

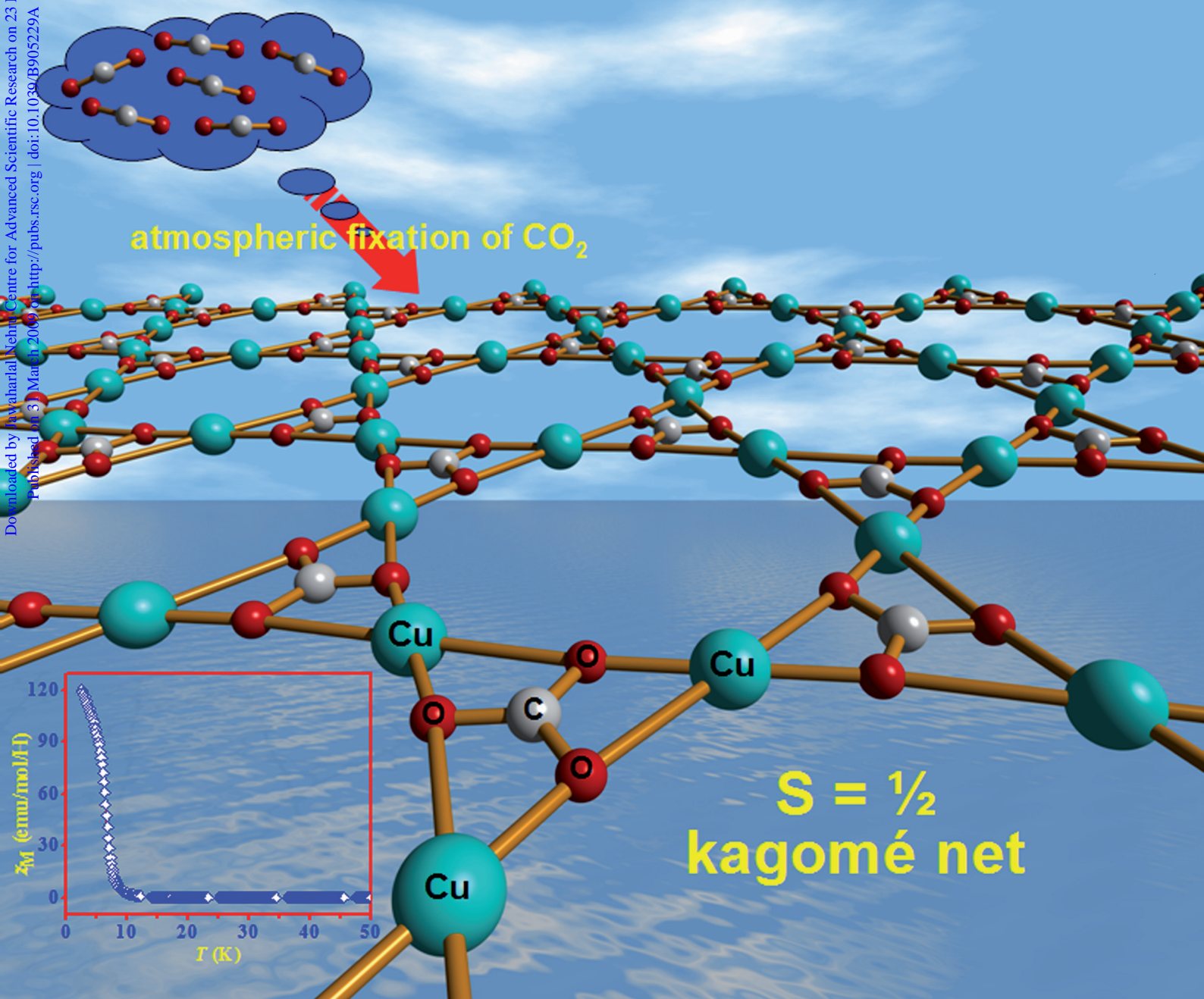
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A planar Cu²⁺ (S = 1/2) kagomé network pillared by 1,2-bis(4-pyridyl)ethane with interesting magnetic properties†

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The reaction of Cu(ClO₄)₂·6H₂O and 1,2-bis(4-pyridyl)ethane (bpe) in basic aqueous solution yields a 3D compound, {[Cu₃(CO₃)₂(bpe)₃·2ClO₄]_n} (1) through the atmospheric fixation of CO₂ composing Cu(CO₃) kagomé layers pillared by the bpe linker that exhibit weak antiferromagnetic interaction in the kagomé layer and interlayer ferromagnetic coupling at low temperature.

Geometrical frustration is common in many low-dimensional insulating systems. Magnetic frustration generally arises due to geometrical effects with competing magnetic interactions.^{1–3} Recently, there has been a large number of theoretical and experimental studies on various aspects of magnetic frustration in kagomé systems.^{4–16} Most of these systems belong to the family of materials known as jarosites.^{10,11,16} Jarosites and analogous materials with Fe³⁺ ions exhibit characteristics of frustrated low-temperature antiferromagnetism and occasional long-range antiferromagnetic ordering in the ground state.^{3,10,11} However, V³⁺ and Cr³⁺ jarosites are known to exhibit ferromagnetism and low-temperature antiferromagnetism,^{12–15} respectively while Cu²⁺ atacamite containing Zn²⁺ shows low-temperature polarized behaviour.¹⁶ Since jarosite-type materials are difficult to obtain in pure single crystalline form, novel synthetic routes, such as the hydrothermal methods have been employed recently by one of us to prepare organically templated kagomé compounds with interesting magnetic properties.^{4,7,17} Redox-based techniques have been employed very recently by Nocera's group to prepare single crystalline kagomé compounds with almost 100% coverage of magnetic ions.^{5,11,16} Beyond magnetism, recently, kagomé type compounds are also finding interest as porous materials.¹⁸ Of particular interest, Barth *et al.* constructed a chiral nanoporous kagomé lattice by the self assembly of simple ditopic organic molecules.¹⁹

Among the kagomé systems reported so far, there exists only one report on the S = 1/2 kagomé structure in pure form.²⁰ Since magnetic behaviour arises due to the electronic spin, which is

purely quantum in nature, the S = 1/2 moment represents the true quantum behaviour of a frustrated system. In our efforts to investigate kagomé compounds, specially with the S = 1/2 system, we have been able to synthesize a new compound 1 of the formula {[Cu₃(CO₃)₂(bpe)₃·2ClO₄]_n}. In this communication, we report the synthesis, structure and magnetic properties of a 3D metal–organic framework, (1) consists of 2D Cu(CO₃) kagomé layers pillared by the bpe organic linker.

Deep violet hexagonal crystals of 1 were prepared by the reaction of Cu(ClO₄)₂ and bpe in aqueous NH₃.† The IR spectrum (Fig. S1†) shows bands around 1621 cm⁻¹ and 1444 cm⁻¹ corroborating the ν(C=C) stretching of the pyridyl group and ν(COO) of the CO₃²⁻, respectively. The sharp bands in the region 1080–1104 cm⁻¹ arise from the ν(Cl–O) of the ClO₄⁻ anions. The purity of the compound was confirmed by elemental analysis and similarity between simulated and experimental PXRD patterns (Fig. S2†). The framework of 1 is thermally stable up to 260 °C (Fig. S3†).

Compound 1 crystallizes in the hexagonal *P*-6 space group§ and structure determination reveals a 3D pillared layer framework of Cu²⁺ composed of the mixed ligands CO₃²⁻ anion and bpe linker (Fig. 1). There are two crystallographically independent CO₃²⁻ dianions and both of them act as a tridentate tris-chelated ligand and connect three different Cu1 atoms forming a 2D [Cu(CO₃)_n] layer in the crystallographic *ab* plane (Fig. 1a, *top right* and Fig. S4†). All the oxygen atoms from the CO₃²⁻ anions act as a μ₂-oxo bridge between the Cu1 centres. Each Cu1 atom chelated to the two different CO₃²⁻ anions *via* O1, O1_{-l} and O2, O2_{-k} (l = -x + y, 1 - x; k = -x + y, -x, -z) forming a perfectly planar kagomé layer (Fig. 1a). Each layer is further pillared by the bpe organic linker resulting in a 3D pillared-layer framework with 1D hexagonal channels along the crystallographic *c*-axis occupied by the ClO₄⁻ anions, which neutralizes the remaining charge of the framework (Fig. 1b and Fig. S5†). The ClO₄⁻ anions in the channels are in symmetry related disorder and C atoms (ethanylene part, C81 and C82) of the bpe molecules are in orientational disorder with the occupancy ratio 0.5:0.5. The crystal is racemic twin with a 48:52 ratio. In the 3D framework Cu1–O bond distances are in the range of 1.949(4)–2.763(5) Å and the Cu–N bond distance is 1.987(3) Å, suggesting Jahn–Teller distortion around each octahedral Cu²⁺ centre. In the 2D kagomé layer the Cu1–O1–Cu1 and Cu1–O2–Cu1 angles are 173.0(3) and 175.5(3)°, respectively. Cu ··· Cu separations along the μ-O1, μ-O2 in the kagomé layer are 4.703, 4.625 Å, respectively and along the μ-bpe is 13.313 Å. The source of CO₃²⁻ is believed to be atmospheric by the nucleophilic fixation of CO₂ in the basic aqueous solution of Cu²⁺. Isolation of such carbonato bridged complexes from the reaction of nitrogen

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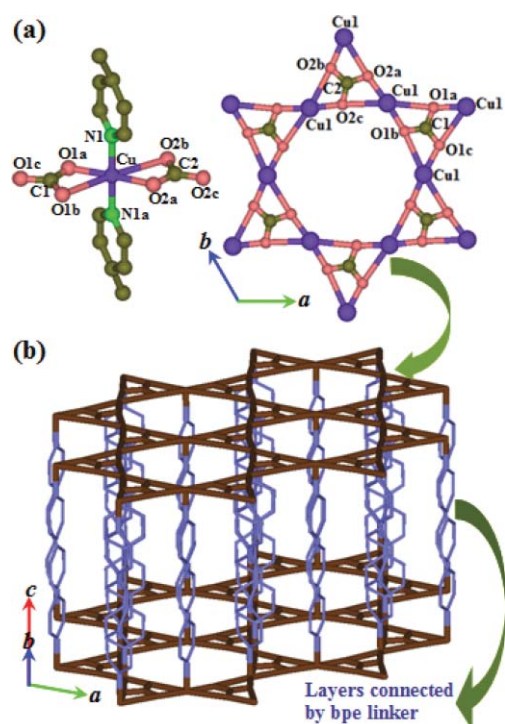


Fig. 1 Crystal structure of **1**: (a) *Left*: Coordination environment of Cu^{2+} ; Selected bond distances (Å): Cu–O1a, 1.949(4); Cu–O2a, 1.959(4); Cu–N1, 1.987(3); Cu–N1a, 1.987(3); Cu–O1b, 2.763(5); Cu–O2b, 2.669(5). *Right*: View of the 2D kagomé layer along the c axis. (b) View of the 3D framework inclined down to the b axis showing 2D kagomé layers are pillared by the bpe linker along the c axis.

containing ligands under aqueous basic conditions with transition metal ions is well documented^{21–24} and is also relevant to certain metalloenzymes, like carbonic anhydrase, D-ribulose *etc.*²⁵ The coordination chemistry of CO_3^{2-} is very rich and its different binding mode can generate complexes with different nuclearity leading to a wide variety of magnetic behaviour from strong to moderate or weak coupling which is either antiferromagnetic or ferromagnetic.^{23,24,26,27}

As can be seen from Fig. 2, the magnetic susceptibility is small down to 70 K and starts rising with a bigger slope as the

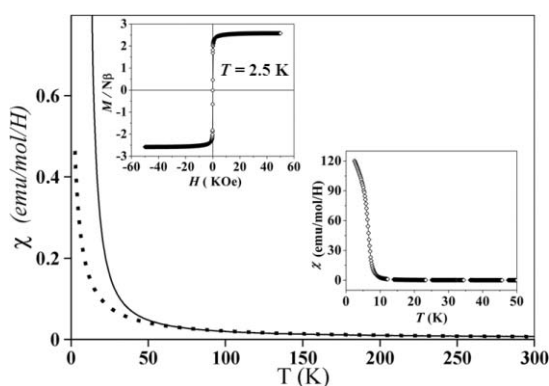


Fig. 2 Molar magnetic susceptibility (χ) as a function of T for **1** (solid line) at 100 Oe. Curie–Weiss fitting is shown as the dotted line. *Inset* (lower right): Temperature dependence of χ at 100 Oe at low temperature; *Inset* (upper left) Magnetic hysteresis loop for **1** at 2.5 K.

temperature decreases further down from $T = 12$ K. The high temperature data was fitted with the Curie–Weiss formula and the Weiss temperature (θ) and Curie constant (C) were found to be -2.13 K and $2.114 \text{ cm}^3 \text{ mol}^{-1}$, respectively. The fitted data is shown as a dotted line with the experimental data, where the T_N can be evaluated to be 70 K. The negative θ value suggests an overall antiferromagnetic exchange coupling in the layered structure. However, the strong rise of susceptibility at low-temperature suggests quite a different mechanism, as the T is lowered. The zero-field-cooled magnetic susceptibility *versus* temperature is shown as an inset of Fig. 2 (lower right) and a plot of $\chi_M T$ vs T is given in Fig. S6.† Increase in susceptibility as the temperature is lowered in both the plots suggests ferromagnetic interaction at low temperature. Magnetization (M) *versus* field (H) plot (Fig. 2 inset, upper left) shows a rapid increase and saturation above 2 kOe and a small hysteric loop with a coercive field of 8.5 Oe suggesting **1** behaves as a soft magnet (Fig. S7†). The saturation magnetization value at 50 kOe is $2.56 \text{ N}\beta$ close to three ferromagnetically coupled Cu^{2+} centres. The shape of the M vs H curve strongly supports ferromagnetic interaction of **1** at low temperature.

A closer look at the structure reveals that each magnetic ion is surrounded by four such ions through oxygens. The Cu–O–Cu angles are found to be $173.0(3)$ and $175.5(3)^\circ$ and it is symmetric for all magnetic ions. According to Goodenough–Kanamori rules, the super exchange processes through oxygens for this angle would be antiferromagnetic. Thus, in the layer, the interactions between Cu^{2+} centers are antiferromagnetic, with a small magnitude of exchange constants (θ value), as also can be seen from the small values of the susceptibility data down to $T = 12$ K (Fig. 2, inset *lower right*). In the kagomé layer each bridging oxygen atom is equatorially positioned to one copper atom and axially to another copper. As, oxygen bridging is of the axial–equatorial type with one shorter and one longer Cu–O bond, the magnetic coupling would be through $d_{x^2-y^2}$ and d_{z^2} orbitals; note that the latter has very low electron density. Consequently, the antiferromagnetic coupling would be smaller which is experimentally observed in the high-temperature region. Note that the θ value found in $\text{Cu}(1,3\text{-bdc})$ ²⁰ is -33 K, much higher than in our case. This is due to the fact that in $\text{Cu}(1,3\text{-bdc})$, the exchange is through the equatorial in plane COO-group. The magnetic moment calculated from the susceptibility data turns out to be $4.26 \mu\text{B}$ at room temperature for three Cu^{2+} ions, slightly higher than the theoretically calculated value. As has been discussed, the kagomé layers are connected through bpe pillars comprising of conjugated pyridine rings with ethylene ($-\text{CH}_2-\text{CH}_2-$) linkers. The overall angle between the Cu^{2+} centers through two adjacent bpe ligands varies quite considerably due to the sp^3 bonding in intervening CH_2 groups. The potential energy landscape for the C–C single bond rotation between two extreme conformers is quite small allowing flexibility in the structural disorder. However, magnetically, the higher energy conformation would allow for a canted spin configuration, according to exchange rules. Furthermore, accessing such a conformation is very unlikely at high temperature and the exchange process is dominated by the in-plane antiferromagnetic coupling. However, since the antiferromagnetic coupling itself is quiet small in magnitude, as the temperature is lowered further and at very low temperature, such conformation can be stable leading to magnetic polarization in the susceptibility data.

To understand two different regimes of interaction as the T is lowered, we have carried out specific heat measurements on **1** in the temperature range 2.5–25 K (Fig. 3). As can be seen, C_p/T keeps increasing with T , with no peak within this temperature range. The low T behavior does not conform to simple T^2 dependence. The data below 4 K can be fitted with linear dependence with a slope of 9.01. Above 4 K, the data can be fitted to a quadratic equation. The linear region at very low temperatures clearly suggests spin polarized interactions, while the quadratic term indicates in-plane interactions which are antiferromagnetic in nature.

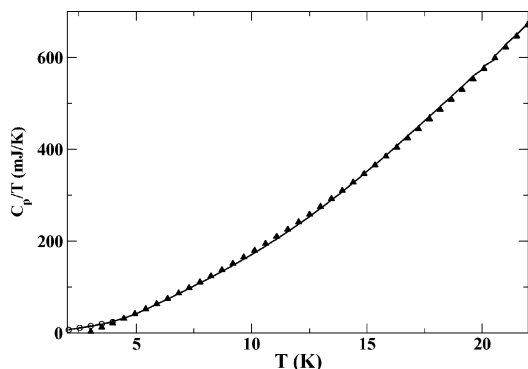


Fig. 3 Temperature dependence of the specific heat of **1** measured at zero field (solid line). Linear fit (open circles) of specific heat up to 4 K and quadratic fit (filled triangles).

In summary, **1** possesses a perfectly planar $S = 1/2$ kagomé layer pillared by an organic linker, forming a 3D pillared-layer framework. The low-temperature magnetic properties indicate the coexistence of two interactions, antiferromagnetic within the layer and ferromagnetic spin coupling between the layers in the framework. Materials with $S = 1/2$ ions on a frustrated lattice are of special interest in lieu of the theoretical predictions that such systems should exhibit spin liquid or an even more exotic behaviour due to strong quantum spin fluctuations. Compound **1** is therefore, interesting for the exploration of quantum spin fluctuation at different energy scales with dimension dependence.

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Notes and references

‡ Synthesis of **1**: Compound **1** was synthesized by a simple reaction at room temperature. The metal solution was prepared by dissolving 0.370 g (1 mmol) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 25 mL aqueous ammonia (20%). To the metal solution, 25 mL of equimolar (0.184 g) aqueous solution of 1,2-bis(4-pyridyl)ethane was added drop wise and stirred for 1 h. The mouth of the reaction vessel containing supernatant blue solution was wrapped with parafilm and kept undisturbed for slow evaporation of ammonia. After two days, ammonia evaporates slowly and hexagonal plate shaped crystals separate out. After about 5 days, the solution becomes

colourless leaving only violet crystals of compound **1**. The product was filtered and washed with distilled water several times. The crystals were examined under a microscope and a good single crystal was picked for X-ray diffraction study. Yield: 90.81% relative to copper. Anal. Calcd. for $\text{C}_{38}\text{H}_{36}\text{Cu}_3\text{N}_6\text{O}_{14}\text{Cl}_2$: C, 42.93; H, 3.39; N, 7.91. Found: C, 42.74; H, 2.98; N, 8.07. IR (KBr, cm^{-1}): 3100–3050w, aromatic $\nu(\text{C-H})$; 2935w, $\nu(\text{CH}_2)$; 1618 s, $\nu(\text{C=C})$; 1506w, 1443vs, $\nu_{\text{as}}(\text{C-O})$; 1346 m, $\nu_{\text{as}}(\text{CO}_2)$; 1103 s, 1088vs, $\nu(\text{ClO}_4)$; 1033w, $\nu_s(\text{CO})$; 842 s, $\delta(\text{CO}_2)$.

§ Crystal data for **1**: Formula, $\text{C}_{38}\text{H}_{30}\text{Cl}_2\text{Cu}_3\text{N}_6\text{O}_{14}$, $M_w = 1056.20$, Hexagonal, Space group $P-6$ (No. 174), $a = b = 9.3139(6)$ Å, $c = 13.3133(9)$ Å, $V = 1000.18(11)$ Å³, $Z = 1$, $\rho_{\text{calc}} = 1.754$ g cm^{-3} , $\mu(\text{MoK}\alpha) = 1.792$ mm⁻¹, $F(000) = 533$, $T = 100$ K; $\lambda(\text{MoK}\alpha) = 0.71073$ Å, $\theta_{\text{max}} = 27.3^\circ$, Total data = 9471, Unique data = 1560, $R_{\text{int}} = 0.040$, Observed data [$I > 2\sigma(I)$] = 1417, $R = 0.0437$, $R_w = 0.1127$, $GOF = 1.08$, Flack (x) = 0.48(3).

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