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Cation-size-controlled assembly of the Ni(Ac)₂–1,4-H₂NDC system: geminal dicationic ionothermal syntheses, crystal structures and magnetic properties†

Bing An,^a Yan Bai,^{*a,b} Jun-Li Wang^a and Dong-Bin Dang^{*a}

Geminal dicationic ionic liquids with different alkyl spacer lengths regularly tune four MOF structures of two structure types in the Ni(Ac)₂–1,4-H₂NDC system, which in turn bring about the magnetic properties divided into antiferromagnetic and ferromagnetic couplings consistent with the structures.

Ionic liquids (ILs), which are credited with a number of unusual properties such as low vapor pressure, weak coordination and high thermal/chemical stability, have received considerable attention as “green alternatives” for synthesis and application.¹ Geminal dicationic ionic liquids (DILs), which carry two positive unit charges, are a class of materials with a growing portfolio of the proposed applications as catalysts, solvents, lubricants, electrolytes, *etc.*² In contrast to monocationic ionic liquids (MILs) with monovalent cations, DILs have been shown to possess superior physical and chemical properties in terms of higher densities and viscosities, greater thermal stabilities and wider liquid ranges.

The family of metal–organic frameworks (MOFs) is rapidly expanding with their rich structural aesthetics and optical, electric, magnetic and other potential applications.³ Recently, directional design and synthesis of functional MOFs have become a hot topic that most chemists make efforts to catch up with, such as understanding and chemically controlling the structures and the properties of these materials.⁴ The development of new synthetic methods is undoubtedly an effective strategy to achieve the above target. Ionothermal synthesis, being advantageous over the traditional hydro/solvo-thermal methods, may open up new research directions: (a) ILs show a

range of properties, which make them suitable for use as reaction media. (b) The variation of cations and/or anions of ILs can often make them function as “structure directing agents” which may provide a means to direct the structures of MOFs. (c) ILs can act as charge-compensating groups and offer an additional and effective way of reaction control to form ionic liquid crystals (ILCs).⁵

Although a remarkable increase of ILs participating in the synthesis of MOFs has been reported, all of them are MILs under investigation, especially imidazole-containing MILs. Mostly 1-alkyl-3-methylimidazolium MILs were used to study the influence on different metal–organic ligand systems.⁶ So far, only a few studies have explored how the alkyl chain length of a 1-alkyl-3-methylimidazolium cation (abbreviated as [C_nMIm]⁺) impacts the structures.^{5c,7} Compared to MILs, DILs contain two tunable functional terminal cation groups, which may give rise to significant changes in the MOF structures, but there is no study on this aspect and it needs more research activities. In the present work, we synthesized and used four sorts of geminal 1,3-bis(3-methylimidazolium-1-yl)alkyl bromide DILs with different alkyl spacer lengths from three to six carbons as solvents. In order to isolate the effect of the cation parts, we have fixed all the other variables such as the anion of DILs, the type of reagent metal ion and the ligand. In comparison with the flexible and long organic carboxylic acid ligands, the size of rigid 1,4-H₂NDC (1,4-H₂NDC = 1,4-naphthalenedicarboxylate acid) is suitable to study the size of ionic liquids, and it also has the role in controlling the aesthetically pleasing molecular structures.⁸ Therefore, by adopting the Ni(Ac)₂–1,4-H₂NDC system, four MOFs in two structure types were obtained: [C₃(MIm)₂][Ni(1,4-ndc)Br]₂ **1** and [C₄(MIm)₂][Ni(1,4-ndc)Br]₂ **2** (type A), [Ni₃(1,4-ndc)₄(MIm-C₅Im)₂(H₂O)₂] **3** and [Ni₃(1,4-ndc)₄(MIm-C₆Im)₂(H₂O)₂] **4** (type B).[‡] Surprisingly, the magnetic properties of **1–4** are also divided into two types, dominant antiferromagnetic (AFM) and ferromagnetic (FM) coupling interactions, which correspond to the structure types A and B, respectively.

The single crystal X-ray diffraction analysis reveals that the structures of **1** and **2** feature a two-dimensional anionic layer

^aHenan Key Laboratory of Polyoxometalate Chemistry, Institute of Molecular and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, P.R. China

^bState Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P.R. China. E-mail: baiyan@henu.edu.cn, dangdb@henu.edu.cn; Fax: (+86)-371-23881589; Tel: (+86)-371-23881589

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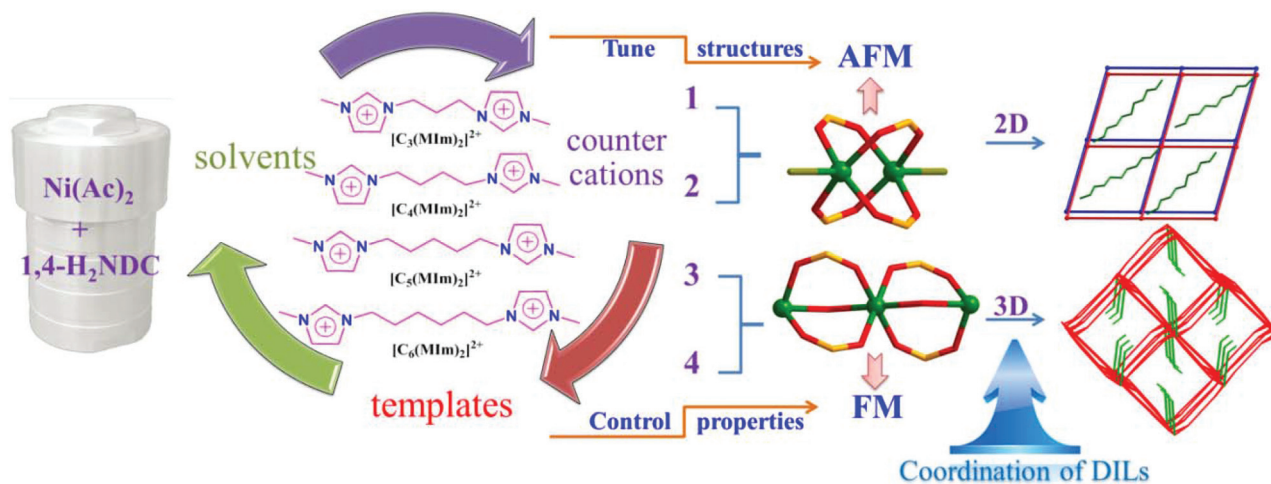


Fig. 1 Schematic representations of the reactions, the SBUs and the structures of 1–4 in two structure types with DILs as multifunctional roles in the ionothermal synthesis. Note that the DILs tune structures to bring about the magnetic properties with antiferromagnetic and ferromagnetic couplings, respectively.

sandwiched by DIL cations, $[\text{C}_3(\text{MIm})_2]^{2+}$ and $[\text{C}_4(\text{MIm})_2]^{2+}$, respectively (Fig. 1). Both structures consist of two $[\text{Ni}(1,4\text{-ndc})\text{Br}]^-$ units and one DIL cation, in which $1,4\text{-ndc}^{2-}$ serves as a tetradentate ligand bridging four nickel ions through four monodentate carboxylate oxygen atoms (Scheme S1†). The Ni(II) site lies in five-coordinated square pyramidal geometry with an O_4Br set from one Br^- and four $1,4\text{-ndc}^{2-}$ ligands. A pair of Ni centres is bridged by O–C–O rods from four cross-linked $1,4\text{-ndc}^{2-}$ ligands to form a paddlewheel-like cluster $[\text{Ni}_2(\text{O}_2\text{C})_4]$ as a secondary building unit (SBU). The Ni...Ni separations are 2.85 Å for 1 and 2.84 Å for 2. Each SBU extends out to connect four adjacent SBUs by the bridging interaction of $1,4\text{-ndc}^{2-}$ ligands giving rise to a 2D (4,4)-anionic layer (Fig. S3†). The adjacent layers are stacked in an AB sequence, and the DIL cations are located at the interlayer spaces.

The isostructural 3 and 4 are 3D network structures consisting of centro-symmetric trinuclear nickel SBUs and two crystallographically independent $1,4\text{-ndc}^{2-}$ ligands. The two $1,4\text{-ndc}^{2-}$ adopt $\mu_2(\eta_1)-(\eta_1)$ and $\mu_4-(\mu_2-\eta_1:\eta_1)-(\mu_2-\eta_1:\eta_1)$ bridging modes. What merits our attention is that the $[\text{MIm}-\text{C}_5\text{Im}]^+$ and $[\text{MIm}-\text{C}_6\text{Im}]^+$ segments come from the *in situ* decomposition of the corresponding raw material DILs, $[\text{C}_5(\text{MIm})_2]^{2+}$ and $[\text{C}_6(\text{MIm})_2]^{2+}$. Both of them lose one methyl to participate in coordination. Each of the two equivalent terminal Ni1 atoms is hexa-coordinated by four oxygen atoms of four $1,4\text{-ndc}^{2-}$ ligands in the equatorial plane of the octahedron, one O1W of the bridging water molecule and N1 of $[\text{MIm}-\text{C}_5\text{Im}]^+$ or $[\text{MIm}-\text{C}_6\text{Im}]^+$ located in the axial positions. The coordination geometry around the central metal ion Ni2 is also a distorted octahedron involving four $1,4\text{-ndc}^{2-}$ ligands, oxygen atoms from each of the four bridging bidentate carboxyl groups constituting the equatorial plane. The apical positions are occupied by two symmetric bridging water molecules. The linkages of Ni1 and Ni2 are two $\mu_2-\eta_1:\eta_1$ carboxyl groups and $\mu_2\text{-H}_2\text{O}$.

The distance between Ni1 and Ni2 is about 3.5 Å, indicating the absence of any bond between the two nickel centres. The Ni1–O1W–Ni2 angle in the bridge part is 113.6° for 3 and 115.9° for 4. Each Ni_3 segment formed by distorted corner-sharing octahedra is double-cross-linked to eight different Ni_3 segments through two types of $1,4\text{-ndc}^{2-}$ backbones to generate a 3D framework. N-donor imidazole segments pointing to the voids of the framework have no contribution to dimension expansion (Fig. S10†). If each Ni_3 unit acts as a node, the overall framework can be simplified as eight-connected CsCl-type topology (Fig. S11†).⁹

The solid-state direct current (dc) magnetic measurements for 1–4 were performed in the temperature range of 1.8–300 K and in a magnetic field of 1 kOe (Fig. 2). The magnetic behaviors indicate that both 1 and 2 (type A) are antiferromagnetic Ni(II)–Ni(II) exchange couplings inside their dimeric structures, while that of linear Ni(II) trimers in 3 and 4 (type B) exhibits the presence of weak ferromagnetic interactions. The distances between two nickel(II) ions within a well-isolated paddlewheel Ni(II) dimer unit connected through carboxyl groups in 1 and 2 suggest the existence of the super-exchange coupling interactions among the metal centers.¹⁰ The magnetic data of 1 and 2 have been analyzed using the Bleaney–Bowers equation

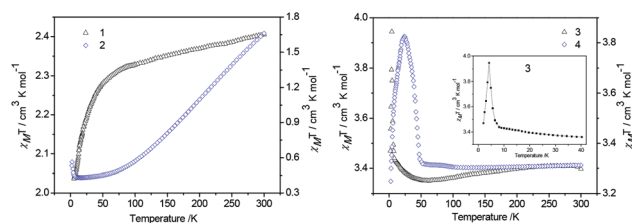


Fig. 2 Temperature variations of the magnetic susceptibility of 1–4 as $\chi_M T$ vs. T . 1 and 2 show antiferromagnetic couplings (left); 3 and 4 (type B) exhibit the presence of weak ferromagnetic interactions (right).

(ESI† eqn 1) derived from the isotropic spin Heisenberg Hamiltonian $H = -2JS_1S_2$ ($S = 1$) and the exchange coupling constants of the fitting results are $J = -29.76 \text{ cm}^{-1}$ for **1** and $J = -3.44 \text{ cm}^{-1}$ for **2**. Note that the magnetic coupling may also include a zero field splitting (ZFS) contribution, as it is customarily observed in most Ni(II) complexes.¹¹ We also fit the magnetic properties considering the ZFS factor in ESI†. The result indicates that polymer **2** has a larger ZFS parameter than polymer **1**, which may cause the differences (χ_{MT} vs. T shape and J value) in **1** and **2**.

For **3** and **4**, we have fitted the magnetic data to the simple model derived for a centrosymmetrical $S = 1$ linear trimer with the Hamiltonian $H = -2J(S_1S_2 + S_2S_3)$, where S_2 is the spin state of the central Ni(II) ion. The consequence of J values is positive ($J = 2.78 \text{ cm}^{-1}$ for **3** and $J = 4.88 \text{ cm}^{-1}$ for **4**), which suggests that the exchange couplings between neighboring nickel centers are ferromagnetic. The structure of **3** and **4** shows that three Ni(II) ions are connected by an aqua and a carboxylate bridge. For the aqua pathways, the Ni–O–Ni bond angles are out of the range of 80–100° for ferromagnetic coupling. Hence, the overall ferromagnetic interaction should originate from the ferromagnetic contribution of carboxylate bridges that is larger than the antiferromagnetic contribution of aqua bridges.¹² In short, the structures generated from different sorts of metal centers by ionothermal synthesis have some relationship with the magnetic properties (see ESI† for details).

Remarkably, the crystal structures of **1–4** reveal that multiple chemical identities of DILs participate in the architecture of the final materials. As discussed above, type A is a typical (4,4) grid framework comprising the paddle-wheel SBUs, in which DIL cations as structure directing agents are located at the interlayer spaces as well as Br[−] anions enter the final structures. Rich π electronic imidazole DILs have an advantage of generating $\pi \cdots \pi$ interactions to make them stable. Besides, the grid size of the overall rigid framework can also be restrained by the size of the ligand. Just as **1** and **2** even including the reported isostructural Cd–H₂NDC structure of [EMIm]⁺, small sized ILs can perfectly and stably accommodate inside.¹³ With increasing length of the alkyl spacer of geminal DIL cations, owing to steric hindrance and charge repulsion, the DIL cations may be unstable to fill the voids, and the structure turns out to be a 3D type B framework with the linear trinuclear Ni(II) SBUs. Apparently, there is a characteristic in type B that partially decomposed DILs act as flexible ligands coordinating to Ni(II) ions. According to the previously reported thermal stability and degradation mechanism of ILs, imidazole MILs incline to decompose into an alkyl halogen and the residual imidazole group.¹⁴ As a consequence, this *in situ* reaction of DILs provides a specific coordination access to generate a diversity of MOF architectures.

Up to now, a large number of chemists have focused on “how anions of MILs tune the structures on different metal-carboxylic acid systems”, but only a few have paid regular attention to the MOFs controlled by cation sizes with different alkyl chain lengths. Particularly on DIL syntheses, there is no

report to the best of our knowledge. In our study, DILs as multiple functional reaction media are adopted for the first time to synthesize new MOFs. The systematic investigation and analysis about the influence of the alkyl spacer lengths of DIL cations on the structures as well as the magnetic properties of the products show that DILs can bring about a variety of magnetic properties by means of tuning the structures into different groups, which gives a possible way to synthesize functional MOF materials with structural controllability. Further studies on these aspects are called for.

In conclusion, we have explored the ionothermal synthesis of the Ni(Ac)₂–1,4-H₂NDC system in a host of DIL media, four geminal 1,3-bis(3-methylimidazolium-1-yl)alkyl bromide DILs with the alkyl spacer length varying from propyl to hexyl. Interestingly, we obtained four frameworks grouped into two structure types, in which type A exhibits AFM coupling interactions and type B exhibits FM coupling interactions. It is expected to be of importance in investigating the relationship between features which are controlled by ILs and resulting magnetic properties. Certainly, our work is just the beginning of such a paramount task, and a large volume of research needs to be done.

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Notes and references

† Syntheses. A mixture of 1,4-H₂NDC (1 mmol), Ni(Ac)₂·6H₂O (1.5 mmol) and DILs (1.5 g) was transferred to a 25 mL Teflon-lined steel autoclave and kept at 180 °C for 3 days under autogenous pressure. After cooling down to room temperature, green crystals of **1–4** were obtained, respectively.

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