An ionothermally-prepared S = ½ vanadium oxyfluoride kagome lattice

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Frustrated magnetic lattices offer the possibility of many exotic ground states of great fundamental importance. Of particular significance is the hunt for frustrated spin ½ networks as candidates for quantum spin liquids (QSLs), which would have exciting and unusual magnetic properties at low temperatures. The few reported QSL candidate materials have all been based on d^9 ions. Here we report the ionothermal synthesis of $[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$, an inorganic-organic hybrid solid that contains a S = ½ kagome network of d^1 V^{4+} ions. The compound exhibits a high degree of magnetic frustration, with significant antiferromagnetic interactions but no long-range magnetic order or spin-freezing above 2 K, and appears to be an excellent candidate for realising a QSL ground state in a spin ½ kagome network.

Antiferromagnetic solids based on the kagome lattice are of great interest because of their geometrically-induced magnetic frustration[1,2]. The kagome structure comprises a planar array of corner sharing triangles, as shown in Figure 1a. The geometric constraints inherent when magnetic centres are located at the vertices of the triangles lead to a situation where competing antiferromagnetic interactions cannot be simultaneously satisfied. This is the classic example of a frustrated magnetic system. Kagome lattices based on $S = \frac{1}{2}$ spins are one of the prime targets in the search for quantum spin liquid (QSL) ground state materials. The degeneracies inherent in such ground states can persist to low temperatures, and this leads to enhanced quantum fluctuations which can suppress magnetic order[3]. In QSL materials the fluctuations are strong enough to overcome the tendency towards ordering even at zero temperature. The realisation of a QSL state is a great challenge to physicists that has not yet been fully demonstrated. For kagome lattices with $S > \frac{1}{2}$, of which there are many examples known, quantum fluctuations are not strong enough to suppress ordering and so $S = \frac{1}{2}$ lattices constitute a special class of materials.

Candidate compounds for $S = \frac{1}{2}$ QSLs are extremely rare, and the corresponding challenge to chemists is to synthesise such materials. The recent review by Balents[3] lists only five potential QSLs amongst materials studied so far. Two of the best candidates are $S = \frac{1}{2}$ kagome lattices; herbertsmithite ($ZnCu_3(OH)_6Cl_2$) and vesignieite ($BaCu_3V_2O_8(OH)_2$), both of which are composed of 2D kagome arrays of d^9 Cu^{2+} magnetic centres. However, neither possesses a 'perfect' 2D kagome array of coplanar, corner-linked equatorial triangles, with each node representing a single magnetic ion. In vesignieite the three-fold symmetry of the kagome lattice is broken and the compound has monoclinic symmetry with two inequivalent Cu^{2+} sites and Cu-Cu distances per triangular unit. Very recent work suggests that there is a transition to a partial spin-glass phase around 9 K[4] and so vesignieite may not be a realistic QSL candidate. Herbertsmithite retains 3-fold symmetry with equilateral triangular motifs, but there is an intrinsic non-stoichiometry as around 15% of the Zn^{2+} sites between layers are occupied by Cu^{2+} so that the magnetic two-dimensionality is potentially broken. . Nevertheless, the relatively recent synthesis[5] of herbertsmithite has ignited huge interest in this field, and there are many reports of detailed physical characterisation and theoretical models[6-9], so that herbertsmithite remains a prime candidate for a QSL material.[10,11] Other Cu^{2+} - based systems, such as a recently reported metal organic framework, Cu(1,3-benzenedicarboxylate)[12] and an inorganic fluoride, $Rb_2SnCu_3F_{12}$[13], have also been of interest. Despite this progress, local or global symmetry-lowering associated with the generally large magnitude of d^9 Cu^{2+} Jahn-Teller distortions

may ultimately limit the utility of these materials, and alternative non-d^9 S = ½ kagome lattices are targets of great potential significance.

In particular, there are no known examples of kagome lattices based on d^1 ions. Such a lattice will likely have significantly different structural and electronic properties from a Cu^{2+} lattice (for example stemming from the different Jahn-Teller effects on the local structure around the ions, and the location of the unpaired spin in different orbitals). Vanadium (IV) is an obvious d^1 ion to target but to date no V^{4+} –based kagome system has been prepared. There are however many examples of frustrated d^2 (S = 1) V^{3+} systems based on the Jarosite structure.[14-16] The poor control over the final oxidation state and the propensity for V^{4+}-containing materials to form low dimensional structures[17,18] make this a chemically-challenging system in which to prepare the extended 2D framework solids necessary for frustration to occur.

In our recent work we have concentrated on altering the chemistry of the preparative system away from traditional hydrothermal and solvothermal approaches towards ionothermal methods. Ionothermal synthesis is the use of ionic liquids as the solvent (and often provider of organic structure directing agent) for the preparation of materials.[19,20] Originally designed for the synthesis of new zeolitic solids,[21] the ionothermal method has recently been extended to show wide ranging and general applicability, with impact through the preparation of important and unexpected new solids in areas as disparate as inorganic porous materials,[22,23] hybrid coordination polymers[24,25] and organic polymers.[26] The key to the preparation of new solids with quite different structural, chemical and physical properties to those forthcoming from other synthesis techniques is the radical change from molecular to ionic solvent species. The binary nature of ionic liquids leads to a wide range of available solvent chemistry (e.g. from very hydrophobic to very hydrophilic) simply by combining different cations and anions, which directly affects the nature of resultant materials. Such large changes in chemistry inevitably lead to the preparation of new solids, and the hypothesis we explored in this work was that the change to ionothermal synthesis may well be used to stabilise oxidation states that are difficult to access using more traditional methods.

Here we describe the use of the ionothermal approach in the synthesis of $[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$ (**1**). This material contains both V^{4+} and V^{3+}, but only the former is incorporated in an S = ½ kagome layer. The material shows no magnetic ordering down to 2 K, indicative of significant frustration, and does not possess the types of Jahn-Teller instabilities or symmetry-lowering inherent in the well-studied Cu^{2+}-based systems.

This new material is therefore a distinct new QSL candidate, which has significantly different chemistry to those available so far.

Results and Discussion

Compound **1** was prepared ionothermally at 170 ^{o}C using 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, (EMIM-NTf$_2$) as the solvent and quinuclidine as an added structure directing agent. Despite being ionic EMIM-NTf$_2$ is relatively hydrophobic in character and the rather unusual properties of the solvent appear to be key in enabling the synthesis of 2D networks such as **1**. In our previous studies of the hydrothermal and solvothermal chemistry of vanadium fluorides and oxyfluorides there is a clear correlation between increasing reaction temperature and the synthesis of materials with increasing dimensionality (i.e. 0D $\rightarrow$ 1D $\rightarrow$ 2D with increasing T). However, there is also a trend towards reduced vanadium species, particularly V^{3+} with increasing temperature.[17] The challenge for the synthesis of multidimensional V^{4+}-containing materials is to ensure that the temperature of the reaction system is high enough to promote condensation into extended solids while simultaneously ensuring the chemistry of the system does not overly favour reduction of V^{4+} to V^{3+}. This challenge is difficult in hydrothermal and traditional solvothermal methods, and the only example of a layered V^{4+}-containing fluoride prepared solvothermally contains more V^{3+} than V^{4+} (ref. 27).

The only layered purely V^{4+}-containing oxyfluoride material that has been prepared as yet is [C$_6$H$_6$N][V$_2$O$_2$F$_5$], which was synthesised using the same ionic liquid as that used to prepare **1**.[28] Although [C$_6$H$_6$N][V$_2$O$_2$F$_5$] is not magnetically frustrated, its synthesis did give some vital clues as to how to target other 2D V^{4+} structures using the same solvent. Our strategy was therefore to explore the ionothermal synthesis of vanadium oxyfluorides at elevated temperatures (>150°C) under conditions where other solvent systems produce predominantly V^{3+} containing solids. The strategy has proved successful and allowed the preparation of **1**.

Small blue single crystals suitable for X-ray diffraction studies could be recovered from the reaction system. Powder X-ray diffraction and chemical analysis (see Supplementary material) are consistent with a phase-pure material. The structure of the solid (Figures 1 and 2) consists of isolated pillared double layers of stoichiometry [V$_7$O$_6$F$_{18}$]$^{3-}$. These layers are built of two V^{4+}–containing kagome sheets that are pillared by a V^{3+} ion. Within each

of these layers resides the NH_4^+ cation, and between these layers along the c-axis lies the quinuclidinium cation, which is crystallographically disordered over two sites (Figure 2). The ammonium ions in **1** come from partial breakdown of the organic moieties under acidic conditions – something that is well known in ionothermal synthesis.[29]

The structure of **1** may be understood by breaking it down into its constituent building blocks. Each pillared double layer can be described as comprising a heptameric, pyrochlore-like building unit consisting of two $V^{4+}_3O_3F_{12}$ triangles linked by a further V^{3+} ion (Figure 1c). These heptameric building units are then connected to form the double layer (Figure 1d). There are two crystallographically distinct vanadium sites, V(1) sits on a site of high symmetry (-3m), whereas V(2) sits on a mirror plane: the refinement unambiguously shows the O/F ordering such that each V(2) has one short vanadyl (V=O) bond, whereas V(1) is surrounded exclusively by F^- ligands. The structure around V(2), particularly the presence of the vanadyl bond, is indicative of V^{4+}, while that around V(1) suggests that this is V^{3+}. In addition to this chemical nature, bond valence sum analysis supports this assignment of V(1) as V^{3+} and V(2) as V^{4+} (See supplementary material). The bond lengths and the bond valence sum analysis also strongly suggests that the V(2) site contains only V^{4+}; i.e. there is no V^{3+}/V^{4+} disorder in the kagome layer.

It is instructive to compare the structure of **1** with that of other S = ½ kagome materials such as herbertsmithite and vesignieite. The V(1) sites in **1** act to link adjacent kagome planes along the c-axis into the pillared double layer described above. However, in the case of herbertsmithite this linkage is extended infinitely in this direction giving rise to overall 3D connectivity. In the ideal herbertsmithite structure, i.e. stoichiometric, cation-ordered $ZnCu_3(OH)_6Cl_2$, the kagome layers would be separated by magnetically inert Zn^{2+} ions which provides the necessary dimensional reduction. In real samples however, the best characterisation shows that there is likely significant non-stiochiometry and partial Cu^{2+} occupancy on the Zn^{2+} site between the kagome layers.[10] Compound **1** shows a different and unique kind of dimensional reduction in which double pillared layers are separated by large organic cations and are therefore magnetically isolated. In the double layer itself the two constituent kagome nets are linked by a V^{3+} unit.

Within the kagome layer itself, the detailed geometry of **1** may be also be compared with that of herbertsmithite and vesignieite. Firstly, unlike in vesignieite, the 3-fold symmetry

of each triangle is retained. However, in herbertsmithite all the triangles in the kagome sheets are the same size, whereas in **1** there are two distinct near-neighbour V–V contacts of about 3.60 and 3.75 Å, which leads to two different sized equilateral triangles (marked 1 and 2 in Figure 1b) which alternate in a periodic manner. This is easily rationalised because the VOF_5 distorted octahedra that make up the kagome net are tilted so that in one triangle all three terminal vanadyl bonds point in towards a point parallel to the 3-fold axis of the triangle, while in the adjacent triangle all three vanadyl groups point away from the 3-fold axis. This is clearly seen in Figure 1b. This 'alternating' kagome sheet is an unusual feature of compound **1**, which is not seen in other kagome structures (although something similar is seen in the bi-layer alloy Fe_3Sn_2,[30] which is a ferromagnetic metal). Magnetic frustration is not lowered through having inequivalent interactions in the alternating triangles of the kagome lattice so this alternating Kagome lattice remains an excellent geometry for QSL formation, and is not sensitive to Jahn-Teller distortion.

The M-L-M (M = V or Cu, L = F or O, respectively) angles may also be compared: 119° in herbertsmithite versus 132 and 147° in **1**; this shows an interesting point that, despite the fact that the kagome net itself (ie. considering only cation-cation contacts) is more regular in herbertsmithite than in **1**, the reverse is true when one considers the full $[ML_2]_n$ kagome sheet, which is much more puckered in herbertsmithite than in **1**. Finally, the out-of-plane ligand distances are significantly different, due to the Cu^{2+} Jahn-Teller distortion (Cu-Cl 2.77 Å versus V-O, V-F 1.582(6), 2.150(5) Å). Note that in herbertsmithite the in-plane O-atoms are also coordinated to the interlayer (Zn) site, whereas they are not in the case of **1** and instead the apical F(1) sites are bonded to V(1).

The inverse magnetic susceptibility versus T plot (Figure 3a) is described well by a Curie-Weiss law above 150 K. The paramagnetic moment of μ_{eff} = 5.11 μ_B derived from the slope is in excellent agreement with the value of 5.10 μ_B expected for a formula unit of six V^{4+} (S = ½) and one V^{3+} (S = 1) spin-only ions. This supports the above structural model and the assignments of V(1) and V(2) as V^{3+} and V^{4+} respectively. The substantial negative Weiss constant of θ = -81 K shows that strong antiferromagnetic exchange interactions are present – this is also seen in the plot of χT versus T (Supplementary) which does not saturate at 300 K. However, no magnetic ordering transition (T_M) is observed down to the lowest measured temperature of 2 K. This shows that spin order is highly frustrated, as quantified by the frustration index[2], f = $-\theta/T_M$, which is at least 40 (a value greater than 10

signifies strong frustration). No significant divergence between zero-field and field cooled susceptibilities is observed (Figure 3b), showing that no spin freezing occurs down to at least 2 K. An equivalent experiment on a separately-prepared sample produced results which were in excellent agreement with the above, demonstrating that the magnetic response is intrinsic and that the synthetic method reproducibly provides a pure sample of **1**, with no observable impurities. It is difficult to separate contributions of the V^{4+} kagome layers and the orbitally-degenerate d^2 V^{3+} ions to the low temperature susceptibility and other bulk measurements, and site-specific probes of spin dynamics such as muon spin rotation[6] will be used in future work.

The relative magnitudes of the V^{4+}-V^{4+} superexchange interactions within the kagome planes and V^{3+}-V^{4+} interactions between pairs of planes will determine whether **1** will show pure kagome or kagome bilayer behaviour. Unpaired V^{4+} d-electrons are localised in d_{xy} type orbitals that generate strong in-plane antiferromagnetic V^{4+}-F-V^{4+} interactions through mutual overlap with the intermediate fluoride p_π orbitals. However, V^{3+}-V^{4+} magnetic exchange is expected to be much weaker, as the $V^{4+}d_{xy}$ orbitals are perpendicular to the long V-F bonds that connect each V^{4+} to a V^{3+} ion, so no good superexchange orbital overlap pathway is available. Hence, compound **1** is expected to show S = ½ single kagome layer magnetism below temperatures ~$|\theta|$, possibly changing to kagome bilayer behaviour at much lower temperatures if weak V^{3+}-V^{4+} interactions are significant. Frustration in kagome bilayer (pyrochlore slab) structures is also of interest and has been studied in the disordered S = 3/2 materials $SrCr_{9x}Ga_{12-9x}O_{19}$ and $Ba_2Sn_2ZnCr_{7x}Ga_{10-7x}O_{22}$ [31].

Aside from the natural comparisons with herbertsmithite and vesignieite, there are several previous examples of S > 1/2 kagome nets in transition metal fluoride chemistry.[32] Perhaps the simplest compound, FeF_3, exists in both hexagonal tungsten bronze (HTB) and pyrochlore polymorphs.[33] Both of these are 3-D framework structures consisting of layers with the same vertex-linked octahedral style as present in **1** but with differing connectivity between layers. Other interesting phases have been observed in the fluorides $Cs_2ZrCu_3F_{12}$[34,35] $Cs_2LiMn_3F_{12}$[36] and related phases. In these cases, 3-D *chemical* connectivity is again preserved, but magnetic connectivity is reduced to 2-D by the presence of an inert 'blocking' cation in the site linking two adjacent kagome layers. In

most of these cases there is evidence of long-range magnetic ordering, caused in some cases by Jahn-Teller symmetry effects, so these are not QSL candidates. However, in $Rb_2SnCu_3F_{12}$ very recent results have revealed the first experimentally verified example of a so-called 'pinwheel valence-bond-solid'[13], which exhibits a different manifestation of the valence-bond state to that seen in QSLs, but may nevertheless provide further clues towards tailoring QSL behaviour via crystal-chemical tuning.

The successful strategy we used to prepare compound **1** is based on the use of an EMIM-NTf_2 ionic liquid as a solvent and quinuclidine as an added structure directing agent (SDA) in order to balance the competing phenomena of V^{4+} to V^{3+} reduction and 0D/1D to 2D condensation with increasing temperature. An important question to answer is how specific are the conditions that will allow the successful synthesis of a material like **1**? The three main variables are the nature of the solvent, the nature of the SDA and the temperature of the reaction. Varying each of these in turn yields important information regarding which features are important for the control of the overall reaction.

Ionic liquids have been referred to as 'designer solvents' as their properties, including melting point, density, viscosity and miscibility with water, can be easily altered by judicious choice of cations and anions.[37] The role of the anion is particularly important. For example, changing from Br^- to the NTf_2^- anion dramatically decreases the melting point (from 81^oC to -3^oC) and the water solubility (from highly water-soluble to 1.4 wt% water content saturated at 20^oC).[38] Varying the anion in ionothermal synthesis has already been shown to exert interesting influence over how a reaction proceeds, even to the point of inducing chirality in materials that contain no asymmetric centres.[39,40]

In this system when the EMIM-NTf_2 solvent is replaced by EMIM-Br or a deep eutectic solvent such as choline chloride/urea (both of which are characterised as hydrophilic ionic liquids) only 0D and 1D V^{4+}-containing materials were recovered at low reaction temperatures (<120 ^oC)[41]. Higher temperatures should promote the formation of multidimensional materials, and indeed this is the case but these materials only contain reduced V^{3+} species and never V^{4+}. The patterns using different kinds of hydrophilic ionic liquid solvents are therefore similar to those seen in the hydrothermal and solvothermal synthesis of vanadium fluorides and oxyfluorides[17,18,42,43] in that it is difficult to form multidimensional V^{4+}-lattices using these approaches. It appears that the specific solvent

properties of the EMIM-NTF$_2$ ionic liquid stabilise the higher +4 oxidation state enough at high temperature (170°C) to allow condensation of V^{4+}-containing units into 2D layers. Higher temperatures than this (up to 200-220 ^{o}C) lead to the formation of a new phase, whose structure is as yet unknown, but spectroscopy and its colour indicates that it is likely to contain predominantly V^{3+}.

The last important variable in the synthesis is the quinuclidine SDA which we have replaced in the synthesis of **1** with various other nitrogen-containing species. This set of SDAs includes 1,4-diazabicyclo[2.2.2]octane (DABCO) a molecule with the same size and shape as quinuclidine but two nitrogen atoms instead of one, and pyridine and piperidine which are single rings (rather than the multiple rings of quinuclidine) but with one nitrogen atom. None of these SDAs produced a material with a kagome lattice under similar conditions as those used to prepare **1**. Interestingly, combining quinuclidine as an SDA with a hydrophobic liquid such as EMIMBr failed to produce any solid product at all under these conditions. This indicates that the quinuclidine is vital to the success of the synthesis, but only in combination with a solvent of the correct type. With DABCO the resulting structure is a novel low dimensional material (see supporting information) and with piperidine a polycrystalline solid with unit cell metrics and symmetry unrelated to those of a kagome lattice is produced. The use of pyridine as the SDA did produce a V^{4+}-containing material with a square 2D lattice (previously reported in reference 28), which strongly supports the hypothesis that it is the EMIM-NTf$_2$ ionic liquid that promotes the formation of multidimensional S = ½ frameworks.

Conclusions

The chemistry behind the synthesis of compound **1** shows how careful choice of synthetic methodology, such as ionothermal synthesis, can yield novel materials. Here we have shown for the first time how the ionothermal method can be extended to include control over oxidation state that is difficult in other solvent systems. Compound **1** presents the first example of a d^1, S = ½ kagome net and the first example of an 'alternating' kagome network. Although the compound still does not display the 'perfect' 2D kagome lattice which might be expected to provide the ideal basis for QSL behaviour, the significant point is that it does *not* display the types of local imperfection which might disrupt QSL behaviour in the Cu^{2+}-based systems, *viz.* loss of the 3-fold symmetry and layer-puckering due to the Jahn-Teller effect or the inter-layer cation site mixing. Given the absence of *any*

model compound exhibiting a 'perfect' 2D S = ½ kagome lattice, the discovery of a model system with a *different* type of deviation from perfection may provide a significant step forward in understanding the key chemical features which underpin the ground states adopted in these systems. Clearly further studies of this compound's ground state will be very important with the aim of identifying QSL behaviour. This is a challenging problem, and will likely require a combination of techniques. The lack of long-range magnetic ordering down to the millikelvin range needs to be demonstrated by susceptibility or heat capacity measurements combined with more specific probes of localised spin dynamics, such as muon spin rotation or inelastic neutron scattering.

The key to the successful synthesis of **1** is the careful choice of the synthesis chemistry. The use of an ionic liquid solvent such as EMIM-NTf$_2$ clearly promotes the stability of V^{4+} at a high enough temperature to allow multidimensional frameworks to form. Combining this with added organic structure directing agents can lead to different multidimensional structures, including compound **1.** Now that the chemical strategies of how to target d^1 kagome lattices such as **1** are beginning to be understood there is also great scope to alter the chemistry in order to prepare other similar materials with subtle differences.

In summary, we have prepared and characterised a novel hybrid material which exhibits a unique double layered topology, incorporating an S = ½ kagome net that appears to be an excellent candidate for realising a spin-liquid ground state. This is the first example of a d^1 kagome net, and adds a significant new paradigm to this highly topical and exciting area. We expect that this study will prompt further experimental and theoretical work from both the chemistry and physics communities.

Methods

Compound **1** was synthesised under ionothermal conditions. A mixture of VOF$_3$ (0.124g, 1mmol), HF (48 wt% in H$_2$O) (0.09 mL, 2.45 mmol), the ionic liquid [EMIM][NTf$_2$] (4g, ~10mmol) and quinuclidine (0.111g, 1mmol) in a 15 mL steel autoclave (PTFE lining) was heated to 170°C for 20 h. Upon cooling to room temperature, the blue crystals were filtered, washed with methanol and dried in air for 24 h. The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMIM][NTf$_2$] was prepared by standard methods. For additional details of the synthesis, chemical analysis and powder X-ray diffraction see Supplementary material.

Crystallographic data for **1**: $Z = 3$, $M_r = 942.82$ g mol^{-1}, trigonal, space group R-3m, a = 7.354(4) Å, c = 43.220(5) Å, V = 2024.2(16) Å^3, ρ_c = 2.32 g cm^{-3}, F(000) = 1368, λ = 0.71073 Å, T = 93 K, μ = 2.471 mm^{-1}, 6879 reflections, of which 517 were independent, R_{int}= 0.168. The structure was solved using direct methods and refined against F^2 (θ_{max}= 25.27°), R1= 0.0709, wR2=0.1798, GOF = 1.139. CCDC <mark>xxx</mark> contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Magnetic susceptibility data for **1** were collected on a Quantum Design MPMS SQUID. Data were recorded in a 10000 Oe field while warming the sample from 2 to 300K in 4 K steps, following consecutive zero-field cooling (ZFC) and field cooling (FC) cycles.

Author contributions:

FHA and DWA carried out the synthetic chemistry. FHA solved the crystal structure, with the assistance of AMZS. FHA and RJG analysed the magnetic data, under the guidance of JPA. PL and REM initiated the research and co-wrote the paper. PL coordinated the project.

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Figure 1 | The structure of the kagome and double pillared layers in $[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$. a, the archetypal kagome lattice. **b,** the V^{4+}-containing kagome lattice in **1**, viewed parallel to the crystallographic *c*-axis. The crystallographically distinct triangles in the lattice are marked 1 and 2 respectively. The V-V distances in triangle 1 are 3.601 Å, while in triangle 2 they are 3.753 Å. **c,** the pyrochlore-like heptameric building unit of the inorganic framework in **1**. V2 represents the V^{4+} site which forms the kagome layers; V1 is the V^{3+} site which links adjacent layers. Bond lengths: V(1)-F(1) (x 6) 1.927(5) Å, V(2)-O(1) 1.582(6) Å, V(2)-F(1) 2.150(5) Å, V(2)-F(2) (x 2) 1.972(2) Å, V(2)-F(3) (x 2) 1.956(2) Å. **d,** a view of the pillared double layer in **1** viewed parallel to the crystallographic *b*-axis, showing the position of the occluded ammonia cations. Key: Cyan = V^{4+}, blue = V^{3+}, green = F, red = O, purple = N, white = H.

Figure 2 | Polyhedral views of the structure of $[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$. a, a view of the pillared double layer perpendicular to the crystallographic *c*-axis showing the *AB*-type hexagonal stacking of the two kagome arrays that make up the layer. **b,** the complete structure viewed parallel to the crystallographic *b*-axis showing one of the possible orientations of the quinuclidinium cations in the interlayer space. Key: V^{4+}-centred polyhedral are shown in cyan, V^{3+}-centred polyhedral are shown in blue. Grey = C, purple = N and white = H.

Figure 3 | Magnetic properties of $[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$. a, Inverse magnetic susceptibility and Curie-Weiss fit above 150 K (right-hand axis) and the raw susceptibility data over the entire range (left-hand axis). **b,** Field-cooled (FC) and Zero field-cooled (ZFC) plots for χ from 0 to 50 K**.**

Table of Contents Summary:

A novel hybrid material featuring a unique $S = \frac{1}{2}$ kagome lattice has been isolated using ionothermal synthesis. Despite strong antiferromagnetic interactions, $[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$ exhibits no-long range magnetic order down to 2 K, and appears to be an excellent candidate for a novel spin liquid ground state.