Organically-templated Kagomé compounds containing two transition metal ions†

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Kagomé compounds containing two transition metal ions, Co^{II} and Ni^{II}, in different proportions have been synthesized, and their magnetic properties have been found to exhibit interesting differences.

Transition metal compounds with the Kagomé lattice have been of great interest due to their novel magnetic properties, since the Kagomé lattice formed by corner-shared triangles of unpaired spins is expected to show magnetic frustration.[1] A majority of the Kagomé systems belong to the family of jarosites containing Fe^{III} ions.[2] These compounds generally show characteristics of frustrated low-temperature antiferromagnetism and occasional long-range antiferromagnetic ordering in the ground state.[3] Thus, antiferromagnetic ordering at 61.4 K has been reported recently in a pure iron jarosite.[3a] Magnetic properties of Co^{II} ($S = 3/2$) compounds are comparable to those of Fe^{III} ($S = 5/2$) compounds.[4] V^{III} ($S = 1$) and Cr^{III} ($S = 3/2$) jarosites are found to exhibit ferromagnetic coupling within the triangles of the Kagomé layers.[5,6] Ferromagnetic interactions occur in Fe^{II} ($S = 2$) as well as mixed-valent Fe^{II}/Fe^{III} Kagomé compounds.[7] Magnetic frustration in a Cu^{II} ($S = 1/2$) Kagomé compound has also been reported.[8] A Ni^{II} ($S = 1$) sulfate with the Kagomé lattice is shown to exhibit canted antiferromagnetism with magnetic polarization at low temperatures.[9]

There have been several theoretical studies of magnetic frustration in Kagomé compounds.[10] Kagomé compounds comprising transition metal ions with integer spins are suggested to give rise to ferro/ferrimagnetic interactions, while odd-half integer spins would show frustrated ground states. In the light of these observations, we considered it important to explore Kagomé compounds containing two transition metals with different spin configurations. A mixed transition metal compound, $(Co_xNi_{1-x})_3V_2O_8$, with an arbitrary composition has been reported without proper structural characterization.[11a] Kagomé compounds containing Cu^{II} and a non-magnetic divalent ion (Zn^{II} and Cd^{II}) have been examined.[8b,11b] We have sought to examine compounds with the Kagomé structure formed by Co^{II} ($S = 3/2$) and Ni^{II} ($S = 1$) and have been able to synthesize two organically templated mixed metal sulfates of the formulae, $[C_4N_2H_{12}][NH_4]_2[Co_2NiF_6(SO_4)_2]$, **1**, and $[C_4N_2H_{12}][NH_4]_2[CoNi_2F_6(SO_4)_2]$, **2**, containing Co^{II} and

Ni^{II} ions in 2:1 and 1:2 ratios. We have characterized them with respect to the chemical composition as well as the structure. While both **1** and **2** possess the Kagomé structure, their magnetic properties are significantly different.

Compounds **1** and **2** were synthesized under solvothermal conditions at 180 °C by varying the ratio of Co^{II} and Ni^{II} in the starting compositions (see ESI†). Chemical analysis of **1** and **2** was satisfactory. Both EDAX and ICP-OES analyses on single crystals of **1** and **2** indicated the ratio of Co : Ni to be 2 : 1 and 1 : 2 respectively (Fig. S1, ESI†).

Compounds **1** and **2** crystallize in the monoclinic crystal system with the $C2/m$ space group.[12] The asymmetric unit of both **1** and **2** consists of two metal atoms with occupancy of 0.5 and 0.25. We have assigned Co^{II} and Ni^{II} to the atoms with occupancy 0.5 and 0.25 in **1** and 0.25 and 0.5 in **2**, respectively, by considering the corresponding metal ratios from EDAX, ICP analysis and the ratios used in the synthesis. Structure determination of **1** reveals a 2D Kagomé network of Co^{II} and Ni^{II} connected by the F^- and SO_4^{2-} anions (Fig. 1(a) and 1(c)). The anionic $[Co_2NiF_6(SO_4)_2]^{4-}$
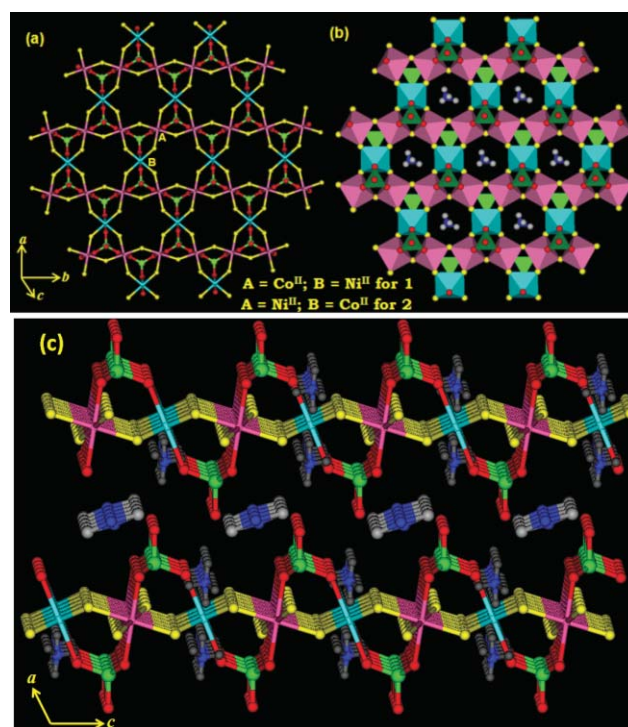

Fig. 1 (a) Ball-and-stick representation of the hexagonal Kagomé layer in **1** or **2**. (b) Polyhedral view of the Kagomé layer in **1**, showing the hexagonal channels occupied by NH_4^+ ions. (c) View down the b axis showing the stacking of the layers in **1**.

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† Electronic supplementary information (ESI) available: Synthetic procedures for **1** and **2**, EDAX and ICP-OES data, Fig. S2 and S3, crystallographic tables, bond distances and angles of **1** and **2**. CCDC reference numbers 768970 and 768971. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00445f

or $[CoNi_2F_6(SO_4)_2]^{4-}$ layer is templated by diprotonated piperizine (H_2PIP) and NH_4^+ cations, the SO_4^{2-} acts as a tridentate tris chelating ligand, connecting two Co^{II} and one Ni^{II} in **1** (one Co^{II} and two Ni^{II} in the case of **2**) at the corners of a triangle, interconnected by F^- bridges (Fig. 1 and Fig. S2, ESI†). Each triangle is extended in two-dimensions resulting in an ordered structure. The environment around each Co^{II} and Ni^{II} center is a distorted octahedron formed by two oxygen atoms (O2 and O2a) from the SO_4^{2-} tetrahedra in the axial positions and four bridging F^- anions in the equatorial positions forming a $Co^{II}F_4O_2$ or $Ni^{II}F_4O_2$ octahedron (Fig. S2, ESI†). These octahedra and SO_4^{2-} tetrahedra are fused together by Co–F–Ni, Co–F–Co (Ni–F–Ni), Co–O–S and Ni–O–S bonds in the crystallographic *ab* plane forming a 2D $[Co_2NiF_6(SO_4)_2]^{4-}$ or $[CoNi_2F_6(SO_4)_2]^{4-}$ Kagomé layer (Fig. 1(a) and 1(b)). In **1**, each $Co^{II}F_4O_2$ octahedron shares four of its Co–F vertices with two nearest $Co^{II}F_4O_2$ and $Ni^{II}F_4O_2$ octahedrons. The remaining two Co–O vertices share corners with the SO_4^{2-} tetrahedra. In **2**, the connectivity of the octahedra is comparable to that of **1**, except that the hexagonal channel of the Kagomé lattice is formed by the *cis*-corner-sharing of four $Ni^{II}F_4O_2$ and two $Co^{II}F_4O_2$ octahedra, while it is formed by four $Co^{II}F_4O_2$ and two $Ni^{II}F_4O_2$ in **1** (Fig. 1(a) and 1(b)). The M^{II}–O bonds (M = Co and Ni) are canted from the *ab*-plane and the M^{II}–O vertex forces a three ring trio of apical M^{II}–O bonds closer together to allow them to be capped by the SO_4^{2-} tetrahedra (Fig. S2, ESI†). The M^{II}–O/F bond distances in **1** are in the range of 2.025(2)–2.071(3) Å, and in **2** in the range of 2.015(4)–2.069(4) Å. Bond valence sum (BVS) calculations[13] give a valence sum of 2.16 for Co^{II}, 1.94 or Ni^{II} in **1** and 2.2 for Co^{II}, 1.97 for Ni^{II} in **2**. It is worth noticing that we did not succeed in the preparation of the Kagomé compound with 1 : 1 Co : Ni ratio, since the Kagomé lattice has a triangle structure and cannot be stable in such metal ratio.

We show the variable temperature magnetic susceptibility data of **1** recorded at 100 Oe under zero-field-cooled (ZFC) and field-cooled (FC) conditions in Fig. 2. The high temperature susceptibility data give a Weiss temperature of −89 K, with effective magnetic moment 7.2 μ_B per formula unit. The ZFC and FC data

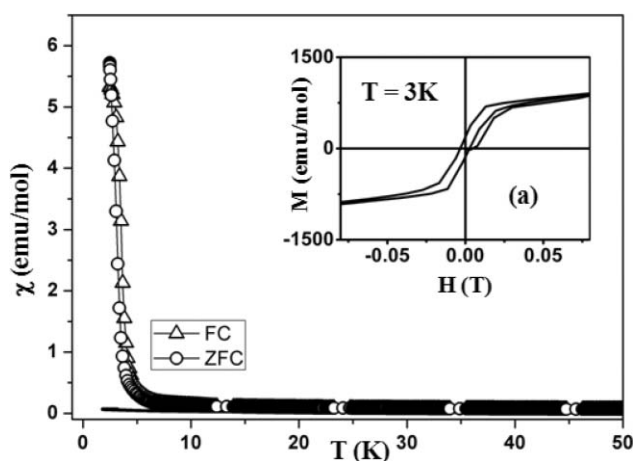of **1** show a small divergence, but there is no clear indication of frustration as in the case of the pure Co^{II} Kagomé compound.[4] Instead, we observe a very small magnetic hysteresis loop at low fields at 3 K (Fig. 2, inset (a)). In Fig. 3, we show ZFC and FC susceptibility data of **2** recorded at 100 Oe. In this case, the Weiss temperature is −101 K, with an effective magnetic moment of 6.45 μ_B per formula unit. The ZFC magnetic susceptibility of **2** starts rising around 8.5 K soon after deviating from the FC component as *T* is lowered, with a behavior similar to that of the pure Ni^{II} compound (Fig. 3).[9] **2** also shows distinct magnetic hysteresis at low magnetic fields at 3 K (Fig. 3, insets (a)) similar to the Ni^{II} compound.[9] The magnetic moments of **1** and **2** are higher than their spin-only moment values suggesting effective orbital contribution from the Co^{II} ion, which is quite well known.[14]
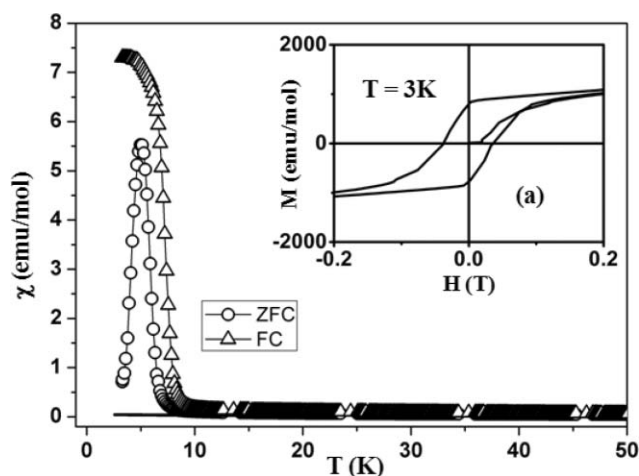

Fig. 3 Temperature dependence of the magnetic susceptibility (χ) of **2** at 100 Oe under field-cooled (FC) and zero-field-cooled (ZFC) conditions. Curie–Weiss fitting is shown as the solid line. Inset (a) shows magnetic hysteresis loop at 3 K.

The relation between the structures and the magnetic properties of **1** and **2** can be understood as follows. The Kagomé lattice has four neighbors with adjacent triangles sharing one lattice point. In case of Kagomé lattice with A and B ions (Fig. S3, ESI†) while every A has two A and two B nearest neighbors, every B has four A as its nearest neighbors. Given two metal ions, it is energetically favorable to form such a lattice with 2 : 1 ratio of metal ions, than causing lattice distortion with edge sharing octahedral topology. Although such geometry has inherent geometrical frustrations, the resulting electronic configuration can be different if the A and B possess different magnitude of spin moments.

In a triangle with three spins, interacting *via* Heisenberg antiferromagnetic exchange, if we consider all the three spins to be half-odd-integer (1/2, 3/2, 5/2 *etc.*), the ground state is multifold degenerate with many possible configurations with same energy. On the other hand, if all the spins are integers, the ground state is a non-degenerate singlet with a unique spin configuration. These two constitute two extreme possibilities. The case with a mixed spin system is very different as has been analyzed before.[10c] If the spin of A is larger than that of B, the ground state would be somewhere between half-odd-integer spin lattice and integer

Fig. 2 Temperature dependence of the magnetic susceptibility (χ) of **1** at 100 Oe under field-cooled (FC) and zero-field-cooled (ZFC) conditions. Curie–Weiss fitting is shown as the solid line. Inset (a) shows the magnetic hysteresis loop at 3 K.

spin lattice, depending strongly on the relative spin magnitudes. However, if the spin magnitude of B is larger than that of A, the resulting spin configuration would be close to that of an integer spin system.

Compounds **1** and **2** synthesized by us represent the above two cases of mixed spin Kagomé systems. **1** is expected to show properties reminiscent of a mixed behavior somewhere between Co^{II} and Ni^{II} compounds. On the other hand, **2** with each Co^{II} ($S = 3/2$) interacting with four Ni^{II} ($S = 1$) should behave like the integer-spin pure Ni^{II} Kagomé compound.[9] Thus, the Weiss temperature of **1** (−89 K), is larger than that of the pure Co^{II} Kagomé compound.[4] As can be seen in Fig. 2, at high temperatures, **1** exhibits an antiferromagnetic behavior and as temperature is lowered, the ZFC and FC curves follow each other down to low-temperatures, beyond which the FC susceptibility increases faster than its ZFC counterpart, deviating at low temperature. The antiferromagnetic coupling observed in **1** is in accordance with Goodenough–Kanamori–Anderson superexchange rules, as the M–F–M angle is in the range of ~ 130°.[15] We conclude that the Kagomé unit cell in **1** is somewhat polarizable at low-temperatures due to the geometry-related energy scale whose magnitude is smaller than the Weiss constant. The very small hysteresis suggests polarization at low-temperatures (see Fig. 2, inset (a)).

The Weiss constant of **2** in the high temperature limit is close to the value reported for the pure Ni^{II} Kagomé system.[9] Also, like in the pure Ni^{II} compound, **2** is magnetically polarized. While in the pure Ni^{II} Kagomé compound, polarization is due to Dzyaloshinsky–Moriya interactions in the out-of-plane direction, in **2** the mixed nature of spin interactions within the unit cell has a magnetic polarization component at low-temperatures. The hysteresis behavior of **2** is comparable to that of the pure Ni^{II} Kagomé compound [9] as can be seen in Fig. 3 (inset (a)).

In conclusion, we have been able to synthesize two Kagomé compounds containing Co^{II} and Ni^{II} ions in different proportions and characterize them by elemental analysis and single crystal X-ray crystallography. Our magnetic studies show marked differences in the magnetic properties, particularly at low temperatures depending on the Co^{II} : Ni^{II} ratio, due to the inherent geometrical frustration in the lattice.

Acknowledgements

Notes and references

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