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Accessory Publication:

Two New Three-Dimensional Networks Constructed on Polyoxovanadates

Fig.S1. The different $\{V_4O_{12}\}$ building units in compounds **1** and **2**.

Fig.S2. The Space-filling diagram of the 2D network of $[Cu(biim)V_4O_{12}]$ (a) and $[Cu(biim)_2]$ (b) in compound **1**.

Fig.S3. Polyhedral representation of the 2D network of compound **2**. For the sake of clarity, all the hydrogen atoms are omitted.

Fig. S4. Space-filling diagram of the 3D open framework of **2**, showing the 1D channels. Hydrogen and solvated water molecules are omitted for clarity.

Fig. S5. The cyclic voltammograms of compound **2** in 1 M H_2SO_4 at different scan rates (from inner to outer: 20, 30, 40, 50 ,60 ,70 ,80, 90, 110,120 and 130 mV s^{-1}).

Fig S6. IR spectrum of compound **1**.

Fig. S7. IR spectrum of compound **2**.

Fig. S8. TG curve of compound **1**.

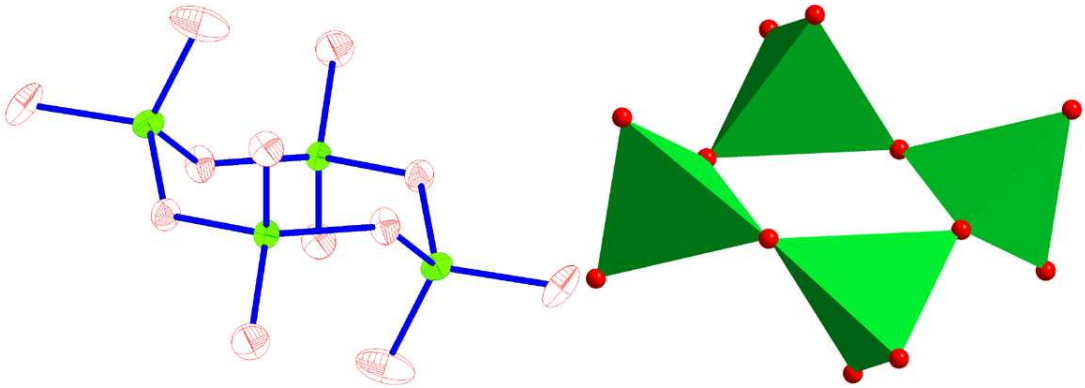
Fig. S9. TG curve of compound **2**.

Fig. S10. TG curve of compound **2'**.

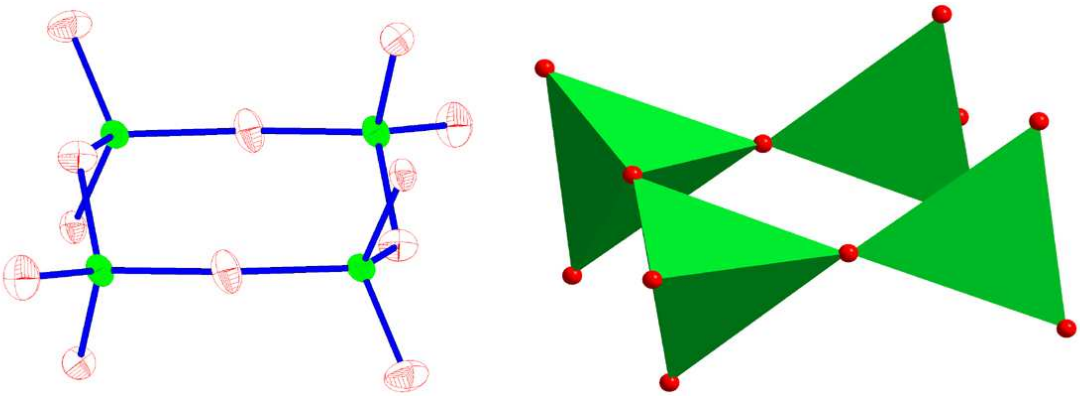
Fig. S11. XRPD patterns of the (a) Simulated of **1** and (b) evacuated of **2**.

Table S1 to S5 crystallographic tables of compound **1**

Table S6 to S10 crystallographic tables of compound **2**

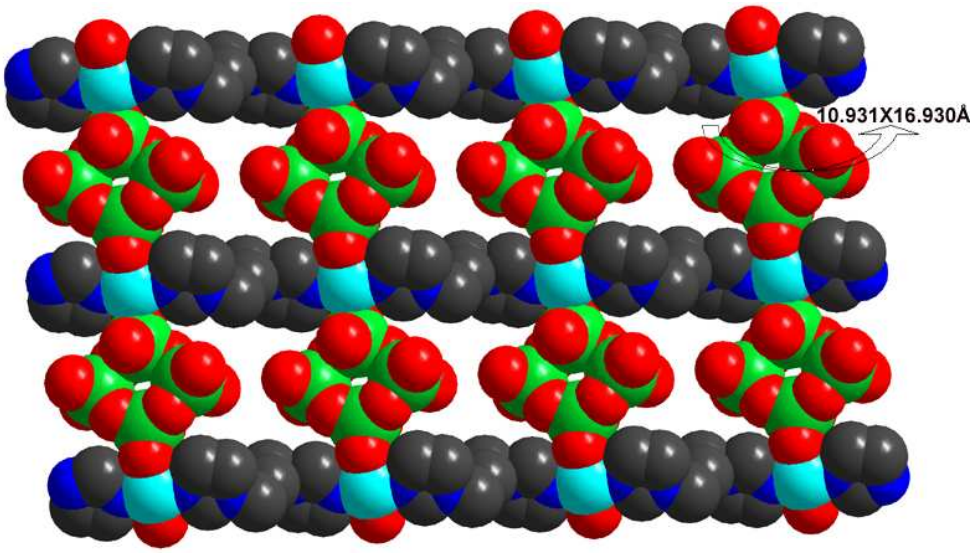


(a)

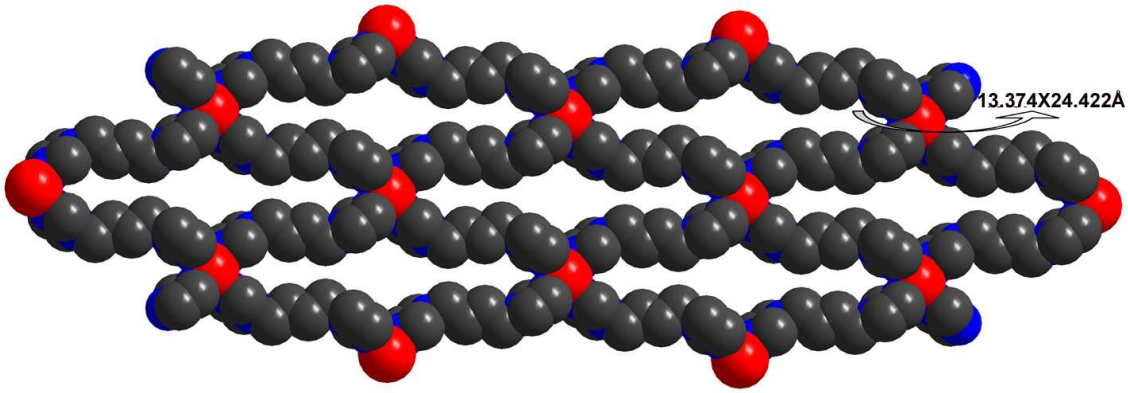


(b)

Fig.S1.



(a)



(b)

Fig. S2.

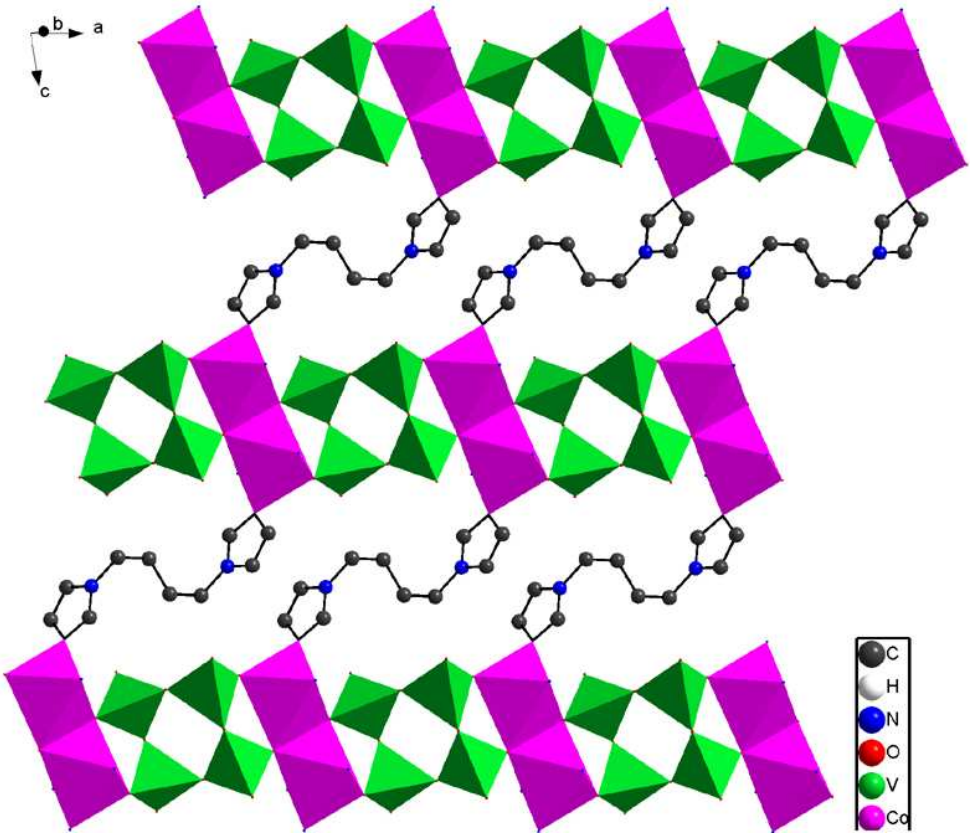


Fig. S3

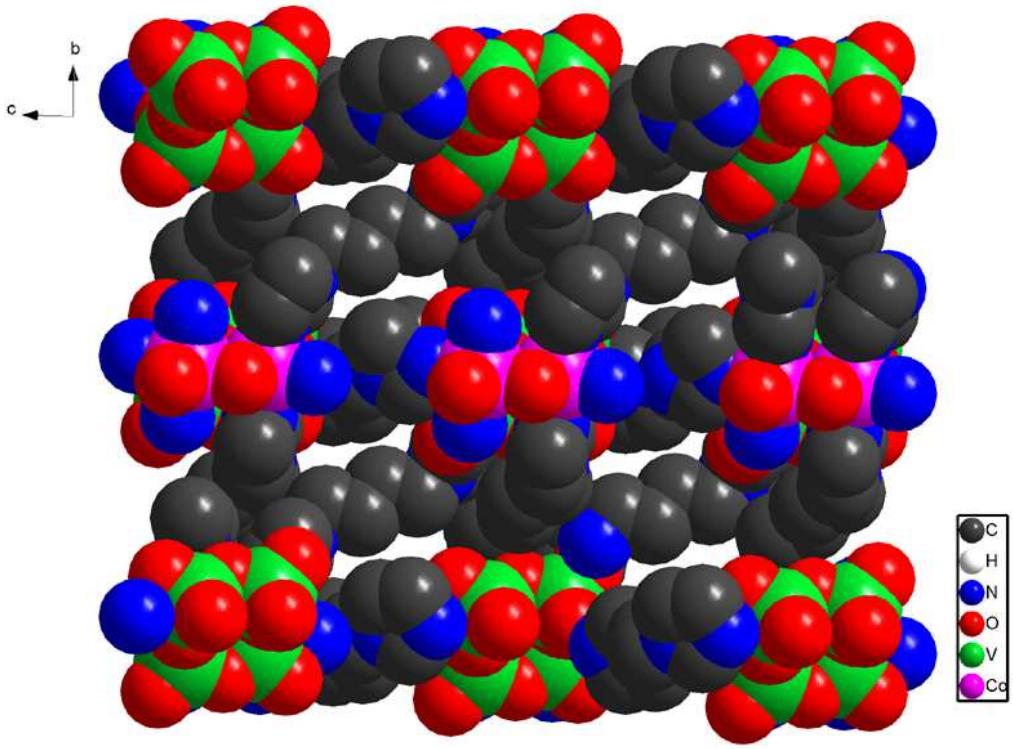


Fig. S4

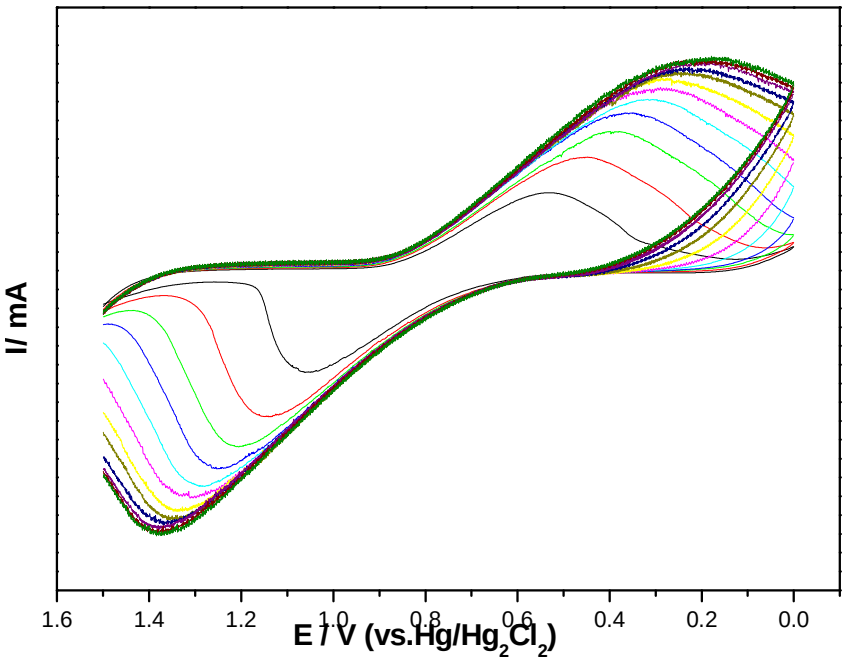
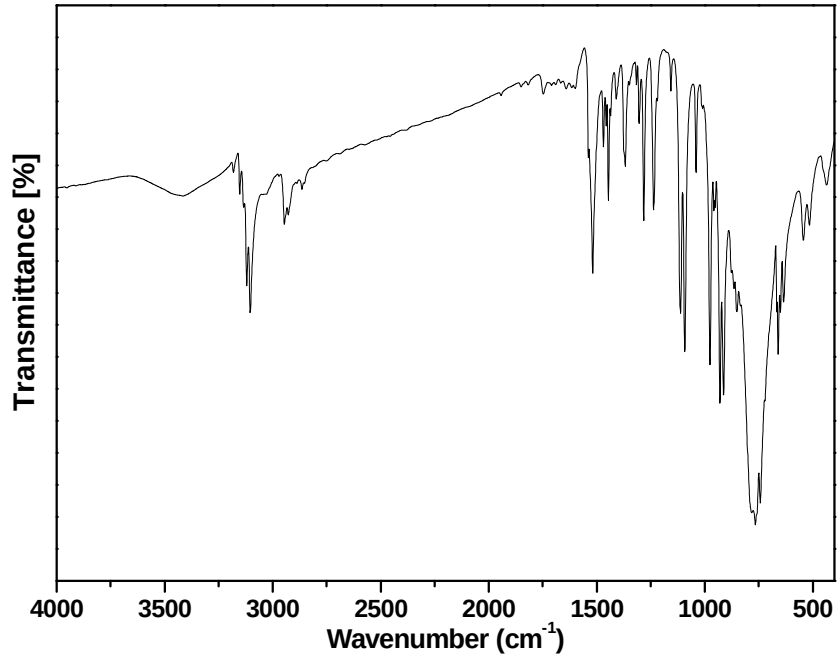


Fig.S5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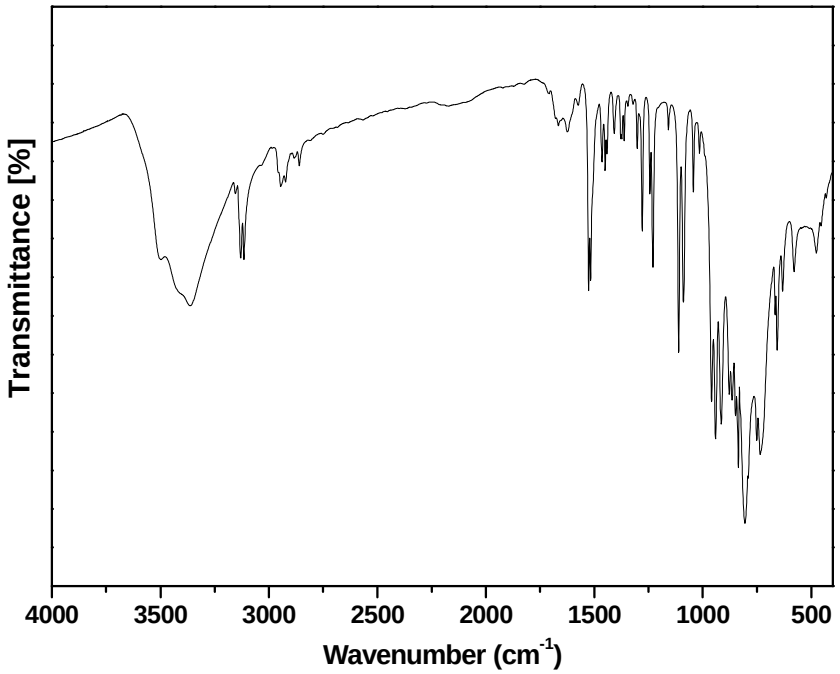
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

Fig S6.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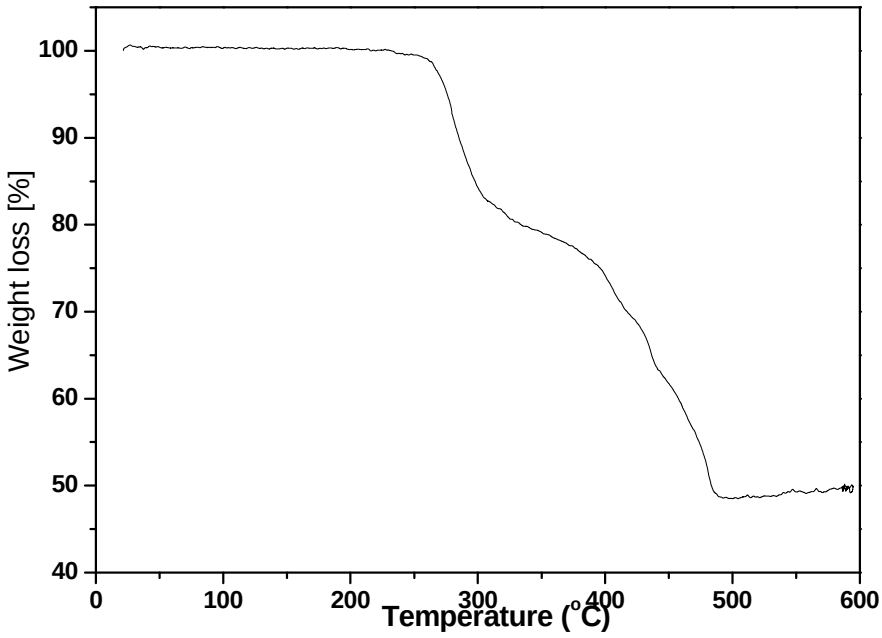
Wavenumber (cm-1)

Fig. S7.


Weight loss [%]
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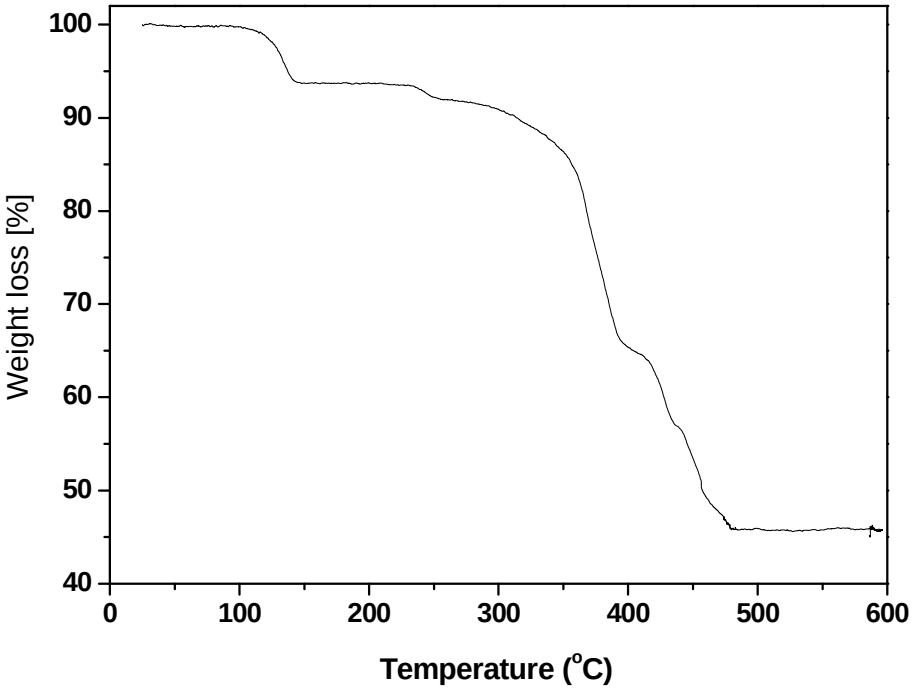
80
70
60
50
40
0
100
200
300
400
500
600
Temperature (°C)

Fig. S8


Weight loss [%]
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40
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300
400
500
600
Temperature (°C)

Fig. S9

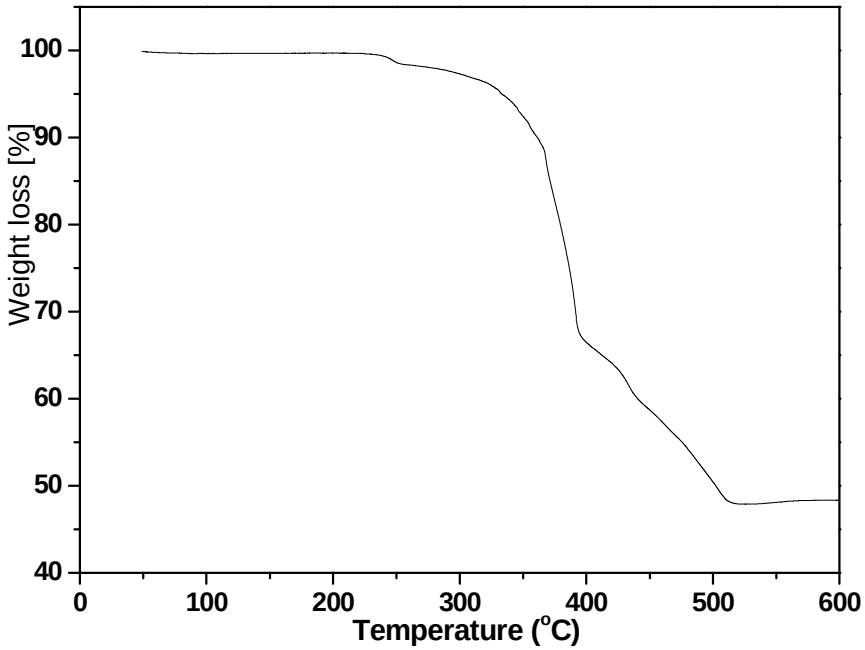

Fig. S10.

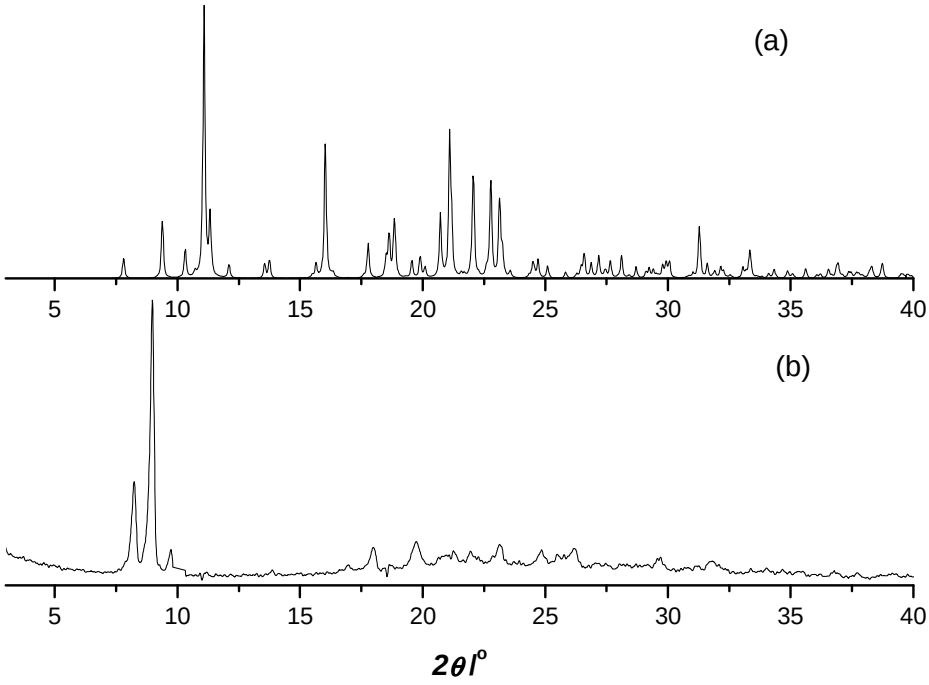

Fig. S11.

Table S1 Crystal data and structure refinement for Complex **1.**

Empirical formula	$C_{15}H_{21}CuN_6O_6V_2$
Formula weight	546.80
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, *P-1*
Unit cell dimensions	a = 9.5040(19)Å alpha = 72.13(3)^o
	b = 10.650(2) Å beta = 76.02(3) ^{o}
	c = 11.993(2) Å gamma = 65.40(3) ^{o}
Volume	1041.4(4) Å^3
Z, Calculated density	2, 1.744 Mg/m^3
Absorption coefficient	1.936 mm^{-1}
F(000)	552
Crystal size	0.31 x 0.26 x 0.21 mm
θ range for data collection	3.12 to 27.40 deg.
Limiting indices	-12<=h<=12, -13<=k<=13, -15<=l<=15
Reflections collected / unique	10059 / 4681 [R(int) = 0.0621]
Completeness to θ = 27.40	98.8 %
Absorption correction	Multi scan
Max. and min. transmission	0.666 and 0.554
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4681 / 0 / 274
Goodness-of-fit on F^2	1.092
Final R indices [I>2sigma(I)]	R1 = 0.0492, wR2 = 0.1267
R indices (all data)	R1 = 0.0664, wR2 = 0.1583
Largest diff. peak and hole	0.830 and -1.104 e.Å^{-3}

Table S2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for Complex **1**. U (eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
V(1)	10823(1)	10960(1)	2837(1)	21(1)
V(2)	7885(1)	11873(1)	5031(1)	25(1)
Cu(1)	5000	15000	5000	28(1)
Cu(2)	10000	10000	0	29(1)
O(1)	8780(6)	12564(5)	5467(3)	64(1)
O(2)	6024(4)	13050(3)	4858(3)	41(1)
O(3)	8843(4)	11465(3)	3625(3)	32(1)
O(4)	11353(4)	12313(4)	2241(3)	43(1)
O(5)	12182(4)	9684(3)	3865(3)	30(1)
O(6)	10854(4)	10276(4)	1763(3)	34(1)
C(1)	6153(6)	14838(5)	2510(4)	41(1)
C(2)	5332(7)	17014(5)	2654(4)	41(1)
C(3)	5818(7)	16988(6)	1488(4)	45(1)
C(4)	6849(7)	15127(7)	296(4)	53(2)
C(5)	5503(8)	15425(6)	–333(5)	55(2)
C(6)	7296(5)	10818(5)	1883(4)	27(1)
C(7)	6559(5)	10427(6)	512(4)	36(1)
C(8)	5318(5)	10671(5)	1394(4)	35(1)
C(9)	4926(5)	11168(5)	3413(3)	28(1)
C(10)	5488(5)	9872(5)	4411(3)	29(1)
C(11)	9867(6)	5954(5)	1525(4)	37(1)
C(12)	10903(6)	7301(5)	1824(4)	33(1)
C(13)	9628(6)	7131(5)	649(4)	32(1)
C(14)	11092(7)	5082(5)	3413(4)	42(1)
C(15)	9733(7)	5418(5)	4397(4)	41(1)
N(1)	5536(5)	15638(4)	3294(3)	37(1)
N(2)	6309(5)	15620(4)	1403(3)	37(1)
N(3)	7789(4)	10526(4)	828(3)	25(1)
N(4)	5812(4)	10933(4)	2256(3)	26(1)
N(5)	10289(4)	7980(4)	827(3)	32(1)
N(6)	10688(5)	6057(4)	2268(3)	34(1)

Table S3 Bond lengths [Å] and angles [º] for Complex **1**

V(1)–O(4)	1.624(3)	V(2)–O(1)	1.585(4)
V(1)–O(6)	1.653(3)	V(2)–O(2)	1.707(4)
V(1)–O(5)	1.820(3)	V(2)–O(5)#1	1.791(3)
V(1)–O(3)	1.826(3)	V(2)–O(3)	1.800(3)
Cu(1)–O(2)	1.935(3)	Cu(2)–N(5)#3	2.004(4)
Cu(1)–O(2)#2	1.935(3)	Cu(2)–N(5)	2.004(4)
Cu(1)–N(1)	1.960(4)	Cu(2)–N(3)	2.017(3)
Cu(1)–N(1)#2	1.960(4)	Cu(2)–N(3)#3	2.017(3)
C(1)–N(1)	1.327(6)	C(6)–N(3)	1.324(5)
C(1)–N(2)	1.344(6)	C(6)–N(4)	1.338(5)
C(1)–H(1A)	0.9300	C(6)–H(6A)	0.9300
C(2)–C(3)	1.367(7)	C(7)–N(3)	1.364(6)
C(2)–N(1)	1.386(6)	C(7)–C(8)	1.373(6)
C(2)–H(2A)	0.9300	C(7)–H(7A)	0.9300
C(3)–N(2)	1.362(7)	C(8)–N(4)	1.374(5)
C(3)–H(3A)	0.9300	C(8)–H(8A)	0.9300
C(4)–N(2)	1.475(6)	C(9)–N(4)	1.473(5)
C(4)–C(5)	1.513(9)	C(9)–C(10)	1.518(6)
C(4)–H(4A)	0.9700	C(9)–H(9A)	0.9700
C(4)–H(4B)	0.9700	C(9)–H(9B)	0.9700
C(5)–C(5)#4	1.510(11)	C(10)–C(10)#5	1.524(8)
C(5)–H(5A)	0.9700	C(10)–H(10A)	0.9700
C(5)–H(5B)	0.9700	C(10)–H(10B)	0.9700
C(11)–C(13)	1.340(6)	C(12)–N(5)	1.322(6)
C(11)–N(6)	1.372(6)	C(12)–N(6)	1.349(6)
C(11)–H(11A)	0.9300	C(12)–H(12A)	0.9300
C(13)–N(5)	1.385(6)	C(14)–N(6)	1.470(5)
C(13)–H(13A)	0.9300	C(14)–C(15)	1.525(8)
C(15)–C(15)#6	1.527(8)	C(14)–H(14A)	0.9700
C(15)–H(15A)	0.9700	C(14)–H(14B)	0.9700
C(15)–H(15B)	0.9700	O(6)–V(1)–O(5)	111.44(16)
O(4)–V(1)–O(6)	107.88(18)	O(4)–V(1)–O(3)	112.25(18)
O(4)–V(1)–O(5)	108.31(16)	O(2)–V(2)–O(5)#1	109.13(16)
O(6)–V(1)–O(3)	107.71(16)	O(1)–V(2)–O(3)	110.2(2)
O(5)–V(1)–O(3)	109.28(14)	O(2)–V(2)–O(3)	108.16(15)
O(1)–V(2)–O(2)	109.4(2)	O(5)#1–V(2)–O(3)	111.66(15)
O(1)–V(2)–O(5)#1	108.27(18)	O(2)–Cu(1)–O(2)#2	180.000(1)
O(2)–Cu(1)–N(1)	89.49(15)	N(5)#3–Cu(2)–N(5)	180.000(1)
O(2)#2–Cu(1)–N(1)	90.51(15)	N(5)#3–Cu(2)–N(3)	93.19(15)
O(2)–Cu(1)–N(1)#2	90.51(15)	N(5)–Cu(2)–N(3)	86.81(15)
O(2)#2–Cu(1)–N(1)#2	89.49(15)	N(5)#3–Cu(2)–N(3)#3	86.81(15)
N(1)–Cu(1)–N(1)#2	180.000(1)	N(5)–Cu(2)–N(3)#3	93.19(15)
V(2)–O(3)–V(1)	137.60(18)	N(3)–Cu(2)–N(3)#3	180.0(2)

V(2)#1–O(5)–V(1)	131.61(18)	V(2)–O(2)–Cu(1)	130.9(2)
N(1)–C(1)–N(2)	111.7(4)	H(4A)–C(4)–H(4B)	107.9
N(1)–C(1)–H(1A)	124.1	C(5)#4–C(5)–C(4)	113.3(6)
N(2)–C(1)–H(1A)	124.1	C(5)#4–C(5)–H(5A)	108.9
C(3)–C(2)–N(1)	108.0(4)	C(4)–C(5)–H(5A)	108.9
C(3)–C(2)–H(2A)	126.0	C(5)#4–C(5)–H(5B)	108.9
N(1)–C(2)–H(2A)	126.0	C(4)–C(5)–H(5B)	108.9
N(2)–C(3)–C(2)	107.8(4)	H(5A)–C(5)–H(5B)	107.7
N(2)–C(3)–H(3A)	126.1	N(3)–C(6)–N(4)	112.1(4)
C(2)–C(3)–H(3A)	126.1	N(3)–C(6)–H(6A)	123.9
N(2)–C(4)–C(5)	112.0(5)	N(4)–C(6)–H(6A)	123.9
N(2)–C(4)–H(4A)	109.2	N(3)–C(7)–C(8)	109.4(4)
C(5)–C(4)–H(4A)	109.2	N(3)–C(7)–H(7A)	125.3
N(2)–C(4)–H(4B)	109.2	C(8)–C(7)–H(7A)	125.3
C(5)–C(4)–H(4B)	109.2	C(7)–C(8)–N(4)	106.1(4)
C(7)–C(8)–H(8A)	126.9	C(10)–C(9)–H(9B)	109.2
N(4)–C(8)–H(8A)	126.9	H(9A)–C(9)–H(9B)	107.9
N(4)–C(9)–C(10)	112.2(4)	C(9)–C(10)–C(10)#5	111.0(5)
N(4)–C(9)–H(9A)	109.2	C(9)–C(10)–H(10A)	109.4
C(10)–C(9)–H(9A)	109.2	C(10)#5–C(10)–H(10A)	109.4
N(4)–C(9)–H(9B)	109.2	C(9)–C(10)–H(10B)	109.4
N(6)–C(11)–H(11A)	126.8	C(10)#5–C(10)–H(10B)	109.4
N(5)–C(12)–N(6)	110.6(4)	H(10A)–C(10)–H(10B)	108.0
N(5)–C(12)–H(12A)	124.7	C(13)–C(11)–N(6)	106.4(4)
N(6)–C(12)–H(12A)	124.7	C(13)–C(11)–H(11A)	126.8
C(11)–C(13)–N(5)	109.8(4)	N(6)–C(14)–H(14B)	109.3
C(11)–C(13)–H(13A)	125.1	C(15)–C(14)–H(14B)	109.3
N(5)–C(13)–H(13A)	125.1	H(14A)–C(14)–H(14B)	108.0
N(6)–C(14)–C(15)	111.6(4)	C(14)–C(15)–C(15)#6	110.5(6)
N(6)–C(14)–H(14A)	109.3	C(14)–C(15)–H(15A)	109.5
C(15)–C(14)–H(14A)	109.3	C(15)#6–C(15)–H(15A)	109.5
H(15A)–C(15)–H(15B)	108.1	C(14)–C(15)–H(15B)	109.5
C(1)–N(1)–C(2)	105.8(4)	C(15)#6–C(15)–H(15B)	109.5
C(1)–N(1)–Cu(1)	126.9(3)	C(6)–N(3)–C(7)	105.6(4)
C(2)–N(1)–Cu(1)	127.3(3)	C(6)–N(3)–Cu(2)	126.6(3)
C(1)–N(2)–C(3)	106.6(4)	C(7)–N(3)–Cu(2)	127.0(3)
C(1)–N(2)–C(4)	127.6(4)	C(6)–N(4)–C(8)	106.7(3)
C(3)–N(2)–C(4)	125.8(4)	C(6)–N(4)–C(9)	126.5(4)
C(12)–N(6)–C(11)	107.6(4)	C(8)–N(4)–C(9)	126.6(4)
C(12)–N(6)–C(14)	125.7(4)	C(12)–N(5)–C(13)	105.7(4)
C(11)–N(6)–C(14)	126.3(4)	C(12)–N(5)–Cu(2)	124.7(3)
C(13)–N(5)–Cu(2)	128.3(3)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+2,-z+1 #2 -x+1,-y+3,-z+1

	#3 -x+2,-y+2,-z	#4 -x+1,-y+3,-z	#5 -x+1,-y+2,-z+1
	#6 -x+2,-y+1,-z+1		

Table S4 Anisotropic displacement parameters ($Å^2 \times 10^3$) for Complex **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \ldots + 2 h k a^* b^* U_{12}]$

U11	U22	U33	U23	U13	U12
V(1)	21(1)	23(1)	17(1)	–3(1)	–1(1)	–7(1)
V(2)	33(1)	24(1)	18(1)	–7(1)	–2(1)	–9(1)
Cu(1)	30(1)	23(1)	17(1)	–4(1)	–1(1)	1(1)
Cu(2)	22(1)	24(1)	23(1)	4(1)	7(1)	–5(1)
O(1)	106(4)	80(3)	40(2)	–14(2)	–10(2)	–66(3)
O(2)	47(2)	26(2)	26(2)	–4(1)	3(1)	4(2)
O(3)	27(2)	45(2)	24(1)	–16(1)	1(1)	–10(2)
O(4)	47(2)	35(2)	42(2)	3(2)	–9(2)	–18(2)
O(5)	28(2)	27(2)	32(2)	–2(1)	–8(1)	–8(1)
O(6)	36(2)	44(2)	24(2)	–13(1)	2(1)	–16(2)
C(1)	53(3)	32(2)	24(2)	–9(2)	–1(2)	–2(2)
C(2)	58(3)	25(2)	30(2)	–8(2)	3(2)	–8(2)
C(3)	59(3)	42(3)	22(2)	0(2)	0(2)	–14(3)
C(4)	62(4)	65(4)	27(2)	–22(2)	10(2)	–20(3)
C(5)	82(5)	49(3)	27(2)	–8(2)	1(3)	–23(3)
C(6)	25(2)	41(2)	20(2)	–13(2)	1(2)	–15(2)
C(7)	28(2)	55(3)	25(2)	–17(2)	1(2)	–13(2)
C(8)	29(2)	58(3)	26(2)	–17(2)	–1(2)	–21(2)
C(9)	30(2)	43(2)	15(2)	–14(2)	5(2)	–17(2)
C(10)	31(2)	39(2)	21(2)	–8(2)	4(2)	–19(2)
C(11)	45(3)	34(2)	29(2)	–2(2)	–2(2)	–17(2)
C(12)	41(3)	31(2)	29(2)	–1(2)	–9(2)	–17(2)
C(13)	39(3)	34(2)	28(2)	–6(2)	–7(2)	–17(2)
C(14)	68(4)	28(2)	27(2)	4(2)	–14(2)	–18(3)
C(15)	62(3)	42(3)	29(2)	11(2)	–14(2)	–39(3)
N(1)	43(2)	32(2)	23(2)	–5(2)	–4(2)	–4(2)
N(2)	45(2)	37(2)	24(2)	–12(2)	–2(2)	–8(2)
N(3)	23(2)	30(2)	17(2)	–5(1)	3(1)	–9(2)
N(4)	26(2)	40(2)	11(1)	–4(1)	4(1)	–14(2)
N(5)	29(2)	31(2)	20(2)	4(2)	1(1)	–7(2)
N(6)	45(2)	29(2)	21(2)	1(2)	–3(2)	–13(2)

Table S5 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for Complex **1.**

	x	y	z	U(eq)
H(1A)	6441	13856	2704	49
H(2A)	4935	17815	2963	50
H(3A)	5814	17767	864	54
H(4A)	7450	14113	473	63
H(4B)	7529	15598	–222	63
H(5A)	4859	16428	–453	66
H(5B)	5914	15212	–1105	66
H(6A)	7910	10931	2314	33
H(7A)	6560	10226	–190	43
H(8A)	4341	10662	1404	42
H(9A)	3829	11406	3392	33
H(9B)	5028	11968	3566	33
H(10A)	6573	9655	4457	35
H(10B)	5421	9063	4249	35
H(11A)	9540	5214	1612	45
H(12A)	11412	7635	2172	40
H(13A)	9097	7344	16	39
H(14A)	11986	5154	3606	50
H(14B)	11381	4114	3357	50
H(15A)	8907	5178	4284	49
H(15B)	9320	6428	4364	49

Table S6 Crystal data and structure refinement for Complex **2**

Empirical formula	$C_{15}H_{25}CoN_6O_8V_2$
Formula weight	578.22
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.0373(18) Å alpha = 87.80(3)°.
	b = 10.577(2) Å beta = 81.71(3)°
	c = 11.947(2) Å gamma = 85.29(3)°
Volume	1125.8(4) $Å^3$
Z, Calculated density	2, 1.706 Mg/m^3
Absorption coefficient	1.594 mm^{-1}
F(000)	588
Crystal size	0.20 x 0.19 x 0.18 mm
Theta range for data collection	3.05 to 25.00°
Limiting indices	-10<=h<=10, -12<=k<=12, -14<=l<=14
Reflections collected / unique	8168 / 3641 [R(int) = 0.1071]
Completeness to theta = 25.00	91.8 %
Absorption correction	Empirical
Max. and min. transmission	0.7623 and 0.7410
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3641 / 0 / 285
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0774, wR2 = 0.1502
R indices (all data)	R1 = 0.1295, wR2 = 0.1799
Extinction coefficient	0.0071(17)
Largest diff. peak and hole	1.283 and -0.642 e. $Å^{-3}$

Table S7 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for Complex **2**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
V(1)	872(2)	1318(1)	8539(1)	24(1)
V(2)	1748(2)	976(1)	11004(1)	23(1)
Co(1)	4599(1)	33(1)	8654(1)	22(1)
O(6)	3523(6)	418(5)	10523(5)	26(1)
O(5)	2498(6)	543(5)	8145(5)	29(1)
O(4)	949(6)	1860(6)	9921(5)	33(2)
O(3)	1686(7)	1895(6)	12049(5)	41(2)
O(2)	–611(6)	306(6)	8588(5)	41(2)
O(1)	641(8)	2522(6)	7687(5)	44(2)
OW1	1286(10)	4229(8)	5961(7)	80(3)
OW2	1206(15)	3908(12)	3661(11)	141(5)
C(2)	6527(10)	2408(8)	8382(7)	30(2)
C(6)	2666(10)	–2216(8)	8745(7)	29(2)
C(7)	4882(10)	–2951(8)	9017(7)	29(2)
C(1)	4454(10)	2772(8)	7720(7)	31(2)
C(3)	6670(11)	3471(9)	7748(7)	36(2)
C(9)	1315(9)	–4181(8)	8850(8)	32(2)
C(8)	4035(10)	–3943(8)	9045(7)	32(2)
C(12)	6473(11)	–1200(10)	5307(8)	46(3)
C(11)	5602(10)	–1323(9)	6322(8)	38(2)
C(10)	754(10)	–4736(9)	10007(8)	36(2)
C(13)	6521(11)	439(9)	6317(7)	37(2)
C(5)	5251(13)	4444(9)	5372(8)	45(3)
C(4)	4941(12)	4750(9)	6571(8)	45(3)
C(14)	8134(11)	509(11)	4421(8)	48(3)
C(15)	9702(11)	–72(12)	4443(8)	57(3)
N(3)	4004(7)	–1843(7)	8830(6)	27(2)
N(1)	5139(7)	1958(7)	8354(5)	26(2)
N(6)	7055(9)	–56(8)	5319(6)	39(2)
N(5)	5642(7)	–316(7)	6970(6)	29(2)
N(4)	2628(8)	–3483(6)	8865(6)	28(2)
N(2)	5333(8)	3716(7)	7329(6)	31(2)

Table S8 Bond lengths [Å] and angles [º] for Complex **2.**

V(1)–O(1)	1.619(6)	Co(1)–N(3)	2.093(7)
V(1)–O(5)	1.639(6)	Co(1)–O(6)#2	2.094(5)
V(1)–O(2)	1.775(6)	Co(1)–O(5)	2.099(5)
V(1)–O(4)	1.782(6)	Co(1)–N(5)	2.128(7)
V(2)–O(3)	1.604(6)	Co(1)–N(1)	2.138(7)
V(2)–O(6)	1.690(6)	Co(1)–O(6)	2.340(6)
V(2)–O(4)	1.771(6)	O(6)–Co(1)#2	2.094(5)
V(2)–O(2)#1	1.779(6)	O(2)–V(2)#1	1.779(6)
C(2)–C(3)	1.336(12)	C(8)–N(4)	1.368(11)
C(2)–N(1)	1.383(10)	C(8)–H(8A)	0.9300
C(2)–H(2A)	0.9300	C(12)–C(11)	1.356(13)
C(6)–N(3)	1.321(10)	C(12)–N(6)	1.360(12)
C(6)–N(4)	1.345(10)	C(12)–H(12A)	0.9300
C(6)–H(6A)	0.9300	C(11)–N(5)	1.347(11)
C(7)–C(8)	1.345(11)	C(11)–H(11A)	0.9300
C(7)–N(3)	1.389(11)	C(10)–C(10)#3	1.518(16)
C(7)–H(7A)	0.9300	C(10)–H(10B)	0.9700
C(1)–N(1)	1.303(11)	C(10)–H(10A)	0.9700
C(1)–N(2)	1.354(10)	C(13)–N(5)	1.325(11)
C(1)–H(1A)	0.9300	C(13)–N(6)	1.330(11)
C(3)–N(2)	1.376(11)	C(13)–H(13A)	0.9300
C(3)–H(3A)	0.9300	C(5)–C(4)	1.463(12)
C(9)–N(4)	1.450(10)	C(5)–C(5)#4	1.525(18)
C(9)–C(10)	1.516(12)	C(4)–N(2)	1.447(11)
C(9)–H(9A)	0.9700	C(4)–H(4A)	0.9700
C(9)–H(9B)	0.9700	C(4)–H(4B)	0.9700
C(5)–H(5B)	0.9700	C(14)–N(6)	1.485(11)
C(5)–H(5A)	0.9700	C(14)–C(15)	1.501(14)
C(15)–C(15)#5	1.525(18)	C(14)–H(14A)	0.9700
C(15)–H(15B)	0.9700	C(14)–H(14B)	0.9700
C(15)–H(15A)	0.9700		
O(1)–V(1)–O(5)	109.8(3)	O(3)–V(2)–O(6)	111.8(3)
O(1)–V(1)–O(2)	111.0(3)	O(3)–V(2)–O(4)	107.4(3)
O(5)–V(1)–O(2)	110.9(3)	O(6)–V(2)–O(4)	110.3(3)
O(1)–V(1)–O(4)	109.6(3)	O(3)–V(2)–O(2)#1	109.7(3)
O(5)–V(1)–O(4)	105.8(3)	O(6)–V(2)–O(2)#1	110.3(3)
O(2)–V(1)–O(4)	109.6(3)	O(4)–V(2)–O(2)#1	107.1(3)
N(3)–Co(1)–O(6)#2	91.5(2)	V(2)–O(6)–Co(1)#2	132.0(3)
N(3)–Co(1)–O(5)	88.1(2)	V(2)–O(6)–Co(1)	128.2(3)
O(6)#2–Co(1)–O(5)	169.0(2)	Co(1)#2–O(6)–Co(1)	99.7(2)
N(3)–Co(1)–N(5)	90.0(3)	V(1)–O(5)–Co(1)	142.9(3)
O(6)#2–Co(1)–N(5)	98.1(2)	V(2)–O(4)–V(1)	125.5(3)
O(5)–Co(1)–N(5)	93.0(2)	V(1)–O(2)–V(2)#1	160.1(4)

N(3)–Co(1)–N(1)	175.6(3)	C(3)–C(2)–N(1)	110.4(8)
O(6)#2–Co(1)–N(1)	92.1(2)	C(3)–C(2)–H(2A)	124.8
O(5)–Co(1)–N(1)	88.8(2)	N(1)–C(2)–H(2A)	124.8
N(5)–Co(1)–N(1)	87.1(3)	N(3)–C(6)–N(4)	112.1(8)
N(3)–Co(1)–O(6)	90.5(2)	N(3)–C(6)–H(6A)	123.9
O(6)#2–Co(1)–O(6)	80.3(2)	N(4)–C(6)–H(6A)	123.9
O(5)–Co(1)–O(6)	88.7(2)	C(8)–C(7)–N(3)	108.8(8)
N(5)–Co(1)–O(6)	178.3(2)	C(8)–C(7)–H(7A)	125.6
N(1)–Co(1)–O(6)	92.5(2)	N(3)–C(7)–H(7A)	125.6
N(1)–C(1)–N(2)	111.2(8)	C(11)–C(12)–H(12A)	105.5(8)
N(1)–C(1)–H(1A)	124.4	N(6)–C(12)–H(12A)	127.3
N(2)–C(1)–H(1A)	124.4	N(5)–C(11)–C(12)	127.3
C(2)–C(3)–N(2)	105.8(8)	N(5)–C(11)–H(11A)	111.4(9)
C(2)–C(3)–H(3A)	127.1	C(12)–C(11)–H(11A)	124.3
N(2)–C(3)–H(3A)	127.1	C(9)–C(10)–C(10)#3	124.3
N(4)–C(9)–C(10)	112.0(7)	C(9)–C(10)–H(10B)	109.9(9)
N(4)–C(9)–H(9A)	109.2	C(10)#3–C(10)–H(10B)	109.7
C(10)–C(9)–H(9A)	109.2	C(9)–C(10)–H(10A)	109.7
N(4)–C(9)–H(9B)	109.2	C(10)#3–C(10)–H(10A)	109.7
C(10)–C(9)–H(9B)	109.2	H(10B)–C(10)–H(10A)	108.2
H(9A)–C(9)–H(9B)	107.9	N(5)–C(13)–N(6)	112.7(8)
C(7)–C(8)–N(4)	107.8(8)	N(5)–C(13)–H(13A)	126.1
C(7)–C(8)–H(8A)	126.1	N(6)–C(14)–H(14B)	109.3
N(4)–C(8)–H(8A)	109.7	C(15)–C(14)–H(14B)	109.3
C(11)–C(12)–N(6)	123.6	N(2)–C(4)–C(5)	114.2(8)
N(6)–C(13)–H(13A)	123.6	N(2)–C(4)–H(4A)	108.7
C(4)–C(5)–C(5)#4	111.3(10)	C(5)–C(4)–H(4A)	108.7
C(4)–C(5)–H(5B)	109.4	N(2)–C(4)–H(4B)	108.7
C(5)#4–C(5)–H(5B)	109.4	C(5)–C(4)–H(4B)	108.7
C(4)–C(5)–H(5A)	109.4	H(4A)–C(4)–H(4B)	107.6
C(5)#4–C(5)–H(5A)	109.4	N(6)–C(14)–C(15)	111.5(9)
H(5B)–C(5)–H(5A)	108.0	N(6)–C(14)–H(14A)	109.3
C(15)–C(14)–H(14A)	109.3	C(15)#5–C(15)–H(15B)	108.7
H(14A)–C(14)–H(14B)	108.0	C(14)–C(15)–H(15A)	108.7
C(14)–C(15)–C(15)#5	114.2(11)	C(15)#5–C(15)–H(15A)	108.7
C(14)–C(15)–H(15B)	108.7	H(15B)–C(15)–H(15A)	107.6
C(6)–N(3)–C(7)	105.1(7)	C(13)–N(6)–C(12)	106.6(8)
C(6)–N(3)–Co(1)	125.4(6)	C(13)–N(6)–C(14)	126.3(8)
C(7)–N(3)–Co(1)	129.5(5)	C(12)–N(6)–C(14)	127.0(8)
C(1)–N(1)–C(2)	105.4(7)	C(13)–N(5)–C(11)	103.8(7)
C(1)–N(1)–Co(1)	124.1(5)	C(13)–N(5)–Co(1)	126.4(6)
C(2)–N(1)–Co(1)	125.9(6)	C(11)–N(5)–Co(1)	129.7(6)
C(6)–N(4)–C(8)	106.1(7)	C(1)–N(2)–C(3)	107.1(7)
C(6)-N(4)-C(9)	125.5(7)	C(1)-N(2)-C(4)	125.7(8)

C(8)-N(4)-C(9)	128.3(7)	C(3)-N(2)-C(4)	127.2(8)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+2 #2 -x+1,-y,-z+2 #3 -x,-y-1,-z+2

#4 -x+1,-y+1,-z+1 #5 -x+2,-y,-z+1

Table S9 Anisotropic displacement parameters ($Å^2 \times 10^3$) for Complex **2** the anisotropic displacement factor exponent takes the form:-2 π^2 [h^2 a^{*2} U_{11} + ... + 2 h k a* b* U_{12}]

	U11	U22	U33	U23	U13	U12
V(1)	17(1)	27(1)	27(1)	5(1)	–4(1)	–1(1)
V(2)	16(1)	29(1)	25(1)	–2(1)	–2(1)	–2(1)
Co(1)	17(1)	24(1)	24(1)	0(1)	–2(1)	–4(1)
O(6)	21(3)	27(3)	30(3)	3(2)	–4(2)	–5(3)
O(5)	14(3)	34(3)	38(4)	–3(3)	–7(2)	4(3)
O(4)	26(3)	39(4)	32(4)	–2(3)	–9(3)	9(3)
O(3)	40(4)	46(4)	36(4)	–19(3)	–11(3)	6(3)
O(2)	22(3)	49(4)	52(4)	9(3)	–7(3)	–13(3)
O(1)	51(4)	41(4)	42(4)	16(3)	–15(3)	–6(3)
OW1	96(7)	82(6)	56(5)	23(5)	1(5)	–3(6)
C(2)	25(5)	37(5)	30(5)	3(4)	–9(4)	–1(4)
C(6)	25(5)	19(5)	39(5)	–2(4)	3(4)	1(4)
C(7)	30(5)	27(5)	31(5)	–3(4)	–6(4)	–7(4)
C(1)	32(5)	24(5)	37(5)	–7(4)	–3(4)	–5(4)
C(3)	43(6)	41(6)	24(5)	6(4)	0(4)	–19(5)
C(9)	25(5)	25(5)	46(6)	–7(4)	1(4)	–6(4)
C(8)	31(5)	26(5)	36(5)	–1(4)	1(4)	–6(4)
C(12)	46(6)	48(7)	44(6)	–21(5)	–2(5)	–11(6)
C(11)	35(5)	45(6)	33(6)	–6(4)	0(4)	–12(5)
C(10)	34(5)	36(5)	40(6)	3(4)	0(4)	–13(5)
C(13)	44(6)	41(6)	26(5)	–8(4)	–2(4)	–8(5)
C(5)	71(8)	36(6)	28(5)	7(4)	–6(5)	–13(6)
C(4)	68(8)	27(5)	43(6)	18(4)	–13(5)	–11(5)
C(14)	39(6)	84(8)	19(5)	–2(5)	7(4)	–13(6)
C(15)	41(6)	101(10)	28(6)	–6(6)	8(5)	–19(6)
N(3)	16(4)	35(4)	29(4)	–5(3)	–2(3)	–7(4)
N(1)	25(4)	32(4)	20(4)	0(3)	–3(3)	–2(3)
N(6)	37(5)	52(5)	28(5)	–4(4)	–1(3)	–12(4)
N(5)	21(4)	38(4)	28(4)	2(3)	–1(3)	–6(4)
N(4)	24(4)	26(4)	33(4)	–2(3)	0(3)	–13(3)
N(2)	39(5)	28(4)	24(4)	11(3)	–8(3)	0(4)

Table S 10 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for Complex **2**

	x	y	z	U(eq)
H(2A)	7257	2026	8786	37
H(6A)	1847	–1667	8617	34
H(7A)	5891	–2999	9107	35
H(1A)	3487	2714	7558	37
H(3A)	7502	3947	7617	43
H(9A)	1561	–4862	8317	38
H(9B)	523	–3618	8592	38
H(8A)	4351	–4790	9166	38
H(12A)	6639	–1777	4725	55
H(11A)	5047	–2016	6543	45
H(10B)	656	–4083	10567	55
H(10A)	1471	–5407	10214	55
H(13A)	6742	1230	6533	44
H(5B)	4731	3709	5243	67
H(5A)	6318	4233	5166	67
H(4A)	5492	5469	6695	54
H(4B)	3880	5004	6758	54
H(14A)	8109	1416	4527	57
H(14B)	7836	382	3688	57
H(15B)	10364	317	3839	85
H(15A)	9728	–968	4290	85