Electronic Supplementary Information (ESI) for

Influence of structure-directing polyhedra and heterocyclic ligands on the

chain structures and O/F ordering in a series of zinc vanadium oxyfluorides

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Figure S1. Experimental and calculated powder X-ray diffraction patterns for compound 1



Figure S2. Experimental and calculated powder X-ray diffraction patterns for compound 2



Figure S3. Experimental and calculated powder X-ray diffraction patterns for compound 3



Figure S4. TGA diagrams for compounds 1–3



Figure S5. Powder X-ray diffraction patterns of compound 1 at different temperatures



Figure S6. Powder X-ray diffraction patterns of compound 2 at different temperatures



Figure S7. Powder X-ray diffraction patterns of compound 3 at different temperatures



	Zn(1)–N(1)	2.039(4)	V(1)-O(1)/F(1)	1.688(5)
Zn(1)-F(4)		2.147(2)	V(1)-O(2)/F(2)	1.734(4)
	Zn(1)–F(5)	2.143(2)	V(1)–F(3)	2.077(4)
	Zn(2)–N(3)	2.011(5)	V(1)–F(3)	2.133(4)
	Zn(2)–N(5)	2.001(4)	V(1)–F(4)	1.918(2)
	Zn(2)–O(2)/F(2)	2.158(4)	V(2)–O(3)	1.589(5)
	Zn(2)–F(6)	2.102(4)	V(2)–F(5)	1.955(2)
	V(2)–F(6)	1.914(4)	V(2)–F(7)	2.173(4)
	V(2)–F(7)	1.969(4)		
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	O(1)/F(1)-V(1)-F(3)	161.45(18)	F6-V(2)-F(7)	159.46(17)
	O(1)/F(1)-V(1)-F(4)	95.88(9)	O(3)–V(2)–F(5)	99.01(8)
	O(2)/F(2) - V(1) - F(3)	97.94(18)	O(3)–V(2)–F(6)	101.7(2)
	O(2)/F(2) - V(1) - F(4)	93.64(8)	O(3)–V(2)–F(7)	98.9(2)
	F(4)–V(1)–F(4)	164.80(17)	F(5)–V(2)–F(6)	87.20(8)
	O(2)/F(2)–Zn(2)–F(6)	179.66(17)	F(4)-Zn(1)-F(5)	179.63(10)

Table S1. Selected bond distances (\AA) and bond angles (degree) for compound 1

Table S2. Selected bond distances (Å) and bond angles (degree) for compound 2

elected bond dista	nces (A) and bond	angles (degree) lo	r compound 2
Zn(1)–N(1)	2.002(2)	V(1)–O(1)	1.6013(17)
Zn(1)–N(3)	2.012(2)	V(1)–O(3)	2.0690(18)
Zn(2)–N(5)	1.991(2)	V(1)–F(1)	1.9152(13)
Zn(1)-F(1)	2.1069(13)	V(1)–F(2)	1.9138(14)
Zn(1)–F(6)	2.0711(14)	V(1)–F(3)	2.1796(14)
V(2)–N(7)	2.105(3)	V(1)–F(4)	1.9352(13)
V(2)–F(4)	2.2139(15)	V(2)–O(2)	1.5836(15)
V(2)–F(5)	1.9467(17)	V(2)–F(3)	1.9684(13)
V(2)–F(6)	1.9190(14)		

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O(1)–V(1)–O(3)	93.40(8)	O(2)–V(2)–F(3)	101.66(9)
O(1)–V(1)–F(1)	102.55(8)	O(2)–V(2)–F(4)	172.26(9)
O(1)–V(1)–F(2)	102.04(9)	O(2)–V(2)–F(5)	101.18(11)
O(1)–V(1)–F(4)	102.80(8)	O(2)–V(2)–F(6)	102.41(9)
O(3)–V(1)–F(1)	88.08(7)	O(3)–V(1)–F(4)	91.11(7)
O(3)–V(1)–F(2)	164.24(8)	F(1)–Zn(1)–F(6)	178.91(6)

Table S3.	Selected	bond	distances	(Å)	and	bond	angles	(degree)	for	compoun	d 3

	()	0 (1011)	1
Zn(1)–N(1)	2.004(6	V(1)-O(1)	1.599(5)
Zn(1)–N(3)	2.001(7)	V(1)–N(7)	2.179(7)
Zn(1)–N(5)	1.993(7)	V(1)–F(1)	2.045(4)
Zn(1)–F(3)	2.023(4)	V(1)–F(2)	1.922(4)
Zn(1)–F(12)	2.111(4)	V(1)–F(3)	1.948(4)
Zn(2)–N(9)	1.999(7)	V(1)–F(4)	1.946(4)
Zn(2)–N(11)	1.982(6)	V(2)–O(2)	1.593(6)
Zn(2)-N(13)	2.008(7)	V(2)–F(5)	1.841(5)
Zn(2)–F(4)	2.046(4)	V(2)–F(6)	1.893(4)
Zn(2)–F(7)	2.118(4)	V(2)–F(7)	1.888(4)
Zn(2)–N(15)	1.991(6)	V(2)–F(8)	1.926(4)
Zn(2)-N(17)	1.991(7)	V(3)–O(3)	1.573(6)
Zn(2)–N(19)	1.987(7)	V(3)–F(9)	1.906(4)
Zn(2)–F(8)	2.118(4)	V(3)–F(10)	1.861(5)
Zn(2)–F(9)	2.042(4)	V(3)–F(11)	1.871(5)
		V(3)–F(12)	1.932(4)

O(1)-V(1)-F(1) 170.0(2) O(2)-V(2)-F(5) 11	0.3(3)
O(1)–V(1)–F(2) 100.2(2) O(2)–V(2)–F(6) 11	0.6(3)
O(1)–V(1)–F(3) 99.2(2) O(2)–V(2)–F(7) 10	3.4(3)
O(1)–V(1)–F(4) 98.3(2) O(2)–V(2)–F(8) 10	3.6(3)
O(1)-V(1)-N(7) 89.9(3) O(3)-V(3)-F(9) 10	3.1(3)
F(3)–Zn(1)–F(12) 177.69(18) O(3)–V(3)–F(10) 11	3.7(3)
F(7)–Zn(2)–F(4) 172.74(18) O(3)–V(3)–F(11) 11	1.9(3)
F(8)-Zn(3)-F(9) 177.1(2) O(3)-V(3)-F(12) 10	2.1(3)

Table S4. EDX results for compounds 1–3

	Compound 1	Compound 2	Compound 3
C K	21.91	29.77	14.95
N K	18.30	22.25	13.80
ОК	13.92	24.15	8.65
F K	20.67	14.00	9.20
Zn L	1.00	1.00	1.00
V K	1.11	1.40	1.18

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Zn(1)	2.055	Zn(2)	2.098	V(1)	3.989
V(2)	4.020	O(1)/F(1)	1.296	O(2)/F(2)	1.145
F(3)	0.671	F(4)	0.795	O(3)	1.693
F(5)	0.745	F(6)	0.832	F(7)	0.761
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		1			
Zn(1)	2.168	V(1)	3.931	V(2)	4.063
O(1)	1.638	O(2)	1.726	O(3)	0.462
F(1)	0.827	F(2)	0.561	F(3)	0.758
F(4)	0.779	F(5)	0.513	F(6)	0.845

Table S6. Bond valence sum for compound 2

 Table S7. Bond valence sum for compound 3

		1				
Zn(1)	2.216	Zn(2)	2.204	Zn(3)	2.237	
V(1)	4.057	V(2)	4.097	V(3)	4.153	
O(1)	1.648	O(2)	1.675	O(3)	1.768	
F(1)	0.500	F(2)	0.549	F(3)	0.848	
F(4)	0.831	F(5)	0.683	F(6)	0.594	
F(7)	0.862	F(8)	0.803	F(9)	0.892	
F(10)	0.647	F(11)	0.803	F(12)	0.799	

Proposed Mechanism for the Reduction of Vanadium(V) to Vanadium(IV)

It is interesting that the oxidation states for all vanadium cations in the reported compounds have been reduced from 5 to 4 during the synthesis. HF was used as a mineralizer as well as the source of fluoride in the hydrothermal reactions. Here, the acidic hydrothermal reactions could lead the reduction of vanadium(V) to vanadium(IV). The calculated BVS of all the reported compounds clearly suggest that all the vanadium atoms have been reduced from vanadium(V) to vanadium(IV). The driving force for the reduction of vanadium(V) should be highly pH dependent. Vanadium(V) cations in acidic media exist as dioxovanadium, VO_2^+ and act as a strong oxidant. Both the inner- and outer-sphere electron-transfer pathways are proposed for the reduction of vanadium(V) using various organic and inorganic compounds in acidic conditions.¹⁻⁵ Here, the reduction of vanadium(V) using pyrazole and 3-methylpyrazole ligands in presence of HF is presented. At first, vanadium(V) forms the dioxovanadium(V), VO2+ in aqueous HF. The reduction of vanadium(V) involves the rapid complexation of VO_2^+ by the reductant pyrazole analogue as an intermediate, followed by the inner-sphere one electron transfer from the pyrazole ligands to VO_2^+ , and produce the oxovanadium(IV), VO^{2+} and pyrazole free-radical. Finally, VO²⁺ forms the oxyfluoride anions, and the free radical generates dimer through the coupling with another free radical. Thus, in the present study, it can be assumed that the reaction proceeds via a free-radical mechanism, wherein dioxovanadium(V) undergoes a one-electron reduction by pyrazole analogue ligands.

The detailed reaction mechanism for the reduction of vanadium(V) to vanadium(IV) and subsequent formation of oxyfluoride anions can be expressed in Scheme 1.



Scheme 1. Reduction of vanadium(V) to vanadium(IV) with pyrazole analogue in acidic media.

Pyrazole and 3-methylpyrazole ligands may reduce the dioxovanadium(V), VO_2^+ in aqueous acidic solutions according to the following equation, where HL represents for pyrazole/3-methylpyrazole ligands.

$$2HL + VO_2^+ + 4HF \rightarrow [VOF_4]^{2-} + [L-L] (Dimer) + H_2O + 4H^+$$

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