

Spin Frustration from *cis*-Edge or -Corner Sharing Metal-Centered Octahedra

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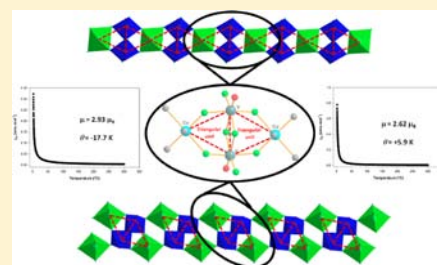
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S Supporting Information

ABSTRACT: A new strategy using *cis*-edge or -corner sharing metal-centered octahedra is described which enables interesting frustrated spin lattices to be targeted. The examination of “CuV₂” triangular motifs in the two new compounds [enH₂]₂[Cu(H₂O)₂][V₂O₂F₈] (1) and [Cu(H₂O)(2,2'-bpy)]₂[V₂O₂F₈] (2) (where enH₂ = ethylenediammonium and 2,2'-bpy = 2,2'-bipyridyl) reveals that the [VOF₄]²⁻ anions, which exhibit *cis* structure directing properties, lead to frustrated lattices owing to the competing ferro and antiferromagnetic interactions. There is direct coordination through two *cis* F⁻ ligands (i.e., the F⁻ ligand *trans* to O²⁻ and one equatorial F⁻ ligand) in both 1 and 2 owing to the significant π -bonding between the vanadium and the oxide ligand. We emphasize that most of triangular motifs reported in the literature are built of *cis*-edge or -corner sharing metal-centered octahedra, thus they can be used to target new materials exhibiting interesting magnetism such as spin frustration.



INTRODUCTION

Magnetic properties of transition metals have an important role in solid-state chemistry, physics, and material science, and in the past decades, there have been numerous applications in the electronic information technology.^{1,2} Recently, more attention has been focused on frustrated systems owing to their interest for different physical properties such as superconductivity and spin chirality and for the exotic inherent behavior in the ground state.^{3–5} In the search of new frustrated systems, materials with spin $S = 1/2$ are interesting because quantum effects suppressing magnetic orders are strong. High magnetic frustration can occur in materials based on triangular arrangement of antialigned spins (such as Li₃Mg₂RuO₆ or [NH₄]₂[C₇H₁₄N][V₇O₆F₁₈]) or in which ferromagnetic (F)- and antiferromagnetic (AF)-interactions compete (such as [MnGd₂O(O₂CPh)₃(O₂CMe)(dapdo)(dapdoH)₂] or [MnGd₂(OH)₂(NO₃)₄(hmp)₄(H₂O)₄](NO₃)₂).^{6–11} In the exception of topologies such as Kagomé lattices, the magnetic frustration resulting from these two categories of triangular interactions is relatively similar. However, few strategies to target magnets based on such arrangement have been developed by chemists. Up to now, every synthetic approach reports the use of secondary building units (SBUs).^{12–18} These SBUs, which are usually triangular, are built by coordinating metal ions through organic ligands that crystallize into Kagomé lattices which are known to induce greater frustration compared to other topologies.¹⁹ However, the resulting materials exhibit

moderate frustrations because the long metal–metal distances decrease the strength of the antiferromagnetic interactions. For this reason, frustrations comparable to those found in purely inorganic Kagomé lattices such as volborthite (Cu₃V₂O₇(OH)₂·2H₂O), vesignieite (BaCu₃(VO₄)₂(OH)₂) or [NH₄]₂[C₇H₁₄N][V₇O₆F₁₈] have not been reported.^{11,20–22}

The two new compounds [enH₂]₂[Cu(H₂O)₂][V₂O₂F₈] (1) and [Cu(H₂O)(2,2'-bpy)]₂[V₂O₂F₈] (2) reported in this article crystallize in two different structures, but they are built from the same triangular spin-1/2 “CuV₂” fragments. The investigation of the crystal structures reveals that the metal-centered octahedra, which direct the coordination in *cis*, favor the formation of these triangular spin-1/2 motifs which are frustrated owing to the competing F and AF interactions mediate by V–F–V and V–F–Cu bonds, respectively. The magnetic frustration index ($f = |\theta|/T_N$) measured in compound 1 is similar to the ones of 2D Kagome lattices which were previously obtained using SBUs.^{17,18}

EXPERIMENTAL SECTION

Synthesis. Hydrofluoric acid is toxic and corrosive! It must be handled with extreme caution and the appropriate protective gear.^{23–25} Both compounds were synthesized by hydrothermal method with similar starting materials. Mixtures of VO₂ (1.99 mmol, Aldrich

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99.9%), CuO (4.02 mmol, Alfa Aesar 99.995%), and 48% aqueous HF (27.8 mmol, Aldrich) with ethylenediamine (29.9 mmol, Aldrich 99%) for compound **1** and 2,2'-dipyridyl (2.56 mmol, Aldrich 99%) for compound **2** were placed in two Teflon pouches.²⁶ The pouches were placed into a 125 mL Parr autoclave with a backfill of 45 mL distilled water. The autoclave was heated to 150 °C for 24 h and slowly cooled to room temperature at 6 °C/h. Single crystals of compounds **1** and **2** were recovered by vacuum filtration.

Structure Determination. Single-crystal X-ray diffraction experiments were conducted at 100 K using a Bruker-APEX II CCD diffractometer with monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The crystal-to-detector distance was 60 mm, and data integrations were made using SAINT-V7.23A program.²⁷ Absorption corrections were processed using SADABS.²⁸ The structures were determined by direct methods and completed by Fourier difference syntheses using SIR97 and then refined using SHELXL-97.^{29,30} Additional symmetry elements were checked using the program PLATON.³¹ Anisotropic displacement parameters were refined using SHELXL-97. Hydrogen atoms of organic molecules were constrained to ride at distances of 0.97 Å from the associated C atoms with Uiso(H) = 1.5Ueq(C) and 0.89 Å from the associated N atoms with Uiso(H) = 1.5Ueq(N). Crystallographic data are reported in Table 1.

Table 1. Crystal Data, Structure Solutions and Refinements for 1 and 2

compound	1	2
space group	<i>P</i> -1 (2)	<i>P</i> 2 ₁ / <i>c</i> (14)
<i>a</i> (Å)	6.6154 (3)	7.107 (3)
<i>b</i> (Å)	6.8546 (3)	17.2400 (7)
<i>c</i> (Å)	7.4796 (3)	12.1314 (18)
α (°)	82.032 (2)	90
β (°)	67.561 (5)	125.491 (12)
γ (°)	71.9979 (18)	90
<i>V</i> (Å ³)	298.06 (2)	1210.2 (5)
<i>T</i> (°K)	100(2)	100(2)
<i>Z</i>	1	4
maximum θ	36.4°	36.8°
λ (Mo K α) (Å)	0.71073	0.71073
ρ_{calcd} (g·cm ⁻³)	2.493	2.089
<i>R</i> _{int}	0.023	0.028
<i>R</i> ₁	0.019	0.023
<i>wR</i> ₂	0.052	0.057
goodness-of-fit	0.93	1.08

Magnetic Measurements. Magnetic measurements were performed using a SQUID magnetometer with vibrating sample under field cooled conditions in the temperature range of 2–300 K. The high-field magnetization was measured in a pulsed magnetic field by an induction method using a multilayer pulse magnet at ISSP, the University of Tokyo.

RESULTS

Structure Description. *[enH₂][Cu(H₂O)₂][V₂O₂F₈]* (**1**). The compound **1** crystallizes in the space group *P*-1. [Cu(H₂O)₂]²⁺ cations and [V₂O₂F₈]⁴⁻ anions form infinite chains running along *a* (Figure 1a). Ethylenediammonium (enH₂)²⁺ cations isolated by hydrogen bonding counterbalance the negative charge of the inorganic chains. [V₂O₂F₈]⁴⁻ anions are built by two crystallographically equivalent [VOF₄]²⁻ units. The shortest bond (the vanadyl bond V1=O1 (1.6022(7) Å)) is in *trans* position of the longest one V1–F1 (2.1551(6) Å). The equatorial V1–F bond distances are in the range 1.9161(6) Å ≤ *d*_{V–F} ≤ 1.9628(6) Å. The Cu1–F3 and Cu1–F4 bond distances are 2.2557(6) and 1.9293(6) Å, respectively. The difference between Cu1–F3 and Cu1–F4 distances is due to the first-

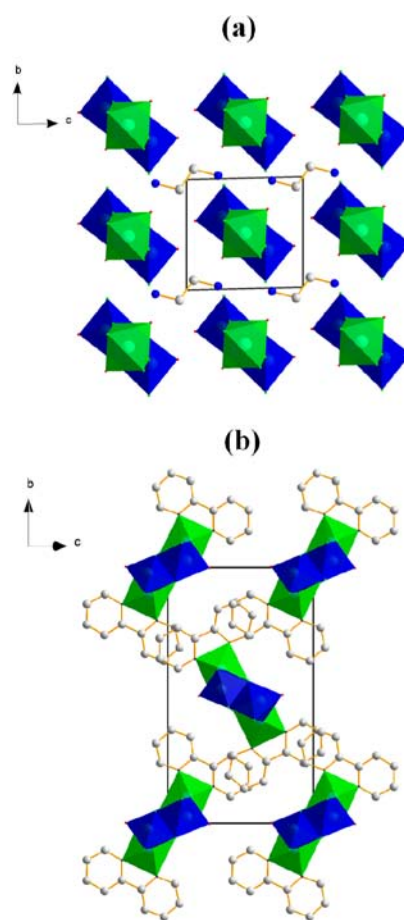


Figure 1. View along the “CuV” chains of (a) [enH₂][Cu(H₂O)₂][V₂O₂F₈] and (b) [Cu(H₂O)(2,2'-bpy)]₂[V₂O₂F₈]. Blue and green octahedra represent vanadium-centered anions and copper-centered cations, respectively.

order Jahn–Teller distortion of Cu²⁺. The bond length between Cu1 and Ow1 atom of the water ligand is 1.9622(7) Å. The Jahn–Teller distortions of the early transition metals and the analysis of the bond valence sums (BVS) allow for the unambiguous distinction between Cu²⁺ and V⁴⁺ sites (the BVS for V⁴⁺ and Cu²⁺ are 4.0 and 2.1, respectively).

[Cu(H₂O)(2,2'-bpy)]₂[V₂O₂F₈] (**2**). The compound **2** crystallizes in the space-group *P*2₁/*c*. Two [Cu(H₂O)(2,2'-bpy)]²⁺ cations and one [V₂O₂F₈]⁴⁻ anion form infinite chains running along *a* (Figure 1b). Similar to compound **1**, [V₂O₂F₈]⁴⁻ anions are built of two crystallographically equivalent [VOF₄]²⁻ units. The shortest bond (vanadyl bond V1=O1 (1.5914(9) Å)) is in *trans* position of the longest one V1–F4 (2.2455(8) Å). The equatorial V1–F bond distances are in the range 1.8856(8) Å ≤ *d*_{V–F} ≤ 2.0325(8) Å. The Cu1–F1, Cu1–F2, and Cu1–F3 bond distances are 2.2533(11), 1.9820(8) Å and 2.2595(11) Å, respectively. The difference between Cu1–F1/F3 and Cu1–F2 distances is due to the first-order Jahn–Teller distortion of Cu²⁺. The bond length between Cu1 and Ow1 atom of the water ligand is 1.9927(8) Å. The Cu1–N1 and Cu1–N2 internuclear distances are 1.9864(10) and 1.9750(9) Å, respectively. The Jahn–Teller distortions of the early transition metals and the analysis of the BVS allow for the unambiguous distinction between Cu²⁺ and V⁴⁺ sites (the BVS for V⁴⁺ and Cu²⁺ are 4.0 and 2.2, respectively).

Magnetic Measurements. Above 100 K, the inverse magnetic susceptibility versus temperature measured in an external field of 1000 Oe can be well described by the Curie–Weiss law (Figure 2). The magnetic moment calculated from

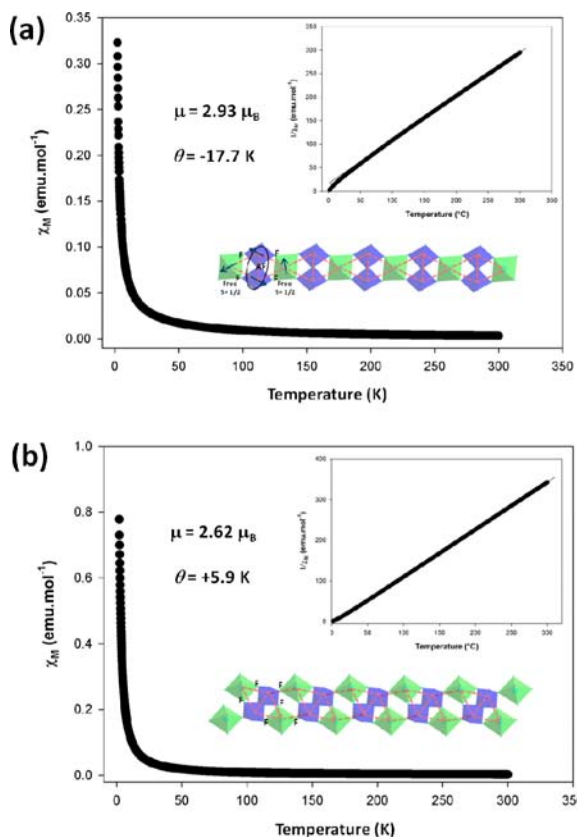


Figure 2. Magnetic data for compounds (a) 1 and (b) 2. The insets represent the inverse magnetic susceptibility and the Curie–Weiss fit.

the slope is $2.93 \mu_B$ for compound 1 and $2.62 \mu_B$ for compound 2. These values are in agreement with the theoretical ones: $3 \mu_B$ for two V^{4+} and one Cu^{2+} (compound 1) and $2.45 \mu_B$ for one V^{4+} and one Cu^{2+} (compound 2). A negative Weiss constant (-17.7 K) is obtained for compound 1, whereas a positive Weiss constant ($+5.9$ K) is observed in compound 2. In order to evaluate the magnetic frustration, one can calculate the frustration index, $f = \theta/T_N$, where T_N is the minimum temperature which does not exhibit magnetic ordering. Materials with $f \sim 3$ are considered as moderately frustrated, while materials with $f > 5$ – 10 indicate strong frustration.^{11,32–34} For compound 1, no antiferromagnetic ordering is observed down to the lowest measured temperature which is 2 K. The calculated frustration index is also larger than 9 for this compound revealing a strong frustration.

Since V–F–V bond angles of 107.8° (compound 1) and 106.9° (compound 2) are close to 106° in an antiferromagnet $[dpaH_2]_2[V_2O_2F_8]$ ($dpa = 2,2'$ -dipyridylamine), antiferromagnetic V–V interactions are expected.³⁵ This antiferromagnetic interaction has also been reported in materials based on the $[V_2O_2F_8]^{4-}$ dimer such as $CsVOF_3$, $RbVOF_3$, $[C_{12}H_{12}N_2]_{0.5}[VOF_3]$, or $[pyH][VO_2F_5]$.^{36,37} Considering the negative Weiss constant for compound 1 with one V–V and four V–Cu paths and positive Weiss constant for compound 2 with one V–V and six V–Cu paths, V–Cu interaction should be ferromagnetic. The strong frustration which suppressed the long-range

magnetic ordering is due to the competition between these ferromagnetic and antiferromagnetic interactions.

The susceptibility data of compound 1 deviated from the Curie–Weiss law below 40 K. This can be understood by assuming the formation of V–V spin singlet. The remaining Cu spin behaves as a free spin and gives larger susceptibility than the Curie–Weiss law with negative Weiss constant. The data at 1 T below 50 K were fitted to the equation:

$$\begin{aligned}\chi &= \chi_0 + \chi_{Cu} + \chi_{dimer} \\ &= \chi_0 + C_{Cu}/(T - \theta) + \frac{3C_{dimer}/T}{(3 + e^{\Delta/T})}\end{aligned}$$

where χ_0 is the temperature-independent term, χ_{Cu} is the contribution from the Cu spins with a Curie constant of C_{Cu} and a Weiss constant of θ , and χ_{dimer} is the contribution from isolated spin-1/2 dimers of the V ions.³⁸ The dimer has a spin gap Δ from the singlet ground state to the triplet excited state and a paramagnetic Curie constant C_{dimer} . The fit gave the values $\chi_0 = 0.001(2)$ emu/mol, $C_{Cu} = 0.32(2)$ emu K/mol, $\theta = -0.00(13)$ K, $C_{dimer} = 0.83(21)$ emu K/mol, and $\Delta = 60(5)$ K. These parameters were varied freely during the fit. The estimated C_{Cu} and C_{dimer} are in good agreement with 0.375 and 0.75 emu K/mol expected for a Cu spin and for two V spins, respectively (Figure 3).

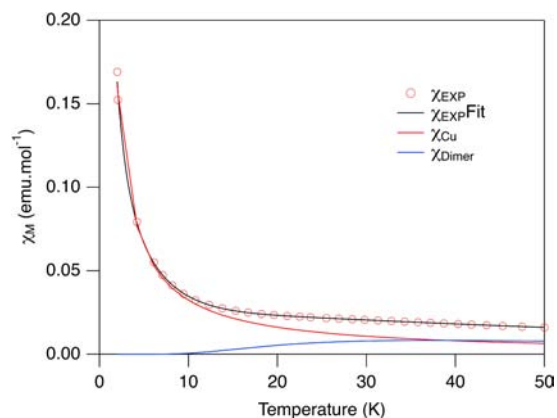


Figure 3. Results of fitting the temperature dependence of magnetic susceptibility below 50 K. The contributions from paramagnetic Cu spins and from V dimers are plotted with red and blue lines, respectively.

Magnetization measurement in a pulsed high-magnetic field was conducted for compound 1. The data at 2 K shown in Figure 4 first show a plateau at $1 \mu_B$, corresponding to the saturation of the Cu-spin magnetization. The broken line shows the Brillouin function for $S = 1/2$ with $g = 1.91$. The good agreement indicates the absence of interaction between the spins. This result confirms that our analysis of susceptibility data with negligible Weiss constant for Cu free spins is valid. The magnetization shows a sudden increase at around 38 T indicating the transition from the singlet ground state to the triplet excited state of V dimers and finally saturates at $3 \mu_B$, full magnetic moment for one Cu and two V spins. The magnitude of spin gap estimated from the crossover field of 38 T is 48.6 K. This value is slightly smaller than that obtained from the fitting of the susceptibility data (60 K), but magnetization data tend to give smaller values in comparison with other methods.³⁹ These results confirmed the formation of V spin-1/2 dimers and the

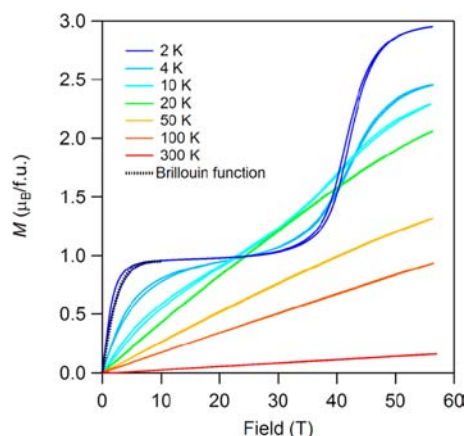


Figure 4. Magnetization curves as a function of temperature for compound **1** measured in a pulsed magnetic field.

paramagnetic behavior of remaining Cu spin-1/2. Thus, the consistency of the number of spins and almost zero Weiss temperature for Cu spins obtained by fitting and the magnetization data are excellent. Also, the contributions of V-dimer and Cu-spins are comparable in the temperature range of 20–50 K. This is also consistent with the susceptibility data that those obeyed the Curie–Weiss law above 40 K.

This class of materials is also of interest owing to the possibility of tuning the degree of frustration. Depending on the ratio between ferromagnetic and antiferromagnetic paths, the Weiss temperature varies from negative to positive. Moreover, the magnetization data show how it is possible to separate the magnetic components of frustrated magnets in which ferromagnetic and antiferromagnetic interactions compete. Thus, the magnetic measurements of such system give more insights on the control and the analysis of new frustrated magnets.

DISCUSSION

The Triangular Fragment. The 1D crystal structures of **1** and **2** are different. In **1**, the “CuV” chains are negatively charged, while they are neutral in **2**. Moreover, the ratio Cu:V is different in **1** (Cu:V = 1:2) and **2** (Cu:V = 1:1), while the organic molecule is isolated in **1** but is coordinated to the chains in **2**. However, both compounds **1** and **2** reported in this paper are built from the same “CuV₂” triangular fragments (Figure 5). These triangular motifs can be described as dimeric [V₂O₂F₈]⁴⁻ anions linked to one octahedral Cu²⁺ cation. The dimeric [V₂O₂F₈]⁴⁻ anion was previously reported in other crystal structures.^{35–37,40,41}

Cis Directing Property of Edge And Corner Sharing Metal-Centered Octahedra and Triangular Spin-1/2 Fragment. In solid-state chemistry, the structure directing properties of different [MO_xF_y]^{z-} anions have been previously investigated.^{42–44} The vanadium-centered anions are of interest because they are *cis*-edge or -corner sharing octahedra. [VOF₅]^{y-} direct coordination through *cis* F⁻ ligands: the F⁻ ligand in *trans* position of O²⁻ and one of the F⁻ ligand in equatorial position. This occurs as a result of the low nucleophilicity of the oxide ligand owing to significant π -bonding between vanadium and the oxide ligand.⁴⁵ The [VOF₅]²⁻ and [VOF₄]²⁻ anions differ from [NbOF₅]²⁻ anion which exhibits *trans* directing properties owing to the high nucleophilicity of the oxide and its *trans* fluoride ligand.

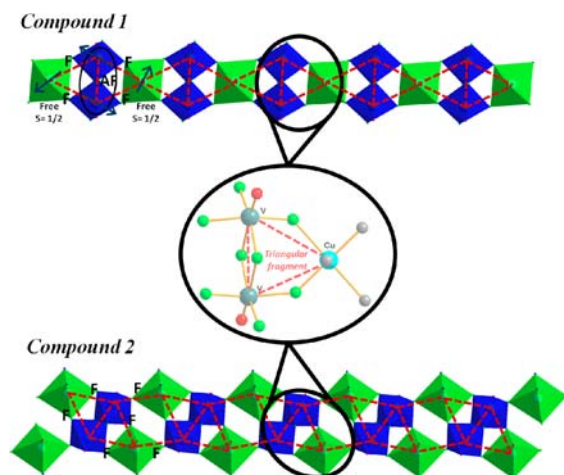


Figure 5. Representation of the “CuV₂” triangular fragment in compounds **1** and **2**. Blue and green octahedra represent vanadium-centered anions and copper-centered cations, respectively.

To our knowledge, the triangular fragments built from octahedral units can be classified in five groups: the three octahedra share (a) one corner (Figure 6a),^{46,47} (b) one edge and one corner (Figure 6b),^{48,49} (c) three corners (Figure

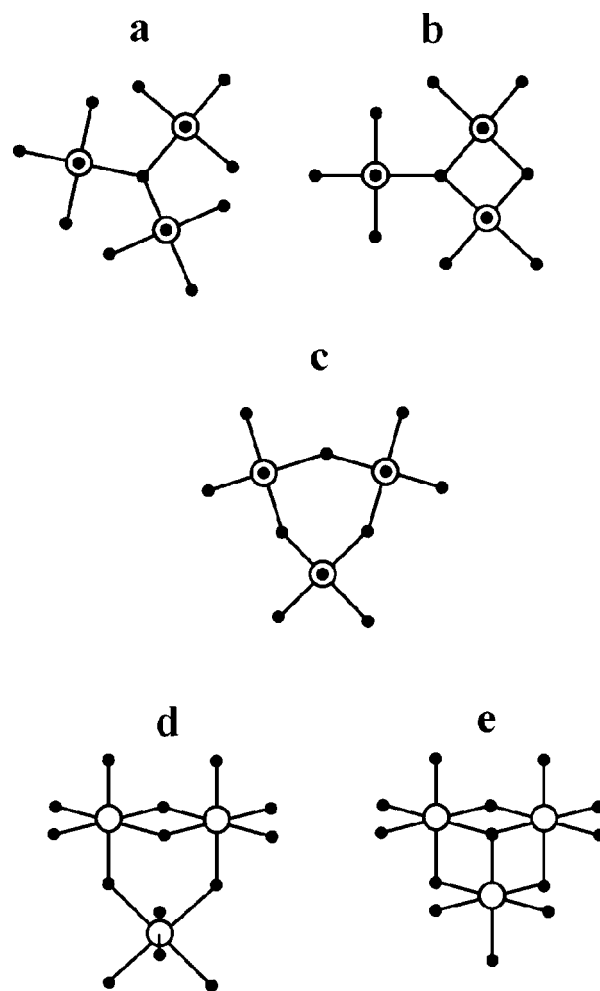


Figure 6. Representation of the possible coordinations of octahedra into triangular motifs. Octahedra are linked through edges or/and corners in *cis* position for (b–e).

6c),^{11,19,50} (d) one edge and two corners (Figure 6d),^{40,51} or (e) three edges (Figure 6e).^{21,52–55} With the exception of the case (a) where no directing property of the octahedral unit is required, every case exhibits *cis*-edge or -corner sharing octahedra within the triangular motif. Metal-centered octahedra exhibiting *cis* directing properties are also of interest to build most of the triangular frustrated fragments. Moreover, this can be extended to other categories of polyhedra. For example, the five coordinated Cu²⁺ cations in La₄Cu₃MoO₁₂ or La₃Cu₂VO₉ can be classified in the group (a) because the polyhedra share one oxygen and form triangular fragments.^{56–58}

In compounds **1** and **2**, the “CuV₂” triangular fragment is formed owing to the *cis* directing properties of the vanadium-centered anions (Figure 7a). In [V₂O₂F₈]⁴⁻ dimer,

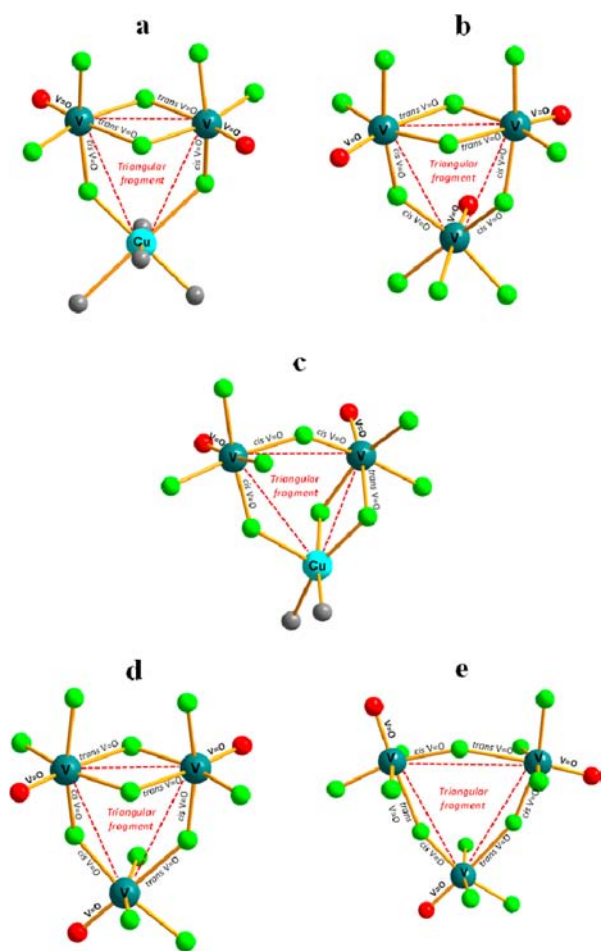


Figure 7. Triangular fragments in (a) compounds **1** and **2**, (b) CsVOF₃·1/2H₂O,⁴⁰ (c) [Cu(2,2'-dipyridylamine)][VOF₄],⁵¹ (d) [C₆N₃H₂₀]₂[V₄O₄F₁₄].2H₂O,⁴¹ and (e) Na_{0.4}K_{0.6}(NMe₄)₂[V₃O₃F₁₂].⁵⁹ The oxide ligands are terminal, while the *trans* fluoride ligand is bonded to another member of the triangular fragment or next nearest triangular fragment (which is not presented for clarity).

[V₂/2O₂/2F₈/2]²⁻ anions share two crystallographically equivalent fluoride ligands. Each of these two fluoride ligands is in *trans*-position of the vanadyl bond of one metal center and in *cis*-position of the vanadyl bond of the other metal center. The three other fluoride ligands in *cis*-position of the vanadyl bond remain available to bond other metal centers. Thus, the Cu²⁺ cations coordinate the two [VOF₄]²⁻ anions in a *cis*-direction and lead to the formation of the triangular “CuV₂” motifs.

In previously reported materials, triangular fragments have also been formed from *cis*-edge or -corner sharing octahedral anions.^{40,51} CsVOF₃·1/2H₂O reported by Walters et al. exhibits spin-1/2 “V₃” triangular motifs (Figure 7b). The dimeric [V₂O₂F₈]⁴⁻ anion is linked to a *cis*-corner sharing vanadium-centered anion. These trimeric fragments form V–O–F chains, but no magnetic frustration was mentioned. In the [Cu(2,2'-dipyridylamine)][VOF₄] compound, a different triangular spin-1/2 “CuV₂” motif is reported (Figure 7c).⁵¹ Within this unit, Cu²⁺ cation is coordinated to [VOF₄]²⁻ anions through the fluoride ligand in the *trans*-position of the vanadyl bond and the fluoride ligand in the *cis*-position of the same vanadyl bond. Another [VOF₄]²⁻ anion bonds the bimetallic units in a *cis*-direction to form the triangular motif. For this material, magnetic frustration was measured and attributed to the three-membered ring units.

The *cis*-directing property is also intrinsic to the V⁵⁺-centered anions.^{42,43} Thus, [C₆N₃H₂₀]₂[V₄O₄F₁₄].2H₂O reported by Aldous et al. is built of “V₃” trimeric fragments (Figure 7d).⁴¹ A dimeric unit anion [V₂O₂F₈]²⁻, structurally similar to [V₂O₂F₈]⁴⁻ of compounds CsVOF₃·1/2H₂O, **2** or **3**, is coordinated to a [VOF₄]⁻ anion. The fluoride ligand in *trans* of the vanadyl bond in the [VOF₄]⁻ anion is bonded to the edge-sharing dimer. In Na_{0.4}K_{0.6}(NMe₄)₂[V₃O₃F₁₂] reported by Hilbers et al., each [VOF₄]⁻ anion share fluorides (the fluoride ligand in *trans* of V=O and another in *cis* of the vanadyl bond) with two members of the triangular fragment (Figure 7e).⁵⁹

In every system reported in Figure 7, the fluoride ligands in *trans*-position of the vanadyl bonds are coordinated to another member of the triangular fragment (or next nearest triangular fragment) owing to their high nucleophilicities. Conversely, the oxide ligands of the vanadyl bonds are terminal because of their low nucleophilicities. Within the VOF₅ octahedra, the equatorial fluoride ligands, which are less nucleophilic than the fluoride ligand in the *trans*-position of the vanadyl bond, are available for coordination to the extended structure.^{42,44}

The Triangular “CuV₂” Fragment in Different Lattices.

The triangular “CuV₂” fragment forms different chains in compounds **1** and **2**. In structure **1**, each Cu²⁺ cation in octahedral environment links two triangular fragments through the four equatorial fluoride ligands, while two water ligands complete the environment of Cu²⁺ in *trans* position (Figure 8).

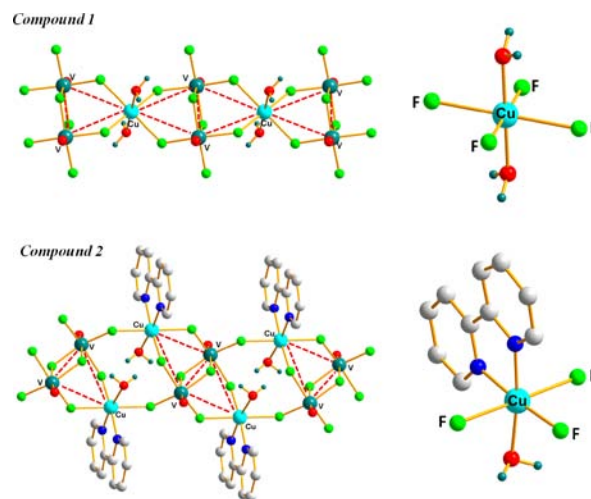


Figure 8. Coordination of copper cations in chains for compounds **1** and **2**.

In structure **2**, each $[\text{Cu}(\text{H}_2\text{O})(2,2'\text{-bpy})]^{2+}$ cation coordinates to only one triangular fragment because of the *cis* coordination of the bidentate organic ligand with Cu^{2+} . Hence, the lattices built from the same triangular fragment differ: the triangular motifs share simultaneously one corner and one edge along the chain in **1**, while double triangular fragments are isolated from each other in **2** (Figures 5 and 8).

The triangular motifs can be targeted in different lattices owing to strong intratriangular interactions. The fluoride ligand in *trans* position of vanadyl bond of $[\text{VOF}_4]^{2-}$ anions interact strongly with the other members of the triangular fragment because of its high nucleophilicity. The equatorial fluoride ligands of the VOF_5 octahedra are less nucleophilic but are able to coordinate to the extended structure. By coordinating the Cu^{2+} cation with the bidentate ligand, the formation of “ CuV_2 ” triangular fragments is not affected, but the interactions of the triangular fragments within the chains are modified resulting in different lattices with different magnetic behaviors.

CONCLUSION

In the search of new methods to engineer magnetic materials, the structure directing properties of $[\text{MO}_x\text{F}_y]^{z-}$ anions (M = transition metal) are shown to be interesting. The formation of triangular motifs based on edge or corner sharing octahedra requires the polyhedra to direct the coordination in *cis* position. The use of $[\text{VOF}_5]^{2-}$ anions exhibiting *cis* directing properties is promising. Triangular motifs could be obtained in different lattices exhibiting long-range frustration. Thus, the magnetic frustration of **1** is equivalent to the frustration of materials previously synthesized using the strategy of SBUs (coordination of the metal ions with organic ligands), but this latter strategy is already fully optimized with the synthesis of kagomé lattices. The use of *cis* directing metal-centered octahedra is also a new, powerful, and promising method to design frustrated magnetic materials.

ASSOCIATED CONTENT

Supporting Information

X-Ray crystallographic files in CIF format for compounds **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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