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Supporting information for article:

Surface-grafted lanthanoid complexes of the tungstosilicate polyanion $[SiW_{12}O_{40}]^{4-}$: a synthetic, structural and computational investigation

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Supporting information

S1. Synthesis of 1,10-phenanthroline-2,9-dicarbaldehyde dioxime Ligand (PDOX)

Synthesis procedure of ligand PDOX is illustrated in Scheme 3.A mixture of neocuproin (3 g) and selenium dioxide (7.5 g) in dioxane containing 4% water (200 ml) was heated under reflux for 3 hours and then filtered through celite while hot. The dialdehyde (2.4g, 70%) was separated from the cold filtrate. A suspension of 1,10-phenanthroline-2,9-dicarbaldehyde (400 mg, 1.69 mmol) in 10 ml of absolute ethanol was stirred at 60 °C for 10 min. NH₂OH.HCl was then progressively added (622 mg, 8.8 mmol). The addition of about 400 mg of hydroxylamine dissolved the dialdehyde within a few minutes to give a brown solution, after which a brown precipitate was obtained (after the complete addition of NH₂OH.HCl). The reaction mixture, in 30 ml of absolute EtOH, was warmed to 80 °C and stirred for 20 minutes. The mixture was stirred at reflux (95°C) for 2 hours after the addition of pyridine (1.64 ml, 20.3 mmol). The reaction mixture was then allowed to cool at room temperature. After removal of the liquid phase, the precipitate was washed with 30 ml of water to eliminate the excess of NH₂OH.HCl (352 mg, yield 78%). IR (KBr) $\tilde{\nu}$: 1617 cm⁻¹ (C=N oxime).

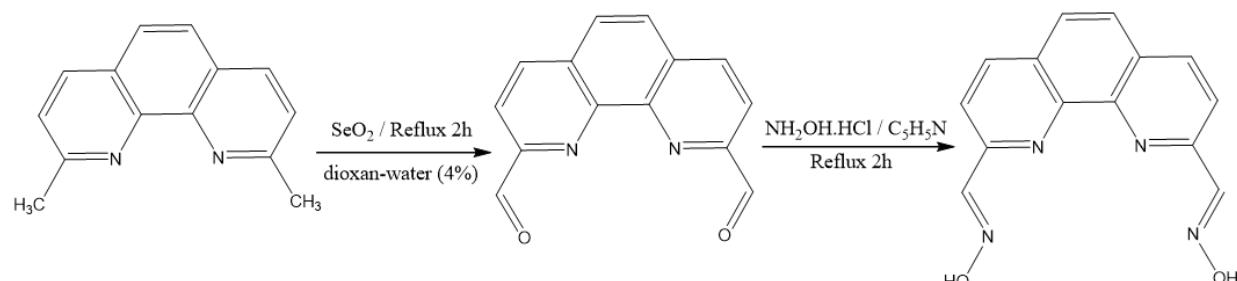


Figure S1 Ligand (PDOX) synthesis procedure.

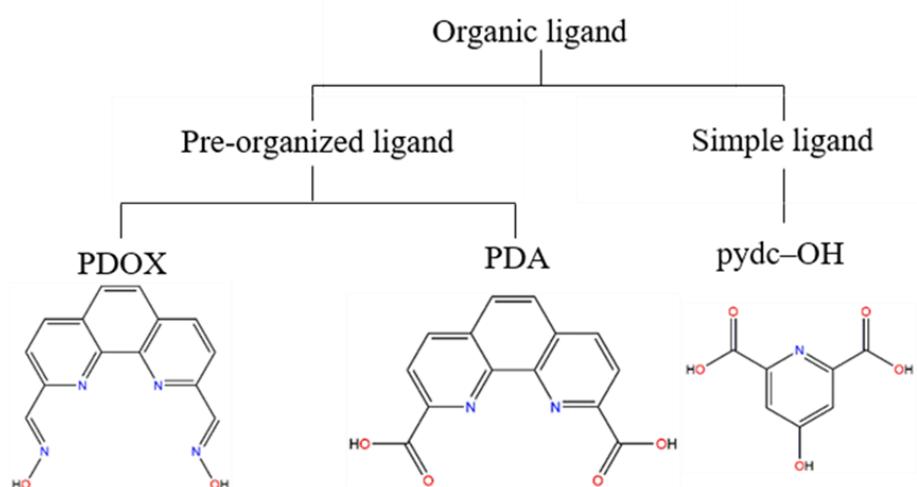


Figure S2 Structures of ligands discussed in this work.

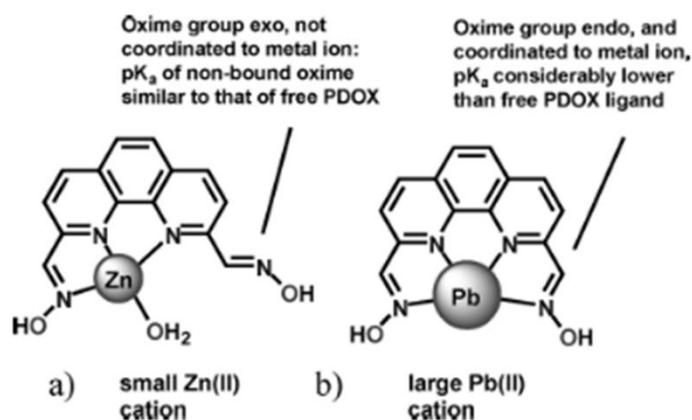


Figure S3 Coordinated PDOX ligands, with at (a) one oxime group exo and not coordinated to the Zn(II) cation, and (b) the coordinated oxime groups both endo, and bound to the large Pb(II) cation (Boone *et al.*, 2011).

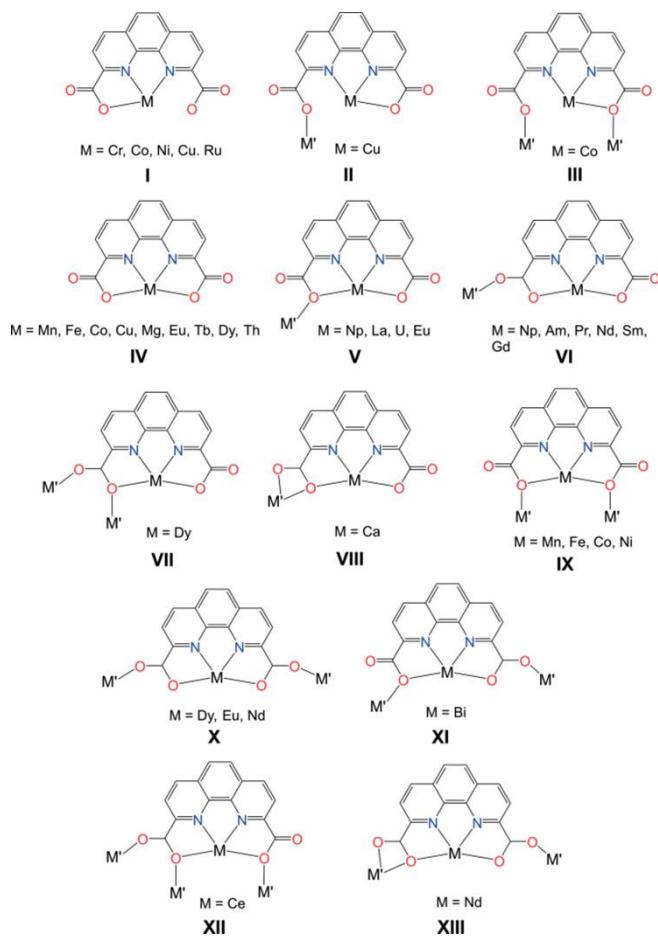


Figure S4 Classification of the coordination modes found for PDA ligands in the CSD. The new mode VII is observed in this work (Alipour *et al.*, 2016).

S2. Crystallographic characteristic data

Table S1 Experimental details for 1.

Crystal data	
Chemical formula	C ₄₂ H ₁₈ Dy ₃ N ₆ NaO _{61.5} SiW ₁₂ ·12(O)
M _r	4527.40
Crystal system, space group	Trigonal, R3
Temperature (K)	130
a, c (Å)	20.3334 (3), 18.7836 (3)
V (Å ³)	6725.60 (19)
Z	3
Radiation type	Cu K α
μ (mm ⁻¹)	41.93
Crystal size (mm)	0.07 × 0.05 × 0.03
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Atlas Gaussian
Absorption correction	CrysAlis PRO 1.171.38.46 (Rigaku Oxford Diffraction, 2015) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T _{min} , T _{max}	0.097, 0.369
No. of measured, independent and observed [I > 2σ(I)] reflections	16672, 5475, 5450
R _{int}	0.030
(sin θ/λ) _{max} (Å ⁻¹)	0.632
Refinement	
R[F ² > 2σ(F ²)], wR(F ²), S	0.036, 0.098, 1.02
No. of reflections	5475
No. of parameters	426
No. of restraints	1
H-atom treatment	H-atom parameters constrained $w = 1/[\sigma^2(F_o^2) + (0.0696P)^2 + 182.8632P]$ where P = (F _o ² + 2F _c ²)/3
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.53, -1.89
Absolute structure	Classical Flack method preferred over Parsons because s.u. lower.
Absolute structure parameter	0.013 (7)

Computer programs: CrysAlis PRO 1.171.38.46 (Rigaku OD, 2015), ShelXT (Sheldrick, 2015), SHELXL (Sheldrick, 2015), Olex2 (Dolomanov *et al.*, 2009).

Table S2 Selected geometric parameters (\AA) for **1**.

W4—O8	1.949 (10)	Na1—O21 ⁱⁱ	2.378 (18)
W4—O12	1.888 (10)	Na1—O21 ⁱ	2.378 (18)
W4—O13	1.725 (11)	Na1—O21	2.378 (18)
W4—O9	2.296 (10)	Na1—O16 ⁱ	2.494 (15)
W4—O14 ⁱ	1.940 (10)	Na1—O16	2.494 (15)
W4—O14	1.870 (10)	Na1—O16 ⁱⁱ	2.494 (15)
W1—O3	1.884 (11)	Na1—O22	2.76 (7)
W1—O11 ⁱ	1.909 (10)	O11—W1 ⁱⁱ	1.909 (10)
W1—O2 ⁱ	1.952 (10)	O2—W1 ⁱⁱ	1.952 (10)
W1—O2	1.924 (10)	O15—Dy1 ⁱⁱ	2.306 (10)
W1—O1	1.719 (11)	O15—C1	1.247 (19)
W1—O4	2.343 (10)	C10—C9	1.41 (3)
W2—O3	1.921 (11)	C10—C6	1.41 (2)
W2—O8	1.896 (11)	C10—N2	1.33 (2)
W2—O6	1.716 (10)	O17—C14	1.29 (2)
W2—O7	1.974 (11)	C9—C8	1.43 (3)
W2—O9	2.332 (9)	C9—C11	1.43 (3)
W2—O5	1.853 (10)	O16—C1	1.25 (2)
W3—O12	1.919 (11)	N1—C6	1.36 (2)
W3—O11	1.886 (11)	N1—C2	1.33 (2)
W3—O7	1.908 (10)	C1—C2	1.49 (2)
W3—O10	1.689 (11)	C4—C3	1.37 (3)
W3—O9	2.356 (9)	C4—C5	1.39 (3)
W3—O5 ⁱⁱ	1.938 (10)	C6—C5	1.41 (2)
Dy1—O15 ⁱ	2.306 (10)	C2—C3	1.40 (2)

Dy1—O13	2.375 (11)	C8—C7	1.34 (3)
Dy1—O17	2.329 (11)	O18—C14	1.26 (2)
Dy1—O20	2.379 (13)	C12—C13	1.44 (3)
Dy1—O16	2.374 (11)	C12—C11	1.34 (3)
Dy1—N1	2.469 (13)	C13—N2	1.32 (2)
Dy1—N2	2.482 (14)	C13—C14	1.48 (3)
Dy1—O19	2.364 (12)	C5—C7	1.45 (3)
Si1—O9	1.633 (10)	O4—W1 ⁱ	2.343 (10)
Si1—O9 ⁱⁱ	1.633 (10)	O4—W1 ⁱⁱ	2.343 (10)
Si1—O9 ⁱ	1.633 (10)	O14—W4 ⁱⁱ	1.940 (10)
Si1—O4	1.615 (19)	O5—W3 ⁱ	1.938 (10)

Symmetry code(s): (i) $-y+1, x-y+1, z$; (ii) $-x+y, -x+1, z$.

Table S3 Selected geometric parameters ($^{\circ}$) for **1**.

O8—W4—O9	73.7 (4)	O9 ⁱ —Si1—O9	109.2 (4)
O12—W4—O8	88.4 (4)	O9 ⁱⁱ —Si1—O9	109.2 (4)
O12—W4—O9	74.9 (4)	O4—Si1—O9 ⁱⁱ	109.8 (4)
O12—W4—O14 ⁱ	157.7 (5)	O4—Si1—O9	109.8 (4)
O13—W4—O8	100.6 (5)	O4—Si1—O9 ⁱ	109.8 (4)
O13—W4—O12	99.6 (5)	O21 ⁱⁱ —Na1—O21 ⁱ	86.1 (7)
O13—W4—O9	172.0 (4)	O21 ⁱⁱ —Na1—O21	86.1 (7)
O13—W4—O14 ⁱ	102.6 (5)	O21 ⁱ —Na1—O21	86.1 (7)
O13—W4—O14	100.6 (5)	O21—Na1—O16 ⁱⁱ	104.8 (4)
O14—W4—O8	158.4 (5)	O21—Na1—O16 ⁱ	162.2 (4)
O14 ⁱ —W4—O8	85.4 (4)	O21—Na1—O16	80.8 (5)
O14—W4—O12	92.6 (5)	O21 ⁱ —Na1—O16 ⁱⁱ	162.2 (4)
O14 ⁱ —W4—O9	82.8 (4)	O21 ⁱ —Na1—O16	104.8 (4)
O14—W4—O9	85.7 (4)	O21 ⁱ —Na1—O16 ⁱ	80.8 (5)
O14—W4—O14 ⁱ	85.6 (6)	O21 ⁱⁱ —Na1—O16	162.2 (4)

O3—W1—O11 ⁱ	86.9 (5)	O21 ⁱⁱ —Na1—O16 ⁱ	104.8 (4)
O3—W1—O2 ⁱ	158.6 (4)	O21 ⁱⁱ —Na1—O16 ⁱⁱ	80.8 (5)
O3—W1—O2	91.7 (4)	O21—Na1—O22	52.0 (5)
O3—W1—O4	85.1 (4)	O21 ⁱ —Na1—O22	52.0 (5)
O11 ⁱ —W1—O2 ⁱ	86.9 (4)	O21 ⁱⁱ —Na1—O22	52.0 (5)
O11 ⁱ —W1—O2	158.5 (5)	O16 ⁱ —Na1—O16	91.0 (6)
O11 ⁱ —W1—O4	84.1 (4)	O16 ⁱⁱ —Na1—O16	91.0 (6)
O2—W1—O2 ⁱ	86.7 (6)	O16 ⁱⁱ —Na1—O16 ⁱ	91.0 (6)
O2—W1—O4	74.4 (4)	O16 ⁱⁱ —Na1—O22	124.5 (4)
O2 ⁱ —W1—O4	73.9 (4)	O16 ⁱ —Na1—O22	124.5 (4)
O1—W1—O3	103.1 (5)	O16—Na1—O22	124.5 (4)
O1—W1—O11 ⁱ	101.7 (5)	W1—O3—W2	150.5 (6)
O1—W1—O2	99.5 (5)	W2—O8—W4	120.3 (5)
O1—W1—O2 ⁱ	98.2 (5)	W4—O12—W3	121.2 (5)
O1—W1—O4	170.1 (5)	W3—O11—W1 ⁱⁱ	151.5 (6)
O3—W2—O7	86.4 (5)	W3—O7—W2	120.0 (5)
O3—W2—O9	83.7 (4)	W1—O2—W1 ⁱⁱ	120.1 (6)
O8—W2—O3	157.4 (4)	C1—O15—Dy1 ⁱⁱ	141.1 (10)
O8—W2—O7	85.9 (4)	C6—C10—C9	119.4 (17)
O8—W2—O9	73.8 (4)	N2—C10—C9	123.5 (16)
O6—W2—O3	101.9 (5)	N2—C10—C6	117.1 (15)
O6—W2—O8	100.3 (5)	W4—O13—Dy1	158.6 (6)
O6—W2—O7	99.0 (5)	C14—O17—Dy1	125.2 (11)
O6—W2—O9	170.9 (4)	C10—C9—C8	118.1 (18)
O6—W2—O5	101.6 (5)	C10—C9—C11	116.9 (18)
O7—W2—O9	73.9 (4)	C11—C9—C8	125.0 (19)
O5—W2—O3	86.0 (5)	Dy1—O16—Na1	118.1 (5)
O5—W2—O8	93.8 (4)	C1—O16—Dy1	125.2 (10)
O5—W2—O7	159.1 (4)	C1—O16—Na1	116.6 (9)
O5—W2—O9	85.9 (4)	C6—N1—Dy1	120.7 (10)
O12—W3—O9	72.9 (4)	C2—N1—Dy1	119.8 (11)

O12—W3—O5 ⁱⁱ	85.8 (5)	C2—N1—C6	119.5 (13)
O11—W3—O12	157.5 (4)	W4—O9—W2	92.2 (3)
O11—W3—O7	93.3 (5)	W4—O9—W3	91.0 (3)
O11—W3—O9	85.6 (4)	W2—O9—W3	91.6 (3)
O11—W3—O5 ⁱⁱ	84.9 (4)	Si1—O9—W4	124.8 (6)
O7—W3—O12	87.5 (5)	Si1—O9—W2	123.7 (5)
O7—W3—O9	74.5 (4)	Si1—O9—W3	123.9 (5)
O7—W3—O5 ⁱⁱ	157.4 (4)	O15—C1—O16	124.7 (14)
O10—W3—O12	99.0 (5)	O15—C1—C2	119.4 (14)
O10—W3—O11	103.0 (5)	O16—C1—C2	116.0 (13)
O10—W3—O7	100.6 (5)	C3—C4—C5	120.2 (16)
O10—W3—O9	170.5 (5)	C10—C6—C5	121.8 (16)
O10—W3—O5 ⁱⁱ	101.7 (5)	N1—C6—C10	116.8 (15)
O5 ⁱⁱ —W3—O9	82.9 (4)	N1—C6—C5	121.3 (15)
O15 ⁱ —Dy1—O13	72.5 (4)	N1—C2—C1	114.1 (14)
O15 ⁱ —Dy1—O17	84.8 (4)	N1—C2—C3	122.0 (16)
O15 ⁱ —Dy1—O20	71.1 (5)	C3—C2—C1	123.9 (15)
O15 ⁱ —Dy1—O16	81.1 (4)	C7—C8—C9	123.0 (17)
O15 ⁱ —Dy1—N1	132.5 (4)	C11—C12—C13	120.2 (16)
O15 ⁱ —Dy1—N2	134.4 (4)	C12—C13—C14	124.9 (15)
O15 ⁱ —Dy1—O19	141.5 (4)	N2—C13—C12	121.1 (17)
O13—Dy1—O20	142.7 (4)	N2—C13—C14	114.0 (16)
O13—Dy1—N1	74.9 (4)	C4—C3—C2	119.0 (16)
O13—Dy1—N2	74.3 (4)	C10—N2—Dy1	121.3 (10)
O17—Dy1—O13	90.6 (4)	C13—N2—Dy1	119.5 (12)
O17—Dy1—O20	94.2 (5)	C13—N2—C10	119.2 (15)
O17—Dy1—O16	165.4 (4)	C4—C5—C6	117.9 (17)
O17—Dy1—N1	129.3 (5)	C4—C5—C7	124.8 (17)
O17—Dy1—N2	65.1 (5)	C6—C5—C7	117.3 (17)
O17—Dy1—O19	88.9 (5)	C12—C11—C9	119.1 (18)
O20—Dy1—N1	126.5 (5)	C8—C7—C5	120.3 (18)

O20—Dy1—N2	140.3 (4)	O17—C14—C13	116.1 (15)
O16—Dy1—O13	88.6 (4)	O18—C14—O17	124 (2)
O16—Dy1—O20	77.8 (4)	O18—C14—C13	120 (2)
O16—Dy1—N1	64.4 (4)	W1 ⁱ —O4—W1 ⁱⁱ	91.6 (5)
O16—Dy1—N2	128.4 (4)	W1—O4—W1 ⁱⁱ	91.6 (5)
N1—Dy1—N2	64.1 (4)	W1 ⁱ —O4—W1	91.6 (5)
O19—Dy1—O13	145.6 (4)	Si1—O4—W1 ⁱ	124.2 (3)
O19—Dy1—O20	71.5 (5)	Si1—O4—W1	124.2 (3)
O19—Dy1—O16	99.9 (5)	Si1—O4—W1 ⁱⁱ	124.2 (3)
O19—Dy1—N1	79.0 (4)	W4—O14—W4 ⁱⁱ	151.9 (6)
O19—Dy1—N2	74.4 (5)	W2—O5—W3 ⁱ	153.0 (6)
O9 ⁱ —Si1—O9 ⁱⁱ	109.2 (4)		

Symmetry code(s): (i) $-y+1, x-y+1, z$; (ii) $-x+y, -x+1, z$.

Table S4 Selected geometric parameters ($^{\circ}$) for **1**.

Dy1 ⁱ —O15—C1—O16	-87 (2)	O9 ⁱ —Si1—O9—W2	177.8 (4)
Dy1 ⁱ —O15—C1—C2	92.5 (19)	O9 ⁱⁱ —Si1—O9—W2	58.5 (10)
Dy1—O17—C14—O18	-178 (2)	O9 ⁱⁱ —Si1—O9—W3	177.8 (4)
Dy1—O17—C14—C13	1 (2)	O9 ⁱ —Si1—O9—W3	-62.9 (10)
Dy1—O16—C1—O15	-172.7 (11)	O9—Si1—O4—W1 ⁱⁱ	178.1 (3)
Dy1—O16—C1—C2	8.1 (18)	O9 ⁱⁱ —Si1—O4—W1	-61.9 (3)
Dy1—N1—C6—C10	0.5 (17)	O9 ⁱ —Si1—O4—W1	178.1 (3)
Dy1—N1—C6—C5	179.4 (12)	O9—Si1—O4—W1	58.1 (3)
Dy1—N1—C2—C1	-2.9 (16)	O9 ⁱⁱ —Si1—O4—W1 ⁱ	178.1 (3)
Dy1—N1—C2—C3	179.6 (12)	O9 ⁱ —Si1—O4—W1 ⁱ	58.1 (3)
Na1—O16—C1—O15	11 (2)	O9—Si1—O4—W1 ⁱ	-61.9 (3)
Na1—O16—C1—C2	-168.5 (10)	O9 ⁱ —Si1—O4—W1 ⁱⁱ	-61.9 (3)
O3—W2—O8—W4	3.7 (15)	O9 ⁱⁱ —Si1—O4—W1 ⁱⁱ	58.1 (3)
O3—W2—O5—W3 ⁱⁱ	-27.3 (13)	C1—C2—C3—C4	-177.1 (15)
O8—W4—O12—W3	72.3 (6)	C4—C5—C7—C8	178.6 (19)

O8—W4—O13—Dy1	145.2 (15)	C6—C10—C9—C8	−1 (2)
O8—W4—O14—W4 ⁱ	39 (2)	C6—C10—C9—C11	−178.3 (16)
O8—W2—O5—W3 ⁱⁱ	130.1 (13)	C6—C10—N2—Dy1	−1.1 (19)
O12—W4—O13—Dy1	55.1 (16)	C6—C10—N2—C13	178.4 (14)
O12—W4—O14—W4 ⁱ	131.1 (14)	C6—N1—C2—C1	178.0 (12)
O12—W3—O11—W1 ⁱ	40 (2)	C6—N1—C2—C3	0 (2)
O11 ⁱⁱ —W1—O3—W2	−24.7 (12)	C6—C5—C7—C8	0 (3)
O6—W2—O8—W4	172.6 (6)	C2—N1—C6—C10	179.7 (13)
O6—W2—O5—W3 ⁱⁱ	−128.6 (13)	C2—N1—C6—C5	−1 (2)
O7—W2—O8—W4	74.2 (6)	C8—C9—C11—C12	−178 (2)
O7—W2—O5—W3 ⁱⁱ	42 (2)	C12—C13—N2—Dy1	−179.8 (13)
O7—W3—O11—W1 ⁱ	130.9 (13)	C12—C13—N2—C10	1 (2)
O2—W1—O3—W2	133.9 (13)	C12—C13—C14—O17	179.3 (18)
O2 ⁱⁱ —W1—O3—W2	49 (2)	C12—C13—C14—O18	−2 (3)
O1—W1—O3—W2	−125.9 (13)	C13—C12—C11—C9	0 (3)
O15—C1—C2—N1	177.7 (13)	C3—C4—C5—C6	−1 (3)
O15—C1—C2—C3	−5 (2)	C3—C4—C5—C7	−180.0 (18)
O10—W3—O11—W1 ⁱ	−127.4 (13)	N2—C10—C9—C8	178.6 (16)
C10—C9—C8—C7	0 (3)	N2—C10—C9—C11	1 (3)
C10—C9—C11—C12	−1 (3)	N2—C10—C6—N1	0 (2)
C10—C6—C5—C4	−179.3 (15)	N2—C10—C6—C5	−178.5 (15)
C10—C6—C5—C7	0 (2)	N2—C13—C14—O17	−1 (3)
O13—W4—O12—W3	172.8 (6)	N2—C13—C14—O18	178 (2)
O13—W4—O14—W4 ⁱ	−128.6 (14)	C5—C4—C3—C2	0 (3)
C9—C10—C6—N1	179.9 (14)	C11—C9—C8—C7	177.5 (19)
C9—C10—C6—C5	1 (2)	C11—C12—C13—N2	0 (3)
C9—C10—N2—Dy1	179.4 (12)	C11—C12—C13—C14	179.6 (19)
C9—C10—N2—C13	−1 (2)	C14—C13—N2—Dy1	0 (2)
C9—C8—C7—C5	0 (3)	C14—C13—N2—C10	−179.3 (15)
O16—C1—C2—N1	−3.0 (19)	O4—W1—O3—W2	59.7 (12)
O16—C1—C2—C3	174.5 (15)	O4—Si1—O9—W4	176.8 (4)

N1—C6—C5—C4	2 (2)	O4—Si1—O9—W2	-61.9 (6)
N1—C6—C5—C7	-179.3 (15)	O4—Si1—O9—W3	57.4 (6)
N1—C2—C3—C4	0 (3)	O14—W4—O12—W3	-86.1 (7)
O9—W4—O12—W3	-1.3 (5)	O14 ⁱⁱ —W4—O12—W3	-1.2 (15)
O9—W4—O14—W4 ⁱ	56.5 (13)	O14 ⁱⁱ —W4—O13—Dy1	-127.2 (15)
O9—W2—O8—W4	-0.3 (5)	O14—W4—O13—Dy1	-39.4 (16)
O9—W2—O5—W3 ⁱⁱ	56.7 (13)	O14 ⁱⁱ —W4—O14—W4 ⁱ	-26.6 (16)
O9—W3—O11—W1 ⁱ	56.8 (13)	O5—W2—O8—W4	-84.9 (6)
O9 ⁱⁱ —Si1—O9—W4	-62.8 (6)	O5 ⁱ —W3—O11—W1 ⁱ	-26.5 (13)
O9 ⁱ —Si1—O9—W4	56.4 (7)		

Symmetry code(s): (i) $-x+y, -x+1, z$; (ii) $-y+1, x-y+1, z$.

Table S5 Experimental details for 2.

Crystal data	
Chemical formula	C ₂₁ H ₃₅ N ₃ NaO ₆₈ Pr ₃ SiW ₁₂ ·9(H ₂ O)·3O
M _r	4307.67
Crystal system, space group	Trigonal, R3
Temperature (K)	100
a, c (Å)	18.119 (3), 21.078 (3)
V (Å ³)	5993 (2)
Z	3
Radiation type	Mo Kα
μ (mm ⁻¹)	19.14
Crystal size (mm)	0.24 × 0.13 × 0.12
Data collection	
Diffractometer	Bruker Smart APEX CCD
Absorption correction	Multi-scan TWINABS (Sheldrick, 2009)
T _{min} , T _{max}	0.09, 0.22
No. of measured, independent and observed [I > 2σ(I)] reflections	74256, 7142, 6106
R _{int}	0.085
(sin θ/λ) _{max} (Å ⁻¹)	0.686
Refinement	
R[F ² > 2σ(F ²)], wR(F ²), S	0.030, 0.065, 1.00
No. of reflections	7142
No. of parameters	385
No. of restraints	241
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.97, -2.07
Absolute structure	Flack x determined using 2688 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons <i>et al.</i> , 2013).
Absolute structure parameter	0.006 (7)

Computer programs: APEX3 (Bruker, 2016), SAINT (Bruker, 2016), SHELXT (Sheldrick, 2015a), SHELXL-2018/1 (Sheldrick, 2015b), DIAMOND (Brandenburg & Putz, 2012), SHELXTL (Bruker, 2016).

Table S6 Selected geometric parameters (\AA) for **2**.

Na1—O2 ⁱ	2.333 (13)	Si1—O22	1.629 (9)
Na1—O2 ⁱⁱ	2.333 (13)	Si1—O22 ⁱ	1.629 (9)
Na1—O2	2.333 (13)	Si1—O22 ⁱⁱ	1.629 (9)
Na1—O26	2.53 (5)	Si1—O23	1.633 (16)
Na1—O26 ⁱⁱ	2.53 (5)	O1—C1	1.264 (19)
Na1—O26 ⁱ	2.53 (5)	O2—C1	1.282 (19)
Na1—Pr1 ⁱ	4.137 (4)	O3—C7	1.276 (17)
Na1—Pr1	4.137 (4)	O4—C7	1.247 (18)
Na1—Pr1 ⁱⁱ	4.137 (4)	O5—C4	1.36 (2)
W1—O10	1.724 (9)	O5—H5	0.8399
W1—O14	1.890 (9)	O6—H6A	0.8699
W1—O15	1.906 (9)	O6—H6B	0.8701
W1—O16	1.927 (10)	O7—H7A	0.8699
W1—O14 ⁱⁱ	1.938 (8)	O7—H7B	0.8701
W1—O22 ⁱ	2.320 (8)	O8—H8A	0.8701
W2—O11	1.714 (10)	O8—H8B	0.8701
W2—O17	1.864 (10)	O9—H9A	0.8700
W2—O18	1.911 (9)	O9—H9B	0.8701
W2—O16	1.911 (9)	N1—C2	1.318 (18)
W2—O21 ⁱ	1.969 (9)	N1—C6	1.340 (19)
W2—O22 ⁱ	2.321 (8)	C1—C2	1.52 (2)
W3—O13	1.708 (11)	C2—C3	1.39 (2)
W3—O21	1.879 (9)	C3—C4	1.38 (2)
W3—O19	1.884 (10)	C3—H3	0.9500
W3—O17	1.936 (10)	C4—C5	1.37 (2)
W3—O15 ⁱⁱ	1.945 (9)	C5—C6	1.40 (2)
W3—O22	2.367 (9)	C5—H5A	0.9500
W4—O12	1.693 (10)	C6—C7	1.51 (2)
W4—O18	1.897 (10)	O24—H24A	0.8700

W4—O20 ⁱ	1.919 (10)	O24—H24B	0.8700
W4—O20	1.922 (10)	O26—H26A	0.8692
W4—O19	1.926 (10)	O26—H26B	0.8697
W4—O23	2.357 (8)	O27—H27A	0.8700
Pr1—O1	2.407 (11)	O27—H27B	0.8700
Pr1—O3 ⁱⁱ	2.468 (10)	O28—H28A	0.8699
Pr1—O2 ⁱⁱ	2.477 (11)	O28—H28B	0.8702
Pr1—O6	2.496 (13)	O29—H29A	0.8701
Pr1—O9	2.509 (12)	O29—H29B	0.8698
Pr1—O10	2.554 (9)	O29A—H29C	0.8702
Pr1—N1 ⁱⁱ	2.567 (12)	O29A—H29D	0.8699
Pr1—O8	2.567 (11)	O29B—H29E	0.8698
Pr1—O7	2.593 (12)	O29B—H29F	0.8701

Symmetry code(s): (i) $-y+1, x-y+1, z$; (ii) $-x+y, -x+1, z$.

Table S7 Selected geometric parameters ($^{\circ}$) for **2**.

O10—W1—O14	101.6 (4)	N1 ⁱⁱ —Pr1—Na1	93.1 (3)
O10—W1—O14 ⁱⁱ	102.5 (4)	C1—O1—Pr1	148.2 (10)
O10—W1—O15	98.3 (4)	Na1—O2—Pr1 ⁱ	118.7 (5)
O10—W1—O16	99.4 (4)	C1—O2—Pr1 ⁱ	122.8 (10)
O10—W1—O22 ⁱ	169.9 (4)	C1—O2—Na1	118.2 (10)
O14—W1—O14 ⁱⁱ	86.4 (5)	C7—O3—Pr1 ⁱ	126.1 (9)
O14—W1—O15	92.6 (4)	C4—O5—H5	108.1
O14—W1—O16	158.7 (4)	Pr1—O6—H6B	109.3
O14—W1—O22 ⁱ	86.3 (3)	Pr1—O6—H6A	109.1
O14 ⁱⁱ —W1—O22 ⁱ	84.0 (3)	H6A—O6—H6B	109.5
O15—W1—O14 ⁱⁱ	159.0 (4)	Pr1—O7—H7B	109.5
O15—W1—O16	87.9 (4)	Pr1—O7—H7A	109.0
O15—W1—O22 ⁱ	75.0 (3)	H7A—O7—H7B	109.5
O16—W1—O14 ⁱⁱ	85.6 (4)	Pr1—O8—H8B	109.2
O16—W1—O22 ⁱ	73.2 (3)	Pr1—O8—H8A	109.5
O11—W2—O16	101.3 (5)	H8A—O8—H8B	109.5

O11—W2—O17	101.7 (4)	Pr1—O9—H9B	109.3
O11—W2—O18	100.7 (5)	Pr1—O9—H9A	109.4
O11—W2—O21 ⁱ	99.9 (4)	H9A—O9—H9B	109.5
O11—W2—O22 ⁱ	171.1 (4)	W1—O10—Pr1	165.8 (5)
O16—W2—O21 ⁱ	86.1 (4)	W1—O14—W1 ⁱ	150.4 (5)
O16—W2—O22 ⁱ	73.4 (4)	W1—O15—W3 ⁱ	120.7 (5)
O17—W2—O16	92.3 (4)	W2—O16—W1	121.2 (5)
O17—W2—O18	86.8 (4)	W2—O17—W3	151.8 (5)
O17—W2—O21 ⁱ	158.2 (4)	W4—O18—W2	151.4 (6)
O17—W2—O22 ⁱ	85.9 (4)	W3—O19—W4	153.0 (5)
O18—W2—O16	157.7 (4)	W4 ⁱⁱ —O20—W4	121.9 (5)
O18—W2—O21 ⁱ	86.6 (4)	W3—O21—W2 ⁱⁱ	122.2 (5)
O18—W2—O22 ⁱ	84.3 (4)	W1 ⁱⁱ —O22—W2 ⁱⁱ	92.2 (3)
O21 ⁱ —W2—O22 ⁱ	72.8 (3)	W1 ⁱⁱ —O22—W3	91.1 (3)
O13—W3—O15 ⁱⁱ	98.8 (4)	W2 ⁱⁱ —O22—W3	91.9 (3)
O13—W3—O17	102.4 (4)	Si1—O22—W1 ⁱⁱ	123.8 (5)
O13—W3—O19	103.0 (4)	Si1—O22—W2 ⁱⁱ	123.7 (4)
O13—W3—O21	102.2 (5)	Si1—O22—W3	124.6 (5)
O13—W3—O22	170.7 (4)	W4—O23—W4 ⁱⁱ	90.9 (4)
O15 ⁱⁱ —W3—O22	73.2 (3)	W4—O23—W4 ⁱ	90.9 (4)
O17—W3—O15 ⁱⁱ	85.3 (4)	W4 ⁱⁱ —O23—W4 ⁱ	90.9 (4)
O17—W3—O22	82.0 (3)	Si1—O23—W4	124.7 (3)
O19—W3—O15 ⁱⁱ	157.6 (4)	Si1—O23—W4 ⁱⁱ	124.7 (3)
O19—W3—O17	85.0 (4)	Si1—O23—W4 ⁱ	124.7 (3)
O19—W3—O22	85.5 (4)	H24A—O24—H24B	109.5
O21—W3—O15 ⁱⁱ	87.6 (4)	Na1—O26—H26B	120.6
O21—W3—O17	155.2 (4)	Na1—O26—H26A	101.6
O21—W3—O19	92.8 (4)	H26A—O26—H26B	91.2
O21—W3—O22	73.2 (3)	H27A—O27—H27B	109.5
O12—W4—O18	101.7 (5)	H28A—O28—H28B	109.5
O12—W4—O19	101.6 (4)	H29E—O29B—H29F	109.5

O12—W4—O20 ⁱ	100.7 (5)	H29C—O29A—H29D	109.5
O12—W4—O20	100.9 (5)	H29A—O29—H29B	109.5
O12—W4—O23	171.9 (5)	Pr1 ⁱ —Na1—Pr1	108.75 (14)
O18—W4—O19	84.7 (4)	Pr1 ⁱ —Na1—Pr1 ⁱⁱ	108.75 (14)
O18—W4—O20 ⁱ	90.7 (4)	Pr1—Na1—Pr1 ⁱⁱ	108.75 (14)
O18—W4—O20	157.2 (4)	O2 ⁱ —Na1—Pr1 ⁱ	77.1 (3)
O18—W4—O23	84.4 (4)	O2 ⁱⁱ —Na1—Pr1 ⁱ	121.4 (4)
O19—W4—O23	84.2 (4)	O2—Na1—Pr1 ⁱ	31.7 (3)
O20 ⁱ —W4—O19	157.7 (4)	O2 ⁱ —Na1—Pr1	121.4 (4)
O20—W4—O19	87.2 (4)	O2 ⁱⁱ —Na1—Pr1	31.7 (3)
O20 ⁱ —W4—O20	88.7 (6)	O2—Na1—Pr1	77.1 (3)
O20 ⁱ —W4—O23	73.6 (4)	O2 ⁱ —Na1—Pr1 ⁱⁱ	31.7 (3)
O20—W4—O23	73.6 (4)	O2 ⁱⁱ —Na1—Pr1 ⁱⁱ	77.1 (3)
O22—Si1—O22 ⁱ	110.0 (4)	O2—Na1—Pr1 ⁱⁱ	121.4 (4)
O22—Si1—O22 ⁱⁱ	110.0 (4)	O2 ⁱ —Na1—O2 ⁱⁱ	94.0 (5)
O22 ⁱ —Si1—O22 ⁱⁱ	110.0 (4)	O2 ⁱ —Na1—O2	94.0 (5)
O22—Si1—O23	108.9 (4)	O2 ⁱⁱ —Na1—O2	94.0 (5)
O22 ⁱ —Si1—O23	108.9 (4)	O2 ⁱ —Na1—O26	71.8 (14)
O22 ⁱⁱ —Si1—O23	108.9 (4)	O2 ⁱⁱ —Na1—O26	151.8 (13)
O1—Pr1—O2 ⁱⁱ	75.1 (4)	O2—Na1—O26	110.8 (12)
O1—Pr1—O3 ⁱⁱ	131.7 (4)	O2 ⁱ —Na1—O26 ⁱⁱ	151.8 (13)
O1—Pr1—O6	73.0 (4)	O2 ⁱⁱ —Na1—O26 ⁱⁱ	110.8 (12)
O1—Pr1—O7	125.0 (4)	O2—Na1—O26 ⁱⁱ	71.8 (14)
O1—Pr1—O8	125.9 (3)	O2 ⁱ —Na1—O26 ⁱ	110.8 (12)
O1—Pr1—O9	69.7 (4)	O2 ⁱⁱ —Na1—O26 ⁱ	71.8 (14)
O1—Pr1—O10	68.9 (3)	O2—Na1—O26 ⁱ	151.8 (13)
O1—Pr1—Na1	51.4 (3)	O26—Na1—Pr1 ⁱ	80.0 (12)
O1—Pr1—N1 ⁱⁱ	124.3 (4)	O26 ⁱⁱ —Na1—Pr1 ⁱ	78.6 (14)
O2 ⁱⁱ —Pr1—O6	85.6 (4)	O26 ⁱ —Na1—Pr1 ⁱ	165.0 (13)
O2 ⁱⁱ —Pr1—O7	66.6 (4)	O26—Na1—Pr1	165.0 (13)
O2 ⁱⁱ —Pr1—O8	139.6 (4)	O26 ⁱⁱ —Na1—Pr1	80.0 (12)

O2 ⁱⁱ —Pr1—O9	144.2 (4)	O26 ⁱ —Na1—Pr1	78.6 (14)
O2 ⁱⁱ —Pr1—O10	76.6 (3)	O26—Na1—Pr1 ⁱⁱ	78.6 (14)
O2 ⁱⁱ —Pr1—Na1	29.7 (3)	O26 ⁱⁱ —Na1—Pr1 ⁱⁱ	165.0 (13)
O2 ⁱⁱ —Pr1—N1 ⁱⁱ	63.5 (4)	O26 ⁱ —Na1—Pr1 ⁱⁱ	80.0 (12)
O3 ⁱⁱ —Pr1—O2 ⁱⁱ	125.7 (4)	O26—Na1—O26 ⁱⁱ	90.2 (18)
O3 ⁱⁱ —Pr1—O6	141.3 (4)	O26—Na1—O26 ⁱ	90.2 (18)
O3 ⁱⁱ —Pr1—O7	102.9 (4)	O26 ⁱⁱ —Na1—O26 ⁱ	90.2 (18)
O3 ⁱⁱ —Pr1—O8	69.6 (4)	C2—N1—Pr1 ⁱ	120.3 (10)
O3 ⁱⁱ —Pr1—O9	76.4 (4)	C2—N1—C6	119.9 (13)
O3 ⁱⁱ —Pr1—O10	74.7 (3)	C6—N1—Pr1 ⁱ	119.6 (10)
O3 ⁱⁱ —Pr1—Na1	153.4 (3)	O1—C1—O2	122.7 (15)
O3 ⁱⁱ —Pr1—N1 ⁱⁱ	63.0 (4)	O1—C1—C2	120.6 (15)
O6—Pr1—O7	66.3 (5)	O2—C1—C2	116.7 (15)
O6—Pr1—O8	71.8 (4)	N1—C2—C1	114.5 (14)
O6—Pr1—O9	90.4 (4)	N1—C2—C3	123.9 (14)
O6—Pr1—O10	140.9 (4)	C3—C2—C1	121.6 (14)
O6—Pr1—Na1	63.7 (4)	C2—C3—H3	121.7
O6—Pr1—N1 ⁱⁱ	134.0 (4)	C4—C3—H3	121.7
O7—Pr1—Na1	77.4 (3)	C4—C3—C2	116.6 (15)
O8—Pr1—O7	73.6 (4)	O5—C4—C3	120.5 (16)
O8—Pr1—Na1	133.7 (3)	O5—C4—C5	119.5 (15)
O9—Pr1—O7	142.2 (4)	C5—C4—C3	119.8 (15)
O9—Pr1—O8	70.8 (4)	C4—C5—H5A	119.8
O9—Pr1—O10	84.6 (3)	C4—C5—C6	120.5 (14)
O9—Pr1—Na1	119.8 (3)	C6—C5—H5A	119.8
O9—Pr1—N1 ⁱⁱ	134.7 (4)	N1—C6—C5	119.3 (14)
O10—Pr1—O7	132.4 (4)	N1—C6—C7	115.9 (13)
O10—Pr1—O8	140.3 (3)	C5—C6—C7	124.7 (13)
O10—Pr1—Na1	85.4 (3)	O3—C7—C6	115.0 (13)
O10—Pr1—N1 ⁱⁱ	66.7 (3)	O4—C7—O3	126.4 (14)
N1 ⁱⁱ —Pr1—O7	70.2 (4)	O4—C7—C6	118.6 (13)

N1ⁱⁱ—Pr1—O8 109.7 (4)

Symmetry code(s): (i) $-y+1, x-y+1, z$; (ii) $-x+y, -x+1, z$.

Table S8 Selected geometric parameters ($^{\circ}$) for **2**.

O14—W1—O10—Pr1	−127 (2)	O22 ⁱ —Si1—O23—W4	−58.5 (3)
O15—W1—O10—Pr1	138 (2)	O22 ⁱⁱ —Si1—O23—W4	−178.5 (3)
O16—W1—O10—Pr1	49 (2)	O22—Si1—O23—W4 ⁱⁱ	−58.5 (3)
O14 ⁱⁱ —W1—O10—Pr1	−39 (2)	O22 ⁱ —Si1—O23—W4 ⁱⁱ	−178.5 (3)
O22 ⁱ —W1—O10—Pr1	91 (3)	O22 ⁱⁱ —Si1—O23—W4 ⁱⁱ	61.5 (3)
O10—W1—O14—W1 ⁱ	131.2 (10)	O22—Si1—O23—W4 ⁱ	−178.5 (3)
O15—W1—O14—W1 ⁱ	−129.8 (10)	O22 ⁱ —Si1—O23—W4 ⁱ	61.5 (3)
O16—W1—O14—W1 ⁱ	−39.1 (17)	O22 ⁱⁱ —Si1—O23—W4 ⁱ	−58.5 (3)
O14 ⁱⁱ —W1—O14—W1 ⁱ	29.2 (11)	Pr1—O1—C1—O2	−78 (3)
O22 ⁱ —W1—O14—W1 ⁱ	−55.0 (10)	Pr1—O1—C1—C2	103 (2)
O11—W2—O17—W3	123.6 (11)	Na1—O2—C1—O1	13 (2)
O18—W2—O17—W3	23.4 (11)	Pr1 ⁱ —O2—C1—O1	−160.3 (11)
O16—W2—O17—W3	−134.3 (11)	Na1—O2—C1—C2	−168.4 (10)
O21 ⁱ —W2—O17—W3	−49.0 (18)	Pr1 ⁱ —O2—C1—C2	18.4 (18)
O22 ⁱ —W2—O17—W3	−61.1 (11)	C6—N1—C2—C3	1 (2)
O12—W4—O18—W2	127.5 (12)	Pr1 ⁱ —N1—C2—C3	−174.0 (11)
O20 ⁱ —W4—O18—W2	−131.4 (12)	C6—N1—C2—C1	178.7 (12)
O20—W4—O18—W2	−42.9 (19)	Pr1 ⁱ —N1—C2—C1	3.9 (16)
O19—W4—O18—W2	26.7 (12)	O1—C1—C2—N1	164.6 (13)
O23—W4—O18—W2	−57.9 (11)	O2—C1—C2—N1	−14.1 (19)
O13—W3—O19—W4	130.1 (13)	O1—C1—C2—C3	−17 (2)
O21—W3—O19—W4	−126.7 (13)	O2—C1—C2—C3	163.8 (14)
O17—W3—O19—W4	28.6 (12)	N1—C2—C3—C4	−1 (2)
O15 ⁱⁱ —W3—O19—W4	−36 (2)	C1—C2—C3—C4	−178.3 (13)
O22—W3—O19—W4	−53.8 (12)	C2—C3—C4—O5	176.9 (13)
O13—W3—O21—W2 ⁱⁱ	−171.8 (5)	C2—C3—C4—C5	1 (2)
O19—W3—O21—W2 ⁱⁱ	84.3 (6)	O5—C4—C5—C6	−177.3 (14)
O17—W3—O21—W2 ⁱⁱ	0.2 (13)	C3—C4—C5—C6	−1 (2)

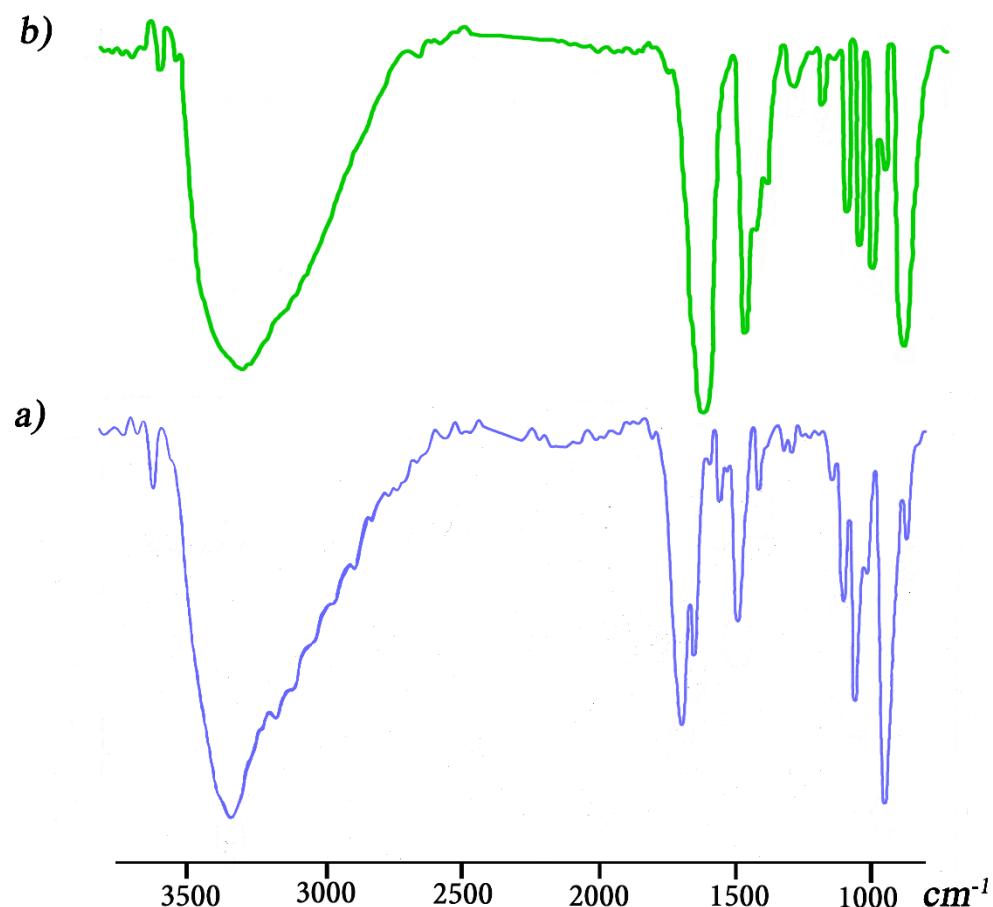
O15 ⁱⁱ —W3—O21—W2 ⁱⁱ	−73.3 (5)	C2—N1—C6—C5	−1 (2)
O22—W3—O21—W2 ⁱⁱ	−0.1 (4)	Pr1 ⁱ —N1—C6—C5	173.7 (10)
O22 ⁱ —Si1—O22—W1 ⁱⁱ	−58.1 (6)	C2—N1—C6—C7	−176.7 (12)
O22 ⁱⁱ —Si1—O22—W1 ⁱⁱ	63.2 (6)	Pr1 ⁱ —N1—C6—C7	−1.9 (15)
O23—Si1—O22—W1 ⁱⁱ	−177.4 (3)	C4—C5—C6—N1	1 (2)
O22 ⁱ —Si1—O22—W2 ⁱⁱ	−178.2 (3)	C4—C5—C6—C7	176.4 (13)
O22 ⁱⁱ —Si1—O22—W2 ⁱⁱ	−56.9 (9)	Pr1 ⁱ —O3—C7—O4	173.4 (11)
O23—Si1—O22—W2 ⁱⁱ	62.4 (5)	Pr1 ⁱ —O3—C7—C6	−9.0 (16)
O22 ⁱ —Si1—O22—W3	61.3 (9)	N1—C6—C7—O4	−175.5 (13)
O22 ⁱⁱ —Si1—O22—W3	−177.5 (4)	C5—C6—C7—O4	9 (2)
O23—Si1—O22—W3	−58.1 (5)	N1—C6—C7—O3	6.6 (17)
O22—Si1—O23—W4	61.5 (3)	C5—C6—C7—O3	−168.6 (13)

Symmetry code(s): (i) $-y+1, x-y+1, z$; (ii) $-x+y, -x+1, z$.

Table S9 Selected hydrogen-bond parameters for **2**.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H (Å)	H··· <i>A</i> (Å)	<i>D</i> ··· <i>A</i> (Å)	<i>D</i> —H··· <i>A</i> (°)
O6—H6A···O26 ⁱ	0.87	2.12	2.91 (6)	151
O7—H7A···O11 ⁱⁱ	0.87	2.36	3.084 (17)	141
O7—H7A···O21 ⁱⁱⁱ	0.87	2.29	2.988 (18)	138
O7—H7B···O4 ^{iv}	0.87	2.16	2.956 (19)	152
O8—H8A···O12 ^v	0.87	2.17	2.929 (15)	146
O8—H8B···O4 ^{iv}	0.87	2.40	3.103 (17)	138
O9—H9A···O29B ⁱ	0.87	2.50	3.09 (4)	123
C5—H5A···O29	0.95	2.64	3.28 (3)	126
O24—H24A···O11 ^{vi}	0.87	2.48	3.109 (19)	130
O26—H26A···O7 ⁱ	0.87	2.23	3.10 (6)	180
O26—H26B···O27 ^{vii}	0.87	1.97	2.84 (6)	179
O27—H27A···O24	0.87	2.42	2.94 (3)	120
O27—H27B···O29B	0.87	1.79	2.51 (4)	138.4
O28—H28A···O7	0.87	2.09	2.75 (3)	132
O29—H29A···O11 ^{viii}	0.87	2.59	3.18 (3)	127
O29A—H29C···O5 ^{ix}	0.87	1.96	2.83 (4)	180
O29A—H29D···O24 ^x	0.87	1.91	2.78 (4)	175
O29B—H29F···O12 ^{xi}	0.87	2.27	3.03 (4)	146

Symmetry code(s): (i) $-x+y, -x+1, z$; (ii) $-y+1/3, x-y+2/3, z-1/3$; (iii) $-x+y-2/3, -x+2/3, z-1/3$; (iv) $x-2/3, y-1/3, z-1/3$; (v) $-x+y-1/3, -x+1/3, z-2/3$; (vi) $-x+y+1/3, -x+2/3, z-1/3$; (vii) $-x+y+1/3, -x+5/3, z-1/3$; (viii) $-y+1, x-y+1, z$; (ix) $x+1/3, y+2/3, z-1/3$; (x) $-x+y+1, -x+2, z$; (xi) $x+2/3, y+1/3, z-2/3$.

S3. IR spectroscopy**Figure S5** IR spectra of a) hybrids **1** and b) **2**

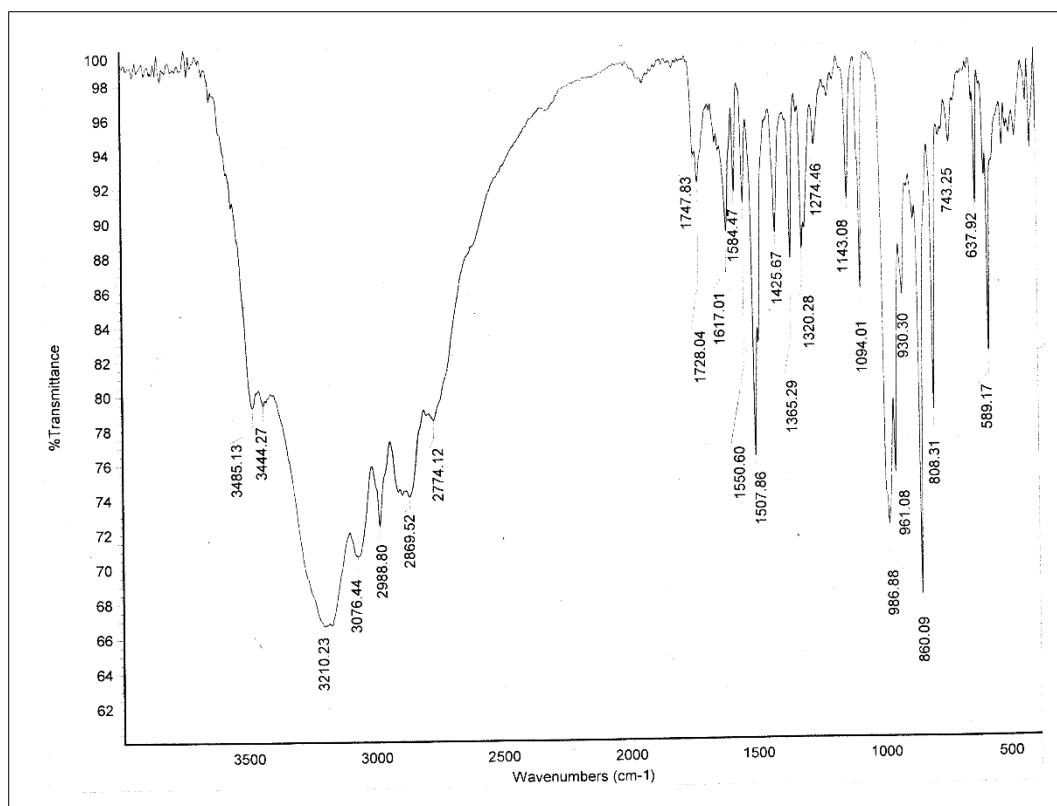


Figure S6 FT-IR spectra of PDOX.

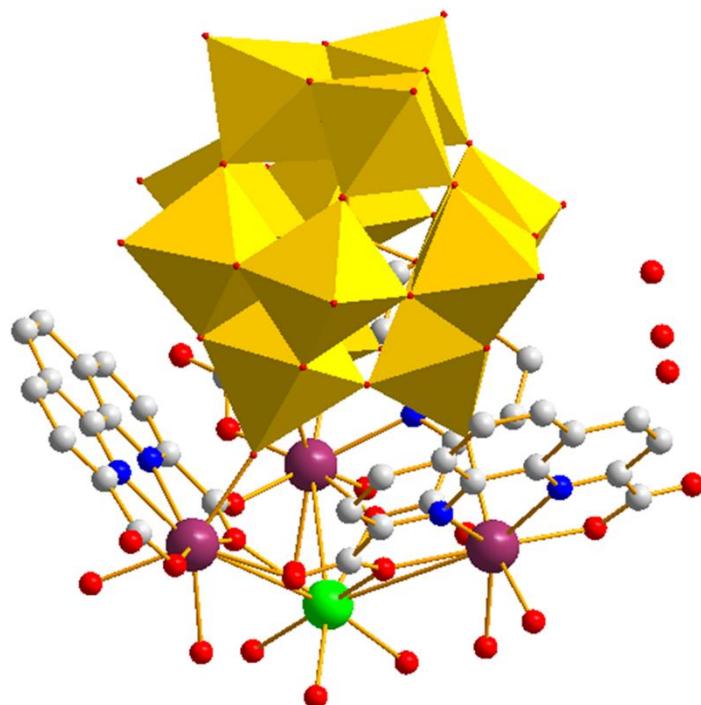


Figure S7 View of the molecular structure of **1**; hydrogen atoms omitted for more clarity (Dy, purple; O, red; W, yellow; Na, green; N, blue; C, gray).

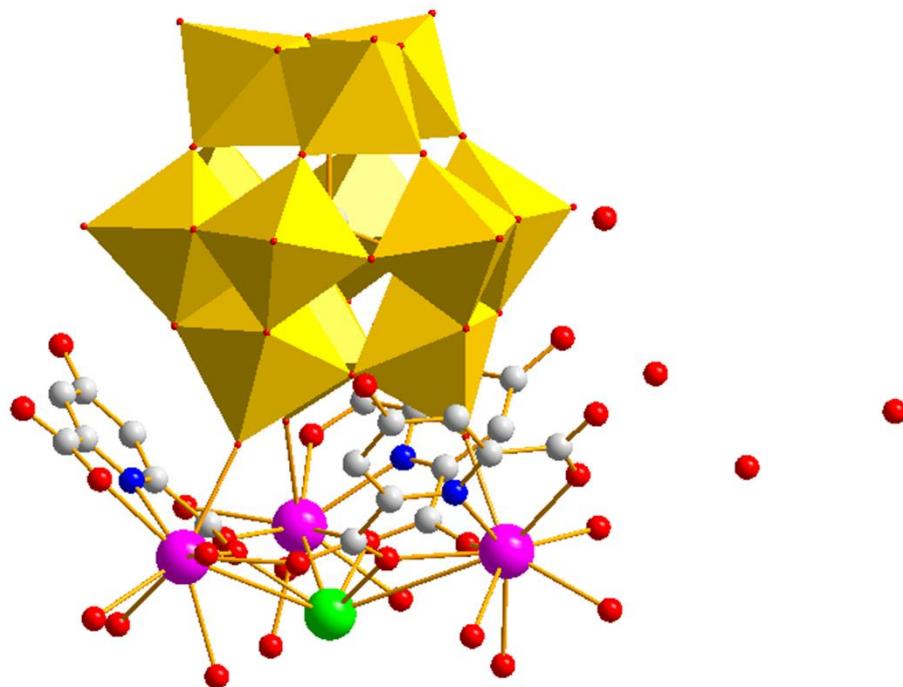


Figure S8 View of the molecular structure of **2**; hydrogen atoms omitted for more clarity (Pr, magenta; O, red; W, yellow; Na, green; N, blue; C, gray).