

# Synthesis of layered (2-D) V-based bimetallic oxalates from non-aqueous media that cannot be synthesized from aqueous media

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The reaction of  $(\text{NBu}_4)_3[\text{V}^{\text{III}}(\text{ox})_3]$  (**1**, ox = oxalate) and  $\text{M}(\text{II})$  ( $\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$ ) ions in MeCN, leads to the isolation of V-based coordination polymers of  $[\text{N}(n\text{-Bu})_4][\text{Fe}^{\text{II}}\text{V}^{\text{III}}(\text{ox})_3] \cdot 0.30\{[\text{N}(n\text{-Bu})_4](\text{BF}_4)\}$  (**2**),  $[\text{N}(n\text{-Bu})_4][\text{Co}^{\text{II}}\text{V}^{\text{III}}(\text{ox})_3] \cdot 0.75\{[\text{N}(n\text{-Bu})_4](\text{BF}_4)\}$  (**3**),  $[\text{N}(n\text{-Bu})_4][\text{Ni}^{\text{II}}\text{V}^{\text{III}}(\text{ox})_3] \cdot 0.20\{[\text{N}(n\text{-Bu})_4](\text{BF}_4)\} \cdot 0.20\text{MeCN}$  (**4**), and  $[\text{N}(n\text{-Bu})_4][\text{Cu}^{\text{II}}\text{V}^{\text{III}}(\text{ox})_2](\text{BF}_4)_2$  (**5**) composition. Due to the lability of  $[\text{V}^{\text{III}}(\text{ox})_3]^{3-}$  to dissociate  $\text{ox}^{2-}$ , these compounds cannot be prepared from aqueous media. **5** is best described as  $[\text{N}(n\text{-Bu})_4][\text{V}^{\text{III}}\text{Cu}^{\text{II}}(\text{ox})_2](\text{BF}_4)_2$ , and **2**, **3**, **4**, and **5** are proposed to have a layered (2-D) motif for the  $\text{M}^{\text{II}}\text{M}(\text{ox})_x$  ( $x = 2, 3$ ) extended framework. The  $[\text{V}^{\text{III}}\text{Cu}^{\text{II}}(\text{ox})_2]$  composition of **5** is reported for the first time for a bimetallic oxalate. **2** shows a weak antiferromagnetic interaction between  $\text{Fe}(\text{II})$ ,  $S = 2$  and  $\text{V}(\text{III})$ ,  $S = 1$  ions ( $\theta = -9.4$  K) within the 2-D layers. **3** and **5** do not magnetically order above 2 K. **4** magnetically order as ferromagnets below 2.55 K [taken as the onset of magnetization in  $\chi''(T)$ ], and has a glass transition temperature ( $\chi''_{\text{max}}$  at 1000 Hz) at 2.26 K.

## Introduction

The contemporary interest in molecule-based magnetic materials reflects not only their relevance to the design and construction of new magnetic materials from molecular building blocks, but also their potential applications to a myriad of applications for magnet including storage devices.<sup>1</sup> Detailed studies of the first organic-containing molecule-based magnet,  $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^{+}[\text{TCNE}]^{-}$  (TCNE = tetracyanoethylene), with a 4.8 K  $T_c$  led to the discovery of the room-temperature organic magnet,  $\text{V}(\text{TCNE})_{x,y}(\text{solvent})$  ( $T_c \sim 400$  K).<sup>2</sup> Furthermore, in addition to this V-based magnet,<sup>3</sup>  $\text{K}_{0.058}\text{V}^{\text{III}}_{0.57}\text{V}^{\text{III}}_{0.43}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.79}(\text{SO}_4)_{0.058}$ <sup>4a</sup> and  $\text{KV}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot \text{H}_2\text{O}$ <sup>4b</sup> have the highest  $T_c$ s and they also possess a vanadium ion linking the  $[\text{Cr}(\text{CN})_6]^{3-}$  ions. Since tris(oxalato)chromates(III) and ferrates(III) were first reported to make 2-D molecule-based magnets by Okawa, magnetic materials based on tris(oxalato)metallate(III) having a general formula  $\text{A}[\text{M}^{\text{II}}\text{M}^{\text{III}}(\text{ox})_3]$  ( $\text{A} =$  bulky monovalent cation;  $\text{M}^{\text{II}} = \text{Mn}, \text{Fe}, \text{Ni}, \text{Co}, \text{Cu}, \text{Zn}$ ;  $\text{M}^{\text{III}} = \text{Cr}, \text{Fe}, \text{Ru}$ ) have been extensively studied.<sup>5</sup>

While magnets based upon  $[\text{M}^{\text{III}}(\text{ox})_3]^{3-}$  ( $\text{M} = \text{Cr}, \text{Fe}, \text{Ru}$ ) have been extensively studied, two-dimensional (2-D) oxalate-bridged compounds containing  $\text{V}(\text{III})$  and/or  $\text{V}(\text{II})$  ions have been very limited, due in part to its lability in aqueous solution. Recently, we reported the aqueous synthesis and magnetic properties of 2-D V-based tris(oxalato)vanadate(III), *i.e.*  $[\text{N}(n\text{-Bu})_4][\text{V}^{\text{II}}\text{V}^{\text{III}}(\text{ox})_3]$  and  $[\text{N}(n\text{-Bu})_4][\text{Mn}^{\text{II}}\text{V}^{\text{III}}(\text{ox})_3]$ .<sup>6</sup> These materials magnetically order as ferrimagnets, and exhibit ferro- or antiferromagnetic interactions depending on the  $\text{M}(\text{II})$  ions. Previously, we were unsuccessful in attempts to obtain  $[\text{N}(n\text{-Bu})_4][\text{M}^{\text{II}}\text{V}^{\text{III}}(\text{ox})_3]$  ( $\text{M}^{\text{II}} = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$ ) due to the lability of  $[\text{V}(\text{ox})_3]^{3-}$  in aqueous solution, but isolated  $[\text{M}^{\text{II}}(\text{ox})(\text{OH})_2]$  that exhibited antiferromagnetic coupling.<sup>6</sup>

Herein, we report the synthesis of  $[\text{N}(n\text{-Bu})_4][\text{Fe}^{\text{II}}\text{V}^{\text{III}}(\text{ox})_3] \cdot 0.30\{[\text{N}(n\text{-Bu})_4](\text{BF}_4)\}$  (**2**),  $[\text{N}(n\text{-Bu})_4][\text{Co}^{\text{II}}\text{V}^{\text{III}}(\text{ox})_3] \cdot 0.75\{[\text{N}(n\text{-Bu})_4](\text{BF}_4)\}$  (**3**),  $[\text{N}(n\text{-Bu})_4][\text{Ni}^{\text{II}}\text{V}^{\text{III}}(\text{ox})_3] \cdot 0.20\{[\text{N}(n\text{-Bu})_4](\text{BF}_4)\} \cdot 0.20\text{MeCN}$  (**4**), and  $[\text{N}(n\text{-Bu})_4][\text{V}^{\text{III}}\text{Cu}^{\text{II}}(\text{ox})_2](\text{BF}_4)_2$  (**5**) from acetonitrile, and which cannot be prepared from aqueous media, and report their magnetic properties.

**Experimental**

## General

### General

Infrared spectra ( $\pm 1$   $\text{cm}^{-1}$ ) were recorded with a Bruker Tensor 37 FT-IR spectrophotometer. Elemental analyses were performed by Complete Analysis Laboratories, Inc. or GCL & Chemisar Laboratories. X-Ray powder diffraction (XRPD) data were recorded on a Bruker AXS diffractometer at 40 kV and 40 mA for  $\text{CuK}\alpha$  ( $\lambda = 1.5406$  Å) with a scan speed of  $0.24^\circ \text{min}^{-1}$  and a step size of  $0.02^\circ$  in  $2\theta$ . All compounds studied by XRPD were sealed in quartz capillaries in an oxygen-free ( $<0.5$  ppm  $\text{O}_2$ ) dry box. Magnetic susceptibilities were measured in applied fields of 300 and/or 1000 Oe between 2 and 300 K on a Quantum Design MPMS superconducting quantum interference device (SQUID). Ac susceptibilities were measured on the MPMS at 10, 100, and 1000 Hz. Diamagnetic corrections were made by using Pascal's constants.

### Synthesis

All chemicals used in the synthesis were of reagent grade and used without further purification.  $[\text{Fe}(\text{NCMe})_6](\text{BF}_4)_2$ ,  $[\text{Co}(\text{NCMe})_6](\text{BF}_4)_2$ ,  $[\text{Ni}(\text{NCMe})_6](\text{BF}_4)_2$ , and  $[\text{Cu}(\text{NCMe})_4](\text{BF}_4)_2$  were synthesized by a literature procedure.<sup>7</sup>  $(\text{NBu}_4)_3[\text{V}(\text{ox})_3]$  (**1**) was prepared by a slightly modified literature procedure.<sup>8</sup> as  $\text{VCl}_3$  and  $(\text{NBu}_4)_2\text{ox}^9$  were used instead of  $\text{V}_2\text{O}_5$ , and  $\text{K}_2\text{ox}/\text{H}_2\text{ox}$ , and diethyl ether/THF was added to precipitate **1**. Solvents were distilled from the appropriate drying agents under nitrogen before use. All syntheses were performed in an oxygen-free ( $<0.5$  ppm  $\text{O}_2$ ) dry box.

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**[N(*n*-Bu)<sub>4</sub>][Fe<sup>II</sup>V<sup>III</sup>(ox)<sub>3</sub>]-0.30{[N(*n*-Bu)<sub>4</sub>](BF<sub>4</sub>)} (2).** An MeCN solution (2 mL) of [Fe(NCMe)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> (91 mg, 0.192 mmol) was added dropwise to an MeCN solution (2 mL) of (NBu<sub>4</sub>)<sub>3</sub>[V(ox)<sub>3</sub>] (200 mg, 0.192 mmol) at room temperature, and a brown precipitate immediately formed. After stirring for 1 h the solid was isolated by centrifugation, washed with MeCN, and dried *in vacuo* (yield: 70 mg; 52%). Anal. Calcd<sup>10</sup> for C<sub>26.8</sub>H<sub>46.8</sub>B<sub>0.3</sub>F<sub>1.2</sub>FeN<sub>1.3</sub>O<sub>12</sub>V: C, 45.20; H, 6.62; N, 2.56. Found: C, 44.94; H, 6.62; N, 3.03%. FT-IR (KBr): 2966 (ν<sub>CH</sub>), 2877 (ν<sub>CH</sub>), 1630 (ν<sub>CO</sub>), 1457, 1428, 1297, 811, 534, 479 cm<sup>-1</sup>.

**[N(*n*-Bu)<sub>4</sub>][Co<sup>II</sup>V<sup>III</sup>(ox)<sub>3</sub>]-0.75{[N(*n*-Bu)<sub>4</sub>](BF<sub>4</sub>)} (3).** An MeCN solution (2 mL) of [Co(NCMe)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> (92 mg, 0.192 mmol) was added dropwise to an MeCN solution (2 mL) of (NBu<sub>4</sub>)<sub>3</sub>[V(ox)<sub>3</sub>] (200 mg, 0.192 mmol) at room temperature, and a yellow-brown precipitate immediately formed. After stirring for 1 h the solid was isolated by centrifugation, washed with MeCN, and dried *in vacuo* (yield: 75 mg; 46%). Anal. Calcd for C<sub>34</sub>H<sub>63</sub>B<sub>0.75</sub>F<sub>3</sub>CoN<sub>1.75</sub>O<sub>12</sub>V: C, 47.30; H, 7.36; N, 2.84. Found: C, 47.06; H, 7.15; N, 3.38%. FT-IR (KBr): 2965 (ν<sub>CH</sub>), 2877 (ν<sub>CH</sub>), 1624 (ν<sub>CO</sub>), 1457, 1429, 1297, 813, 535, 479 cm<sup>-1</sup>.

**[N(*n*-Bu)<sub>4</sub>][Ni<sup>II</sup>V<sup>III</sup>(ox)<sub>3</sub>]-0.20{[N(*n*-Bu)<sub>4</sub>](BF<sub>4</sub>)}-0.20MeCN (4).** An MeCN solution (3 mL) of [Ni(NCMe)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> (92 mg, 0.192 mmol) was added dropwise to an MeCN solution (4 mL) of (NBu<sub>4</sub>)<sub>3</sub>[V(ox)<sub>3</sub>] (200 mg, 0.192 mmol) at room temperature, and a green precipitate immediately formed. After stirring for 1 h the solid was isolated by centrifugation, washed with MeCN, and dried *in vacuo* (yield: 83 mg; 63%). Anal. Calcd for C<sub>25.6</sub>H<sub>43.8</sub>B<sub>0.2</sub>F<sub>0.8</sub>N<sub>1.4</sub>NiO<sub>12</sub>V: C, 44.55; H, 6.40; N, 2.84. Found: C, 44.59; H, 6.29; N, 3.16%. FT-IR (KBr): 2964 (ν<sub>CH</sub>), 2877 (ν<sub>CH</sub>), 1623 (ν<sub>CO</sub>), 1462, 1430, 1299, 808, 537, 478 cm<sup>-1</sup>.

**[N(*n*-Bu)<sub>4</sub>][Cu<sup>II</sup>V<sup>III</sup>(ox)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (5).** An MeCN solution (2 mL) of [Cu(NCMe)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> (154 mg, 0.384 mmol) was added dropwise to an MeCN solution (4 mL) of (NBu<sub>4</sub>)<sub>3</sub>[V(ox)<sub>3</sub>] (400 mg, 0.384 mmol) at room temperature, and a green precipitate immediately formed. After stirring for 1 h the solid was isolated by centrifugation, washed with MeCN, and dried *in vacuo* (yield: 180 mg; 67%). Anal. Calcd for C<sub>20</sub>H<sub>36</sub>B<sub>2</sub>F<sub>8</sub>CuNO<sub>8</sub>V: C, 34.00; H, 5.14; N, 1.98. Found: C, 34.05; H, 4.67; N, 1.82%. FT-IR (KBr): 2966 (ν<sub>CH</sub>), 2877 (ν<sub>CH</sub>), 1653 (ν<sub>CO</sub>), 1611 (ν<sub>CO</sub>), 1460, 1423, 1280, 815, 538, 479 cm<sup>-1</sup>.

## Results and discussion

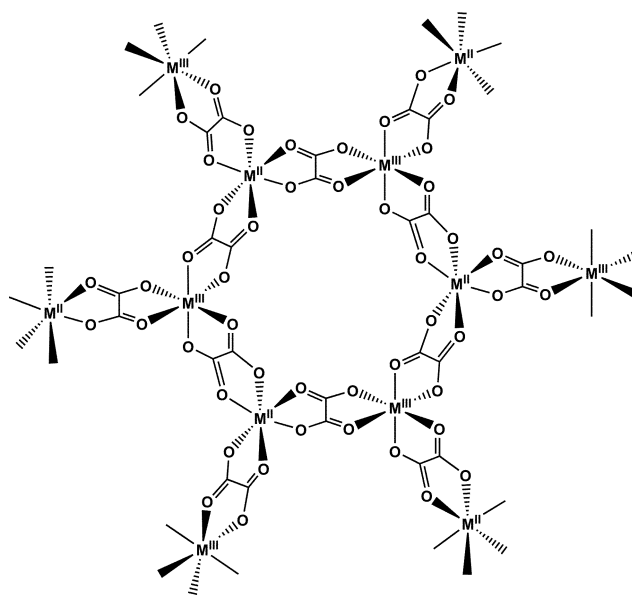
### Synthesis and characterization

The reaction of one equivalent of (NBu<sub>4</sub>)<sub>3</sub>[V(ox)<sub>3</sub>] with [M(NCMe)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> (M = Fe, Co, Ni) or [Cu(NCMe)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> in acetonitrile under anaerobic conditions affords [N(*n*-Bu)<sub>4</sub>][Fe<sup>II</sup>V<sup>III</sup>(ox)<sub>3</sub>]-0.30{[N(*n*-Bu)<sub>4</sub>](BF<sub>4</sub>)} (brown) (2), [N(*n*-Bu)<sub>4</sub>][Co<sup>II</sup>V<sup>III</sup>(ox)<sub>3</sub>]-0.75{[N(*n*-Bu)<sub>4</sub>](BF<sub>4</sub>)} (yellow-brown) (3), [N(*n*-Bu)<sub>4</sub>][Ni<sup>II</sup>V<sup>III</sup>(ox)<sub>3</sub>]-0.20{[N(*n*-Bu)<sub>4</sub>](BF<sub>4</sub>)}-0.20MeCN (green) (4), and [N(*n*-Bu)<sub>4</sub>][Cu<sup>II</sup>V<sup>III</sup>(ox)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (green) (5) in good yield. Due to the very rapid precipitation, [N(*n*-Bu)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>, and sometimes the MeCN solvent, is occluded in the precipitate, and attempts to obtain pure materials by altering the reaction conditions, unlike the water-prepared analogs,<sup>6</sup> were unsuccessful.<sup>11</sup> Use of water, however, leads to the formation of different products.<sup>6</sup> Due to the small particle size 2–5 had to be isolated *via* centrifugation. When

exposed to air for a few hours, the colors and the IR spectra did not change significantly, indicating that these compounds are stable in air. The IR spectra of 2–4 are nearly identical except that the IR spectrum of 5 contains split peaks associated with an oxalate bridging ligand. All of these spectra had peaks characteristic of [BF<sub>4</sub>]<sup>-</sup>, and 4 additionally has ν<sub>CN</sub> absorptions characteristic of uncoordinated MeCN. The ν<sub>CO</sub> were strong, single absorptions at 1630, 1624, and 1623 cm<sup>-1</sup> for 2–4, respectively, while the ν<sub>CO</sub> peak for 5 shows split absorptions at 1653 and 1611 cm<sup>-1</sup>. The genesis of the splitting is unknown, but may be due to the Jahn–Teller distortion of the Cu(II) ion.

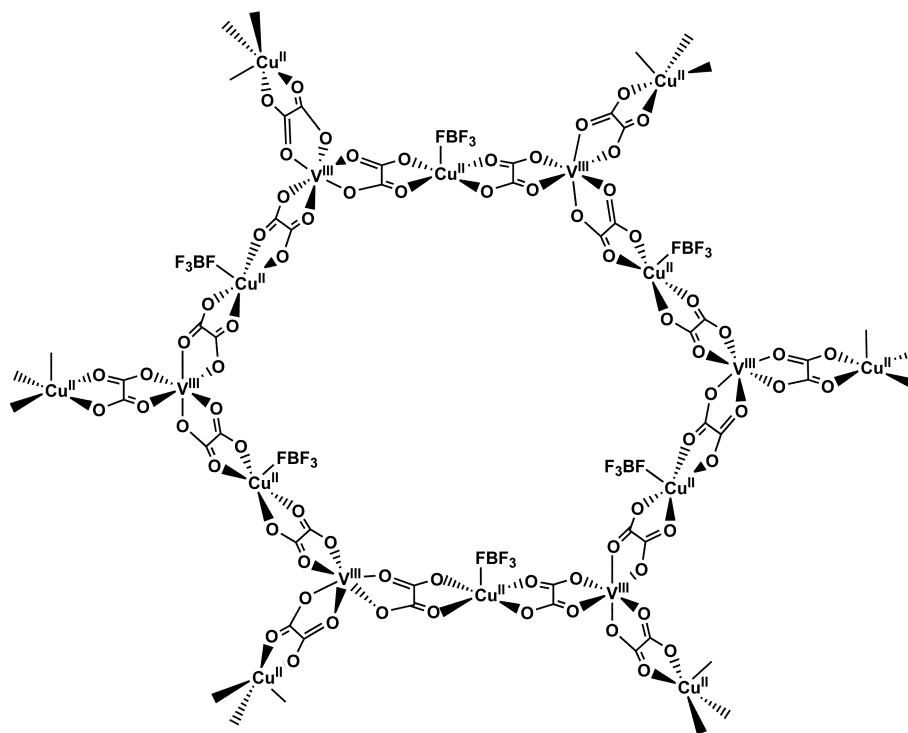
The X-ray powder diffraction (XRPD) patterns of 2–4 are very similar each other, although the determination of the unit cell parameters could not be indexed, due to the broad and weak peaks. Contrary to the XRPDs of 2–4, the pattern of 5 showed three strong peaks at 27.78, 32.19, and 46.21° 2θ, which could be indexed. Compound 5 is decomposed by X-rays as it turned brown upon exposure to the X-ray beam. Hence its structure cannot be determined.

Based on the structure of the large family of compounds of [N(*n*-Bu)<sub>4</sub>][M<sup>II</sup>M<sup>III</sup>(ox)<sub>3</sub>] (M<sup>III</sup> = Cr, Fe, Ru; M<sup>II</sup> = Cr, Mn, Fe, Co, Ni, Cu) composed of each metal ion surrounded by three oxalates (Fig. 1) and the [N(*n*-Bu)<sub>4</sub>]<sup>+</sup> cation sitting above the center of each hexagonal ring,<sup>5,14</sup> this motif is proposed for the framework structures present in 2, 3, and 4. The excess cations and anions presumably occupy interlayer interstitial sites, which limit the crystallinity and hence lead to poor diffraction, as observed.



**Fig. 1** Proposed 2-D structure of [M<sup>II</sup>M<sup>III</sup>(ox)<sub>3</sub>]<sup>-</sup> present in the [N(*n*-Bu)<sub>4</sub>][M<sup>II</sup>M<sup>III</sup>(ox)<sub>3</sub>] moieties of 2, 3, and 4. The [N(*n*-Bu)<sub>4</sub>]<sup>+</sup> cation sits in a site above the center of each hexagonal ring.

Compound 5 has a different composition of [N(*n*-Bu)<sub>4</sub>][Cu<sup>II</sup>V<sup>III</sup>(ox)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>. This indicates [N(*n*-Bu)<sub>4</sub>][V<sup>III</sup>Cu<sup>II</sup>(ox)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> with two oxalates coordinated to the Cu(II)s and the V(III) cation coordinated to three of these units is a better formulation, Fig. 2. As occurs for the [N(*n*-Bu)<sub>4</sub>][M<sup>II</sup>M<sup>III</sup>(ox)<sub>3</sub>] family of magnets, the [N(*n*-Bu)<sub>4</sub>]<sup>+</sup> in 5 is proposed to reside above the center of the hexagonal ring, and the anions presumably occupy interstitial



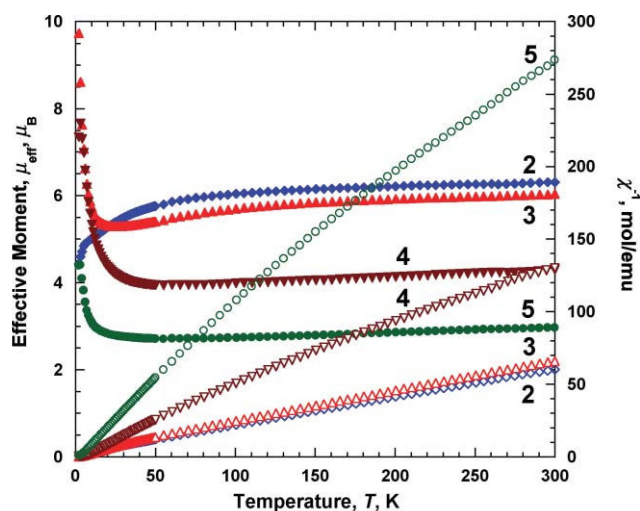
**Fig. 2** Proposed 2-D structure of  $[\text{V}^{\text{III}}\text{Cu}^{\text{II}}(\text{ox})_2](\text{BF}_4)$  present in  $[\text{N}(n\text{-Bu})_4][\text{Cu}^{\text{II}}\text{V}^{\text{III}}(\text{ox})_2](\text{BF}_4)_2$  (**5**) with the  $[\text{N}(n\text{-Bu})_4]^+$  cation residing above the center of each hexagonal ring.

sites, which lead to poor crystallinity and poor diffraction, as observed. This composition and structure has yet to be reported for a bimetallic oxalate, but several examples of  $[\text{Cu}(\text{ox})_2(\text{OH}_2)]^{2-12}$  have been reported. Formation of  $[\text{N}(n\text{-Bu})_4][\text{V}^{\text{III}}\text{Cu}^{\text{II}}(\text{ox})_2](\text{BF}_4)_2$  undoubtedly arises from the ability of  $[\text{V}^{\text{III}}(\text{ox})_3]^{3-}$  to dissociate  $\text{ox}^{2-}$ , which forms less labile  $[\text{Cu}(\text{ox})_2(\text{OH}_2)]^{2-}$ . The presence of  $[\text{N}(n\text{-Bu})_4]^+$  forms the needed template for formation of the 2-D lattice as originally reported by Okawa and co-workers for the smaller  $[\text{M}^{\text{II}}\text{M}^{\text{III}}(\text{ox})_3]^-$  framework,<sup>5b</sup> and this requires the second  $[\text{BF}_4]^-$  anion to balance the charge.

### Magnetic properties

The magnetic susceptibilities,  $\chi$ , of **2** to **5** were measured between 2 and 300 K, and are plotted as  $\chi^{-1}(T)$  and  $\mu_{\text{eff}}(T)$  [ $\mu_{\text{eff}} = (8\chi T)^{1/2}$ ], Fig. 3. Compound **2** has a 300 K effective magnetic moment of  $6.31 \mu_{\text{B}}$  that decreases monotonically with decreasing temperature to  $4.43 \mu_{\text{B}}$  at 2 K. This exceeds the  $5.66 \mu_{\text{B}}$  expected for independent  $g = 2$ ,  $S = 2$ ,  $\text{Fe}^{\text{II}}$  and  $S = 1$ ,  $\text{V}^{\text{III}}$  spins and is attributed to a high effective Landé  $g$  value, *i.e.*  $g_{\text{eff}} = 2.23$ , typical of  $\text{Fe}^{\text{II}}$ . Between 2 and 300 K, the data can be fit to the Curie–Weiss expression with  $\theta = -9.4$  K, in accord with a weak antiferromagnetic interaction (Fig. 3). This value is comparable to that of  $[\text{N}(n\text{-Bu})_4][\text{Cr}^{\text{II}}\text{Cr}^{\text{III}}(\text{ox})_3]$ , which possesses a weak antiferromagnetic coupling, *i.e.*  $\theta = -12.7$  K, and does not magnetically order.<sup>13</sup>

Compound **3** has an effective magnetic moment of  $6.03 \mu_{\text{B}}$  at 300 K, which decreases upon cooling to minimum of  $5.29 \mu_{\text{B}}$  at 26 K, and then increases to maximum of  $9.73 \mu_{\text{B}}$  at 2 K, Fig. 3. This is indicative of ferrimagnetic behavior. This magnetic moment at 300 K exceeds the expected one ( $4.80 \mu_{\text{B}}$ ) for independent  $g = 2$ ,  $S = 3/2$ ,  $\text{Co}^{\text{II}}$  and  $S = 1$ ,  $\text{V}^{\text{III}}$  spins. This deviation can be attributed



**Fig. 3**  $\mu_{\text{eff}}(T)$  for **2** (◆), **3** (▲), **4** (▼) and **5** (●) and  $\chi^{-1}(T)$  for **2** (◇), **3** (△), **4** (▽) and **5** (○).

to a substantial orbital angular momentum of  $\text{Co}(\text{II})$ , *i.e.*  $g_{\text{eff}} = 2.52$ , as is expected for  $\text{Co}(\text{II})$ .<sup>14</sup> Above 30 K  $\chi^{-1}(T)$  for **3** can be fit to the Curie–Weiss expression with  $\theta = -14$  K indicating weak antiferromagnetic coupling. To ascertain if **3** magnetically orders the in-phase, real,  $\chi'(T)$ , and the out-of-phase, imaginary,  $\chi''(T)$ , components of the ac susceptibility were measured between 2 and 10 K.  $\chi(T)$  increases continuously with decreasing temperatures, irrespective of frequency (10, 100, 1000 Hz) without reaching a maximum. This suggests that **3** magnetically orders below 2 K.

Compound **4** has an effective magnetic moment of  $4.29 \mu_B$  at 300 K, which decreases upon cooling to a minimum of  $3.94 \mu_B$  at 55 K, and then increases to a maximum of  $7.66 \mu_B$  at 3 K, Fig. 3. The value of  $\mu_{\text{eff}}$  at room temperature is slightly larger than the  $4.00 \mu_B$  expected for independent  $S = 1$ ,  $V^{\text{III}}$  ( $g = 2$ ) and  $S = 1$ ,  $Ni^{\text{II}}$  ( $g = 2$ ) spins, and is attributed to a high effective  $g$  value, *i.e.*  $g_{\text{eff}} = 2.15$ . Above 30 K  $\chi^{-1}(T)$  for **4** can be fit to the Curie–Weiss expression with  $\theta = -10$  K indicative of weak antiferromagnetic coupling. To ascertain if **4** magnetically orders the ac susceptibility,  $\chi'(T)$  and  $\chi''(T)$ , was measured below 9 K (Fig. 4 top). The frequency dependent peaks in both  $\chi'(T)$  and  $\chi''(T)$  are characteristic of magnetic ordering. The frequency ( $f$ ) dependence, as evidenced by  $\theta = 0.034 \{ \theta = \Delta T_f / [T_f \Delta(\log f)]$ , where  $T_f$  is the temperature at which the maximum in  $\chi'(T)$  occurs in the lowest frequency (10 Hz) data, and the greater the frequency dependence the larger the value of  $\theta$  } is indicative of spin-glass-like behavior.<sup>15</sup> The poor crystallinity is a source of the disorder and the differing antiferromagnetic couplings leads to sufficient frustration for spin glass behavior to be observed. The glass transition temperature extracted from the peak position at 1000 Hz  $\chi'(T)$  data is 2.26 K.

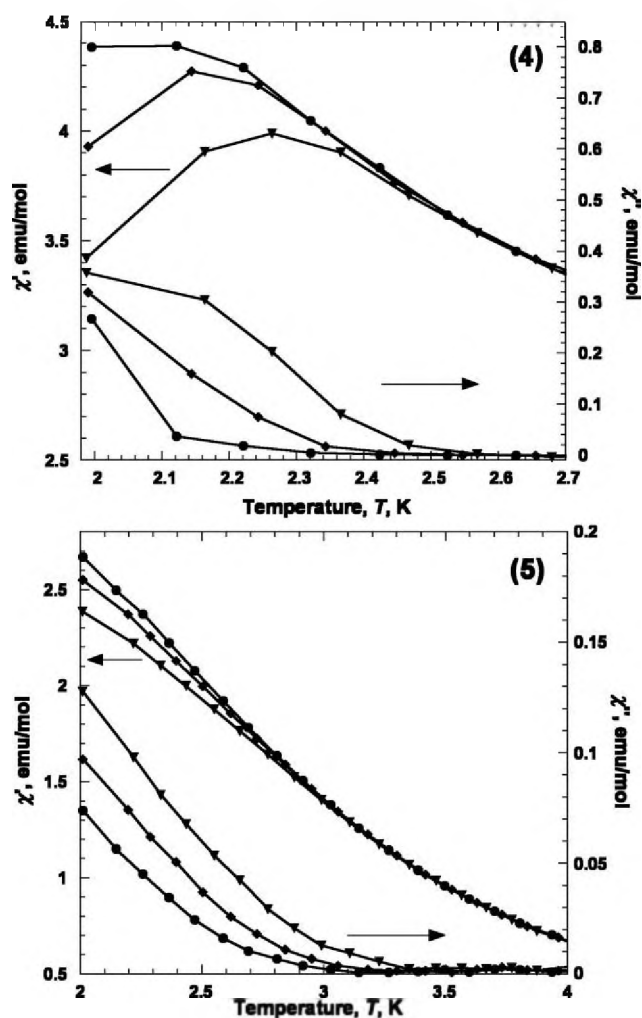


Fig. 4  $\chi'(T)$  and  $\chi''(T)$  for **4** and **5** at 10 (●), 100 (◆), and 1000 (▼) Hz.

Compound **5** has an effective magnetic moment of  $2.96 \mu_B$  at 300 K, which decreases upon cooling to a minimum of  $2.71 \mu_B$  at 55 K, and then increases to a maximum of  $4.40 \mu_B$  at 3 K, Fig. 3. This is less than  $3.32 \mu_B$  expected for independent  $g = 2$ ,  $S = 1/2$ ,  $Cu^{\text{II}}$  and  $S = 1$ ,  $V^{\text{III}}$  spins indicative of weak antiferromagnetic interaction. The effective magnetic moment is lower than the spin-only value, indicative of antiferromagnetic coupling between the  $Cu(\text{II})$  and  $V(\text{III})$  ions. Above 30 K, the data can be fit to the Curie–Weiss expression with  $\theta = -12$  K in accord with a weak antiferromagnetic interaction (Fig. 3). To determine if **5** magnetically orders  $\chi'(T)$  and  $\chi''(T)$  were measured below 7 K (Fig. 4 bottom).  $\chi'(T)$  increases continuously with decreasing temperature to 2 K, irrespective of frequency without reaching a maximum. This suggests that **5** magnetically orders below 2 K. However, **5** shows a frequency dependence below 3 K, although  $\theta$  could not be calculated due to the lack of maxima,<sup>15</sup> and is indicative of spin-glass-like behavior.  $\chi''(T)$  is non-zero below 3.35 K, indicating that the ordering is ferrimagnetic.

At 2 K the remanent magnetizations are 41, 84 and 32 emu Oe mol<sup>-1</sup> and the coercive fields,  $H_{\text{c}}$ , are 14, 13, and 11 Oe for **3** to **5**, respectively. These values are comparable to those reported for  $[M^{\text{II}}\text{Cr}^{\text{III}}(\text{ox})_3]^-$  ( $H_{\text{c}} = 20$  to 320 Oe).<sup>5b</sup> The 2 K field dependence of the magnetization,  $M(H)$ , shows a rapid rise with increasing applied field,  $H$ , for **3** to **5**. The magnetizations at 5 T are 17 400, 12 400, and 6850 emu Oe mol<sup>-1</sup> for **3** to **5**, respectively. The FCM (field-cooled magnetization) and ZFCM (zero-field-cooled magnetization) for **3** to **5** were measured at 5 Oe, however, bifurcation temperatures were not observed. This is attributed to the low temperature  $T_{\text{cs}}$  ( $\sim 2$  K) of the compounds.

## Conclusion

Air stable  $[N(n\text{-Bu})_4][M^{\text{II}}V^{\text{III}}(\text{ox})_3]$  ( $M = \text{Fe}, \text{Co}, \text{Ni}$ ) and  $[N(n\text{-Bu})_4][V^{\text{III}}\text{Cu}^{\text{II}}(\text{ox})_2](\text{BF}_4)_2$  (**5**), albeit with occluded  $[N(n\text{-Bu})_4](\text{BF}_4)$  can be obtained from  $[N(n\text{-Bu})_4]_3[V^{\text{III}}(\text{ox})_3]$  in non-aqueous media, but due to the instability of  $[V^{\text{III}}(\text{ox})_3]^{3-}$  cannot be made from water. Compound **5** exhibits a new composition and structure of a bimetallic oxalate, as it has 2 oxalates, not 3 per pair of metal ions. The MeCN-made materials precipitate much more rapidly than the analogs made from water, and as a consequence occlude other ions and solvent, and pure phases are challenging to make. Furthermore, the precipitates diffract poorly indicative of very small crystallites, and disorder. This is in contrast to the materials made from water.<sup>6</sup> The special ability of water to facilitate the formation of more crystalline materials is also noted for the Prussian blue family<sup>3,4,16</sup> as well as  $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{Cr}^{\text{III}}(\text{CN})_6]$ <sup>17</sup> where MeCN-made materials also exhibit poor diffraction and poor crystallinity. Consequently, the  $T_{\text{cs}}$  of materials prepared from aqueous media range from 11 to  $\sim 30$  K<sup>6</sup> and those from non-aqueous media are reduced to below 3 K. Finally, **2** shows antiferromagnetic coupling between the  $\text{Fe}(\text{II})$  and  $\text{V}(\text{III})$  ions, **3** and **5** order as ferrimagnets below 2 K, and **4** orders as a ferromagnet at 2.3 K.

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