Candidate Quantum Spin Liquid due to Dimensional Reduction of a Two-Dimensional Honeycomb Lattice

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As with quantum spin liquids based on two-dimensional triangular and kagome lattices, the two-dimensional honeycomb lattice with either a strong spin-orbital coupling or a frustrating second-nearest-neighbor coupling is expected to be a source of candidate quantum spin liquids. An ammonium salt [(C3H7)3NH][Cu2(C2O4)3](H2O)2.2 containing hexagonal layers of Cu2+ was obtained from solution. No structural transition or long-range magnetic ordering was observed from 290 K to 2 K from single crystal X-ray diffraction, specific heat and susceptibility measurements. The anionic layers are separated by sheets of ammonium and H2O with distance of 3.5 Å and no significant interaction between anionic layers. The two-dimensional honeycomb lattice is constructed from Jahn-Teller distorted Cu2+ and oxalate anions, showing a strong antiferromagnetic interaction between S = 1/2 metal atoms with θ = −120 (1) K. Orbital analysis of the Cu2+ interactions through the oxalate-bridges suggests a stripe mode pattern of coupling with weak ferromagnetic interaction along the b axis, and strong antiferromagnetic interaction along the a axis. Analysis of the magnetic susceptibility shows that it is dominated by a quasi-one-dimensional contribution with spin chains that are at least as well isolated as those of well-known quasi-one-dimensional spin liquids.

Magnetic systems exhibit, most commonly, classical long-range order at low temperature. To avoid magnetic ordering the interactions between magnetic atoms can be frustrated by the topology of the underlying lattice and/or compete with one another, the dimensionality of the lattice can be reduced by weakening the interactions between planes or chains, or the spin of magnetic units can be reduced to S = 1/2 to promote quantum fluctuation1–5. Examples of geometric frustration include antiferromagnetic materials based on a triangular lattice or a Kagome lattice on which triangles share their corners rather than edges. For a perfect system, this frustration would result in the ground state being inherently highly degenerate, even a spin liquid state3–5. For real systems, the degree of frustration is described by the parameter f = hCW/TN, the Curie-Weiss temperature showing how strong the magnetic interactions are and the Néel temperature defining the onset of magnetic order. An unfrustrated system has f = 1, a spin frustrated system has f = 10 and in an ideal spin frustrated system f tends to infinity2,3.

Quantum spin liquids have attracted particular attention since Anderson proposed their possible connection to the superconductivity of cuprates6,7. But most compounds with triangular-lattices or Kagome lattices showed long-range magnetic order due to structural distortion or crystal defects8–15. In one dimensional system including KCuF3 and copper pyrazine dinitrate the spinon continuum associated with the spin liquid state has been observed directly and it has also been confirmed for the two-dimensional kagome system ZnCu3(OH)6Cl222,24,25.

Quantum spin liquids with two-dimensional lattices should not only be limited to triangular lattices and Kagome lattices2,26. The S = 1/2 honeycomb lattice (Figure 1) with strong spin –orbital coupling described by
the exactly-solvable Kitaev honeycomb model has been proposed as a candidate quantum spin liquid and may exhibit Majorana Fermions that could enable future schemes for quantum computation 27–31. This is an idealization of real systems where Heisenberg-like and next-nearest-neighbor couplings lead to an even richer assortment of phases, including other spin-liquids. However, the best-known model honeycomb compound Na2IrO3 shows long-range magnetic ordering at 13.3 K and other higher spin systems such as Bi3Mn4O12(NO3), Na2Co2TeO6, Na3Co2SbO6, Mn3Al9, Cu3Ni2SbO6, Cu2Co2SbO6, and Ba3Co2O6(CO3)0.2 – all order magnetically 32–37. The quest for honeycomb systems that exhibit strong magnetic frustration therefore continues to excite the physics community, and at the same time challenge the chemistry community.

In 2011, spin fluctuation was observed in a charge-transfer salt (BEDT-TTF)3[Cu2(C2O4)3](CH3OH)2 with forming a distorted honeycomb lattice, the Weiss constant was 29.8(7) K and there was no long-range magnetic ordering observed above 2 K 38. Two sets of spins exist in this compound: one coming from the donor molecules is similar to the triangular lattice in (BEDT-TTF)2Cu2(CN)3, the other coming from the anionic layer forming the honeycomb lattice 16. In order to focus on the properties of the honeycomb lattice, an ammonium salt [(C3H7)3NH]2[Cu2(C2O4)3](H2O)2.2 was synthesized and magnetic ordering was found to be strongly suppressed, setting a lower bound of 60 for the frustration parameter f.

Results

Temperature-dependent single crystal X-ray experiment. 1 crystallizes in a monoclinic system with cell parameters: a = 9.3696(1) Å, b = 16.0340(2) Å, c = 22.7991(4) Å, α = 92.9561(5)°, V = 3420.60(8) Å³, Z = 4, at 290 K. Figure 2a shows the temperature-dependent cell parameters from room-temperature to 100 K. When temperature decreased, the b and c axis contracted, the a axis and the β angle show a negative thermal expansion 39. The negative thermal expansion coefficient as a function of temperature is shown in Figure 2a. Below 140 K, a hydrophilic effect occurs, and above 140 K, the volume decreases. The negative thermal expansion coefficient as a function of temperature is shown in Figure 2a. Below 140 K, the b axis, the c axis and the volume decrease when temperature decreases, and the space group remained P21/n in the X-ray diffraction experimental temperature range.

Crystal structure. At 290 K, there are two (C6H7)3NH+ in an asymmetric unit in 1. One of the propyl groups connects to N1, points in the direction perpendicular to the ab plane and intercalates into a cavity of the anionic honeycomb. The non-hydrogen-atoms on the ammonium of N2 are almost parallel to the ab plane, the hydrogen bond between N–H and O of oxalate anion was found to be N2–H2…O10 2.806 Å/166.96°. H2O molecules exist in five positions with populations of 0.50, 0.50, 0.50, 0.50 and 0.20, so there are 2.2 H2O in an asymmetric unit. There are hydrogen bonds between cation and H2O and between solvent and anionic layer. Two sheets of ammonium exist between the two anion layers and there is no weak interaction between ammoniums. This explains the nature of the crystal effectively, because it is always a thin plate crystal and cleaves easily (Figure S1). In 1, Cu is coordinated by three bisbidentated oxalate anions, Cu1 and Cu2 are neighboring to each other, so a (6,3) honeycomb network is formed on the ab plane. The Cu–O distances are 1.969(2) Å, 2.310(2) Å for Cu1 and 1.966(2) Å, 2.340(2) Å for Cu2, and the Cu–O distances on the equatorial plane are shorter than those in the axial direction as a result of the Jahn-Teller distortion. The elongated bonds on the Jahn-Teller distorted octahedron around the Cu2+ are highlighted with black solid lines (Figure 1e). The cis-O–Cu–O
The oxalate-bridged Cu1 …Cu2 distances are 5.5179(7) Å, 162.86(9), and 9.3696(5) Å. When temperature decreased, the Cu …Cu distance decreasing, a broad maximum was observed at 52 K, and a turning point was observed at 14 K, then the χ value increased quickly and reached 0.0084 cm³ mol⁻¹ at 2 K. At 300 K, the χT value is 0.465 cm³ K mol⁻¹, it is higher than 0.375 cm³ K mol⁻¹ of an isolated Cu²⁺ with S = 1/2, and in the range of Cu²⁺ compounds with S = 1/2. The data above 80 K was fitted to the Curie-Weiss law with C = 0.650(2) cm³ K mol⁻¹ and θ = −120 (1) K. No bifurcation was observed from ZFC/FC/RM measurement above 2 K. This is consistent with the specific heat experiment showing no long-range magnetic ordering and indicates the absence of spin glass freezing. The isothermal magnetization at 2 K increased in a smooth curve and reached 0.012 Nₜ at 10 kOe, then the magnetization increased linearly and reached 0.044 Nₜ at 65 kOe (Figure 3).

Discussion

The distance between two anion layers which are separated by cation and H₂O is longer than 3.5 Å, so there is no significant interaction between two-dimensional anion layers. The starting point for understanding the magnetic properties is therefore consideration of the independent two-dimensional honeycomb layers.

The magnetic configuration of the honeycomb lattice can be postulated from an orbital analysis. The unpaired electron exists in the magnetic orbital dx²-y² on the equatorial plane. The orbital along the elongated octahedral Cu(II) is the dz² orbital as highlighted by black solid lines in Figure 1e, and the dz² orbital is perpendicular to the equatorial plane and the dx²-y² orbital. The relationship between magnetic and structural properties of oxalate-bridged Cu²⁺ atoms was well established from one-dimensional Cu-oxalate compounds, for example, a ferromagnetic interaction was observed in [Cu(bpy)(C₂O₄)₂]H₂O when dx²-y² orbitals on two oxalate-bridged Cu²⁺ atoms are parallel each other. Meanwhile, an antiferromagnetic interaction appeared when dx²-y² orbitals on two oxalate-bridged Cu²⁺ atoms are perpendicular to each other.

Ferromagnetic interaction along the b axis between oxalate-bridged Cu1 and Cu2 and antiferromagnetic interaction along the a axis between oxalate-bridged Cu1 and Cu2 were assumed. Because the antiferromagnetic interaction is stronger than the ferromagnetic interaction between oxalate-bridged Cu²⁺ atoms, antiferromagnetic behavior should be expected in 1 and the magnetic configuration of 1, if it orders, would be that of a system with a stripy antiferromagnetic ground state with a pair of spins up and a pair of spins down alternately on the honeycomb lattice (Figure 1c). This is distinct from the other possible magnetic configurations of honeycomb lattices (Figure 1a,b,d) and the stripy configuration is suggested by theoretical calculations to be the best candidate to lead to a quantum spin liquid.

On the χ-vs-T plot, a broad maximum at 52 K indicates short-range antiferromagnetic interactions in the low-dimensional system of metal atoms. The data above 2 K was fitted to several models: first the anisotropic honeycomb model of Curely et al, which showed good consistency with the orbital analysis above, giving an FM interchain interaction that is around 700 times weaker than the AF intra-chain coupling. The best fit to the data was however given by the 1D Bonner-Fisher model plus a small impurity term, indicating a highly 1D state. This strongly 1D state may be the result of weak interchain coupling plus a further frustration of the interchain coupling J' by the second nearest neighbour interactions J'' (Figure 4).

The parameters obtained from the fitting are: C = 0.4383(8) cm³ mol⁻¹, J = −43.82(7) K, n_impurity = 1.09(2)%, θ_impurity = 1.27(3) K. From the value of J and the absence of magnetic ordering above 2 K we can provide an upper bound on the J'/J ratio of 2.2 × 10⁻⁴, around half that of the benchmark S = 1/2 Heisenberg antiferromagnetic chain system KCuF₃.

The specific heat data shows that neither magnetic ordering, nor a structural transition happened between 200 K and 2 K. The crystal structure at 2 K is the same as the crystal structure at 290 K. The heat capacity at 2 K is 183 mJ K⁻¹ mol⁻¹, which is higher than the value in long-range magnetic ordered
metal-oxalate-honeycomb compounds where the electron spins are frozen into an ordered array of magnetic dipoles. For example, it is 2.17 mJ K$^{-2}$ mol$^{-1}$ in Fe$^{2+}$ ($S = 2$), and 43 mJ K$^{-1}$ mol$^{-1}$ in Co$^{2+}$ ($S = 3/2$). Although there is a strong spin-orbital coupling in the Co$^{2+}$ ($S = 3/2$) case, it is not a candidate spin liquid as it undergoes long range magnetic ordering at 21 K. So the large heat capacity of 1 at 2 K suggests that the spins are in a quantum fluctuating spin liquid state$^{53}$. I is different from reported low-dimensional octahedral coordinated Cu$^{2+}$ compounds where the strong antiferromagnetic interaction and high $J$ value were the result of interchain or interlayer interactions between Cu$^{2+}$ atoms. For example in CuCl$_2$(1,4-dioxane)(H$_2$O)$_2$, the hydrogen bonds through O–H …Cl between chains results in strong antiferromagnetic interaction with $\theta = -71.9$ K, but spin frustration has not been observed$^{54}$. I is an antiferromagnetic compound that our measurements suggest to be candidate for the 1D class of quantum spin liquids. In this case the combination of dimensional reduction and frustration turns a honeycomb system into one where the properties of well-isolated chains dominate the magnetic properties$^{55–57}$.

**Methods**

**Sample preparation and X-ray diffraction experiments.** Blue thin crystal plates of [(C$_3$H$_7$)$_3$NH]$_2$[Cu$_2$(C$_2$O$_4$)$_3$](H$_2$O)$_2$ (1) were obtained from methanol solution of Cu(NO$_3$)$_2$·3H$_2$O, H$_2$C$_2$O$_4$·2H$_2$O and (C$_3$H$_7$)$_3$N$_2$H$_2$ in a 1 : 3 : 5 ratio at room-temperature with yield of 31%. Element analysis: C$_{48}$H$_{96}$O$_{18}$N$_2$Cu$_2$. F.W. = 719.345, calc. C 40.67, H 6.78, N 3.89; exp. C 40.45, H 6.82, N 3.91. A piece of single crystal was selected for single-crystal X-ray diffraction experiments at 290 K, 230 K, 180 K, 140 K and 100 K.

**Specific heat measurement.** The specific heat experiments were carried out on a Quantum Design PPMS-9XL system from 200 K to 2 K under 0 Oe and 80 kOe. The polycrystal was fixed on the sample stage with N-grease. The contribution from sample stage and N-grease was subtracted from the raw data.
Magnetic measurement: The magnetization measurement was performed using a tightly packed 16.26 mg polycrystalline sample which was sealed by 5.62 mg paraffin in capsule on a Quantum Design MPMS-7XL SQUID system. Susceptibility data were corrected for diamagnetism of sample by Pascal constants (−190.4 × 10−6 cm3 mol−1 per Cu2+) and the background was determined by a measurement of the sample holder.

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Author contributions

B.Z. and D.Z. managed the project. Magnetic measurement was carried out by Y.Z., single crystal X-ray diffraction experiment was carried out by Z.W., heat capacity measurement was carried out by D.W. B.Z. synthesised crystal, conducted all experiments and analyzed the data. Paper was written with discussion of B.Z., P.J.B., F.L.P. and D.Z. B.Z., P.J.B. and F.L.P. wrote the main manuscript text. B.Z. prepared figures 1–3 and F.L.P. prepared figure 4. All authors reviewed the manuscript.
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