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# Solvatothermal chemistry of organically-templated vanadium fluorides and oxyfluorides

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Dedicated to Prof. Jonathan R. Dilworth

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### ABSTRACT

The solvatothermal reactions of  $V_2O_5$ , the appropriate organoamine and HF in the temperature range 100–180 °C yielded a series of vanadium fluorides and oxyfluorides. The compounds  $[NH_4][H_3N(CH_2)_2 NH_3$ [[VF<sub>6</sub>] (1) and [H<sub>3</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>3</sub>][VF<sub>5</sub>(H<sub>2</sub>O)] (2) contain mononuclear V(III) anions, while [H<sub>3</sub>N  $(CH_2)_2NH_2(CH_2)_2NH_3]_2$  [VF<sub>5</sub>(H<sub>2</sub>O)]<sub>2</sub>[VOF<sub>4</sub>(H<sub>2</sub>O)] (**3**) exhibits both V(IV) and V(III) mononuclear anions. Both compound **4**, [H<sub>3</sub>NCH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)CH<sub>2</sub>NH<sub>3</sub>][VOF<sub>4</sub>]·H<sub>2</sub>O (**4**·H<sub>2</sub>O) and compound **5**, [HN(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>NH][V<sub>2</sub>O<sub>2</sub>F<sub>6</sub>  $(H_2O)_2$ ] (5) contain binuclear anions constructed from edge-sharing V(IV) octahedra. In contrast,  $[H_3N(CH_2)_2NH_2(CH_2)_2NH_3]_2[V_4O_4F_{14}(H_2O)_2],$  (6) exhibits a tetranuclear unit of edge- and corner-sharing V(IV) octahedra. Compound 7,  $[H_3N(CH_2)_2NH_2][VF_5]$ , contains chains of corner-sharing  $\{V^{IV}F_6\}$  octahedra, while  $[H_2N(C_2H_4)_2NH_2]_3[V_4F_{17}O] \cdot 1.5H_2O$  (8.1.5H<sub>2</sub>O) is two-dimensional with a layer of V(III) and V(IV) octahedra in an edge- and corner-sharing arrangement. In the case of  $[H_3N(CH_2)_2NH_3][V_2O_6]$  (**9**), there was no fluoride incorporation, and the  $\{V_2O_6\}_n^{2n-}$  anion is a one-dimensional chain of corner-sharing V(V) tetrahedra.

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### 1. Introduction

Hydrothermal reaction conditions afford a practical method for the preparation of organic-inorganic hybrid materials, where the inorganic substructure is modified by the introduction of organic components as charge-compensating units and/or as conventional ligands [1–9]. Under such conditions, it is also noted that at the acidic pH range employed for metal oxide-based hybrids, fluoride was essential to effect mineralization and to induce crystallization, although fluoride was not present in the products [10]. However, judicious modification of reaction conditions allows incorporation of fluoride to produce oxyfluorinated materials, a phenomenon initially observed for the aluminum and gallium phosphates and demonstrated to provide even more varied coordination types [11,12]. More recently, fluoride incorporation into oxovanadium and oxomolybdenum organophosphonates has been shown to result in considerable structural complexity and novelty [13-20]. For example the family of oxyfluorovanadates of the general type  ${Cu_2(bisterpy)}^{4+}/V_xO_yF_z^{n-}/{O_3P(CH_2)_nPO_3}^{4-}$  exhibits a range of V/ P/O/F building blocks such as embedded clusters, chains and networks and even three-dimensional frameworks. In addition to generating an expansive structural chemistry, fluoride incorporation also provides enhanced thermal stability of the oxide phases.

Metal oxyfluorides have also attracted considerable interest for properties such as magnetism [21], catalysis [22] and non-linear optical behavior [23]. Systematic studies of the vanadium oxyfluorides by Lightfoot have revealed an extensive structural chemistry, including oligomeric, chain and ladder building blocks [24-28]. However, as noted by this author and others [29-31], the complexity of the hydrothermal reaction domain often results in unusual, unprecedented and inconceivable structures, and it is certain that many metal oxyfluoride structures remain to be discovered. Certainly, variations in temperature, pH, reactant stoichiometry, the presence or absence of organic cations, and even the fill volume can influence the product outcome.

In the course of our own investigations of the hydrothermal chemistry of vanadium oxides in the presence of HF, we have encountered numerous examples of vanadium oxyfluoride phases. Herein, we report the structural chemistry of a number of vanadium fluoride and oxyfluoride materials: the mononuclear [NH<sub>4</sub>]  $[H_3N(CH_2)_2NH_3][VF_6]$  (1),  $[H_3N(CH_2)_2NH_3][VF_5(H_2O)]$  (2) and  $[H_3N(CH_2)_2NH_2(CH_2)_2NH_3]_2[VF_5(H_2O)]_2[VOF_4(H_2O)]$  (3), the binuclear  $[H_3NCH_2(C_6H_4)CH_2NH_3][VOF_4]\cdot H_2O$  (4·H<sub>2</sub>O) and  $[H_2NC_6H_{12} NH_2$ ] [ $V_2O_2F_6(H_2O_2)$ ] (5), the tetranuclear [ $H_3N(CH_2)_2NH_2$ ]  $(CH_2)_2NH_3]_2 [V_4O_4F_{14}(H_2O)_2]$  (6), the one-dimensional  $[H_3N(CH_2)_2 NH_2$  [VF<sub>5</sub>] (7) and the two-dimensional phase [ $H_2NC_4H_8NH_2$ ]<sub>3</sub>





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 $[V_3^{III}V^{IV}F_{17}O] \cdot 1.5H_2O$  (**8**·1.5H<sub>2</sub>O). The structure of the one-dimensional vanadium oxide  $[H_3N(CH_2)_2NH_3][V_2O_6]$  (**9**) is also reported. The magnetic properties of selected phases are discussed.

## 2. Experimental

#### 2.1. General considerations

All chemicals were used as obtained without further purification: vanadium(V) oxide, ethylene diamine, piperazine, diethylene triamine, triethylene diamine, *para*-xylylene diamine, piperazine, ethylene glycol, ethanol, and hydrofluoric acid (48–51%) were purchased from Aldrich. All syntheses were carried out in 23 mL poly(tetrafluoroethylene) lined stainless steel containers under autogeneous pressure. The reactants were stirred briefly and initial pH was measured before heating. Water was distilled above 3.0 M  $\Omega$  in-house using a Barnstead Model 525 Biopure Distilled Water Center. The reactions initial and final pH was measured using Hydrion pH sticks.

# 2.1.1. Synthesis of $[NH_4][H_3N(CH_2)_2NH_3][V^{III}F_6]$ (1)

A solution of  $V_2O_5$  (0.161 g, 0.885 mmol), ethylenediamine (0.240 mL, 3.59 mmol), ethanol (5 mL, 185.59 mmol), and HF (0.200 mL, 5.80 mmol) in the mole ratio 1.00:4.05:209.70:6.55 was heated to 150 °C for 4 days (initial and final pH value of 5.0 and 5.0, respectively). Green blocks of **1** were isolated in 5% yield. IR (KBr pellet, cm<sup>-1</sup>): 3421(s), 3247(m), 2931(w), 1560(m),

# 2.1.2. Synthesis of $[H_3N(CH_2)_2NH_3][V^{III}F_5(H_2O)]$ (2)

A solution of V<sub>2</sub>O<sub>5</sub> (0.159 g, 0.87 mmol), ethylenediamine (0.240 mL, 4.05 mmol), H<sub>2</sub>O (2.50 mL, 138.73 mmol), ethanol (2.50 mL, 42.80 mmol), and HF (1.20 mL, 34.80 mmol) in the mole ratio 1.00:4.66:159.43:49.19:40.00 was stirred briefly before heating to 180 °C for 5 days (initial and final pH value of 1.5 and 1.5, respectively). Light green needles of **2** were isolated in 10% yield. IR (KBr pellet, cm<sup>-1</sup>): 3421(s), 3248(s), 2931(w), 1618 (m), 1508(m), 1055(m), 966(w), 844(w), 533(w). *Anal.* calc. for C<sub>2</sub>H<sub>12</sub>F<sub>5</sub>N<sub>2</sub>OV: C, 10.6; H, 5.31; N, 12.4. Found: C, 10.9; H, 5.45; N, 12.2%.

# 2.1.3. Synthesis of $[H_3N(CH_2)_2NH_2(CH_2)_2NH_3]_2[V^{III}F_5(H_2O)]_2$ $[V^{IV}OF_4(H_2O)]$ (3)

A mixture of  $V_2O_5$  (0.160 g, 0.88 mmol), diethylenetriamine (0.192 mL,1.78 mmol), H<sub>2</sub>O (2.00 mL, 110.99 mmol), ethylene glycol (5.00 mL, 89.68 mmol) and HF (0.400 mL, 11.60 mmol) in the mole ratio 1.00:2.02:126.13:101.91:13.81 was stirred briefly before heating to 150 °C for 48 h. Initial and final pH values of 3.0 and 3.0, respectively, were recorded. Green crystals of **3** suitable for X-ray diffraction were isolated in 60% yield. IR (KBr pellet, cm<sup>-1</sup>): 3239(s), 2944(m), 1610(m), 1509(m), 1453(w), 1050(m),

#### Table 1

Summary of crystallographic data for the structures of  $[NH_4][H_3N(CH_2)_2NH_3][VF_6]$  (1),  $[H_3N(CH_2)_2NH_3][VF_6](2)$ ,  $[H_3N(CH_2)_2NH_2(CH_2)_2NH_3]_2[VF_5(H_2O)]_2[VOF_4(H_2O)]_$ 

	1	2		3		4	5
Empirical formula	$C_2H_{14}F_6N_3V$	$C_2H_{12}F_5N_2OV$		$C_8H_{38}F_{14}N_6O_4V_3$		$C_8H_{16}F_4N_2O_2V$	$C_3H_9F_3NO_2V$
Formula weight	245.10	226.08		701.26		299.17	199.05
Crystal system	monoclinic	monoclinic		monoclinic		monoclinic	monoclinic
Space group	P21/c	$C_2/c$		$P2_1/c$		$P2_1/c$	$P2_1/c$
a (Å)	11.676(2)	12.2147(10)		9.4050(5)		11.3790(6)	7.0857(8)
b (Å)	10.125(2)	12.9834(11)		20.6986(11)		12.1694(6)	7.2338(8)
<i>c</i> (Å)	14.507(3)	10.4855(9)		13.1142(7)		8.8454(5)	12.9537(14)
α (°)	90.	90.		90.		90.	90.
β (°)	90.93(3)	106.007(2)		100.5020(10)		111.9130(10)	99.127(2)
γ (°)	90.	90.		90.		90.	90.
$V(Å^3)$	1714.7(6)	1598.4(2)		2510.2(2)		1136.38(10)	655.56(13)
Z	8	8		4		4	4
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.899	1.879		1.856		1.749	2.017
$\mu ({\rm mm^{-1}})$	1.213	1.281		1.225		0.919	1.513
T (K)	90(2)	90(2)		90(2)		90(2)	90(2)
Wavelength (Å)	0.71073	0.71073		0.71073		0.71073	0.71073
$R_1$	0.0916	0.0558		0.0694		0.0589	0.0398
$wR_2$	0.1807	0.1018		0.1326		0.1337	0.1064
	6		7		8		9
Empirical formula	$C_4H_{18}F_7N_3O_3V_2$		$C_2H_9F_5N_2V$		$C_{12}H_{39}F_{12}$	7N <sub>6</sub> O <sub>2.50</sub> V <sub>4</sub>	$CH_5NO_3V$
Formula weight	391.09		207.04		837.25		130.00
Crystal system	monoclinic		orthorhombi	с	monoclin	ic	monoclinic
Space group	$P2_1/n$		Pnma		P2/c		$P2_1/c$
a (A)	11.7636(8)		10.5231(9)		16.8083(	10)	5.5430(5)
b (A)	10.2859(7)		5.7185(5)		13.5767(	8)	12.6715(12)
<i>c</i> (A)	11.8956(8)		10.1319(8)		12.7430(	7)	5.7127(5)
α (°)	90		90		90		90
β(°)	90		90		107.9370	(10)	97.890(2)
$\gamma$ (°)	90		90		90	<u>,</u>	90
V(A <sup>3</sup> )	1287.06(15)		609.70(9)		2766.6(3	)	397.45(6)
Z	4		4		4		4
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	2.018		2.255		2.010		2.173
$\mu (\text{mm}^{-1})$	1.546		1.656		1.454		2.347
I (K)	90(2)		90(2)		90(2)		90(2)
Wavelength (A)	0.71073		0.71073		0./10/3		0./10/3
K1	0.0287		0.0414		0.0682		0.0269
WK <sub>2</sub>	0.0667		0.1025		0.13//		0.0664

Table 2	
Selected bond lengths (Å) and angles (°) for the compounds of this stud	y.

	0 () 0 ()	1	5
Compound 1 V(1)-F(6) V(1)-F(5) V(1)-F(2) V(1)-F(1) V(1)-F(1) V(1)-F(3) $\sum_{sij}$ V(2)-F(7) V(2)-F(7) V(2)-F(8) V(2)-F(9) V(2)-F(10) V(2)-F(11) V(2)-F(12)	$1.821(4) \\ 1.899(4) \\ 1.947(3) \\ 1.951(4) \\ 1.962(4) \\ 1.963(4) \\ 3.15 \\ 1.829(4) \\ 1.884(4) \\ 1.946(4) \\ 1.951(4) \\ 1.976(4) \\ 1.982(3) \\ 2.12$	F(4)-V(1)-F(2) F(6)-V(1)-F(1) F(5)-V(1)-F(3) F(8)-V(2)-F(10) F(9)-V(2)-F(11) F(7)-V(2)-F(12)	176.11(15) 178.20(18) 173.48(17) 170.70(17) 173.32(16) 179.29(17)
$\sum^{sij}$ Compound 2 V(1)-F(4) V(1)-F(3) V(1)-F(1) V(1)-F(2) V(1)-F(5) V(1)-O(90) $\sum^{sij}$	3.12 1.839(2) 1.9181(19) 1.9219(19) 1.942(2) 1.9679(19) 2.068(2) 3.11	F(3)-V(1)-F(1) F(4)-V(1)-F(2) F(5)-V(1)-O(90)	174.08(9) 176.31(10) 177.83(10)
Compound <b>3</b> V(1)-F(4) V(1)-F(5) V(1)-F(1) V(1)-F(2) V(1)-O(90) $\sum sij$ V(2)-F(9) V(2)-F(6) V(2)-F(6) V(2)-F(7) V(2)-F(7) V(2)-F(7) V(2)-O(91) $\sum sij$ V(3)-O(1) V(3)-F(13) V(3)-F(14) V(3)-F(12) $\sum sij$	1.761(3) 1.832(2) 1.890(2) 1.942(2) 1.960(2) 2.145(3) 3.37 1.757(3) 1.853(3) 1.924(2) 2.017(2) 2.038(3) 3.37 1.619(3) 1.913(2) 1.940(2) 1.947(2) 2.051(3) 2.070(2) 3.92	$\begin{array}{l} F(1)-V(1)-F(3)\\ F(4)-V(1)-F(2)\\ F(5)-V(1)-O(90)\\ F(6)-V(2)-F(8)\\ F(9)-V(2)-F(7)\\ F(10)-V(2)-O(91)\\ F(13)-V(3)-F(11)\\ F(14)-V(3)-O(92)\\ O(1)-V(3)-F(12) \end{array}$	172.06(10) 171.14(12) 173.96(12) 172.40(11) 175.97(11) 172.19(13) 163.80(12) 168.84(11) 176.03(13)
Compound <b>4</b> V(1)-O(1) V(1)-F(4) V(1)-F(3) V(1)-F(1) V(1)-F(2)#1 V(1)-F(2) $\sum sij$	$\begin{array}{c} 1.598(2) \\ 1.9275(19) \\ 1.9440(19) \\ 1.9475(19) \\ 1.9765(18) \\ 2.2139(18) \\ 3.84 \end{array}$	F(4)-V(1)-F(1) F(3)-V(1)-F(2)#1 O(1)-V(1)-F(2)	165.01(8) 157.62(8) 173.27(10)
$\begin{array}{l} \mbox{Compound 5} \\ V(1)-O(1) \\ V(1)-F(1) \\ V(1)-F(3) \\ V(1)-F(2) \\ V(1)-O(90) \\ V(1)-F(2)\#2 \\ \sum sij \end{array}$	$\begin{array}{c} 1.617(2) \\ 1.9209(17) \\ 1.9347(16) \\ 1.9601(16) \\ 2.034(2) \\ 2.1422(16) \\ 4.23 \end{array}$	$\begin{array}{l} F(1)-V(1)-F(3)\\ O(1)-V(1)-O(90)\\ F(2)-V(1)-O(90)\\ O(1)-V(1)-F(2)\#1 \end{array}$	163.85(7) 101.06(10) 161.75(8) 171.01(9)
Compound <b>6</b> V(1)-O(1) V(1)-F(3) V(1)-F(2) V(1)-F(1) V(1)-O(90) V(1)-F(4) $\sum sij$ V(2)-O(2) V(2)-F(5) V(2)-F(5) V(2)-F(7)#3 V(2)-F(7) $\sum sij$	$\begin{array}{c} 1.6202(13)\\ 1.9089(12)\\ 1.9229(12)\\ 1.9304(12)\\ 2.0370(15)\\ 2.1230(11)\\ 3.94\\ 1.6080(14)\\ 1.9309(11)\\ 1.9429(11)\\ 1.9473(11)\\ 1.9579(11)\\ 2.1825(11)\\ 3.84 \end{array}$	$\begin{array}{l} F(3)-V(1)-F(2)\\ O(1)-V(1)-F(1)\\ F(1)-V(1)-O(90)\\ O(1)-V(1)-F(4)\\ F(5)-V(2)-F(7)\#3\\ O(2)-V(2)-F(7)\\ V(2)-F(4)-V(1)\\ V(2)\#1-F(7)-V(2) \end{array}$	$\begin{array}{c} 165.95(5)\\ 100.65(6)\\ 165.91(6)\\ 171.63(6)\\ 155.58(5)\\ 173.22(6)\\ 142.16(6)\\ 106.82(5) \end{array}$

Table 2 (continued)			
Compound 7			
V(1)-F(1)#4	1.760(2)	F(2)-V(1)-F(4)	165.03(11)
V(1)-F(1)	1.760(2)	F(1)-V(1)-F(3)#5	171.46(8)
V(1)-F(2)	1.915(3)	F(1)#1-V(1)-F(3)	171.46(8)
V(1)-F(4)	1.916(2)	V(1)-F(3)-V(1)#6	180.0
V(1)-F(3)#5	2.1317(5)		
V(1)-F(3)	2.1317(5)		
$\sum sij$	3.42		
Compound 8			
V(1)-O(1)	1.704(3)	F(4) - V(1) - F(1)	165.85(12)
V(1)-F(4)	1.900(3)	F(3)-V(1)-F(6)	167.01(8)
V(1)-F(1)	1.911(3)	F(2)-V(1)-F(5)	169.55(12)
V(1)-F(3)	1.9575(7)	F(7)-V(2)-F(8)	170.17(12)
V(1) - F(6)	2.028(2)	F(5)-V(2)-F(14)	169.59(11)
V(1)-F(5)	2.142(2)	F(9)-V(2)-F(6)	173.25(10)
$\sum sij$	3.87	F(13)-V(3)-F(10)	172.77(11)
V(2)-F(7)	1.857(3)	F(11)–V(3)–F(12)#7	173.06(10)
V(2)-F(8)	1.895(2)	F(9)-V(3)-F(12)	175.84(11)
V(2) - F(5)	1.925(2)	F(16)-V(4)-F(19)	178.27(11)
V(2) - F(14)	1.954(2)	F(17) - V(4) - F(14)	175.38(11)
V(2) - F(9)	1.964(2)	F(18) - V(4) - F(15)	176.45(11)
V(2) - F(6)	2.010(2)	V(1)#2-F(3)-V(1)	178.6(2)
∑sij	3.06	V(2) - F(5) - V(1)	101.32(10)
V(3) - F(11)	1.862(2)	V(2)-F(6)-V(1)	102.43(10)
V(3) - F(13)	1.871(2)	V(2) - F(9) - V(3)	148.32(14)
V(3) - F(10)	1.911(2)	V(3)#1-F(12)-V(3)	102.15(10)
V(3) - F(9)	1.990(2)	V(2)-F(14)-V(4)	156.93(15)
V(3) - F(12) # 7	1.998(2)	V(4)#3-F(15)-V(4)	152.4(2)
V(3) - F(12)	2.019(2)		
$\sum sij$	3.02		
V(4) - F(16)	1.906(2)		
V(4) - F(19)	1.913(3)		
V(4) - F(17)	1.916(2)		
V(4) - F(18) V(4) - F(14)	1.924(3)		
V(4) - F(14) V(4) - F(15)	1.903(2)		
V(4) - F(15)	1.9876(11)		
$\sum sij$	3.04		
Compound <b>9</b>			
V(1)-O(3)	1.6452(16)	O(3)-V(1)-O(1)	109.41(8)
V(1)-O(1)	1.6457(15)	O(3)-V(1)-O(2)#8	110.66(7)
V(1)-O(2)#8	1.8057(15)	O(1)-V(1)-O(2)#8	107.33(8)
V(1)-O(2)	1.8079(15)	O(3)-V(1)-O(2)	110.11(7)
$\sum sij$	4.68	O(1)-V(1)-O(2)	111.36(7)
		O(2)#1-V(1)-O(2)	107.93(5)
		V(1)#2-O(2)-V(1)	132.52(9)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z + 2; #2 -x,-y,-z + 1; #3 -x + 1,-y + 2,-z; #4 x,-y + 1/2,z; #5 -x + 1,y + 1/2,-z + 1; #6 -x + 1,-y,-z + 1; #7 -x + 1,y,-z + 3/2; #8 x,-y + 3/2,z + 1/2; #9 x,-y + 3/2,z-1/2.

966(m), 520(m), 489(m). *Anal.* calc. for C<sub>8</sub>H<sub>38</sub>F<sub>14</sub>N<sub>6</sub>O<sub>4</sub>V<sub>3</sub>: C, 13.7; H, 5.42; N, 12.0. Found: C, 13.4; H, 5.21; N, 12.3%.

# 2.1.4. Synthesis of $[H_3NCH_2(C_6H_4)CH_2NH_3][V^{IV}OF_4] \cdot 1H_2O(4)$

A solution of V<sub>2</sub>O<sub>5</sub> (0.161 g, 0.89 mmol), *para*-xylylenediamine (0.244 g, 1.79 mmol), H<sub>2</sub>O (2.00 mL, 110.99 mmol), ethylene glycol (5.00 mL, 89.68 mmol), and HF (0.300 mL, 8.70 mmol) in the mole ratio 1.00:2.01:124.71:100.76:9.78 was heated at 135 °C for 48 h (initial and final pH values of 3.5 and 3.0, respectively). Blue plates of **4** were isolated in 40% yield. IR (KBr pellet, cm<sup>-1</sup>): 3239(s), 2944(m), 1611(m), 1509(m), 1453(w), 1050(m), 966(m), 843(w), 520(m), 489(m). *Anal.* calc. for  $C_8H_{16}F_4N_2O_2V$ : C, 32.1; H, 5.35; N, 9.36. Found: C, 32.4; H, 5.21; N, 9.25%.

#### 2.1.5. Synthesis of $[HN(C_2H_4)_3NH][V^{IV}_2O_2F_6(H_2O)_2]$ (5)

A solution of  $V_2O_5$  (0.162 g, 0.89 mmol), diaminobicyclooctane (DABCO) (0.197 g, 1.76 mmol), H<sub>2</sub>O (2.0 mL, 110.99 mmol), ethylene glycol (5.0 mL, 89.68 mmol) and HF (0.400 mL, 11.60 mmol) with the mole ratio 1.00:1.98:124.71:100.76:13.03 was stirred briefly before heating to 150 °C for 48 h (initial and final pH values of 2.0 and 2.0, respectively). Blue crystals of **5** were isolated in 25% yield. IR (KBr pellet, cm<sup>-1</sup>): 3239(s), 2944(m), 1611(m), 1509(s),

1050(m), 966(s), 843(w), 520(s), 489(s). *Anal.* calc. for C<sub>3</sub>H<sub>9</sub>F<sub>3</sub>NO<sub>2</sub>V: C, 18.1; H, 4.52; N, 7.04. Found: C, 18.3; H, 4.46; N, 7.11%.

## 2.1.6. Synthesis of $[H_3N(CH_2)_2NH_2(CH_2)_2NH_3]_2[V^{IV}_4O_4F_{14}(H_2O)_2]$ (6)

A solution of  $V_2O_5$  (0.160 g, 0.88 mmol), diethylenetriamine (0.192 mL, 1.78 mmol), H<sub>2</sub>O (2.00 g, 110.99 mmol), ethylene glycol (5.00 mL, 89.68 mmol) and HF (0.400 mL, 11.60 mmol) in the mole ratio 1.00:2.02:126.13:101.91:13.81 was stirred briefly before heating to 100 °C for 48 h (initial and final pH values of 3.0 and 3.0, respectively). Blue crystals of **6** suitable for X-ray diffraction were isolated in 15% yield. IR (KBr pellet, cm<sup>-1</sup>): 3239(s), 2944(m), 1611(m), 1509(m), 1453(w), 1050(m), 966(m), 520(m), 489(m). Anal. calc. for C<sub>4</sub>H<sub>18</sub>F<sub>7</sub>N<sub>3</sub>O<sub>3</sub>V<sub>2</sub>: C, 12.3; H, 4.60; N, 10.7. Found: C, 12.5; H, 4.48; N, 10.4%.

#### 2.1.7. Synthesis of $[H_3N(CH_2)_2NH_2][V^{IV}F_5]$ (7)

A solution of  $V_2O_5$  (0.158 g, .87 mmol), ethylenediamine (0.240 mL, 4.05 mmol),  $H_2O$  (2.50 mL, 138.73 mmol), ethanol (2.5 mL, 42.80 mmol) and HF (0.200 mL, 5.8 mmol) in the mole ratio 1.00:4.50:159.46:49.20:6.67 was heated to 120 °C for 60 h (initial and final pH values of 5.0 and 4.5, respectively). Blue rods of **7** were

isolated in 60% yield. IR (KBr pellet,  $cm^{-1}$ ): 3239(s), 2944(m), 1611(m), 1508(m), 1050(m), 966(s), 843(w), 521(s), 489(s). *Anal.* calc. for C<sub>2</sub>H<sub>9</sub>F<sub>5</sub>N<sub>2</sub>V: C, 11.6; H, 4.34; N, 13.5. Found: C, 11.8; H, 4.22; N, 13.3%.

#### 2.1.8. Synthesis of $[H_2NC_4H_8NH_2]_3[V_4F_{17}O] \cdot 1.5 H_2O(\mathbf{8})$

A mixture of  $V_2O_5$  (0.181 g, 1.00 mmol), piperazine (0.283 g, 3.28 mmol), H<sub>2</sub>O (2.00 mL, 110.99 mmol), ethylene glycol (5.00 mL, 89.68 mmol) and HF (0.800 mL, 23.20 mmol) in the mole ratio 1.00:3.28:110.99:89.68:23.20 was stirred briefly before heating to 150 °C for 48 h (initial and final pH values of 2.0 and 1.5, respectively). Brown blocks of **8** suitable for X-ray diffraction were isolated in 80% yield. IR (KBr pellet, cm<sup>-1</sup>): 3239(s), 2944(m), 1611(m), 1509(s), 1050(m), 966(s), 843(w), 520(s), 489(s). *Anal.* calc. for C<sub>12</sub>H<sub>39</sub>F<sub>17</sub>N<sub>6</sub>O<sub>2.5</sub>V<sub>4</sub>: C, 17.3; H, 4.68; N, 10.1. Found: C, 17.6; H, 4.78; N, 9.84%.

## 2.1.9. Synthesis of $[H_3N(CH_2)_2NH_3][V_2O_6]$ (9)

A solution of  $V_2O_5$  (0.163 g, .90 mmol), ethylenediamine (0.240 mL, 4.05 mmol),  $H_2O$  (5.0 mL, 277.47 mmol), and HF (0.100 mL, 2.90 mmol) in the mole ratio 1.00:4.50:308.30:3.22







Fig. 2. Polyhedral representation of the  $\{VF_4O(H_2O)\}^{2-}$  and  $\{VF_5(H_2O)\}^{2-}$  anions and ball and stick representation of the  $\{H_3N(CH_2)_2NH_2(CH_2)_2NH_3\}^{3+}$  cations of 3.

was stirred briefly before heating to 100 °C for 48 h (initial and final pH values of 6 and 5.5, respectively). Brown blocks of **9** were isolated in 5% yield. IR (KBr pellet, cm<sup>-1</sup>): 3421(s), 3248(m), 2931(w), 1509(m), 1498(m), 1054(m), 966(w), 844(w), 533(m).

2.2. X-ray crystallography

X-ray measurements were performed on a Bruker-AXS SMART-CCD diffractometer at low temperature (90 K) using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda_{MO K\alpha}$  = 0.71073 Å) [32]. The data were

#### Table 3

Selected structural characteristics of vanadium fluorides and oxyfluorides.

	5			
Chemical formula	Dimensionality	Structural unit	Ox. state	Reference
Na <sub>3</sub> VOF <sub>5</sub>	molecular	monomer	IV	[51]
Na <sub>2</sub> VOF <sub>5</sub>	molecular	monomer	V	[52]
$Cs_2VOF_4(H_2O)$	molecular	trans-monomer	IV	[46]
Cs <sub>2</sub> VF <sub>6</sub>	molecular	monomer	IV	[43]
$[NH_4]_3[VO_2F_4]$	molecular	<i>cis</i> -monomer	V	[53]
Na <sub>3</sub> VF <sub>6</sub>	molecular	monomer	III	[54]
$K_2VF_5(H_2O)$	molecular	monomer	III	[45]
$RbVF_4(H_2O)_2$	molecular	trans-monomer	III	[55]
$[C_6N_4H_{22}][VOF_4(H_2O)]_2 \cdot H_2O$	molecular	monomer	IV	[27]
$[NH_4][H_3N(CH_2)_2NH_3][VF_6]$ (1)	molecular	monomer	III	this work
$[H_3N(CH_2)_2NH_3][VF_5(H_2O)]$ (2)	molecular	monomer	III	this work
$[H_3N(CH_2)_2NH_2(CH_2)_2NH_3]_2[VF_5(H_2O)]_2[VF_4O(H_2O)] (3)$	molecular	monomer	III/IV	this work
$(NMe_4)_3V_2F_9$	molecular	binuclear, face-sharing octahedra	III	[56]
$Cs_3V_2O_2F_7$	molecular	binuclear, face-sharing octahedra	IV	[57]
$[NH_4]_3[V_2O_4F_5]$	molecular	binuclear, face-sharing octahedra	V	[56]
$[NMe_4]_2[V_2O_2F_6(H_2O)_2]$	molecular	binuclear, edge-sharing octahedra (axial H <sub>2</sub> O)	IV	[47]
$[C_6N_2H_{14}][V_2O_2F_6(H_2O)_2]$	molecular	binuclear, edge-sharing octahedra (F bridge)	IV	[27]
$[C_6N_4H_{22}][V_2O_2F_8]$	molecular	binuclear, edge-sharing octahedra (F bridge)	IV	[27]
$[H_3NCH_2(C_6H_4)CH_2NH_3][VF_4O] \cdot H_2O$ (4)	molecular	binuclear, edge-sharing octahedra (F bridge)	IV	this work
$[HN(C_2H_4)_3NH][V_2F_6O_2(H_2O)_2]$ (5)	molecular	binuclear, edge-sharing octahedra (F bridge)	IV	this work
$[NMe_4]Cs[V_2O_2F_8(H_2O)]$	molecular	binuclear, corner-sharing octahedra (F bridge)	V	[58]
$K_2[NMe_4][V_2O_2F_9]$	molecular	binuclear, corner-sharing octahedra (F bridge)	V	[58]
$Na[NMe_4]_2[V_3O_3F_{12}]$	molecular	trinuclear, corner-sharing octahedra (F bridge)	V	[58]
$Ba_3V_2O_4F_8$	molecular	tetranuclear, corner-sharing octahedra	V	[59]
$[C_6N_4H_{21}]_2[V_4O_4F_{14}]\cdot 3H_2O$	molecular	tetranuclear, edge- and corner-sharing octahedra	IV	[27]
$[C_6N_3H_20][V_4O_4F_{14}]0.5 \cdot H_2O$	molecular	tetranuclear, edge- and corner-sharing octahedra	IV	[27]
$[C_4N_2H_{12}]_4[V_4O_3F_{17}]\cdot 4H_2O$	molecular	tetranuclear, edge- and corner-sharing octahedra	III/IV	[26]
$[H_3N(CH_2)_2NH_2(CH_2)_2NH_3]_2[V_4F_{14}O_4(H_2O)]_2$ (6)	molecular	tetranuclear, edge- and corner-sharing octahedra (F bridges)	IV	this work
$Na_{6}[H_{6}V_{12}O_{30}F_{2}]\cdot 22H_{2}O$	Molecular cluster	polyanion $[H_6V_{12}O_{30}F_2]^{6-}$	IV/V	[60]
$[H_3N(C_2H_4)_nNH_3]_4[V_{14}O_{36}F_4]$	Molecular cluster	polyanion $\left[V_{14}O_{36}F_4 ight]^{8-}$	IV/V	[42]
$[C_4H_{12}N_2]_3[V_7F_{27}]$	1-D	chain of corner-sharing octahedra (F bridges)	III	[25]
$[C_4N_2H_{12}]_4[V_5O_3F_{20}]\cdot 2H_2O$	1-D	chain of edge- and corner-sharing octahedra	III/IV	[26]
$[C_4N_2H_{12}][VF_5]\cdot H_2O$	1-D	chain of corner-sharing octahedra	III	[26]
$[H_3N(CH_2)_2NH_2][VF_5]$ (7)	1-D	chain of corner-sharing octahedra (F bridges)	IV	this work
$[H_2NC_4H_8NH_2]_3[V_4F_{17}O] \cdot 1.5 H_2O(8)$	2-D	layer of edge- and corner-sharing octahedra (F bridges)	III/IV	this work

 Table 4

 Summary of Curie–Weiss parameters for the magnetic susceptibilities of compounds 4–7.

Compound	Vanadium sites	g	θ (K)
4	2  imes V(IV)	1.99	${\sim}0.0$
5	$2 \times V(IV)$	2.10	-1.9
6	$4 \times V(IV)$	2.03	${\sim}0.0$
7	V(IV)	2.06	-8.9

corrected for Lorentz and polarization effects and absorption using sADABS [33]. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. After all of the non-hydrogen atoms were located, the model was refined against  $F^2$ , initially using isotropic and later anisotropic thermal displacement parameters. Hydrogen atoms were introduced in calculated positions and refined isotropically. Neutral atom scattering coefficients and anomalous dispersion corrections were taken from the *International Tables*, Vol. C. All calculations were performed using sHELXTL crystallographic software packages [34,35]. The crystallographic details for the X-ray crystallographic studies of compounds **1–9** are summarized in Table 1. Selected bond lengths and angles for the compounds of this study are given in Table 2.

#### 2.3. Magnetic susceptibilities

Magnetically susceptibility measurements were performed on a 7 T Quantum Design MPMS SQUID magnetometer. Measurements of magnetization as a function of temperature were performed from 5 to 300 K and in a 5000 G field. The samples were prepared by packing ~15 mg between cotton plugs in a gelatin capsule, cooled in zero applied field, and measured upon warming. Diamagnetic corrections were applied on the basis of Pascal's constants. The data were corrected for the diamagnetism of the sample holder. For compounds **5** and **6**, magnetic data were recorded on 50.6 and 56.2 mg samples, respectively, in the 2–300 K temperature range using a Quantum Design MPMS-XL-7 SQUID spectrometer. Calibrating and operating procedures have been reported previously [36]. The temperature dependent data were obtained at a magnetic field of H = 1000 Oe after zero field cooling.

#### 3. Results and discussion

The vanadium fluorides and oxyfluorides of this study were prepared by conventional hydrothermal methods [37–40], which provide suitable conditions for solubilizing and crystallizing organic/ inorganic hybrid materials [41]. The reaction mixtures consisted of a vanadate source, an organoammonium cation and HF with reaction times of 48–120 h at temperatures of 100–180 °C. While HF is generally introduced into hydrothermal reactions as a mineralizer to promote solubility and crystal growth and not as a component of the final product, fluorinated and oxyfluorinated products have been reported for hybrid materials of both vanadium and molybdenum oxides [13–20,42]. In these studies, it was observed



Fig. 3. Polyhedral view of the  $\{V_2F_8O_2\}^{4-}$  dimer of 4 and its hydrogen-bonding interactions with the  $\{H_3NCH_2(C_6H_4)CH_2NH_3\}^{2+}$  cations.



Fig. 4. Mixed polyhedral and ball and stick representation of the  $\{V_2F_6O_2(H_2O)_2\}^{2-}$  anion and  $\{HN(C_2H_4)_3NH\}^{2+}$  cations of 5.



Fig. 5. A polyhedral representation of the  $\{V_4F_{14}O_4(H_2O)\}_2^6$  cluster of 6 and its hydrogen-bonding interactions with the  $\{H_3N(CH_2)_2NH_2(CH_2)_2NH_3\}^{3*}$  cations.

that fluoride incorporation depended on the HF/V molar ratio, with increased molar ratios favoring fluoride uptake into the product.

It is also noteworthy that although V(V) starting materials were used exclusively, the products contained reduced vanadium. Thus, compounds **4**, **5**, **6**, and **7** contain only V(IV) and compounds **1** and **2** are V(III) materials while compounds **3** and **8** are mixed valence V(III)/V(IV) species. Reduction of vanadium in the presence of nitrogenous compounds under hydrothermal conditions is not unusual. However, reduction from V(V) to V(III) generally occurs only in the presence of HF and most commonly with excess fluoride and concomitant fluoride incorporation.

The structural characteristics of the compounds of this study and related vanadium fluorides and oxyfluorides are summarized in Table 3. The structures of compounds 1-6 consist of discrete molecular cations and anions. As shown in Fig. 1a, the structure of 1 consists of distorted octahedral V(IV) sites with V–F distances in the range 1.821(4)-1.982(3)Å, hydrogen-bonded to the ethylenediammonium cations. The metrical parameters for the



**Fig. 6.** Polyhedral view of the  $\{VF_5\}_n^{2n-}$  chain of **7**.

 $\{VF_6\}^{2-}$  anion are similar to those previously reported for  $Na_3VF_6$  [54].

The structure of the anion of  $[H_3N(CH_2)_2NH_3][VF_5(H_2O)]$  (2) is shown in Fig. 1b. The vanadium is in the +3 oxidation, as confirmed by valence sum calculations [44]. The V–F bond distances in the VF<sub>4</sub> plane are in the range 1.839(2)–1.942(2) Å, while that *trans* to the aqua ligand is 1.968(2)Å, indicative of a weak *trans* influence. There is hydrogen-bonding between the fluorine ligands and the ethylenediammonium cations. The structure of the anion is comparable to those previously reported for K<sub>2</sub>[VF<sub>5</sub>(H<sub>2</sub>O)] [45] and [H<sub>3</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>3</sub>] [VF<sub>5</sub>(H<sub>2</sub>O)]<sub>2</sub> [27].

As shown in Fig. 2, the structure of **3** consists of discrete  $[H_3N(CH_2)_2NH_2(CH_2)NH_3]^{3+}$  cations and both  $\{VF_5(H_2O)\}^{2-}$  and  $\{VOF_4(H_2O)\}^{2-}$  anions with hydrogen-bonding interactions between the fluoride ligands and the cations. The  $\{VF_5(H_2O)\}^{2-}$  anion is structurally comparable to that discussed for compound **2**. The  $\{VOF_4(H_2O)\}^{2-}$  anion exhibits a *cis*-disposition of the oxo-group and the aqua ligand, with V–O distances of 1.619(3) and 2.051(3) Å, respectively. The V–F distances are in the range 1.913(2)–1.947(2) Å for the fluorides *cis* to the oxo-group, while the V–F distance *trans* to this group is 2.070(3)Å, a significant lengthening attributed to the *trans*-influence of the multiply bonded oxo-group. Valence bond calculations are in agreement with the assignment of the +4 oxidation state to the vanadium. Curiously, this results in mixed valence character for compound **3**, as a result of incorporation of two different anionic components.

It is also noteworthy that the  $\{VOF_4(H_2O)\}^{2-}$  anions of  $K_2[VF_8(H_2O)]$  [46] and  $[H_3NCH_2CH_2NH_3][VOF_4(H_2O)]$  [28] exhibit *trans*-oxo-aqua ligation, while  $[H_3N(CH_2)_2NH_2(CH_2)_2NH_2(CH_2)_2-NH_3][VOF_4(H_2O)]_2 \cdot H_2O$  exhibits both *cis*- and *trans*-isomers [27].

As shown in Fig. 3, the structure of **4**·H<sub>2</sub>O contains discrete  $[H_3NCH_2(C_6H_4)CH_2NH_3]^{2+}$  cations,  $\{V_2O_2F_8\}^{4-}$  anions and water molecules of crystallization. Once again, hydrogen-bonding between the fluoride ligands and the cations is significant. The  $\{V_2O_2F_8\}^{4-}$  anion consists of edge-sharing  $\{VOF_5\}$  octahedra, linked through two bridging fluorides. The vanadium oxo-bonds are thus *exo-* to the bridge and in the equatorial plane  $\{VO_2F_4\}$  with the bridging fluoride groups. The *trans* influence of the terminal oxogroup is evident in the V–F bond distance of 2.214(2) Å for the *trans* fluoride, compared to an average of 1.949(3) Å for the cisoid V–F bonds. The structure of the anion of **4** is similar to that previously reported for  $[H_3N(CH_2)_2NH_2(CH_2)_2NH_3][V_2O_2F_8]$  [27].

The structure of the DABCO derivative **5**, shown in Fig. 4, consists of discrete  $H_2DABCO^{2+}$  cations and  $[V_2O_2F_6(H_2O)_2]^{2-}$  anions. The binuclear anion is constructed from  $\{V^{IV}O_2F_4\}$  octahedra sharing an edge through two bridging fluorides. The vanadium-oxo and vanadium-aqua distances are 1.617(2)-2.034(2) Å, respectively. The vanadium-fluoride distances *trans* to the oxo-ligand are 2.142(2)Å, compared to an average of 1.939(3)Å for the axial set of fluorides. The equatorial plane  $\{V_2O_2F_2(H_2O)_2\}$  contains the oxo-group, the aqua ligands and the bridging fluorides. Two other examples with the  $[V_2O_2F_6(H_2O)_2]^{2-}$  anion have been reported

 $[NMe_4]_2[V_2O_2F_6(H_2O)_2]$  [47] and  $[H_3N(CH_2)_2NH_2(CH_2)_2NH_2(CH_2)_2-NH_3]$   $[V_2O_2F_6(H_2O)_2]$  [27]. Curiously, in both cases, the aqua ligand adopts an axial orientation rather than the equatorial position of **5**.

As shown in Fig. 5, the structure of 6 contains discrete  $[H_3N(CH_2)_2NH_2(CH_2)_2NH_3]^{3+}$  cations and  $[V_4O_4F_{14}(H_2O)_2]^{6-}$  and ions. The structure of the anion consists of a chain of corner- and edge-sharing V(IV) octahedra. The central pair of octahedra are fused along a common edge through bridging fluorides. Each central vanadium site in turn corner-shares with a terminal vanadium octahedra through a bridging fluoride. The central {V2O2F8} binuclear unit is similar to that of compound 4 with oxo-groups trans to the bridging fluorides. The peripheral vanadium octahedra exhibits cis oxo and aqua ligands, with the aqua ligand trans to the bridging fluoride. Tetranuclear anions of the type  $[V_4O_4F_{14}]^{6-1}$ been reported for [(H<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N][V<sub>4</sub>O<sub>4</sub>F<sub>14</sub>] and have  $[H_3N(CH_2)C_2NH_2(CH_2)_2NH_3][V_4O_4F_{14}]$  [27]. However, these are cyclic tetramers, characterized by {V<sub>4</sub>F<sub>4</sub>} rings, in one case with two edge-sharing {V<sub>2</sub>O<sub>2</sub>F<sub>8</sub>} binuclear units fused through cornersharing and in the second by a single {V<sub>2</sub>O<sub>2</sub>F<sub>8</sub>} unit corner-sharing to two {VOF<sub>8</sub>} octahedra.

The one-dimensional  $\{VF_5\}_n^{1n-}$  chain of  $[H_3N(CH_2)_2NH_2][VF_5]$ (7) is shown in Fig. 6. The chain consists of vanadium(III)  $\{VF_6\}$  octahedra sharing *cis* vertices to produce a zig-zag profile. The V–F distances are 1.838(3) and 2.132(5) Å for the terminal and bridging fluorides, respectively. The chain axes align with the crystallographic *b*-axis, and the cations occupy the channels between chains. A curious feature of **7** is the presence of a monoprotonated (Hen)<sup>+</sup> cation. This observation is confirmed by charge-balance considerations and by the magnetic studies (*vide infra*) which establish that **7** is a V(IV) species. The final Fourier difference maps also clearly show three hydrogen atoms associated with one en terminus and two with the other.

The two-dimensional structure of the mixed valence  $\{V_3^{IIV}V^{IV}F_{17}O\}_n^{6n-}$  anion of **8** is shown in Fig. 7a–c. The structure consists of edge- and corner-sharing  $\{VF_6\}$  and  $\{VF_5O\}$  octahedra in an arrangement that generates  $\{V_{18}F_{18}\}$  rings. The building blocks of the layer are edge-sharing and corner-sharing binuclear units. The structure may be described as zig-zag chains of alternate cornerand edge-sharing octahedral units parallel to the crystallographic *c*-axis, connected through  $\{V_2F_{10}\}$  binuclear units along the *a*-axis. The V–F distances exhibit an unusual range. The V-terminal fluorine distances are observed at 1.857(3)-1.924(3) Å, while V-bridging fluoride distances are in the range 1.954(3)-2.142(3) Å.

Compound **9** did not incorporate fluoride and consists of discrete  $[H_3N(CH_2)_2NH_3]^{2+}$  cations and  $VO_{3^n}^{n-}$  chains. As shown in Fig. 8, the chains consist of corner-sharing V(V) tetrahedra. This is a well-known structure type, first reported for potassium meta-vanadate [48]. It has also been reported in organic–inorganic hybrid materials, such as  $[Ni(en)_3][V_2O_6]$  [49,50].

The magnetic susceptibilities of compounds **4–8** were studied in the 2–300 K temperature range. Compounds **4–7** exhibit temperature dependent magnetic susceptibilities consistent with



(a)



(b)



(c)

**Fig. 7.** (a) A view of the layer stacking and interlamellar occupancy of the cations in 8. (b) A polyhedral representation of the  $V_4F_{17}O_n^{2n-}$  layer of 8. (c) The stacking of layers for 8. The blue polyhedra represent the layer beneath the orange polyhedra. The cations occupy interlamellar positions above and below the cavities in the layers.

Curie–Weiss behavior, as shown in Table 4 and Fig. 9. However, the mixed valence **8** showed more complicated magnetic properties. At

300 K, the effective magnetic moment  $\sqrt{8\chi_0 T}$  is 5.11  $\mu_B$ , consistent with three V(III) sites and one V(IV) site per formula unit. The



**Fig. 8.** A polyhedral view of the  $\{VO_3\}_n^{n-}$  chain and its hydrogen-bonding interactions with the  $\{H_3NC_2H_4NH_3\}^{2+}$  cations of **9**.



**Fig. 9.** The temperature dependence of the inverse susceptibility  $1/\chi$  (red triangles) and of the susceptibility-temperature product  $\chi T$  (blue diamonds) for **5** in the 2–300 K temperature range. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

moment decreases with lowering temperature, indicating the existence of dominant antiferromagnetic interactions. The magnetic data were analyzed using the model considering three V(III) (S = 1) dimers and one V(IV) (S =  $\frac{1}{2}$ ) dimer, following Eq. (1) below. The corresponding exchange Hamiltonian is  $H = -2J_1(S1S2 + S3S4 + S5S6) - 2J_2S7S8$  Fig. 10.

$$\chi = \chi_0 + \chi_{\Pi}$$

$$= \frac{Ng^2 \mu_B^2}{kT} \left( \frac{6e^{2J1/k1} + 30e^{6J1/kT}}{1 + 3e^{2J1/kT} + 5e^{6J1/kT}} + \frac{2e^{2J2/kT}}{1 + 3e^{2J2/kT}} \right) + \chi_{\Pi}$$
(1)

The calculated susceptibility was also corrected for exchange interaction zl' between all spins as shown in Eq. (2).

$$\chi' = \frac{\chi_0}{1 - (2zJ'/Ng^2\mu_B^2)}\chi_0$$
(2)

The best fit gives g = 1.97, J1/k = -18.63 K, J2/k = 19.10 K, zJ'/k = -0.45 K and  $\chi_{TI} = -3.94$ E-4 emu/mol.

#### 4. Conclusions

A series of vanadium fluorides and oxyfluorides has been prepared by the solvatothermal reactions of  $V_2O_5$ , an appropriate organoamine and HF in ethanol/water or ethylene glycol/water solvents. Both the identity of the organoammonium component of the product and variations in reaction conditions influence the product identity. For example, with ethylenediammonium cation



Fig. 10. The temperature dependence of the magnetic susceptibility  $\gamma$  (red circles) and of the effective magnetic moment  $\mu_{eff}$  (blue diamonds) for 8 in the 2–300 K temperature range. The line through the circles is the fit to Eq. (1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

 $[H_2en]^{2+}$ ,  $[H_2en][VF_6]$  (1) is isolated at 150 °C and pH 5.0, while [H<sub>2</sub>en][VF<sub>5</sub>(H<sub>2</sub>O)] is the product at 180 °C and pH 1.8. However, at 120 °C and pH 4.5–5.0, the one-dimensional [Hen][VF<sub>5</sub>] (7) is isolated, while at lower temperatures, the oxide  $[H_2en][V_2O_6]$  (9) is the major product. When diethylenetriammonium cation [H<sub>3</sub>tren]<sup>3+</sup> is the cationic component, [H<sub>3</sub>tren]<sub>2</sub>[VF<sub>5</sub>(H<sub>2</sub>O)]<sub>2</sub>[VOF<sub>4</sub>  $(H_2O)$ ] (3) is isolated at 150 °C and pH 3.0 and  $[H_3tren]_2[V_4F_{14}O_4$  $(H_2O)_2$ ] (6) at 100 °C and the same pH. When bis(aminomethyl)benzene, DABCO and piperazine are introduced,  $(H_2O)_2$ ] (**5**) and  $[H_2pip]_3[V_4F_{17}O] \cdot 1.5H_2O$  (**8**  $\cdot 1.5H_2O$ ) are isolated. The temperature dependence of the products of hydrothermal reactions has been well-documented [1,26]. The role of the cation as a structural determinant appears to derive from hydrogenbonding patterns and steric demands, although the limited data set precludes a more systematic analysis. However, it is apparent that the hydrothermal and solvatothermal chemistries of the  $\{V_x F_y\}$ and  $\{V_x F_y O_z\}$  systems remain relatively undeveloped and that further exploration of the hydrothermal parameter space is warranted.

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#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.09.053.

CCDC 719529, 719530, 719531, 719532, 719533, 719534, 719535, 719536 and 719537 contain 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.

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