Controlled One Pot Synthesis of Polyoxofluorovanadate Molecular Hybrids Exhibiting Peroxidase Like Activity

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Contents

Methods

Crystallography. Crystal structure refinement data of **1-3**, and $[XyH_2]_2[V^{IV}{}_2O_2F_6(\mu\text{-}F)_2]$ are provided in Table 1. The intensity data of the complexes were collected on a XCaliburSuperNova 4-cycle diffractometer, equipped with a CCD camera detector, using Cu (λ =1.54184 Å) and Mo (λ =0.71073 Å) radiation. Data acquisition and data reduction was done using the software CrysAlis.[1, 2] The structures were solved by direct methods using the program SHELX–97 and refined by full–matrix least square techniques.[3, 4] All non–hydrogen atoms were generally refined with anisotropic thermal parameters. All the atoms were refined anisotropically. The positions occupied by O and F atoms were determined unambiguously by evaluating the refinement of the structures assigning either to O or F atoms. The positions of hydrogen atoms were calculated from stereochemical considerations and kept fixed isotropic during refinement or found in D*F* map and refined with isotropic thermal parameters. Interatomic bond lengths and angles of compounds can be found in Table S1-xxx.

NMR and EPR Measurements. ^{1}H, ^{13}C and ^{51}V NMR spectra were recorded on a Bruker Avance 500 MHz instrument in 500, 150 and 130 MHz respectively. A 30° pulse was used and a relaxation delay of 2 s for ^{1}H, ^{13}C and 0.5 s for ^{51}V were applied. The chemical shifts are reported with respect to TMS for ^{1}H, ^{13}C and $VOCl_3$ for ^{51}V at 0 ppm. 2D {^{1}H,^{1}H} COSY, {^{1}H,^{13}C} HMQC and {^{1}H,^{13}C} HMBC was acquired using the standard Bruker NMR pulses and parameters. The cw X-band EPR spectra of aqueous solutions of the complexes at 130 K were measured on an ELEXSYS E500 Bruker spectrometer at resonance frequency ~9.5 GHz and modulation frequency 100 MHz. The resonance frequency was accurately measured with solid DPPH (g=2.0036). Simulations of EPR spectra were performed using Easyspin.[5]

Reactivity Studies

The organic substrate (n-butanol or crotyl alcohol) at various quantities (0.10-1.0 mmol) was added in aqueous solution (0.60 mL) of each complex (4.7 μmol). The pH of the solution was adjusted by aqueous HCl (0.1 M) to ~4.8. Then, H_2O_2 (0, 0.12 and 0.24 mmol) was added and the ^{1}H and ^{51}V NMR were acquired at different time intervals: 0, 10 min, 1 hour and 24 hours after the H_2O_2 addition. The experiments were performed in triplicates for complexes obtained from three different preparations. The organic molecules were determined by 2D {^{1}H,^{1}H} COSY, {^{1}H,^{13}C} HMQC and {^{1}H,^{13}C} HMBC experiment.

Magnetic, Electrochemical, UV-Vis measurements, elemental analysis

Room temperature magnetic measurements were carried out on an MK1 MB magnetic susceptibility balance.

Cyclic voltammetry (CV) and round disk voltammetry (RDV) experiments were recorded using an EG&G Princeton Applied Research 273A potentiostat/galvanostat. Electrochemical procedures were performed with a three-electrode configuration: a platinum disk or rotating disk electrode (RDE) as the working electrode, a platinum wire as the auxiliary electrode, and a Ag/AgCl(s) electrode as a reference. All the potential values are referred to Ag/AgCl(s). The electrochemical measurements were carried out in water solutions of KNO_3 (0.1 M) purged with N_2 prior to the measurement at 298 K. Scan rates (ν) of 100 mV s^{-1} and 10 mV s^{-1} were used for cyclic voltammograms and linear sweep voltammetry experiments respectively.

The UV-Vis measurements were recorded on a Photonics UV-Vis spectrophotometer Model 400, equipped with a CCD array, operating in the range 250 to 1000 nm. C, H, N were measured on a Eurovector 2000. The fluoride content was analyzed gravimetrically as PbClF.

The stability of the solutions of the complexes were examined vs time (every 10 min) by UV-Vis spectroscopy under inert and under air atmosphere.

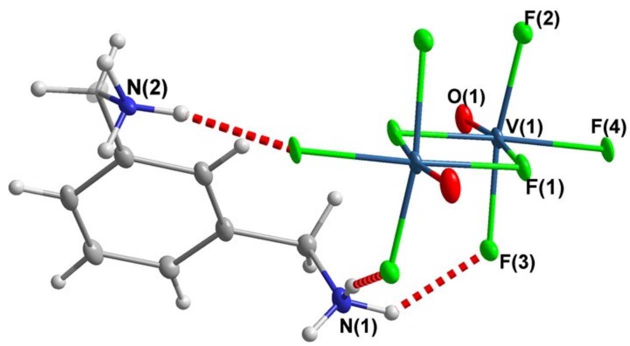

Fig S1. ORTEP diagrams of the anion of $[XyH_2]_2[V^{IV}{}_2O_2F_6(\mu\text{-}F)_2]$ with atomic numbering scheme and thermal ellipsoids at 50% probability level.

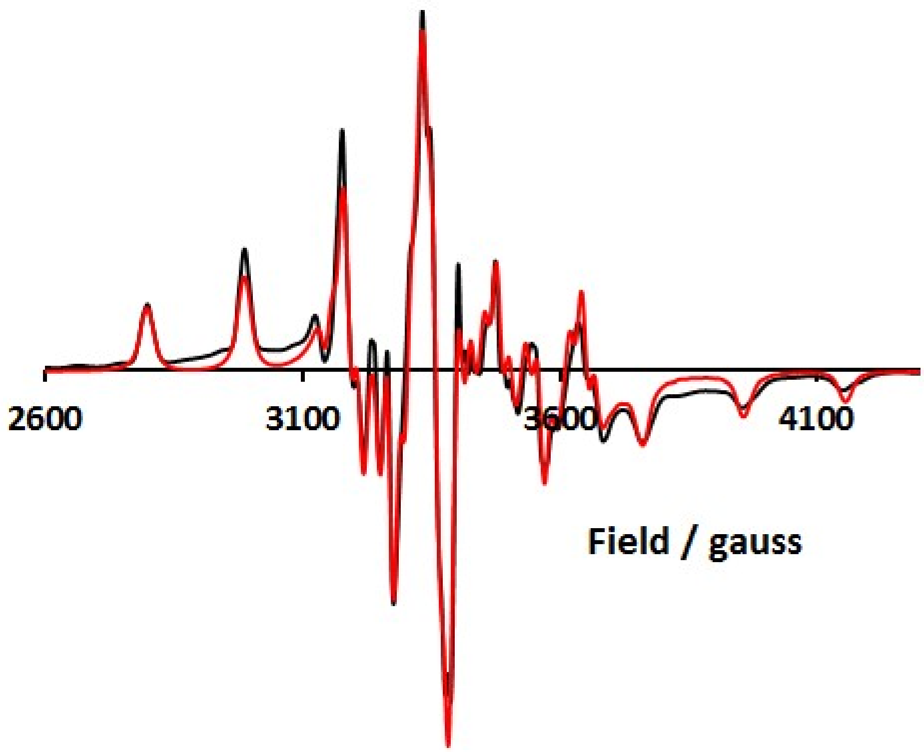

Fig S2. Cw X-band EPR spectrum of $[XyH_2]_2[V^{IV}{}_2O_2F_6(\mu\text{-}F)_2]$ (0.10 mM) in frozen DMSO (black line) and its simulated one (red line). The simulated spectrum were fitted to experimental ones using the following parameters: $g\perp$ = 1.970, $g||$ = 1.934, and $A\perp_{51V}$ = -62.7 x 10^{-4}, $A||_{51V}$ = -175.1 x 10^{-4}, $A\perp_{19F}$ = 21.1 x 10^{-4}, $A||_{19F}$ = 8.6 x 10^{-4}, $A\perp_{19F'}$ = 22.6 x 10^{-4}, $A||_{19F'}$ = 5.8 x 10^{-4} cm^{-1}.

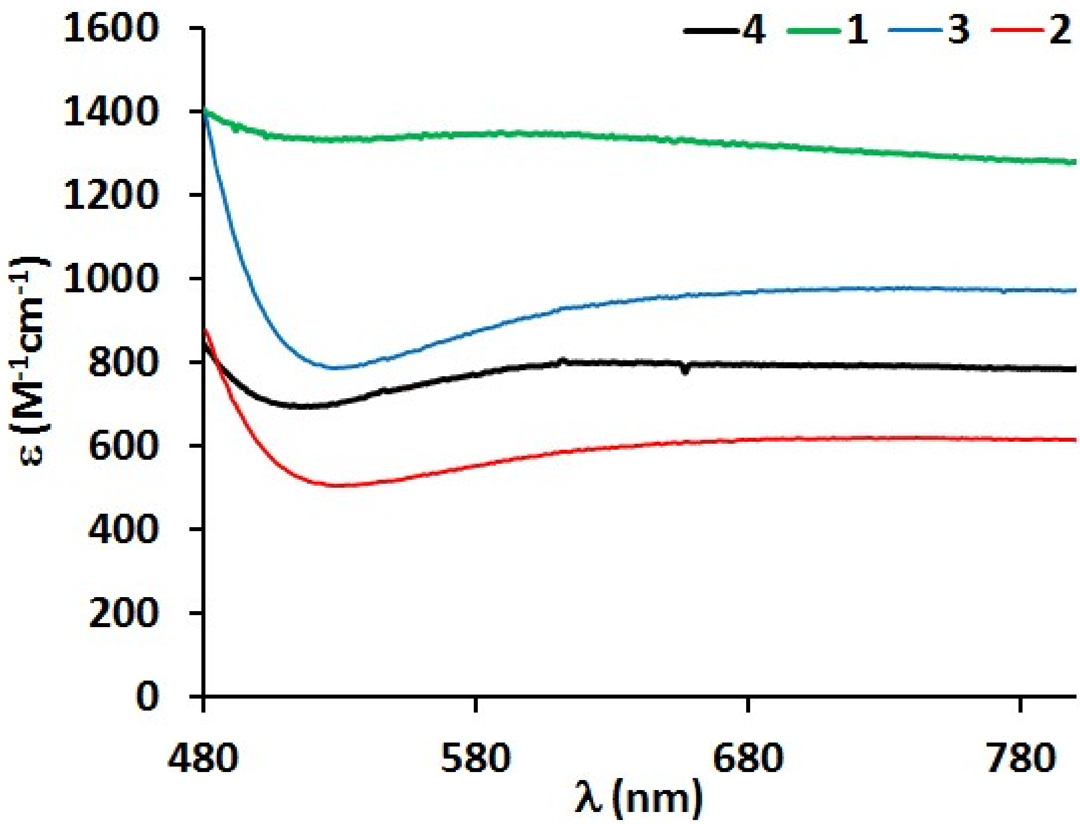

Fig S3. Visible spectra of the aqueous solutions of **1**-**4** (0.50 mmol)**.**

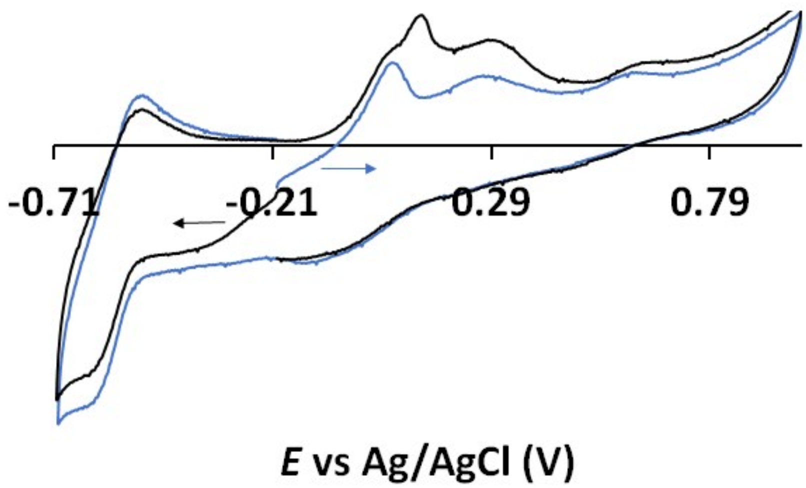

Fig. S4. Cyclic Voltammograph of compound **4** (0.5 mmol) forward scan (blue line) and reverse scan black line) in aqueous solution at pH 4.5 in the presence of 0.1 M KNO_3 at scan rates 100 mV/s. Platinum disk was used as working electrode, platinum wire as counter and Ag/AgCl as reference.

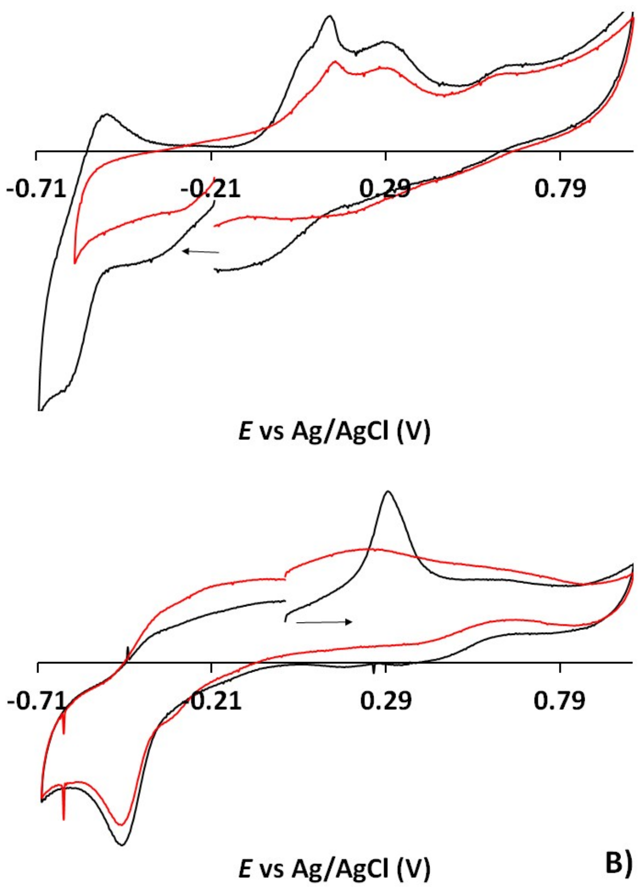

Fig S5. Cyclic Voltammograph of A) compound **1** (0.5 mmol, red line) compound **4** (1.0 mmol, black line) and B) compound 3 (0.5 mmol, red line) compound 2 (1.0 mmol, black line), in aqueous solution at pH 4.5 in the presence of 0.1 M KNO_3 at scan rates 100 mV/s. Platinum disk was used as working electrode, platinum wire as counter and Ag/AgCl as reference.

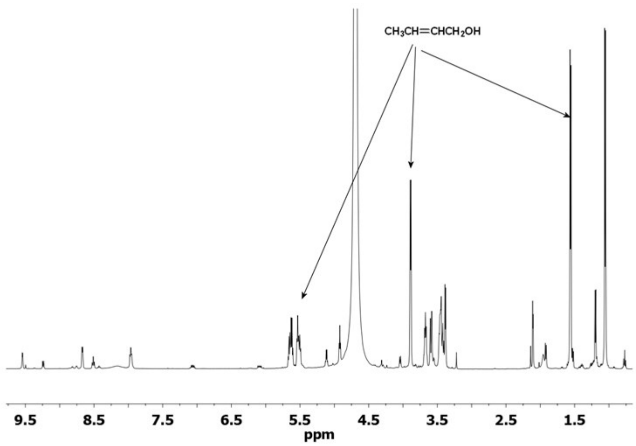

Fig. S6. ^{1}H NMR spectrum of a D_2O (0.60 mL) solution of 5 (10 mg, 4.7 μmol), crotyl alcohol (44 mg, 0.60 mmol) and H_2O_2 (0.12 mmol, 13.6 mg aqueous 30%) at pH 4.8.

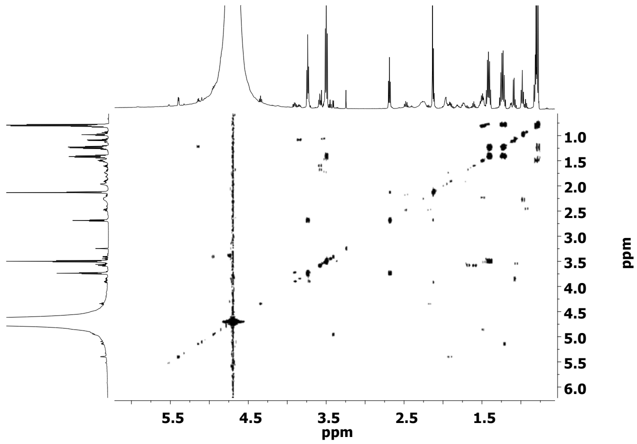

Fig. S7. 2D{[1]H}-COSY NMR spectrum of a D_2O (0.60 mL) solution of 5 (10 mg, 4.7 μmol), n-butanol (44 mg, 0.60 mmol) and H_2O_2 (0.12 mmol, 13.6 mg aquoeus 30%) at pH 4.8.

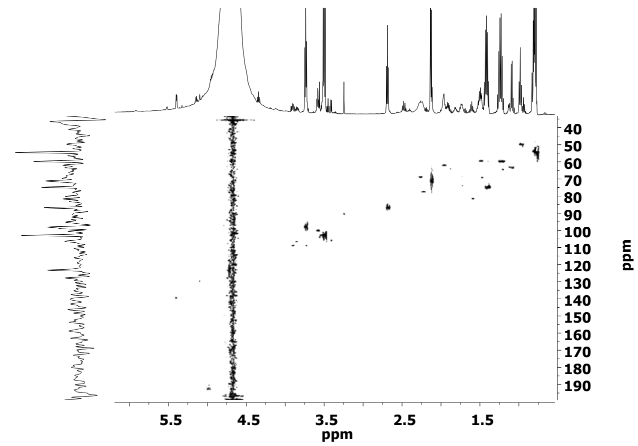

Fig. S8. 2D{[1]H,[13]C}-HSQC NMR spectrum of a D_2O (0.60 mL) solution of **5** (10 mg, 4.**7** μmol), n-butanol (44 mg, 0.60 mmol) and H_2O_2 (0.12 mmol, 13.6 mg aqueous 30%) at pH 4.8.

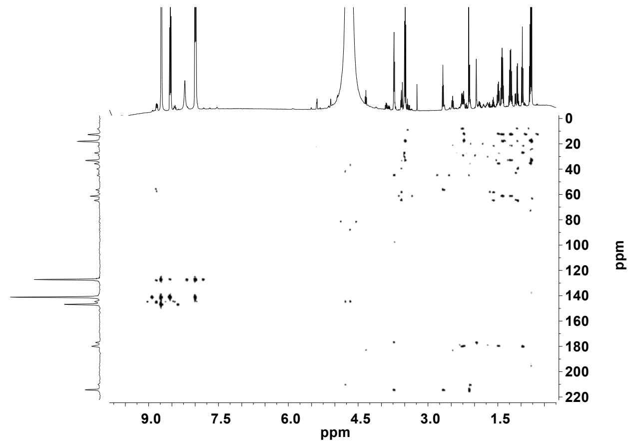

Fig. S9. 2D{^{1}H,^{13}C}-HMBC NMR spectrum of a D_2O (0.60 mL) solution of 5 (10 mg, 4.2 μmol), n-butanol (44 mg, 0.60 mmol) and H_2O_2 (0.12 mmol, 13.6 mg aqueous 30%) at pH 4.8.

Table S1. Selected bonds (Å) and angles (°) of compound **$(XyH_2)_2^{2+}[V^{IV}OF4]_2^{2-}$**.

	$(XyH_2)_2^{2+}[V^{IV}OF4]_2^{2-}$
V(1)-O(1)	1.598(2)
V(1)-F(3)	1.954(2)
V(1)-F(2)	1.922(2)
V(1)-F(1)	1.9852(17)
V(1)-O(2)/F(4)	1.9410(17)
V(1)-F(1)#1	2.1699(17)
O(1)-V(1)-F(3)	96.30(12)
O(1)-V(1)-F(2)	98.68(12)
F(3)-V(1)-F(2)	164.53(8)
O(1)-V(1)-F(1)	97.05(10)
F(3)-V(1)-F(1)	91.57(8)
F(2)-V(1)-F(1)	90.42(8)
O(1)-V(1)-O(2)/F(4)	102.30(10)
F(3)-V(1)-O(2)/F(4)	87.11(8)
F(2)-V(1)-O(2)/F(4)	85.95(8)
F(1)-V(1)-O(2)/F(4)	160.64(7)

Table S2. Selected bonds of compounds **2-4**.

	1 / Å	**2** / Å		**3** / Å	
V(4)-O(5)	1.602(2)	V(6)-O(8)	1.584(3)	V(4)-O(8)	1.603(5)
V(4)-O(13)	1.724(2)	V(6)-O(4)	1.809(3)	V(4)-O(6)	1.829(3)
V(4)-O(16)	2.008(2)	V(6)-O(17)	1.815(3)	V(4)-O(53)	1.983(16)
V(4)-O(4)	1.936(2)	V(6)-O(41)	1.959(3)	V(4)-N(51)	2.161(17)
V(4)-O(14)	1.905(2)	V(6)-N(1)	2.163(4)	V(4)-O(5)	2.280(5)
V(2)-O(2)	1.604(2)	V(6)-O(20)	2.360(3)	V(3)-O(7)	1.605(5)
V(2)-O(13)	1.934(2)	V(26)-O(28)	1.584(3)	V(3)-O(6)	1.938(3)
V(2)-O(6)	1.937(2)	V(26)-O(24)	1.779(3)	V(3)-O(50)	1.992(13)
V(2)-O(12)	1.993(2)	V(26)-O(37)	1.812(3)	V(3)-N(50)	2.146(15)
V(2)-O(11)	1.987(2)	V(26)-O(43)	2.005(3)	V(3)-O(4)	2.290(5)
V(2)-F(1)	2.187(2)	V(26)-N(2)	2.158(4)	V(2)-O(3)	1.582(4)
V(5)-O(7)	1.598(2)	V(26)-O(40)	2.352(3)	V(2)-O(2)	1.790(4)
V(5)-O(6)	1.739(2)	V(1)-O(1)	1.604(3)	V(2)-O(4)	1.902(3)
V(5)-O(14)	1.987(2)	V(1)-O(11)	1.715(3)	V(2)-O(5)	1.924(3)
V(5)-O(17)	1.935(2)	V(1)-O(14)#1	1.923(3)	V(2)-O(6)	2.026(3)
V(5)-O(16)	1.926(2)	V(1)-O(20)	2.021(3)	V(2)-F	2.2864(9)
V(6)-O(8)	1.599(2)	V(1)-O(17)	2.067(3)	V(1)-O(1)	1.605(8)
V(6)-O(15)	1.723(2)	V(1)-F(1)	2.166(3)	V(1)-F	2.297(5)
V(6)-O(4)	1.811(2)	V(2)-O(2)	1.612(4)	Na(1)-O(7)	2.881(5)
V(6)-O(17)	1.800(2)	V(2)-O(13)#1	1.927(3)		
V(3)-O(3)	1.607(2)	V(2)-O(6)	1.927(3)		
V(3)-O(12)	1.737(2)	V(2)-O(12)	1.965(3)		
V(3)-O(16)	1.940(2)	V(2)-O(11)	1.990(3)		
V(3)-O(18)	1.937(2)	V(2)-F(1)	2.194(3)		
V(3)-O(17)	2.074(2)	V(24)-O(25)	1.597(3)		
V(3)-F(1)	2.184(2)	V(24)-O(33)	1.709(3)		
V(1)-O(1)	1.599(2)	V(24)-O(34)	1.944(3)		
V(1)-O(11)	1.736(2)	V(24)-O(24)#2	1.953(3)		

V(1)-O(18)	1.951(2)	V(24)-O(36)	2.009(3)
V(1)-O(14)	1.937(2)	V(25)-O(27)	1.608(4)
V(1)-O(4)	2.080(2)	V(25)-O(26)	1.708(3)
V(1)-F(1)	2.207(2)	V(25)-O(36)	1.911(3)
V(7)-O(9)	1.599(2)	V(25)-O(37)	1.939(3)
V(7)-F(2)	1.815(2)	V(25)-O(34)	2.040(3)
V(7)-O(15)	2.001(2)	V(21)-O(21)	1.605(3)
V(7)-O(18)	2.003(2)	V(21)-O(31)	1.718(3)
V(7)-F(3)	1.914(2)	V(21)-O(34)	1.902(3)
		V(21)-O(40)	2.026(3)
		V(21)-O(37)	2.079(3)
		V(21)-F(2)	2.173(3)
		V(23)-O(23)	1.601(3)
		V(23)-O(32)	1.721(3)
		V(23)-O(36)#2	1.885(3)
		V(23)-O(40)	2.019(3)
		V(23)-O(24)	2.089(3)
		V(23)-F(2)	2.209(3)
		V(22)-O(22)	1.603(3)
		V(22)-O(33)	1.932(3)
		V(22)-O(26)#2	1.936(4)
		V(22)-O(32)	1.983(3)
		V(22)-O(31)	1.996(4)
		V(22)-F(2)	2.187(3)
		V(3)-O(3)	1.594(3)
		V(3)-O(12)	1.717(3)
		V(3)-O(16)	1.900(3)
		V(3)-O(20)	2.024(3)
		V(3)-O(4)	2.062(3)
		V(3)-F(1)	2.238(3)
		V(5)-O(7)	1.603(3)
		V(5)-O(6)	1.703(3)

V(5)-O(16)	1.910(3)
V(5)-O(17)#1	1.925(3)
V(5)-O(14)	2.073(3)
V(4)-O(5)	1.599(3)
V(4)-O(13)	1.717(4)
V(4)-O(4)	1.936(3)
V(4)-O(14)	1.945(3)
V(4)-O(16)	1.993(3)

Table S3. Selected angles of compounds **1-3**.

	1 /°		**2** /°		**3** /°
				O(8)-V(4)-O(6)	101.36(15)
O(5)-V(4)-O(13)	106.31(10)	O(8)-V(6)-O(4)	102.23(16)	O(6)#1-V(4)-O(6)	101.3(2)
O(5)-V(4)-O(16)	101.06(9)	O(8)-V(6)-O(17)	103.01(16)	O(8)-V(4)-O(53)	97.8(5)
O(13)-V(4)-O(16)	96.34(9)	O(4)-V(6)-O(17)	103.30(14)	O(6)#1-V(4)-O(53)	154.6(5)
O(5)-V(4)-O(4)	104.25(10)	O(8)-V(6)-O(41)	102.01(16)	O(6)#1-V(4)-O(53)#1	91.0(4)
O(13)-V(4)-O(4)	94.21(9)	O(4)-V(6)-O(41)	89.10(14)	O(6)-V(4)-O(53)#1	154.6(5)
O(16)-V(4)-O(4)	141.94(9)	O(17)-V(6)-O(41)	148.87(14)	O(53)-V(4)-O(53)#1	69.8(8)
O(5)-V(4)-O(14)	107.59(10)	O(8)-V(6)-N(1)	95.33(16)	O(8)-V(4)-N(51)	98.7(5)
O(13)-V(4)-O(14)	152.59(9)	O(4)-V(6)-N(1)	158.79(15)	O(6)#1-V(4)-N(51)	157.1(5)
O(16)-V(4)-O(14)	76.52(8)	O(17)-V(6)-N(1)	83.94(14)	O(6)-V(4)-N(51)	85.4(5)
O(4)-V(4)-O(14)	77.40(9)	O(41)-V(6)-N(1)	75.56(14)	O(8)-V(4)-N(51)#1	98.7(5)
O(2)-V(2)-O(13)	101.45(9)	O(8)-V(6)-O(20)	175.00(14)	O(6)#1-V(4)-N(51)#1	85.4(5)
O(2)-V(2)-O(6)	100.90(10)	O(4)-V(6)-O(20)	74.89(13)	N(51)-V(4)-N(51)#1	80.7(9)
O(13)-V(2)-O(6)	98.09(9)	O(17)-V(6)-O(20)	73.98(13)	O(8)-V(4)-O(5)	174.4(2)
O(2)-V(2)-O(12)	99.10(9)	O(41)-V(6)-O(20)	82.15(13)	O(6)-V(4)-O(5)	75.26(13)
O(13)-V(2)-O(12)	83.76(8)	N(1)-V(6)-O(20)	88.37(13)	O(53)-V(4)-O(5)	86.7(5)
O(6)-V(2)-O(12)	158.60(8)	O(28)-V(26)-O(24)	104.23(17)	N(51)-V(4)-O(5)	85.5(5)
O(2)-V(2)-O(11)	100.59(10)	O(28)-V(26)-O(37)	104.54(16)	O(7)-V(3)-O(6)	99.98(16)
O(13)-V(2)-O(11)	157.46(9)	O(24)-V(26)-O(37)	102.86(14)	O(6)-V(3)-O(6)#2	94.1(2)
O(6)-V(2)-O(11)	84.22(8)	O(28)-V(26)-O(43)	100.67(16)	O(7)-V(3)-O(50)	102.4(4)
O(12)-V(2)-O(11)	86.20(8)	O(24)-V(26)-O(43)	149.06(14)	O(6)-V(3)-O(50)	92.1(4)
O(2)-V(2)-F(1)	172.80(8)	O(37)-V(26)-O(43)	88.16(14)	O(6)#2-V(3)-O(50)	155.3(4)
O(13)-V(2)-F(1)	84.42(7)	O(28)-V(26)-N(2)	97.31(15)	O(7)-V(3)-O(50)#2	102.4(4)
O(6)-V(2)-F(1)	82.22(8)	O(24)-V(26)-N(2)	84.55(14)	O(6)#2-V(3)-O(50)#2	92.1(4)
O(12)-V(2)-F(1)	74.67(7)	O(37)-V(26)-N(2)	154.20(14)	O(50)-V(3)-O(50)#2	73.0(7)
O(11)-V(2)-F(1)	75.67(7)	O(43)-V(26)-N(2)	74.28(13)	O(7)-V(3)-N(50)	98.6(4)
O(7)-V(5)-O(6)	106.43(11)	O(28)-V(26)-O(40)	179.65(16)	O(6)-V(3)-N(50)	89.4(4)

O(7)-V(5)-O(14)	105.03(10)	O(24)-V(26)-O(40)	75.45(13)	O(6)#2-V(3)-N(50)	160.2(4)
O(6)-V(5)-O(14)	95.20(9)	O(37)-V(26)-O(40)	75.41(12)	N(50)-V(3)-N(50)#2	81.1(8)
O(7)-V(5)-O(17)	105.42(10)	O(43)-V(26)-O(40)	79.68(12)	O(7)-V(3)-O(4)	169.7(2)
O(6)-V(5)-O(17)	94.31(9)	N(2)-V(26)-O(40)	82.82(12)	O(6)-V(3)-O(4)	73.22(13)
O(14)-V(5)-O(17)	144.16(9)	O(1)-V(1)-O(11)	103.77(17)	O(6)#2-V(3)-O(4)	73.23(13)
O(7)-V(5)-O(16)	104.81(10)	O(1)-V(1)-O(14)#1	103.21(15)	O(50)-V(3)-O(4)	85.8(4)
O(6)-V(5)-O(16)	148.54(10)	O(11)-V(1)-O(14)#1	100.20(15)	N(50)-V(3)-O(4)	89.2(4)
O(14)-V(5)-O(16)	76.57(8)	O(1)-V(1)-O(20)	98.84(15)	O(3)-V(2)-O(2)	102.49(19)
O(17)-V(5)-O(16)	77.38(8)	O(11)-V(1)-O(20)	96.17(15)	O(3)-V(2)-O(4)	104.2(2)
O(8)-V(6)-O(15)	106.03(10)	O(14)#1-V(1)-O(20)	148.39(13)	O(2)-V(2)-O(4)	94.63(19)
O(8)-V(6)-O(4)	107.71(11)	O(1)-V(1)-O(17)	98.24(15)	O(3)-V(2)-O(5)	103.2(2)
O(15)-V(6)-O(4)	112.69(10)	O(11)-V(1)-O(17)	157.76(14)	O(2)-V(2)-O(5)	94.40(19)
O(8)-V(6)-O(17)	108.52(10)	O(14)#1-V(1)-O(17)	77.50(13)	O(4)-V(2)-O(5)	148.5(2)
O(15)-V(6)-O(17)	110.57(10)	O(20)-V(1)-O(17)	77.15(13)	O(3)-V(2)-O(6)	100.12(17)
O(4)-V(6)-O(17)	111.07(9)	O(1)-V(1)-F(1)	173.01(14)	O(2)-V(2)-O(6)	157.37(16)
O(3)-V(3)-O(12)	103.82(10)	O(11)-V(1)-F(1)	80.54(13)	O(4)-V(2)-O(6)	80.40(18)
O(3)-V(3)-O(16)	101.25(10)	O(14)#1-V(1)-F(1)	81.18(11)	O(5)-V(2)-O(6)	79.75(17)
O(12)-V(3)-O(16)	96.12(9)	O(20)-V(1)-F(1)	75.06(11)	O(3)-V(2)-F	178.91(19)
O(3)-V(3)-O(18)	101.88(10)	O(17)-V(1)-F(1)	77.25(11)	O(2)-V(2)-F	78.31(18)
O(12)-V(3)-O(18)	96.62(9)	O(1)-V(1)-V(2)	139.62(13)	O(4)-V(2)-F	76.46(13)
O(16)-V(3)-O(18)	150.01(8)	O(11)-V(1)-V(2)	35.85(11)	O(5)-V(2)-F	76.00(13)
O(3)-V(3)-O(17)	97.13(9)	O(14)#1-V(1)-V(2)	88.99(10)	O(6)-V(2)-F	79.07(16)
O(12)-V(3)-O(17)	158.68(8)	O(20)-V(1)-V(2)	88.68(10)	O(1)-V(1)-O(2)#1	103.70(12)
O(16)-V(3)-O(17)	75.75(8)	O(17)-V(1)-V(2)	122.06(9)	O(2)#1-V(1)-O(2)#3	86.2(2)
O(18)-V(3)-O(17)	82.66(8)	F(1)-V(1)-V(2)	44.90(7)	O(1)-V(1)-O(2)#2	103.70(12)
O(3)-V(3)-F(1)	176.18(9)	O(1)-V(1)-V(5)#1	106.21(13)	O(2)#1-V(1)-O(2)#2	152.6(2)
O(12)-V(3)-F(1)	79.85(7)	O(11)-V(1)-V(5)#1	135.00(11)	O(1)-V(1)-O(2)	103.70(12)
O(16)-V(3)-F(1)	76.47(7)	O(14)#1-V(1)-V(5)#1	40.54(10)	O(2)#1-V(1)-O(2)	87.4(2)
O(18)-V(3)-F(1)	79.22(7)	O(20)-V(1)-V(5)#1	111.28(10)	O(2)#3-V(1)-O(2)	152.6(2)
O(17)-V(3)-F(1)	79.27(7)	O(17)-V(1)-V(5)#1	37.10(8)	O(2)#2-V(1)-O(2)	86.2(2)

O(1)-V(1)-O(11)	103.99(11)	F(1)-V(1)-V(5)#1	73.48(7)	O(1)-V(1)-F	180.0(3)
O(1)-V(1)-O(18)	101.00(10)	O(2)-V(2)-O(13)#1	101.19(17)	O(2)-V(1)-F	76.30(12)
O(11)-V(1)-O(18)	96.96(9)	O(2)-V(2)-O(6)	102.26(16)	O(8)-Na(1)-O(8)#2	103.68(19)
O(1)-V(1)-O(14)	104.19(10)	O(13)#1-V(2)-O(6)	96.14(13)	O(8)-Na(1)-O(8)#5	76.32(19)
O(11)-V(1)-O(14)	96.07(8)	O(2)-V(2)-O(12)	102.28(16)	O(8)#4-Na(1)-O(8)#5	103.68(19)
O(18)-V(1)-O(14)	147.80(9)	O(13)#1-V(2)-O(12)	155.83(15)	O(8)-Na(1)-O(7)	68.67(7)
O(1)-V(1)-O(4)	95.05(10)	O(6)-V(2)-O(12)	84.44(13)	O(8)#4-Na(1)-O(7)	111.33(7)
O(11)-V(1)-O(4)	160.56(9)	O(2)-V(2)-O(11)	100.95(16)	O(8)-Na(1)-O(7)#1	68.67(7)
O(18)-V(1)-O(4)	82.99(8)	O(13)#1-V(2)-O(11)	85.06(14)	O(8)#4-Na(1)-O(7)#1	111.33(7)
O(14)-V(1)-O(4)	75.16(8)	O(6)-V(2)-O(11)	156.05(14)	O(7)-Na(1)-O(7)#1	107.88(19)
O(1)-V(1)-F(1)	175.04(9)	O(12)-V(2)-O(11)	84.94(14)	O(7)#4-Na(1)-O(7)#1	72.13(19)
O(11)-V(1)-F(1)	80.20(8)	O(2)-V(2)-F(1)	174.60(14)	O(8)-Na(1)-O(7)#6	111.33(7)
O(18)-V(1)-F(1)	75.66(7)	O(13)#1-V(2)-F(1)	81.15(12)	O(8)#4-Na(1)-O(7)#6	68.67(7)
O(14)-V(1)-F(1)	77.75(8)	O(6)-V(2)-F(1)	82.23(12)	O(7)-Na(1)-O(7)#6	72.12(19)
O(4)-V(1)-F(1)	80.97(7)	O(12)-V(2)-F(1)	74.98(12)	O(7)#4-Na(1)-O(7)#6	107.87(19)
O(9)-V(7)-O(10)/F(2)	108.94(12)	O(11)-V(2)-F(1)	74.30(12)	V(2)#2-F-V(2)	89.25(5)
O(9)-V(7)-O(15)	98.12(11)	O(2)-V(2)-V(1)	131.22(13)	V(2)#1-F-V(2)	90.44(5)
O(10)/F(2)-V(7)-O(15)	89.73(9)	O(13)#1-V(2)-V(1)	79.05(10)	V(2)#3-F-V(2)	174.0(3)
O(9)-V(7)-O(18)	116.66(12)	O(6)-V(2)-V(1)	126.39(10)	V(2)-F-V(1)	87.00(13)
O(10)/F(2)-V(7)-O(18)	134.31(9)	O(12)-V(2)-V(1)	81.22(10)	V(2)-O(4)-V(2)#2	115.2(3)
O(15)-V(7)-O(18)	81.55(8)	O(11)-V(2)-V(1)	30.31(10)	V(2)-O(4)-V(3)	98.33(16)
O(9)-V(7)-N(1)/F(3)	100.76(11)	F(1)-V(2)-V(1)	44.17(7)	V(2)#2-O(4)-V(3)	98.32(16)
O(10)/F(2)-V(7)-N(1)/F(3)	88.86(9)	O(25)-V(24)-O(33)	105.02(17)	V(2)#1-O(5)-V(2)	115.0(3)
O(15)-V(7)-N(1)/F(3)	160.47(8)	O(25)-V(24)-O(34)	107.71(16)	V(2)#1-O(5)-V(4)	95.98(16)
O(18)-V(7)-N(1)/F(3)	85.55(8)	O(33)-V(24)-O(34)	96.52(14)	V(2)-O(5)-V(4)	95.99(16)

O(25)-V(24)-O(24)#2	104.10(15)	V(4)-O(6)-V(3)	143.58(19)
O(33)-V(24)-O(24)#2	94.70(15)	V(4)-O(6)-V(2)	108.59(16)
O(34)-V(24)-O(24)#2	142.05(13)	V(3)-O(6)-V(2)	106.75(16)
O(25)-V(24)-O(36)	103.95(16)	V(2)-O(2)-V(1)	118.4(2)
O(33)-V(24)-O(36)	151.01(14)	V(3)-O(7)-Na(1)	136.2(3)
O(34)-V(24)-O(36)	75.47(13)	V(4)-O(8)-Na(1)	137.7(2)
O(24)#2-V(24)-O(36)	77.25(13)		
O(25)-V(24)-V(25)	119.49(14)		
O(33)-V(24)-V(25)	123.87(10)		
O(34)-V(24)-V(25)	40.43(10)		
O(24)#2-V(24)-V(25)	104.90(9)		
O(36)-V(24)-V(25)	37.03(8)		
O(25)-V(24)-V(23)#2	107.53(13)		
O(33)-V(24)-V(23)#2	130.32(12)		
O(34)-V(24)-V(23)#2	107.84(10)		
O(24)#2-V(24)-V(23)#2	41.46(9)		
O(36)-V(24)-V(23)#2	35.80(9)		
O(27)-V(25)-O(26)	105.67(18)		
O(27)-V(25)-O(36)	106.35(15)		
O(26)-V(25)-O(36)	95.86(14)		
O(27)-V(25)-O(37)	105.82(15)		
O(26)-V(25)-O(37)	95.21(14)		
O(36)-V(25)-O(37)	141.54(14)		
O(27)-V(25)-O(34)	102.41(17)		

O(26)-V(25)-O(34)	151.92(15)
O(36)-V(25)-O(34)	75.45(13)
O(37)-V(25)-O(34)	77.57(12)
O(27)-V(25)-V(24)	117.71(13)
O(26)-V(25)-V(24)	123.04(11)
O(36)-V(25)-V(24)	39.26(10)
O(37)-V(25)-V(24)	105.76(10)
O(34)-V(25)-V(24)	38.18(9)
O(27)-V(25)-V(21)	110.59(13)
O(26)-V(25)-V(21)	128.93(11)
O(36)-V(25)-V(21)	106.73(10)
O(37)-V(25)-V(21)	41.15(9)
O(34)-V(25)-V(21)	36.55(8)
O(21)-V(21)-O(31)	103.80(17)
O(21)-V(21)-O(34)	104.35(16)
O(31)-V(21)-O(34)	100.18(15)
O(21)-V(21)-O(40)	98.75(15)
O(31)-V(21)-O(40)	95.54(15)
O(34)-V(21)-O(40)	147.90(14)
O(21)-V(21)-O(37)	96.91(16)
O(31)-V(21)-O(37)	159.03(15)
O(34)-V(21)-O(37)	77.42(13)
O(40)-V(21)-O(37)	77.94(12)
O(21)-V(21)-F(2)	172.18(14)
O(31)-V(21)-F(2)	80.50(13)
O(34)-V(21)-F(2)	81.03(12)
O(40)-V(21)-F(2)	74.17(11)
O(37)-V(21)-F(2)	78.55(11)
O(21)-V(21)-V(25)	106.03(13)
O(31)-V(21)-V(25)	134.83(11)
O(34)-V(21)-V(25)	39.70(10)
O(40)-V(21)-V(25)	112.32(9)
O(37)-V(21)-V(25)	37.86(8)
F(2)-V(21)-V(25)	74.34(7)

O(21)-V(21)-V(22)	139.80(13)
O(31)-V(21)-V(22)	36.02(11)
O(34)-V(21)-V(22)	89.03(11)
O(40)-V(21)-V(22)	87.46(9)
O(37)-V(21)-V(22)	123.14(10)
F(2)-V(21)-V(22)	44.66(7)
O(23)-V(23)-O(32)	103.56(16)
O(23)-V(23)-O(36)#2	105.29(16)
O(32)-V(23)-O(36)#2	100.61(15)
O(23)-V(23)-O(40)	98.94(15)
O(32)-V(23)-O(40)	95.28(15)
O(36)#2-V(23)-O(40)	146.80(14)
O(23)-V(23)-O(24)	98.87(15)
O(32)-V(23)-O(24)	157.24(14)
O(36)#2-V(23)-O(24)	76.78(13)
O(40)-V(23)-O(24)	77.36(12)
O(23)-V(23)-F(2)	171.97(15)
O(32)-V(23)-F(2)	80.29(12)
O(36)#2-V(23)-F(2)	80.63(12)
O(40)-V(23)-F(2)	73.53(11)
O(24)-V(23)-F(2)	76.98(10)
O(23)-V(23)-V(24)#2	104.94(12)
O(32)-V(23)-V(24)#2	135.29(11)
O(36)#2-V(23)-V(24)#2	38.55(10)
O(40)-V(23)-V(24)#2	113.27(9)

O(24)-V(23)-V(24)#2	38.24(9)
F(2)-V(23)-V(24)#2	76.18(7)
O(23)-V(23)-V(22)	139.35(12)
O(32)-V(23)-V(22)	35.79(10)
O(36)#2-V(23)-V(22)	88.35(10)
O(40)-V(23)-V(22)	87.78(9)
O(24)-V(23)-V(22)	121.64(9)
F(2)-V(23)-V(22)	44.80(7)
O(22)-V(22)-O(33)	102.49(16)
O(22)-V(22)-O(26)#2	103.70(17)
O(33)-V(22)-O(26)#2	95.50(14)
O(22)-V(22)-O(32)	99.80(16)
O(33)-V(22)-O(32)	156.95(14)
O(26)#2-V(22)-O(32)	84.79(14)
O(22)-V(22)-O(31)	99.67(17)
O(33)-V(22)-O(31)	84.22(14)
O(26)#2-V(22)-O(31)	156.09(13)
O(32)-V(22)-O(31)	86.35(14)
O(22)-V(22)-F(2)	172.68(14)
O(33)-V(22)-F(2)	81.62(12)
O(26)#2-V(22)-F(2)	81.74(12)
O(32)-V(22)-F(2)	75.60(11)
O(31)-V(22)-F(2)	74.55(12)
O(22)-V(22)-V(23)	130.31(13)
O(33)-V(22)-V(23)	126.97(10)
O(26)#2-V(22)-V(23)	78.49(9)

O(32)-V(22)-V(23)	30.51(9)
O(31)-V(22)-V(23)	82.62(9)
F(2)-V(22)-V(23)	45.36(7)
O(22)-V(22)-V(21)	130.07(15)
O(33)-V(22)-V(21)	78.84(10)
O(26)#2-V(22)-V(21)	126.05(10)
O(32)-V(22)-V(21)	82.39(10)
O(31)-V(22)-V(21)	30.40(9)
F(2)-V(22)-V(21)	44.31(7)
O(3)-V(3)-O(12)	103.29(17)
O(3)-V(3)-O(16)	103.79(15)
O(12)-V(3)-O(16)	99.46(15)
O(3)-V(3)-O(20)	101.46(15)
O(12)-V(3)-O(20)	95.37(14)
O(16)-V(3)-O(20)	146.75(14)
O(3)-V(3)-O(4)	99.97(15)
O(12)-V(3)-O(4)	156.66(14)
O(16)-V(3)-O(4)	76.60(13)
O(20)-V(3)-O(4)	78.03(13)
O(3)-V(3)-F(1)	174.75(15)
O(12)-V(3)-F(1)	78.61(13)
O(16)-V(3)-F(1)	80.57(11)
O(20)-V(3)-F(1)	73.41(11)
O(4)-V(3)-F(1)	78.04(11)
O(3)-V(3)-V(4)	105.06(12)
O(12)-V(3)-V(4)	133.93(11)
O(16)-V(3)-V(4)	38.60(10)
O(20)-V(3)-V(4)	113.40(10)
O(4)-V(3)-V(4)	38.00(8)
F(1)-V(3)-V(4)	76.45(7)
O(7)-V(5)-O(6)	105.32(17)
O(7)-V(5)-O(16)	106.36(15)
O(6)-V(5)-O(16)	96.02(14)

O(7)-V(5)-O(17)#1	106.79(15)
O(6)-V(5)-O(17)#1	95.72(14)
O(16)-V(5)-O(17)#1	140.31(14)
O(7)-V(5)-O(14)	101.95(15)
O(6)-V(5)-O(14)	152.71(15)
O(16)-V(5)-O(14)	75.01(13)
O(17)#1-V(5)-O(14)	77.30(13)
O(7)-V(5)-V(4)	117.79(12)
O(6)-V(5)-V(4)	122.92(11)
O(16)-V(5)-V(4)	38.79(10)
O(17)#1-V(5)-V(4)	104.95(10)
O(14)-V(5)-V(4)	38.42(8)
O(7)-V(5)-V(1)#1	110.93(13)
O(6)-V(5)-V(1)#1	129.06(12)
O(16)-V(5)-V(1)#1	106.40(10)
O(17)#1-V(5)-V(1)#1	40.37(10)
O(14)-V(5)-V(1)#1	37.08(8)
O(5)-V(4)-O(13)	104.96(17)
O(5)-V(4)-O(4)	105.50(15)
O(13)-V(4)-O(4)	94.77(14)
O(5)-V(4)-O(14)	104.77(15)
O(13)-V(4)-O(14)	96.11(14)
O(4)-V(4)-O(14)	143.83(13)
O(5)-V(4)-O(16)	104.59(16)
O(13)-V(4)-O(16)	150.45(14)
O(4)-V(4)-O(16)	77.47(13)
O(14)-V(4)-O(16)	76.14(13)
O(5)-V(4)-V(5)	118.81(13)
O(13)-V(4)-V(5)	123.45(11)
O(4)-V(4)-V(5)	105.25(10)
O(14)-V(4)-V(5)	41.47(10)

O(16)-V(4)-V(5)	36.90(9)
O(5)-V(4)-V(3)	109.26(13)
O(13)-V(4)-V(3)	129.49(11)
O(4)-V(4)-V(3)	40.96(10)
O(14)-V(4)-V(3)	109.40(10)
O(16)-V(4)-V(3)	36.52(9)
V(21)-F(2)-V(22)	91.03(9)
V(21)-F(2)-V(23)	98.63(10)
V(22)-F(2)-V(23)	89.84(9)
V(1)-F(1)-V(2)	90.93(10)
V(1)-F(1)-V(3)	97.71(10)
V(2)-F(1)-V(3)	89.73(10)
V(23)#2-O(36)-V(25)	129.48(17)
V(23)#2-O(36)-V(24)	105.66(15)
V(25)-O(36)-V(24)	103.71(14)
V(1)#1-O(14)-V(4)	126.37(17)
V(1)#1-O(14)-V(5)	102.38(14)
V(4)-O(14)-V(5)	100.12(13)
V(6)-O(4)-V(4)	140.87(19)
V(6)-O(4)-V(3)	112.68(15)
V(4)-O(4)-V(3)	101.04(14)
V(21)-O(34)-V(24)	126.80(19)
V(21)-O(34)-V(25)	103.74(14)
V(24)-O(34)-V(25)	101.39(14)
V(6)-O(17)-V(5)#1	137.88(18)
V(6)-O(17)-V(1)	113.46(16)
V(5)#1-O(17)-V(1)	102.53(14)
C(45)-O(43)-V(26)	121.5(3)
V(26)-O(37)-V(25)	139.49(18)
V(26)-O(37)-V(21)	111.92(15)
V(25)-O(37)-V(21)	100.99(13)
V(25)-O(26)-	139.83(19)

V(22)#2	
V(3)-O(16)-V(5)	129.52(17)
V(3)-O(16)-V(4)	104.88(15)
V(5)-O(16)-V(4)	104.32(15)
C(52)-O(41)-V(6)	123.8(3)
V(24)-O(33)-V(22)	137.60(18)
V(3)-O(12)-V(2)	116.07(18)
V(1)-O(20)-V(3)	110.13(14)
V(1)-O(20)-V(6)	95.40(13)
V(3)-O(20)-V(6)	94.38(12)
V(26)-O(24)-V(24)#2	143.23(18)
V(26)-O(24)-V(23)	112.48(15)
V(24)#2-O(24)-V(23)	100.30(14)
V(23)-O(40)-V(21)	110.46(14)
V(23)-O(40)-V(26)	94.60(12)
V(21)-O(40)-V(26)	94.72(12)
V(4)-O(13)-V(2)#1	137.90(19)
V(5)-O(6)-V(2)	140.0(2)
V(1)-O(11)-V(2)	113.83(17)
V(23)-O(32)-V(22)	113.69(17)
V(6)-O(4)-V(4)	140.87(19)
V(6)-O(4)-V(3)	112.68(15)
V(4)-O(4)-V(3)	101.04(14)
V(21)-O(34)-V(24)	126.80(19)
V(21)-O(34)-V(25)	103.74(14)
V(24)-O(34)-V(25)	101.39(14)
V(6)-O(17)-V(5)#1	137.88(18)
V(6)-O(17)-V(1)	113.46(16)
V(5)#1-O(17)-V(1)	102.53(14)
C(45)-O(43)-V(26)	121.5(3)
V(26)-O(37)-V(25)	139.49(18)
V(26)-O(37)-V(21)	111.92(15)

V(25)-O(37)-V(21)	100.99(13)
V(25)-O(26)-V(22)#2	139.83(19)
V(3)-O(16)-V(5)	129.52(17)
V(3)-O(16)-V(4)	104.88(15)
V(5)-O(16)-V(4)	104.32(15)
C(52)-O(41)-V(6)	123.8(3)
V(24)-O(33)-V(22)	137.60(18)
V(3)-O(12)-V(2)	116.07(18)
V(1)-O(20)-V(3)	110.13(14)
V(1)-O(20)-V(6)	95.40(13)
V(3)-O(20)-V(6)	94.38(12)
V(26)-O(24)-V(24)#2	143.23(18)
V(26)-O(24)-V(23)	112.48(15)
V(24)#2-O(24)-V(23)	100.30(14)
V(23)-O(40)-V(21)	110.46(14)
V(23)-O(40)-V(26)	94.60(12)
V(21)-O(40)-V(26)	94.72(12)
V(4)-O(13)-V(2)#1	137.90(19)
V(5)-O(6)-V(2)	140.0(2)

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