

Supporting Information

Coordination and supramolecular assembly of {Cd₂Ge₈V₁₂O₄₈} building block and Cucurbit[6] to form rotaxane-shaped hybrids

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‡ Crystal data for **1**: C₅₈H₁₈₀N₄₆O₁₂₈V₂₄Ge₁₆Cd₈; *P*-1; *a* = 12.434(5) Å, *b* = 12.685(5) Å, *c* = 30.441(5) Å; *V* = 4647(3) Å³; *Z* = 1; 26717 reflns measured, 16334 unique (*R*_{int} = 0.0515); final *R*_{*f*} = 0.0549, *wR*₂ = 0.1309 for 16334 observed reflections [*I* > 2σ(*I*)]. CCDC- (1403847) contains 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 for **1**.

‡ Crystal data for **2**: C₄₆H₉₈N₃₄O₆₇V₁₂Ge₈Cd₄; *C*2/*c*; *a* = 15.524(5) Å, *b* = 19.795(5) Å, *c* = 36.902(5) Å; *V* = 11306(5) Å³; *Z* = 4; 32176 reflns measured, 9937 unique (*R*_{int} = 0.0617); final *R*_{*f*} = 0.0675, *wR*₂ = 0.1914 for 9937 observed reflections [*I* > 2σ(*I*)]. CCDC-(1403848) contains 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 for **2**.

Experimental characterization

Materials and Instrumentation

All reagents were of AR grade and used without further purification. IR spectra (4000-400 cm^{-1}) were recorded in KBr discs on a Nicolet Magna 560 IR spectrometer (Resolution: 2 cm^{-1} , Number of scan: 16 times). Powder X-ray diffraction (PXRD) patterns were recorded on a Siemens D 5005 diffractometer with Cu-K α ($\lambda = 1.5418 \text{ \AA}$) radiation in the range of 3-50 $^\circ$ C. TGA was performed on a Perkin-Elmer TGA analyzer heated from room temperature to 900 $^\circ$ C under nitrogen gas with a heating rate of 10 $^\circ$ C/min. Variable temperature magnetic susceptibility measurements were carried out in an applied magnetic field of 1000 Oe in the temperature range of 2-300 K with a Quantum Design MPMS XL-7 magnetometer.

Synthesis of 1.

NH_4VO_3 (0.0432 g, 0.36 mmol), GeO_2 (0.0760 g, 0.74 mmol), $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.1014 g, 0.36 mmol), H_3BO_3 (0.0316 g, 0.52 mmol), and en (0.20 mL) were added to H_2O (10 mL) solution with stirring. The final solution was transferred into a 20 mL Teflon-lined autoclave, before CB6 (0.11 g, 0.11 mmol) was added, then sealed, and kept at 170 $^\circ\text{C}$ for 4 days. After cooling to room temperature, reddish brown crystals were collected (Yield: 0.0518 g, 48.6% based on V). Elem anal. Calcd for $\text{C}_{58}\text{H}_{180}\text{N}_{46}\text{O}_{144}\text{V}_{24}\text{Ge}_{16}\text{Cd}_8$: C, 10.16; H, 2.65; N, 9.40%. Found: C, 10.01; H, 2.33; N, 9.18%. IR (KBr): $\nu = 3331(\text{m}), 3282(\text{m}), 3188(\text{w}), 2929(\text{m}), 2883(\text{w}), 1741(\text{s}), 1682(\text{m}), 1645(\text{m}), 1587(\text{w}), 1483(\text{m}), 1458(\text{w}), 1419(\text{m}), 1383(\text{m}), 1329(\text{m}), 1284(\text{w}), 1242(\text{m}), 1194(\text{m}), 1147(\text{w}), 985(\text{s}), 800(\text{s}), 733(\text{w}), 669(\text{m}), 544(\text{m}) \text{ cm}^{-1}$.

Synthesis of 2.

NH_4VO_3 (0.0154 g, 0.13 mmol), GeO_2 (0.0271 g, 0.26 mmol), $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.0362 g, 0.13 mmol), H_3BO_3 (0.0113 g, 0.19 mmol), and en (0.071 mL) were added to H_2O (5 mL) solution with stirring. The final solution was transferred into a 20 mL Teflon-lined autoclave, before CB6 (0.057 g, 0.057 mmol) was added, then sealed, and kept at 170 $^\circ\text{C}$ for 4 days. After cooling to room temperature, reddish brown crystals were harvested (Yield: 0.0223 g, 53.8% based on V). Elem anal. Calcd for $\text{C}_{23}\text{H}_{54}\text{N}_{17}\text{O}_{40}\text{V}_6\text{Ge}_4\text{Cd}_2$: C, 14.38; H, 2.57; N, 12.40%. Found: C, 14.01; H, 2.35; N, 12.14%. IR (KBr): $\nu = 3344(\text{m}), 3280(\text{m}), 3195(\text{w}), 2931(\text{m}), 2881(\text{w}), 1740(\text{s}), 1682(\text{m}), 1643(\text{m}), 1589(\text{w}), 1481(\text{m}), 1419(\text{m}), 1380(\text{m}), 1329(\text{m}), 1294(\text{w}), 1240(\text{m}), 1194(\text{m}), 1147(\text{w}), 987(\text{s}), 800(\text{s}), 733(\text{w}), 671(\text{m}), 546(\text{m}) \text{ cm}^{-1}$.

X-ray Crystallographic study.

The single-crystal X-ray diffraction measurements were performed at room temperature with a Bruker Apex II CCD using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Absorption corrections were applied using multi-scan technique and performed by using the SADABS program. All of the structures were solved by direct methods¹ and refined by F^2 full-matrix refinement using the SHELXTL package² within WINGX³. Carbon-bonded hydrogen atoms were placed in geometrically calculated positions; hydrogen atoms on water molecules were not assigned or directly included in the molecule formula. Crystallographic data for **1** and **2** are illustrated in Table S1 and selected bond lengths and angles are listed from Table S2 to Table S5, respectively. In addition, the bond valence sums⁴ for terminal O2, O21, O23, O27, O30, O32, O35 and O45 atoms on the Ge atoms in **1** and O3, O4, O18 and O21 atoms on the Ge atoms in **2** are in the range of 0.947 to 1.167, which indicates that these O atoms belong to OH groups. Other

similar OH groups have also been seen in previous reports⁵⁻⁶.

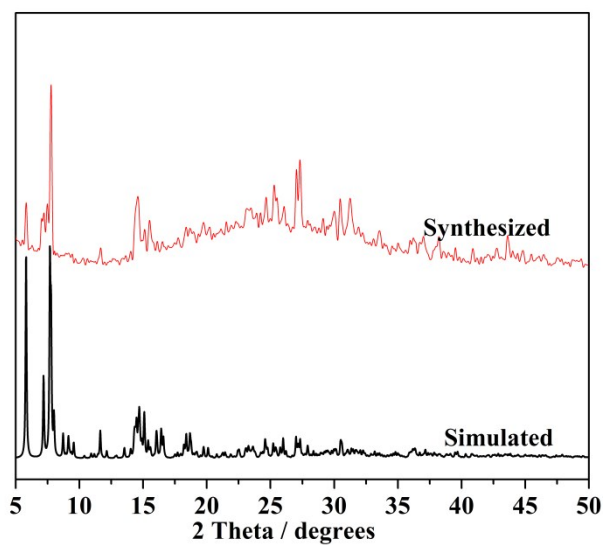


Fig. S1 The experimental and simulated X-ray powder diffraction patterns of **1**.

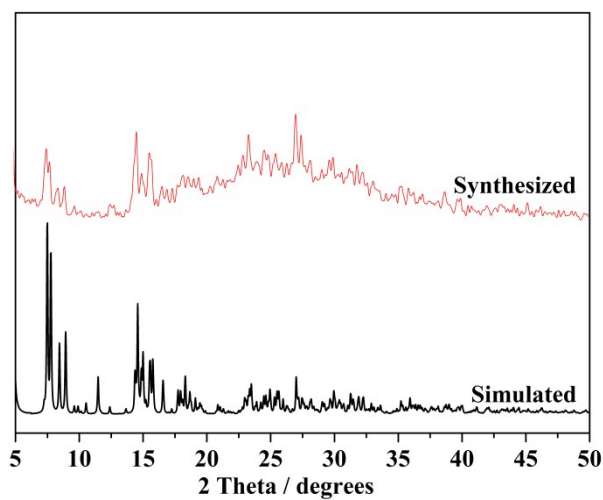


Fig. S2 The experimental and simulated X-ray powder diffraction patterns of **2**.

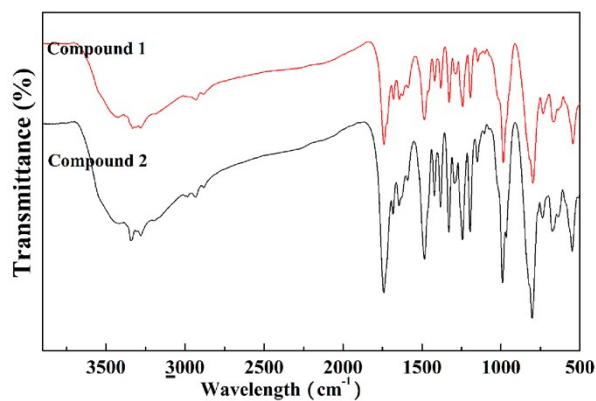


Fig S3. Infrared absorption spectrum of compounds **1** and **2**.

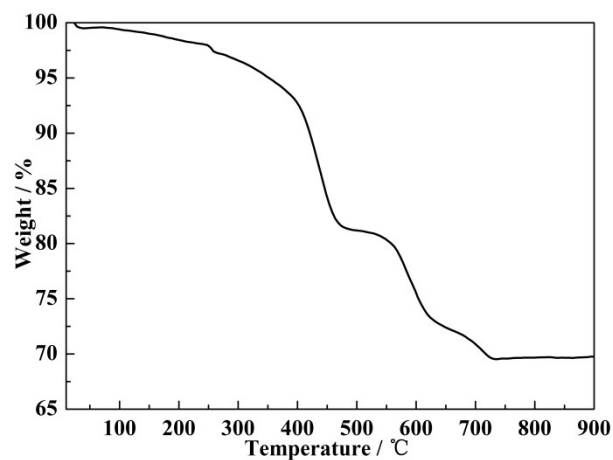


Fig S4. TGA curve of compound **1**.

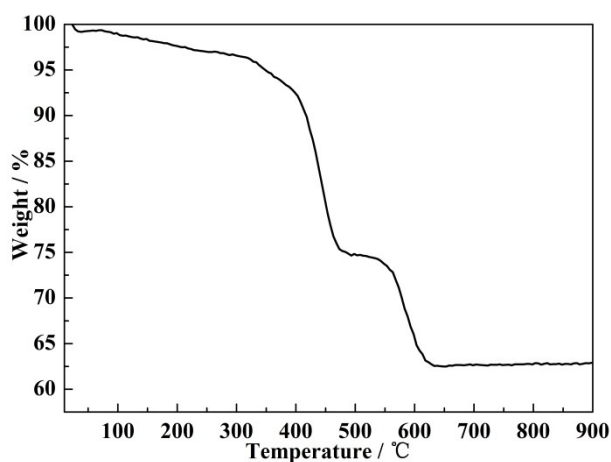


Fig S5. TGA curve of compound **2**.

Table S1. Crystal data and structure refinements for compound **1** and compound **2**.

Compound reference	1	2
Chemical formula	$C_{58}H_{180}N_{46}O_{128}V_{24}Ge_{16}Cd_8$	$C_{46}H_{98}N_{34}O_{67}V_{12}Ge_8Cd_4$
Formula Mass	6853.68	3841.18
Crystal system	Triclinic	Monoclinic
$a/(\text{\AA})$	12.434(5)	15.524(5)
$b/(\text{\AA})$	12.685(5)	19.795(5)
$c/(\text{\AA})$	30.441(5)	36.902(5)
$\alpha/^\circ$	87.927(5)	90.000(5)
$\beta/^\circ$	87.149(5)	94.457(5)
$\gamma/^\circ$	75.801(5)	90.000(5)
Unit cell volume/ $(\text{\AA})^3$	4647(3)	11306(5)

Temperature/K	293(2)	293(2)
Space group	<i>P</i> -1	<i>C</i> 2/ <i>c</i>
No. of formula units per unit cell, <i>Z</i>	1	4
No. of reflections measured	26717	32176
No. of independent reflections	16334	9937
R_{int}	0.0515	0.0617
Final R_I values ($I > 2\sigma(I)$) ^a	0.0549	0.0675
Final $wR(F_2)$ values ($I > 2\sigma(I)$) ^b	0.1309	0.1914
Final R_I values (all data)	0.0974	0.0991
Final $wR(F_2)$ values (all data)	0.1526	0.2158
Goodness of fit on F_2	1.008	1.013

$$^a R_I = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = \sqrt{\sum w(|F_o|^2 - |F_c|^2)^2} / \sum w(F_o^2)^{1/2}$$

Table S2. Selected bond lengths [\AA] for compound **1**.

V(1)-O(22)	1.620(7)	Ge(1)-O(28)	1.715(6)
V(1)-O(10)	1.930(7)	Ge(1)-O(19)	1.730(7)
V(1)-O(25)	1.944(7)	Ge(1)-O(27)	1.760(7)
V(1)-O(9)	1.945(6)	Ge(1)-O(26)	1.768(7)
V(1)-O(24)	1.970(7)	Ge(2)-O(21)	1.717(7)
V(2)-O(29)	1.616(7)	Ge(2)-O(25)	1.731(6)
V(2)-O(15)	1.923(6)	Ge(2)-O(7)	1.767(7)
V(2)-O(47)	1.953(7)	Ge(2)-O(26)	1.782(7)
V(2)-O(31)	1.955(7)	Ge(3)-O(24)	1.727(7)
V(2)-O(28)	1.970(7)	Ge(3)-O(23)	1.740(7)
V(3)-O(46)	1.601(7)	Ge(3)-O(11)	1.761(7)
V(3)-O(15)	1.919(7)	Ge(3)-O(44)	1.772(6)
V(3)-O(47)	1.923(7)	Ge(4)-O(31)	1.734(7)
V(3)-O(36)	1.972(7)	Ge(4)-O(30)	1.743(6)
V(3)-O(17)	2.014(7)	Ge(4)-O(13)	1.745(7)
V(4)-O(16)	1.599(7)	Ge(4)-O(44)	1.771(7)
V(4)-O(15)	1.915(6)	Ge(5)-O(45)	1.712(7)
V(4)-O(20)	1.937(6)	Ge(5)-O(5)	1.714(7)
V(4)-O(19)	1.983(7)	Ge(5)-O(36)	1.737(6)
V(4)-O(17)	1.999(7)	Ge(5)-O(34)	1.767(7)
V(5)-O(18)	1.611(7)	Ge(6)-O(43)	1.722(6)
V(5)-O(8)	1.909(7)	Ge(6)-O(32)	1.728(7)
V(5)-O(20)	1.935(7)	Ge(6)-O(3)	1.744(7)
V(5)-O(7)	1.992(7)	Ge(6)-O(42)	1.777(6)
V(5)-O(19)	1.995(6)	Ge(7)-O(2)	1.708(7)
V(6)-O(6)	1.600(7)	Ge(7)-O(40)	1.727(7)
V(6)-O(8)	1.933(7)	Ge(7)-O(39)	1.741(7)
V(6)-O(9)	1.952(6)	Ge(7)-O(42)	1.758(7)

V(6)-O(7)	1.965(7)	Ge(8)-O(41)	1.709(7)
V(6)-O(39)	1.979(7)	Ge(8)-O(35)	1.736(7)
V(7)-O(1)	1.604(7)	Ge(8)-O(17)	1.737(7)
V(7)-O(20)	1.935(7)	Ge(8)-O(34)	1.761(7)
V(7)-O(41)	1.961(7)	Cd(1)-N(2)	2.271(13)
V(7)-O(8)	1.962(7)	Cd(1)-N(1)	2.333(13)
V(7)-O(40)	1.970(7)	Cd(2)-N(4)	2.285(10)
V(8)-O(4)	1.603(7)	Cd(2)-N(3)	2.384(9)
V(8)-O(38)	1.924(7)	Cd(3)-N(8)	2.282(10)
V(8)-O(10)	1.927(7)	Cd(3)-N(7)	2.295(11)
V(8)-O(3)	1.995(6)	Cd(3)-N(13)	2.434(11)
V(8)-O(11)	1.996(6)	Cd(4)-N(9)	2.257(9)
V(9)-O(12)	1.598(7)	Cd(4)-N(11)	2.281(10)
V(9)-O(37)	1.918(7)	Cd(4)-N(12)	2.298(10)
V(9)-O(38)	1.929(6)	Cd(4)-N(10)	2.325(9)
V(9)-O(13)	1.994(7)	Cd(1)-O(5)	2.299(6)
V(9)-O(11)	1.995(6)	Cd(1)-O(40)	2.304(7)
V(10)-O(14)	1.577(7)	Cd(1)-O(43)	2.362(7)
V(10)-O(37)	1.952(7)	Cd(1)-O(41)	2.366(7)
V(10)-O(47)	1.958(7)	Cd(2)-O(24)	2.307(7)
V(10)-O(36)	1.982(7)	Cd(2)-O(31)	2.317(7)
V(10)-O(13)	1.991(7)	Cd(2)-O(28)	2.325(6)
V(11)-O(33)	1.608(7)	Cd(2)-O(25)	2.348(6)
V(11)-O(38)	1.933(7)	Cd(3)-O(49)	2.304(7)
V(11)-O(37)	1.947(7)	Cd(3)-O(50)	2.428(8)
V(11)-O(43)	1.958(6)	Cd(3)-O(29)	2.432(8)
V(11)-O(5)	1.970(6)	Cd(4)-O(22)	2.425(7)
V(12)-O(48)	1.597(7)	V(1)-V(12)	2.793(2)
V(12)-O(9)	1.913(7)	V(2)-V(3)	2.851(3)
V(12)-O(10)	1.915(6)	V(3)-V(10)	3.003(2)
V(12)-O(3)	2.016(7)	V(3)-V(4)	3.010(3)
V(12)-O(39)	2.018(6)	V(4)-V(5)	3.026(2)
		V(5)-V(7)	2.854(3)
		V(5)-V(6)	3.015(2)
		V(6)-V(12)	3.036(2)
		V(8)-V(12)	3.022(2)
		V(8)-V(9)	3.038(2)
		V(9)-V(11)	2.859(3)
		V(9)-V(10)	3.018(2)

Table S3. Selected angles [deg] for compound **1**.

O(22)-V(1)-O(10)	108.0(3)	O(28)-Ge(1)-O(19)	115.7(3)
O(22)-V(1)-O(25)	109.5(3)	O(28)-Ge(1)-O(27)	112.6(3)
O(10)-V(1)-O(25)	142.4(3)	O(19)-Ge(1)-O(27)	108.6(3)
O(22)-V(1)-O(9)	105.1(3)	O(28)-Ge(1)-O(26)	107.8(3)
O(10)-V(1)-O(9)	84.6(3)	O(19)-Ge(1)-O(26)	104.4(3)
O(25)-V(1)-O(9)	87.8(3)	O(27)-Ge(1)-O(26)	107.2(3)
O(22)-V(1)-O(24)	107.0(3)	O(21)-Ge(2)-O(25)	115.0(3)
O(10)-V(1)-O(24)	87.5(3)	O(21)-Ge(2)-O(7)	107.3(3)
O(25)-V(1)-O(24)	79.7(3)	O(25)-Ge(2)-O(7)	114.8(3)
O(9)-V(1)-O(24)	147.8(3)	O(21)-Ge(2)-O(26)	109.2(3)
O(29)-V(2)-O(15)	104.2(4)	O(25)-Ge(2)-O(26)	106.0(3)
O(29)-V(2)-O(47)	107.6(3)	O(7)-Ge(2)-O(26)	104.0(3)
O(15)-V(2)-O(47)	82.9(3)	O(24)-Ge(3)-O(23)	108.5(3)
O(29)-V(2)-O(31)	111.5(4)	O(24)-Ge(3)-O(11)	115.3(3)
O(15)-V(2)-O(31)	144.2(3)	O(23)-Ge(3)-O(11)	112.6(3)
O(47)-V(2)-O(31)	88.5(3)	O(24)-Ge(3)-O(44)	108.3(3)
O(29)-V(2)-O(28)	104.9(4)	O(23)-Ge(3)-O(44)	106.0(3)
O(15)-V(2)-O(28)	89.6(3)	O(11)-Ge(3)-O(44)	105.7(3)
O(47)-V(2)-O(28)	147.5(3)	O(31)-Ge(4)-O(30)	114.5(3)
O(31)-V(2)-O(28)	79.2(3)	O(31)-Ge(4)-O(13)	114.8(3)
O(46)-V(3)-O(15)	113.4(4)	O(30)-Ge(4)-O(13)	107.7(3)
O(46)-V(3)-O(47)	107.6(3)	O(31)-Ge(4)-O(44)	106.3(3)
O(15)-V(3)-O(47)	83.8(3)	O(30)-Ge(4)-O(44)	108.8(3)
O(46)-V(3)-O(36)	107.2(4)	O(13)-Ge(4)-O(44)	104.1(3)
O(15)-V(3)-O(36)	139.2(3)	O(45)-Ge(5)-O(5)	115.5(3)
O(47)-V(3)-O(36)	80.3(3)	O(45)-Ge(5)-O(36)	105.7(3)
O(46)-V(3)-O(17)	108.3(3)	O(5)-Ge(5)-O(36)	113.7(3)
O(15)-V(3)-O(17)	79.3(3)	O(45)-Ge(5)-O(34)	108.2(3)
O(47)-V(3)-O(17)	144.0(3)	O(5)-Ge(5)-O(34)	106.8(3)
O(36)-V(3)-O(17)	92.1(3)	O(36)-Ge(5)-O(34)	106.5(3)
O(16)-V(4)-O(15)	109.7(3)	O(43)-Ge(6)-O(32)	111.1(4)
O(16)-V(4)-O(20)	112.8(3)	O(43)-Ge(6)-O(3)	111.2(3)
O(15)-V(4)-O(20)	137.4(3)	O(32)-Ge(6)-O(3)	111.9(3)
O(16)-V(4)-O(19)	104.9(4)	O(43)-Ge(6)-O(42)	107.8(3)
O(15)-V(4)-O(19)	88.9(3)	O(32)-Ge(6)-O(42)	108.7(3)
O(20)-V(4)-O(19)	79.1(3)	O(3)-Ge(6)-O(42)	105.9(3)
O(16)-V(4)-O(17)	106.0(4)	O(2)-Ge(7)-O(40)	114.4(3)
O(15)-V(4)-O(17)	79.7(3)	O(2)-Ge(7)-O(39)	105.7(3)
O(20)-V(4)-O(17)	90.1(3)	O(40)-Ge(7)-O(39)	113.8(3)
O(19)-V(4)-O(17)	149.1(3)	O(2)-Ge(7)-O(42)	108.7(3)
O(18)-V(5)-O(8)	112.2(3)	O(40)-Ge(7)-O(42)	107.5(3)
O(18)-V(5)-O(20)	109.8(3)	O(39)-Ge(7)-O(42)	106.3(3)

O(8)-V(5)-O(20)	84.6(3)	O(41)-Ge(8)-O(35)	116.2(4)
O(18)-V(5)-O(7)	108.5(3)	O(41)-Ge(8)-O(17)	112.3(3)
O(8)-V(5)-O(7)	78.5(3)	O(35)-Ge(8)-O(17)	108.2(4)
O(20)-V(5)-O(7)	141.6(3)	O(41)-Ge(8)-O(34)	108.0(3)
O(18)-V(5)-O(19)	110.0(3)	O(35)-Ge(8)-O(34)	105.3(3)
O(8)-V(5)-O(19)	137.7(3)	O(17)-Ge(8)-O(34)	106.0(3)
O(20)-V(5)-O(19)	78.8(3)	O(28)-Ge(1)-O(19)	115.7(3)
O(7)-V(5)-O(19)	91.0(3)	O(28)-Ge(1)-O(27)	112.6(3)
O(6)-V(6)-O(8)	112.2(3)	O(19)-Ge(1)-O(27)	108.6(3)
O(6)-V(6)-O(9)	112.7(3)	O(28)-Ge(1)-O(26)	107.8(3)
O(8)-V(6)-O(9)	135.0(3)	O(19)-Ge(1)-O(26)	104.4(3)
O(6)-V(6)-O(7)	106.4(3)	O(27)-Ge(1)-O(26)	107.2(3)
O(8)-V(6)-O(7)	78.6(3)	O(21)-Ge(2)-O(25)	115.0(3)
O(9)-V(6)-O(7)	88.9(3)	O(21)-Ge(2)-O(7)	107.3(3)
O(6)-V(6)-O(39)	105.0(3)	O(25)-Ge(2)-O(7)	114.8(3)
O(8)-V(6)-O(39)	90.0(3)	O(21)-Ge(2)-O(26)	109.2(3)
O(9)-V(6)-O(39)	78.7(3)	O(25)-Ge(2)-O(26)	106.0(3)
O(7)-V(6)-O(39)	148.6(3)	O(7)-Ge(2)-O(26)	104.0(3)
O(1)-V(7)-O(20)	106.9(3)	O(24)-Ge(3)-O(23)	108.5(3)
O(1)-V(7)-O(41)	106.2(4)	O(24)-Ge(3)-O(11)	115.3(3)
O(20)-V(7)-O(41)	89.3(3)	O(23)-Ge(3)-O(11)	112.6(3)
O(1)-V(7)-O(8)	107.4(3)	O(24)-Ge(3)-O(44)	108.3(3)
O(20)-V(7)-O(8)	83.1(3)	O(23)-Ge(3)-O(44)	106.0(3)
O(41)-V(7)-O(8)	146.3(3)	O(11)-Ge(3)-O(44)	105.7(3)
O(1)-V(7)-O(40)	107.9(3)	O(31)-Ge(4)-O(30)	114.5(3)
O(20)-V(7)-O(40)	145.2(3)	O(31)-Ge(4)-O(13)	114.8(3)
O(41)-V(7)-O(40)	79.2(3)	O(30)-Ge(4)-O(13)	107.7(3)
O(8)-V(7)-O(40)	88.4(3)	O(31)-Ge(4)-O(44)	106.3(3)
O(4)-V(8)-O(38)	113.0(3)	O(30)-Ge(4)-O(44)	108.8(3)
O(4)-V(8)-O(10)	112.4(3)	O(13)-Ge(4)-O(44)	104.1(3)
O(38)-V(8)-O(10)	134.6(3)	O(45)-Ge(5)-O(5)	115.5(3)
O(4)-V(8)-O(3)	103.3(3)	O(45)-Ge(5)-O(36)	105.7(3)
O(38)-V(8)-O(3)	90.7(3)	O(5)-Ge(5)-O(36)	113.7(3)
O(10)-V(8)-O(3)	79.0(3)	O(45)-Ge(5)-O(34)	108.2(3)
O(4)-V(8)-O(11)	107.3(3)	O(5)-Ge(5)-O(34)	106.8(3)
O(38)-V(8)-O(11)	78.3(3)	O(36)-Ge(5)-O(34)	106.5(3)
O(10)-V(8)-O(11)	88.4(3)	O(43)-Ge(6)-O(32)	111.1(4)
O(3)-V(8)-O(11)	149.3(3)	O(43)-Ge(6)-O(3)	111.2(3)
O(12)-V(9)-O(37)	111.6(3)	O(32)-Ge(6)-O(3)	111.9(3)
O(12)-V(9)-O(38)	110.2(3)	O(43)-Ge(6)-O(42)	107.8(3)
O(37)-V(9)-O(38)	83.7(3)	O(32)-Ge(6)-O(42)	108.7(3)
O(12)-V(9)-O(13)	109.7(3)	O(3)-Ge(6)-O(42)	105.9(3)
O(37)-V(9)-O(13)	79.6(3)	O(2)-Ge(7)-O(40)	114.4(3)
O(38)-V(9)-O(13)	140.0(3)	O(2)-Ge(7)-O(39)	105.7(3)

O(12)-V(9)-O(11)	108.9(3)	O(40)-Ge(7)-O(39)	113.8(3)
O(37)-V(9)-O(11)	139.3(3)	O(2)-Ge(7)-O(42)	108.7(3)
O(38)-V(9)-O(11)	78.2(3)	O(40)-Ge(7)-O(42)	107.5(3)
O(13)-V(9)-O(11)	91.3(3)	O(39)-Ge(7)-O(42)	106.3(3)
O(14)-V(10)-O(37)	113.3(4)	O(41)-Ge(8)-O(35)	116.2(4)
O(14)-V(10)-O(47)	110.3(3)	O(41)-Ge(8)-O(17)	112.3(3)
O(37)-V(10)-O(47)	136.4(3)	O(35)-Ge(8)-O(17)	108.2(4)
O(14)-V(10)-O(36)	105.6(4)	O(41)-Ge(8)-O(34)	108.0(3)
O(37)-V(10)-O(36)	88.4(3)	O(35)-Ge(8)-O(34)	105.3(3)
O(47)-V(10)-O(36)	79.2(3)	O(17)-Ge(8)-O(34)	106.0(3)
O(14)-V(10)-O(13)	107.0(4)	O(5)-Cd(1)-O(40)	119.8(2)
O(37)-V(10)-O(13)	78.9(3)	O(5)-Cd(1)-O(43)	65.2(2)
O(47)-V(10)-O(13)	89.5(3)	O(40)-Cd(1)-O(43)	87.4(2)
O(36)-V(10)-O(13)	147.4(3)	O(5)-Cd(1)-O(41)	86.3(2)
O(33)-V(11)-O(38)	109.9(3)	O(40)-Cd(1)-O(41)	64.9(2)
O(33)-V(11)-O(37)	107.1(3)	O(43)-Cd(1)-O(41)	123.3(3)
O(38)-V(11)-O(37)	82.8(3)	O(24)-Cd(2)-O(31)	88.4(2)
O(33)-V(11)-O(43)	105.8(3)	O(24)-Cd(2)-O(28)	122.0(3)
O(38)-V(11)-O(43)	89.2(3)	O(31)-Cd(2)-O(28)	65.2(2)
O(37)-V(11)-O(43)	146.9(3)	O(24)-Cd(2)-O(25)	65.2(2)
O(33)-V(11)-O(5)	105.2(3)	O(31)-Cd(2)-O(25)	119.7(2)
O(38)-V(11)-O(5)	144.8(3)	O(28)-Cd(2)-O(25)	83.9(2)
O(37)-V(11)-O(5)	88.7(3)	O(49)-Cd(3)-O(50)	98.6(3)
O(43)-V(11)-O(5)	79.6(3)	O(49)-Cd(3)-O(29)	71.2(3)
O(48)-V(12)-O(9)	107.4(3)	O(50)-Cd(3)-O(29)	79.4(3)
O(48)-V(12)-O(10)	109.7(3)	N(2)-Cd(1)-N(1)	72.2(5)
O(9)-V(12)-O(10)	85.9(3)	N(4)-Cd(2)-N(3)	74.4(3)
O(48)-V(12)-O(3)	110.1(3)	N(8)-Cd(3)-N(7)	77.0(4)
O(9)-V(12)-O(3)	142.3(3)	N(8)-Cd(3)-N(13)	90.4(4)
O(10)-V(12)-O(3)	78.8(3)	N(7)-Cd(3)-N(13)	96.5(4)
O(48)-V(12)-O(39)	110.2(3)	N(9)-Cd(4)-N(11)	149.8(3)
O(9)-V(12)-O(39)	78.6(3)	N(9)-Cd(4)-N(12)	131.9(3)
O(10)-V(12)-O(39)	139.9(3)	N(11)-Cd(4)-N(12)	77.0(3)
O(3)-V(12)-O(39)	91.3(3)	N(9)-Cd(4)-N(10)	77.2(4)
		N(11)-Cd(4)-N(10)	96.9(4)
		N(12)-Cd(4)-N(10)	119.5(4)

Table S4. Selected bond lengths [\AA] for compound 2.

V(1)-O(8)	1.611(8)	Cd(1)-N(1)	2.351(11)
V(1)-O(9)	1.950(8)	Cd(2)-N(2B)	2.300(10)
V(1)-O(7)	1.954(8)	Cd(2)-N(2A)	2.304(10)
V(1)-O(15)#1	1.980(8)	Cd(3)-N(14)	2.231(16)

V(1)-O(6)	1.983(8)	Cd(1)-O(20)	2.328(8)
V(2)-O(10)	1.602(8)	Cd(1)-O(17)	2.340(7)
V(2)-O(11)	1.920(8)	Cd(2)-O(2)	2.334(8)
V(2)-O(9)	1.922(8)	Cd(2)-O(1)	2.342(8)
V(2)-O(6)	1.971(8)	Cd(3)-O(25)	2.200(11)
V(2)-O(5)	2.015(8)	Cd(3)-O(24)	2.490(10)
V(3)-O(16)	1.610(8)	Cd(3)-O(22)	2.520(11)
V(3)-O(11)	1.918(8)	Ge(1)-O(2)	1.710(8)
V(3)-O(12)	1.937(7)	Ge(1)-O(3)	1.736(8)
V(3)-O(13)	1.988(8)	Ge(1)-O(6)	1.743(7)
V(3)-O(5)	1.995(8)	Ge(1)-O(29)	1.773(8)
V(4)-O(14)	1.605(9)	Ge(2)-O(1)	1.715(8)
V(4)-O(7)#1	1.908(7)	Ge(2)-O(5)	1.737(8)
V(4)-O(12)	1.940(8)	Ge(2)-O(4)	1.741(9)
V(4)-O(13)	2.001(8)	Ge(2)-O(29)	1.757(8)
V(4)-O(15)	2.007(8)	Ge(3)-O(20)	1.706(8)
V(5)-O(22)	1.605(9)	Ge(3)-O(13)	1.735(7)
V(5)-O(11)	1.927(8)	Ge(3)-O(21)	1.738(8)
V(5)-O(17)	1.953(8)	Ge(3)-O(19)	1.770(7)
V(5)-O(9)	1.970(8)	Ge(4)-O(17)#1	1.722(8)
V(5)-O(20)	1.981(7)	Ge(4)-O(18)	1.740(8)
V(6)-O(30)	1.608(8)	Ge(4)-O(15)	1.741(7)
V(6)-O(12)#1	1.945(8)	Ge(4)-O(19)	1.780(8)
V(6)-O(7)	1.955(7)	V(1)-V(2)	3.003(3)
V(6)-O(2)	1.972(8)	V(1)-V(4)#1	3.015(3)
V(6)-O(1)#1	1.980(8)	V(2)-V(5)	2.858(3)
Cd(3)-N(16A)	2.294(9)	V(2)-V(3)	3.013(3)
Cd(3)-N(15B)	2.315(10)	V(3)-V(4)	3.035(3)
Cd(3)-N(15A)	2.319(10)	V(4)-V(6)#1	2.853(3)
Cd(3)-N(16B)	2.329(10)		

Table S5. Selected angles [deg] for compound **2**.

O(8)-V(1)-O(9)	111.4(4)	O(20)#1-Cd(1)-O(20)	123.1(4)
O(8)-V(1)-O(7)	112.7(4)	O(20)#1-Cd(1)-O(17)	85.8(3)
O(9)-V(1)-O(7)	135.9(3)	O(20)-Cd(1)-O(17)	65.9(3)
O(8)-V(1)-O(15)#1	106.1(4)	O(17)#1-Cd(1)-O(17)	119.3(4)
O(9)-V(1)-O(15)#1	88.9(3)	O(2)#1-Cd(2)-O(2)	121.3(4)
O(7)-V(1)-O(15)#1	79.2(3)	O(2)-Cd(2)-O(1)#1	64.9(3)
O(8)-V(1)-O(6)	106.4(4)	O(2)-Cd(2)-O(1)	86.7(3)
O(9)-V(1)-O(6)	79.0(3)	O(1)#1-Cd(2)-O(1)	121.1(4)
O(7)-V(1)-O(6)	88.7(3)	O(25)-Cd(3)-O(24)	98.4(3)
O(15)#1-V(1)-O(6)	147.5(3)	O(25)-Cd(3)-O(22)	70.9(4)
O(10)-V(2)-O(11)	110.4(4)	O(24)-Cd(3)-O(22)	80.6(3)

O(10)-V(2)-O(9)	109.1(4)	O(2)-Ge(1)-O(3)	114.9(4)
O(11)-V(2)-O(9)	84.2(3)	O(2)-Ge(1)-O(6)	114.1(4)
O(10)-V(2)-O(6)	109.5(4)	O(3)-Ge(1)-O(6)	106.3(4)
O(11)-V(2)-O(6)	139.9(3)	O(2)-Ge(1)-O(29)	107.0(4)
O(9)-V(2)-O(6)	80.0(3)	O(3)-Ge(1)-O(29)	108.9(4)
O(10)-V(2)-O(5)	107.6(4)	O(6)-Ge(1)-O(29)	105.2(4)
O(11)-V(2)-O(5)	79.2(3)	O(1)-Ge(2)-O(5)	112.6(4)
O(9)-V(2)-O(5)	143.0(3)	O(1)-Ge(2)-O(4)	116.4(4)
O(6)-V(2)-O(5)	91.9(3)	O(5)-Ge(2)-O(4)	107.2(4)
O(16)-V(3)-O(11)	108.8(4)	O(1)-Ge(2)-O(29)	108.2(4)
O(16)-V(3)-O(12)	112.3(4)	O(5)-Ge(2)-O(29)	106.6(4)
O(11)-V(3)-O(12)	138.9(3)	O(4)-Ge(2)-O(29)	105.2(4)
O(16)-V(3)-O(13)	105.1(4)	O(20)-Ge(3)-O(13)	115.3(4)
O(11)-V(3)-O(13)	89.5(3)	O(20)-Ge(3)-O(21)	113.8(4)
O(12)-V(3)-O(13)	79.0(3)	O(13)-Ge(3)-O(21)	107.4(4)
O(16)-V(3)-O(5)	105.6(4)	O(20)-Ge(3)-O(19)	107.9(4)
O(11)-V(3)-O(5)	79.7(3)	O(13)-Ge(3)-O(19)	104.8(3)
O(12)-V(3)-O(5)	90.4(3)	O(21)-Ge(3)-O(19)	106.9(4)
O(13)-V(3)-O(5)	149.3(3)	O(17)#1-Ge(4)-O(18)	114.3(4)
O(14)-V(4)-O(7)#1	112.0(4)	O(17)#1-Ge(4)-O(15)	115.9(4)
O(14)-V(4)-O(12)	109.0(4)	O(18)-Ge(4)-O(15)	107.3(4)
O(7)#1-V(4)-O(12)	84.8(3)	O(17)#1-Ge(4)-O(19)	106.2(4)
O(14)-V(4)-O(13)	109.8(4)	O(18)-Ge(4)-O(19)	108.5(4)
O(7)#1-V(4)-O(13)	138.0(3)	O(15)-Ge(4)-O(19)	104.0(4)
O(12)-V(4)-O(13)	78.7(3)	O(20)-Cd(1)-N(1)	105.9(4)
O(14)-V(4)-O(15)	108.9(4)	O(17)#1-Cd(1)-N(1)	85.9(3)
O(7)#1-V(4)-O(15)	79.6(3)	O(17)-Cd(1)-N(1)	151.4(4)
O(12)-V(4)-O(15)	142.1(3)	O(20)-Cd(1)-N(1)#1	119.1(4)
O(13)-V(4)-O(15)	90.3(3)	N(2B)-Cd(2)-O(2)#1	109.7(8)
O(22)-V(5)-O(11)	104.1(5)	N(2A)-Cd(2)-O(2)#1	93.4(7)
O(22)-V(5)-O(17)	111.8(5)	N(2A)#1-Cd(2)-O(2)#1	137.5(8)
O(11)-V(5)-O(17)	144.1(3)	N(2B)-Cd(2)-O(2)	116.3(8)
O(22)-V(5)-O(9)	108.0(4)	N(2A)-Cd(2)-O(2)	137.5(8)
O(11)-V(5)-O(9)	82.8(3)	N(2B)-Cd(2)-O(1)	152.6(7)
O(17)-V(5)-O(9)	87.6(3)	N(2B)#1-Cd(2)-O(1)	83.9(7)
O(22)-V(5)-O(20)	103.8(4)	N(2A)-Cd(2)-O(1)	133.2(8)
O(11)-V(5)-O(20)	89.9(3)	N(2A)#1-Cd(2)-O(1)	96.5(7)
O(17)-V(5)-O(20)	80.3(3)	O(25)-Cd(3)-N(14)	90.1(5)
O(9)-V(5)-O(20)	148.2(3)	O(25)-Cd(3)-N(16A)	168.0(5)
O(30)-V(6)-O(12)#1	107.1(4)	O(25)-Cd(3)-N(15B)	81.9(16)
O(30)-V(6)-O(7)	107.3(4)	O(25)-Cd(3)-N(15A)	88.1(16)
O(12)#1-V(6)-O(7)	83.4(3)	O(25)-Cd(3)-N(16B)	144.5(6)
O(30)-V(6)-O(2)	106.2(4)	N(14)-Cd(3)-O(24)	169.4(4)
O(12)#1-V(6)-O(2)	146.7(3)	N(16A)-Cd(3)-O(24)	92.9(5)

O(7)-V(6)-O(2)	88.7(3)	N(15B)-Cd(3)-O(24)	92.7(16)
O(30)-V(6)-O(1)#1	107.1(4)	N(15A)-Cd(3)-O(24)	85.3(16)
O(12)#1-V(6)-O(1)#1	89.6(3)	N(16B)-Cd(3)-O(24)	94.5(5)
O(7)-V(6)-O(1)#1	145.4(3)	N(14)-Cd(3)-O(22)	96.4(5)
O(2)-V(6)-O(1)#1	78.8(3)	N(16A)-Cd(3)-O(22)	115.1(5)
		N(15B)-Cd(3)-O(22)	150.6(15)
		N(15A)-Cd(3)-O(22)	152.5(15)
		N(16B)-Cd(3)-O(22)	144.2(6)

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