AMI = 1-amyli-3-methylimidazolium) as the reaction medium produced a novel 3D mixed-ligand metal-organic framework [AMI][Ni₃(BTC)₂(OAc)(MI)₃] (**1**) (MI = 1-methylimidazole) with [AMI]⁺ incorporated in the framework. The framework is formed by connecting 2D planes, made up of 32- and 48-membered rings, through 1D chains composed of 32-membered rings. The two BTC³⁻ ligands in **1** show the same connectivity mode with two bidentate and one μ_2 bridging carboxylic groups. This is a new connectivity mode to the already existing 17 in the Ni-BTC system. The role of MI and [AMI]Cl in the structure formation is discussed.

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Ionothermal method is an emerging technique in the field of synthetic solid state chemistry. The materials synthesized by this method thus far, which include aerosols [1], nanoparticles [2], zeolites [3–4], zeo-type materials [5–7], and metal-organic frameworks (MOFs) [8–19], indicate that ionothermal method can be applied to the syntheses of a wide range of materials. These examples also demonstrate that this technique can be a means to obtain unusual structural features, especially for MOFs, which may not be possible with the conventional hydrothermal or solvothermal techniques [8–10].

Most of such features can be attributed to the unique yet widely diverse characteristics of ionic liquids (ILs) that are used as the reaction media in ionothermal reactions. ILs are composed of organic cations and mostly inorganic anions [20–24]. The irregularly shaped and fluxional organic cations do not allow close packing of the ionic species into solids, thereby lowering the melting points down to the ambient temperatures [25,26]. At the same time, the ionic interactions make ILs highly ionic conductive, nonflammable, and they have negligible vapor pressures even at high temperatures [27–30]. Furthermore, by varying the structures of cations and/or anions, physicochemical properties of ILs

can be tuned to meet the specific requirements for a given reaction [31,32].

The use of ILs as reaction media for the synthesis of solid materials provides new opportunities to be explored. While the number of existing examples is still small, one may attempt to generalize the influences of ILs to the final MOF products: firstly, the chemical nature of ILs strongly influences the framework structure. Morris' recent paper clearly demonstrated this point by comparing the framework structures from the same reagents in ILs with different hydrophilicity/hydrophobicity [19]. Secondly, the cations of ILs can often function as templates and direct the framework structures [8–10]. Thirdly, the cations of reagents can interact with the anions of the ILs, which, sometimes, yield different results depending on the anions [9,10]. Though not comprehensive at the present, this generalization can be further extended to include many other possibilities of ionothermal method, which calls for more research activities in this field.

In the present paper, as a part of our recent efforts to explore the ionothermal synthesis system between metal cations and 1,3,5-benzentricarboxylic acid (H₃BTC) in various ILs, we synthesized a new MOF, [AMI][Ni₃(BTC)₂(OAc)(MI)₃] (**1**) (MI = 1-methylimidazole), from the reaction between Ni(OAc)₂ and H₃BTC in [AMI]Cl (1-amyli-3-methylimidazolium chloride). The small amount of MI present in [AMI]Cl or produced during the reaction (see below) participated in the framework leading to a new framework structure. The synthesis, crystal structure and other properties of **1** are presented herein.

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[AMI]Cl (pale yellow oil, yield: 72%) was prepared according to the literature method under an inert nitrogen atmosphere condition [6,27]. $^1\text{H-NMR}$ spectrum showed that our [AMI]Cl contained some impurities (Supporting Information; Fig. S1). Compound **1** was obtained from a series of ionothermal synthesis with $n_{\text{Ni}}:n_{\text{H}_3\text{BTC}} = 3.0\text{--}4.0:0.5$ with a step of 0.5 [33], indicating the resulting framework compound is a preferred or thermodynamic product. The crystal structure was determined by single crystal X-ray crystallography [34]. The experimental XRPD pattern for the title compound matches well with the one simulated from the single crystal structure data (Supporting Information; Fig. S2), indicating that **1** was isolated as a single phase.

The structure of **1** features a 3D framework, whose asymmetric unit contains three Ni^{2+} atoms, one AMI^+ cation, two BTC^{3-} , one OAc^- and three neutral MI molecules. As shown in Fig. 1, the three Ni centers are all in six-coordinated octahedra. The coordination sphere around Ni1 is formed by six carboxylic oxygen atoms of three BTC^{3-} ligands (O11, O12 from a chelate carboxylic group, monodentate O16A, and O21B from two BTC^{3-} ligands) and one OAc^- ligand (O1A and O2A). The constraint from the chelate carboxylic group makes a distorted octahedron. The more regular

octahedron around Ni2 is formed by four oxygen atoms from two chelate carboxylic groups (O13/O14 and O25/O26) on two different BTC^{3-} ligands and two nitrogen atoms (N33/N43) each from its own MI ligand. Ni3 functions as a vertex that joins three BTC^{3-} , one OAc^- and one MI ligand. Its equatorial plane is occupied by one chelate carboxylic group (O23D and O24D) and two monodentate carboxylic oxygen atoms (O15 and O22C). The axial positions are occupied by one oxygen (O2) from OAc^- ligand and one nitrogen (N51) from MI ligand.

The framework structure can be best described as a 3D architecture constructed from the interconnection of 2D layers extended along the bc plane with 1D chains along the a -direction. Four BTC^{3-} ligands alternately connect two Ni1 and two Ni2 atoms through monodentate and chelating coordination modes to generate a twisted 32-membered $[\text{Ni}_4(\text{BTC})_4]$ ring. The neighboring 32-membered rings are further connected through Ni1–O11/O12 bonds into 48-membered rings. The two types of rings share their edges and their extension generates a 2D layer along the bc plane (Fig. S3). Similarly, Ni2 and Ni3 centers are linked by four BTC^{3-} ligands through two kinds of connection modes with chelate and chelate/monodentate fashion to create a

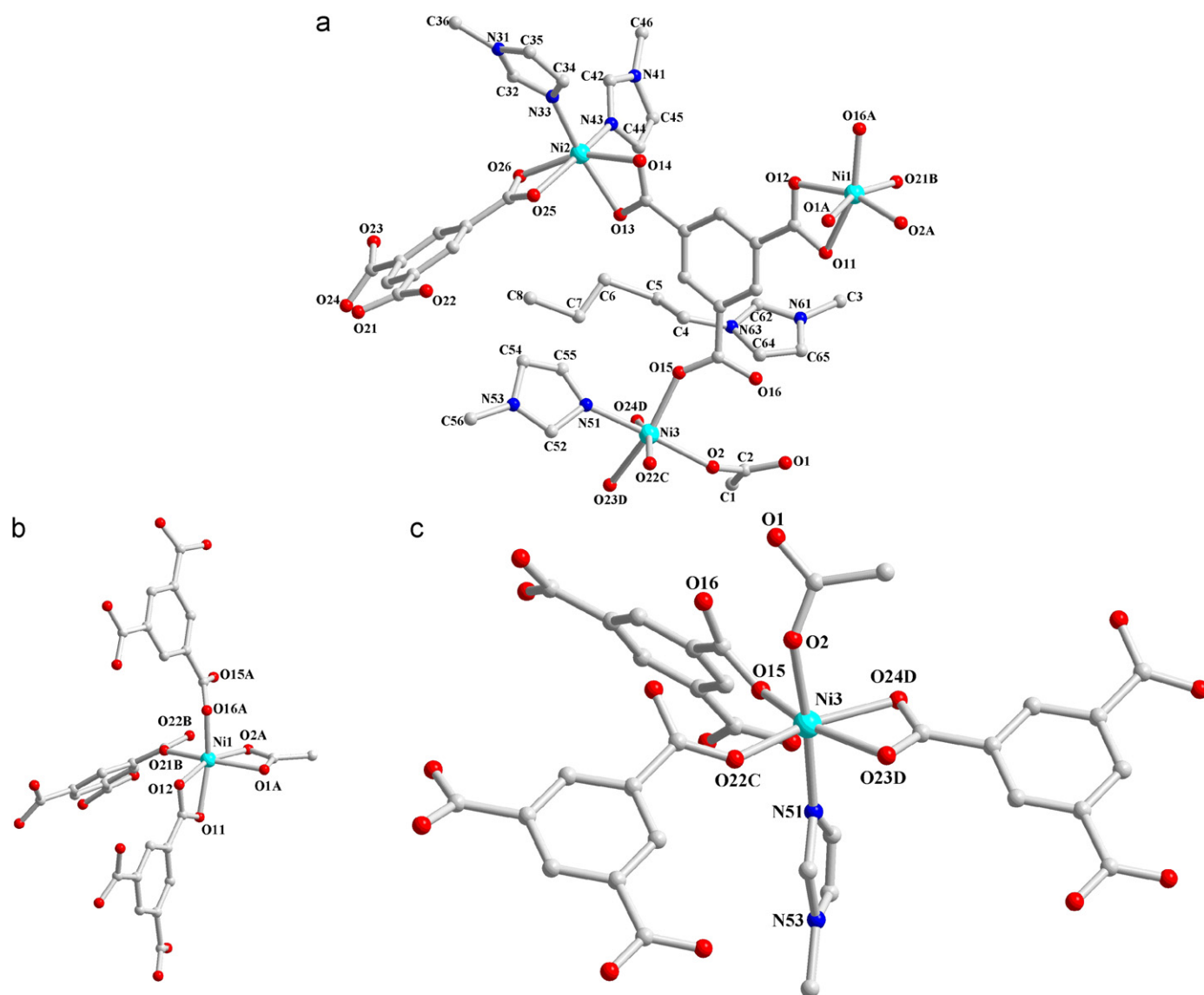


Fig. 1. Structure of **1**: (a) the asymmetric unit and the coordination sphere of Ni2, (b) the coordination sphere of Ni1 and (c) the coordination sphere of Ni3. (Symmetry code: $A = -1/2-x, -1/2+y, -1/2-z$; $B = -1/2+x, 5/2-y, -1/2+z$; $C = 1-x, 3-y, -z$; $D = 2-x, 3-y, -z$; $E = 2-x, 3-y, -z$.)

32-membered ring. These rings further grow into a 1D double chain through Ni3–O22 bonds along the *a*-direction (Fig. S4a). With the terminal Ni3–MI bonds pointing toward the inside the rings, the space of the rings is partially occupied (Fig. S4b). The layers are fused with 1D chains into a 3D network by the Ni2 nodes (Fig. 2). The channels are formed with 27.2% extra-framework volume calculated by PLATON [35], which is fully occupied by the [AMI]⁺ cations between the layers (Fig. 3). There exist $\pi \dots \pi$ stacking (the minimum centroid-to-centroid distance of 3.551 Å between the paired methylimidazole rings of MI) and electrostatic interactions (the distance being 3.907 Å between the AMI⁺ and OAc⁻) to reinforce the structure.

Thermogravimetric (TG) analysis shows that **1** starts to decompose at about 280 °C, which can be assigned to the breakdown of the MOFs, indicating that AMI⁺, MI, OAc⁻ and BTC³⁻ are decomposed synchronously (Fig. S5). XRD data on samples heat-treated at various temperatures also show that **1** loses its crystallinity at around 280 °C (Fig. S6).

The interesting feature of **1** is that its framework is constituted of large-size rings only. There are two Ni-BTC MOFs from ionothermal reactions in the literature, (EMI)₂[Ni₃(BTC)₂(OAc)₂] (EMI = 1-ethyl-3-methylimidazolium) [13] and (BMI)₂[Ni₃(HBTC)₄(H₂O)₂] (BMI = 1-butyl-3-methylimidazolium) [18]. These are all characterized by the tri-nuclear units formed by edge-sharing octahedral around the nickel centers. As a result, their structures are more condensed with 32- and 16-membered rings, respectively. It appears that the large rings in **1** are mainly due to the many monodentate MI ligands that coordinatively saturate Ni²⁺ ions, which otherwise would form more bonds with BTC leading to a more condensed framework with smaller rings. In this sense, **1** may be regarded as an example that gives an insight into an additional design principle for MOFs in IL media. That is, by employing a monodentate ligand along with the metal ions and multidentate linkers, MOFs with large rings can be formed. It would be more desirable if the MI ligands can be removed while the framework of **1** is not destroyed. Unfortunately, however, this

is not the case for **1**, probably because the secondary interaction of the MI ligands is not small. A better designed ligand with a similar function may be able to lead to porous MOFs by this strategy.

It is not clear where the MI ligands are from. The ¹H-NMR spectrum of our [AMI]Cl shows many extra peaks, indicating the

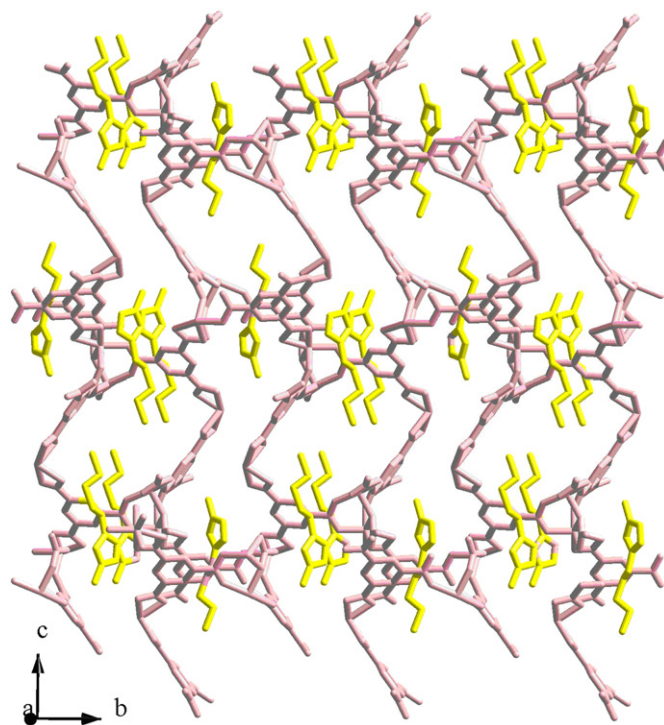


Fig. 3. The 3D network with the channels located by AMI⁺ with MI molecules omitted for clarity. The framework and AMI⁺ are marked as purple and yellow, respectively.

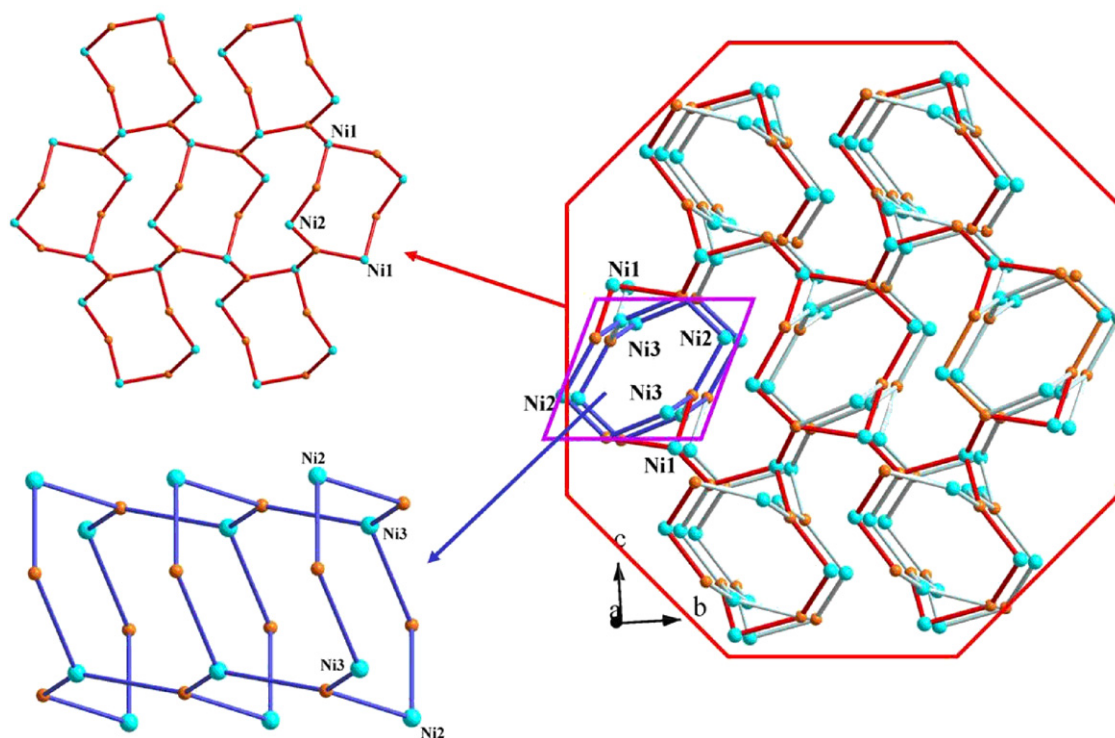


Fig. 2. The 3D framework formed by the linkage of the 2D layers via 1D double chains with MI and AMI⁺ omitted for clarity. BTC ligands are represented by orange balls.

presence of impurities, among which unreacted MI is highly possible. This impure MI could be the source of the MI ligands found in **1**. However, several experiments with deliberately added MI all failed in yielding even a small quantity of **1**, indicating that 'free' MI in the solvent could not be the source of the MI ligands in **1**. This leaves us with the only possibility that MI is produced *in-situ* through the decomposition of [AMI]Cl or other impurities. There are examples of MOFs whose ligands are similarly produced by the decomposition of solvent molecules [36]. Although there is no such example reported on ionothermal systems, such a pathway seems very likely for our system, which could be a new direction for future studies on ionothermal systems.

H₃BTC has been one of the most widely used ligands in MOF studies, and the Ni-BTC system has been extensively studied by the conventional solvothermal and hydrothermal techniques. A survey on the Cambridge Structure Database (CSD version 5.29) revealed that there are already 53 different compounds reported only for the Ni-BTC system; the connectivity modes around the BTC ligand can be grouped into 17 different modes (Supporting Information: Scheme S1 and Table S2). Remarkably, both of the two BTC in **1** show a yet new mode, making up a total of 18 different modes for BTC in the Ni-BTC system. Furthermore, the connectivity mode found in **1** is one of the only three that utilize all the carboxylic oxygen atoms for coordination to Ni centers, probably due to the highly polarizing nature of the IL solvent. These demonstrate the usefulness of the ionothermal technique in exploring reactions and obtaining new compounds with interesting structural features.

In summary, a novel 3D mixed-ligand MOF [AMI][Ni₃(BTC)₂(OAc)(MI)₃] was synthesized by the ionothermal method. The BTC³⁻ ligands alternately connect Ni centers to two kinds of 32- and 48-membered rings to a 3D framework. It appears that the presence of monodentate ligand MI induces the large-sized rings. The newly found connectivity mode of BTC in **1**, in addition to the known 17 modes of the widely explored Ni-BTC system, and its high degree of condensation demonstrate the unique potentials of ionothermal method in synthesizing new MOFs and, more importantly, in finding new structural features of MOFs.

Supporting Information

Physical measurements, XRPD pattern; TG graph, bond distances and angles, Ni-BTC MOFs in the literature. Crystallographic data for the structure reported here has been deposited with the Cambridge Crystallographic Data Centre (Deposition no. CCDC-681306). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2008.08.013](https://doi.org/10.1016/j.jssc.2008.08.013).

References

- [1] S. Dai, Y.H. Ju, J. Gao, J.S. Lin, S.J. Pennycook, C.E. Barnes, Chem. Commun. (2000) 243.
- [2] J. Wang, J.M. Cao, B.Q. Fang, P. Lu, S.G. Deng, H.Y. Wang, Mater. Lett. 59 (2005) 1405.
- [3] E.R. Parnham, P.S. Wheatley, R.E. Morris, Chem. Commun. (2006) 380.
- [4] E.R. Parnham, R.E. Morris, J. Am. Chem. Soc. 128 (2006) 2204.
- [5] E.R. Cooper, C.D. Andrews, P.S. Wheatley, P.B. Webb, P. Wormald, R.E. Morris, Nature 430 (2004) 1012.
- [6] E.R. Parnham, R.E. Morris, Chem. Mater. 18 (2006) 4882.
- [7] E.R. Parnham, R.E. Morris, J. Mater. Chem. 16 (2006) 3682.
- [8] L. Xu, E.Y. Choi, Y.U. Kwon, Inorg. Chem. 46 (2007) 10670.
- [9] L. Xu, E.Y. Choi, Y.U. Kwon, Inorg. Chem. 47 (2008) 1907.
- [10] L. Xu, E.Y. Choi, Y.U. Kwon, Inorg. Chem. Commun. 11 (2008) 150.
- [11] K. Jin, X.Y. Huang, L. Pang, J. Li, A. Appel, S. Wherland, Issue Series Title: Chem. Commun. (2002) 2872.
- [12] N.D. Danil, H.C. Chun, K.M. Kim, Chem. Commun. (2004) 1594.
- [13] Z.J. Lin, D.S. Wragg, R.E. Morris, Chem. Commun. (2006) 2021.
- [14] J.H. Liao, P.C. Wu, W.C. Huang, Cryst. Growth Des. 6 (2006) 1062.
- [15] C.Y. Sheu, S.F. Lee, K.H. Lii, Inorg. Chem. 45 (2006) 1891.
- [16] C.P. Tsao, C.Y. Sheu, N. Nguyen, K.H. Lii, Inorg. Chem. 45 (2006) 6361.
- [17] J.H. Liao, W.C. Huang, Inorg. Chem. Commun. 9 (2006) 1227.
- [18] Z. Lin, A.M.Z. Slawin, R.E. Morris, J. Am. Chem. Soc. 129 (2007) 4880.
- [19] Z. Lin, J.E. Wragg, R.E. Morris, J. Am. Chem. Soc. 129 (2007) 10334.
- [20] K.R. Seddon, J. Chem. Technol. Biotechnol. 68 (1997) 351.
- [21] T. Welton, Chem. Rev. 99 (1999) 2071.
- [22] K. Boutilier, L.R. MacGillivray, S. Subramanian, M.J. Zaworotko, J. Crystallogr. Spectrosc. Res. 23 (1993) 773.
- [23] S. Christie, S. Subramanian, L. Wang, M.J. Zaworotko, Inorg. Chem. 32 (1993) 5415.
- [24] M. Hasan, V.I. Kozhevnikov, M.R.H. Siddiqui, C. Femoni, A. Steiner, N. Winterton, Inorg. Chem. 40 (2001) 795.
- [25] H. Tokuda, K. Hayamizu, K. Ishii, M. Susan, M. Watanabe, J. Phys. Chem. B. 109 (2005) 6103.
- [26] A.S. Larsen, J.D. Holbrey, F.S. Tham, C.A. Reed, J. Am. Chem. Soc. 122 (2000) 7264.
- [27] P. Bonhôte, A.P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, Inorg. Chem. 35 (1996) 1168.
- [28] D. Camper, P. Scovazzo, C. Koval, R. Noble, Ind. Eng. Chem. Res. 43 (2004) 3049.
- [29] K.E. Gutowski, G.A. Broker, H.D. Willauer, J.G. Huddleston, R.P. Swatloski, J.D. Holbrey, R.D. Rogers, J. Am. Chem. Soc. 125 (2003) 6632.
- [30] J. Hoffmann, M. Nuchter, B. Ondruschka, P. Wasserscheid, Green Chem. (2003) 296.
- [31] J.D. Holbrey, K.R. Seddon, J. Chem. Soc. Dalton Trans. (1999) 2133.
- [32] P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, Wiley-VCH: Weinheim, Germany, 2003 (Chapter 3).
- [33] Ni(OAc)₂·4H₂O (3.0–4.0 mmol with a step of 0.5 mmol), H₃BTC (0.5 mmol, 0.105 g), were mixed with 1.0 mL [AMI]Cl (containing some impurities by ¹H-NMR in D₂O) in a 25 mL Teflon-lined stainless-steel autoclave. The mixture was heated at 180 °C for 3 days in a furnace, cooled naturally to obtain suitable green crystals of **1**. Yield based on H₃BTC: 62%. Elemental analysis (%) for C₄₁H₄₃N₈Ni₃O₁₄, found (calcd): C, 45.65 (47.08); H, 4.35 (4.15); N, 10.48 (10.72). IR data (in KBr, cm⁻¹): 3500(s), 3134(w), 3063(w), 2964(w), 2929(w), 2386(m), 2280(m), 1636(s), 1545(s), 1432(s), 1375(s), 1227(w), 1163(w), 1107(m), 937(w), 824(w), 767(m), 725(m), 661(w), 612(w), 527(w), 464(w).
- [34] Crystallographic data for **1**: C₄₁H₄₃N₈Ni₃O₁₄, crystal dimensions: 0.40 × 0.36 × 0.25 mm³, Fw = 1047.96, monoclinic, space group P2₁/n, a = 10.109(2), b = 15.178(3), c = 29.970(6) Å, β = 93.026(4)°, V = 4592.0(15) Å³, Z = 4, D_c = 1.516 g cm⁻³, μ = 1.291 mm⁻¹, F(0 0 0) = 2164, T = 173(2) K, GOF on F² = 1.012, Δρ_{max/min} = 0.007/0.000, Δρ_{max/min} = 2.161/−0.803. 33135 reflection measured, 11183 unique reflections (R_{int} = 0.0504) which were used in all calculations. R₁ = 0.0558, wR₂ = 0.1440 for I > 2σ(I). Bond distances and angles are in the Supporting Information (Table S1).
- [35] A.L. Spek, Acta Crystallogr. A46 (1990) C43.
- [36] S.M. Hawxwell, L. Brammer, Cryst. Eng. Commun. 8 (2006) 473.