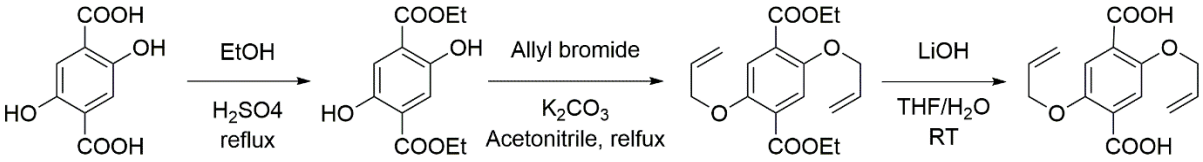
A reversible pressure-induced bond rearrangement of flexible lanthanide 2,5-bis(allyloxy)terephthalate coordination polymer networks.

L. R. Hunter,*[a] J. D. Sellars [b,c] and M. R. Probert [a*]

a. Department of Chemistry, School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK
b. Biosciences Institute, Faculty of Medical Sciences, Newcastle University, Newcastle upon Tyne NE2 4HH, UK
c. School of Pharmacy, Faculty of Medical Sciences, King George VI Building, Newcastle upon Tyne NE1 7RU, UK a-

Supplementary Information

Synthesis of 2,5-bis(allyloxy)terephthalic acid



Synthesis of diethyl 2,5-dihydroxyterephthalate

To a solution of 2,5-dihydroxyterephalic acid (1 g, 5 mmol) in ethanol (20 mL) 5-10 drops of c. H_2SO_4 were added carefully. The solution was stirred and heated under reflux for 12h. When cooling the solution, a yellow solid precipitated, that was collected by filtration and washed with ethanol to afford the title compound as a bright yellow solid (1.1 g, 88 %); δ_H (300 MHz, $CDCl_3$) 10.14 (2H, s, Ar-O*H*), 7.51 (2H, s, Ar-*H*), 4.43 (4H, q, *J* 7, Ar-$CO_2CH_2CH_3$), 1.43 (6H, t, *J* 7, Ar-$CO_2CH_2CH_3$); all data agrees with that given in the literature.[1]

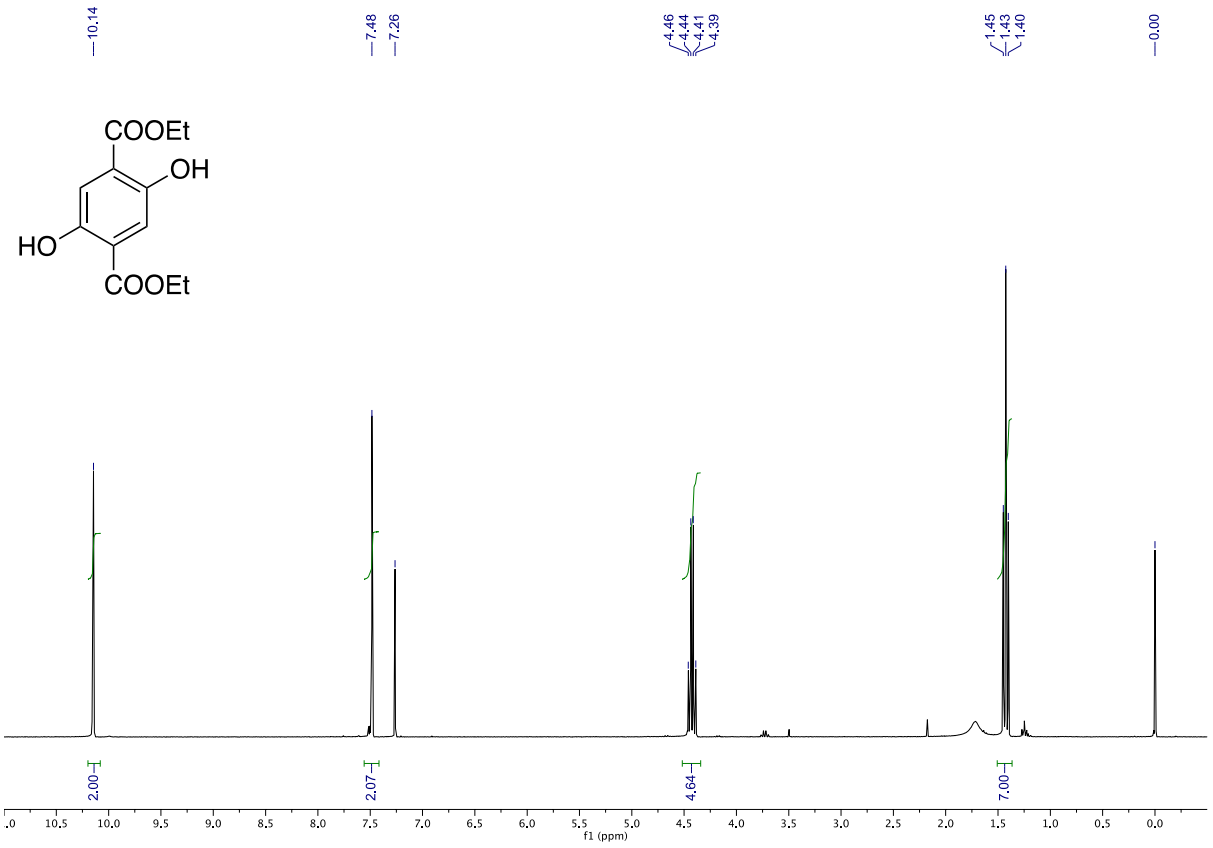
Synthesis of diethyl 2,5-bis(allyloxy)terephthalate

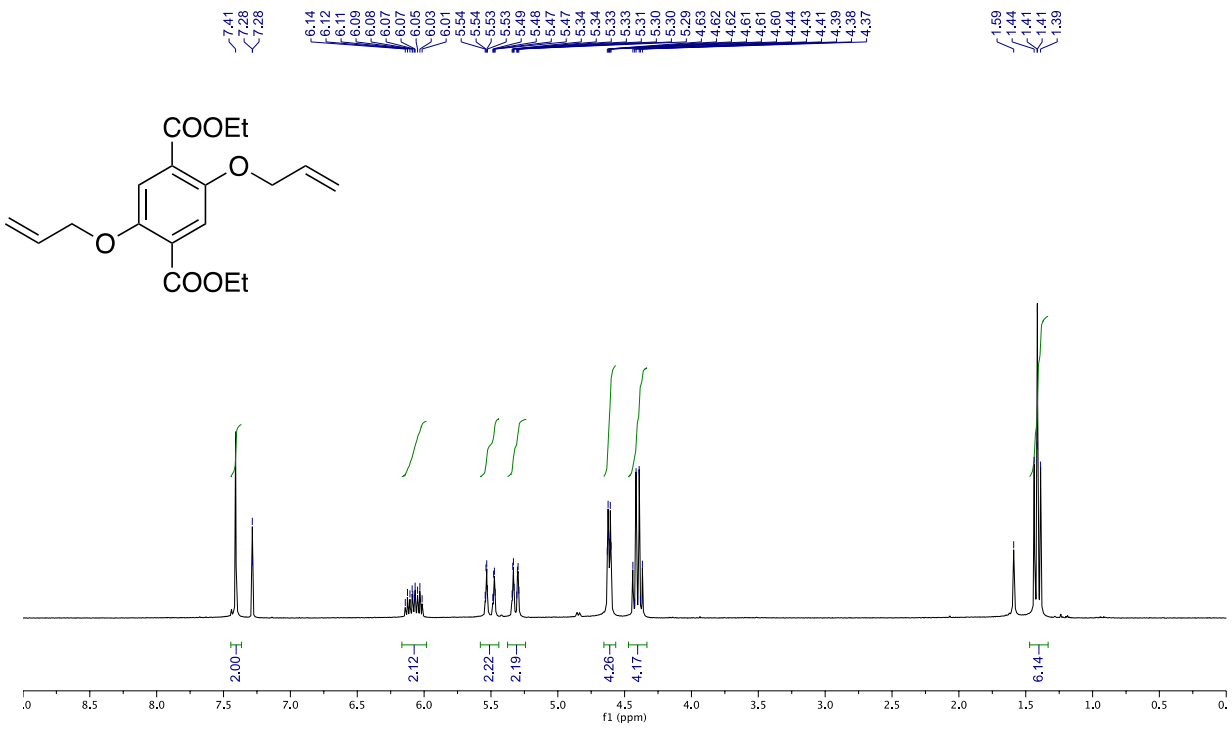
Allyl bromide (3 mL, 18 mmol), diethyl 2,5-dihydroxyterephthalate (0.5 g, 2 mmol) and potassium carbonate (1 g, 8 mmol) were added to acetonitrile (10 mL) and refluxed for 12h under nitrogen. Excess solvent was removed under vacuum and the remaining residue diluted with water before extraction into ethyl acetate. Organics were dried with $MgSO_4$ and concentrated to afford a crude product as pale orange waxy residue. The crude product was passed through a silica plug with *n*-hexane:ethyl acetate [3:1] before being concentrated under vacuum to afford the title compound as a yellow waxy solid (420 mg, 57 %); δ_H (300 MHz, $CDCl_3$) 7.36 (2H, s, Ar-*H*), 6.12-6.00 (2H, m, Ar-OCH_2CH), 5.52-5.44 (2H, m, Ar-OCH_2CH=C*H*H), 5.32-5.27 (2H, m, Ar-OCH_2CH=CH*H*), 4.60-4.58 (4H, m, ArOCH_2), 4.41-4.34 (4H, q, *J* 7, Ar-$CO_2CH_2CH_3$), 1.41-1.36 (6H, t, *J* 7, Ar-$CO_2CH_2CH_3$); all data agrees with that given in the literature.[1]

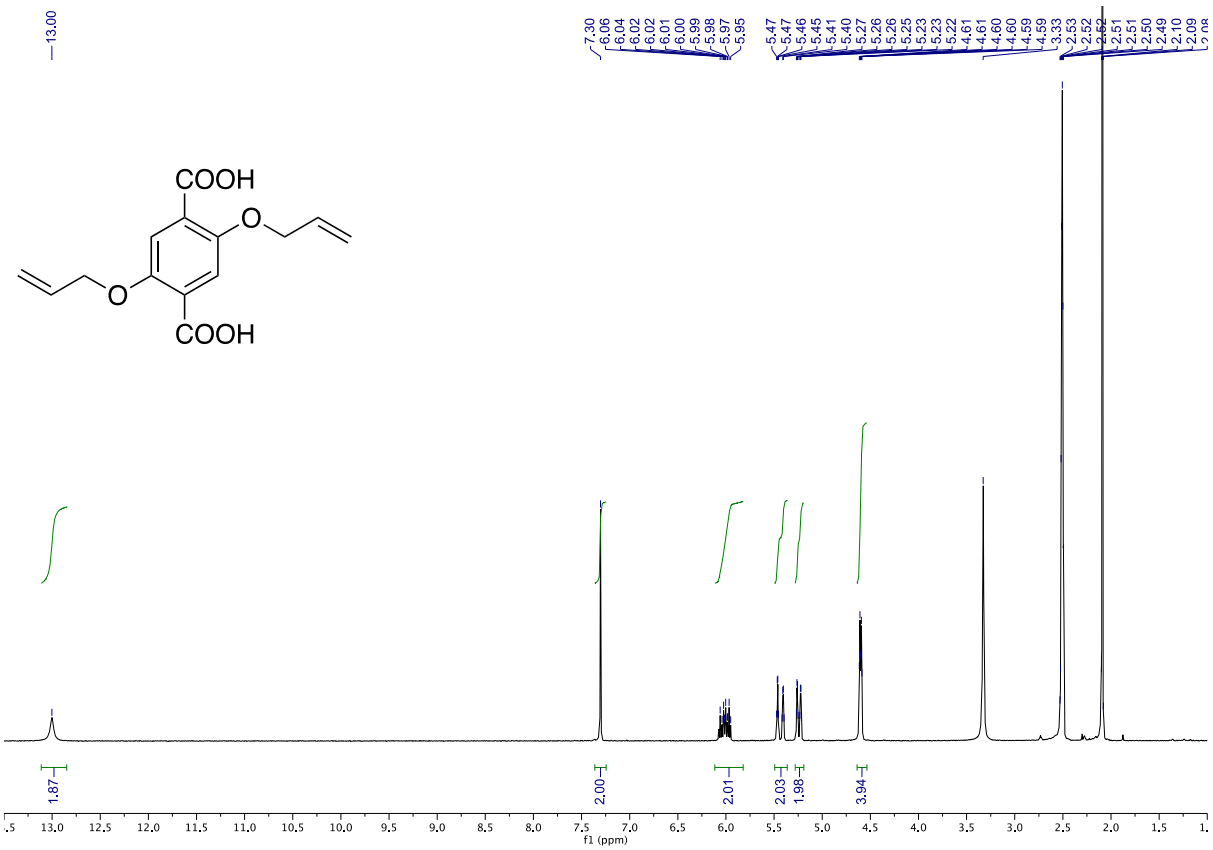
Synthesis of 2,5-bis(allyloxy)terephthalic acid

Three equivalents of LiOH were added to diethyl 2,5-bis(allyloxy)terephthalate (0.4 g, 1.2 mmol) in equal parts THF:H_2O (10 mL) and stirred overnight at room temperature. Solvents were removed by rotary evaporation and the remaining residue diluted with H_2O. The solution was neutralised using 1M HCl to a pH of ~ 2 to precipitate the product. The precipitate was filtered to afford the title compound as a white solid (0.32 g, 97 %); δ_H (300 MHz, DMSO-d_6) 13.00 (2H, bs, CO_2H), 7.30 (2H, s, Ar-*H*), 6.08-5.95 (2H, m, Ar-OCH_2CH), 5.47-5.40 (2H, m, Ar-OCH_2CH=C*H*H), 5.27-5.22 (2H, m, Ar-OCH_2CH=CH*H*), 4.61-4.59 (4H, m, ArOCH_2); all data agrees with that given in the literature.[1]

^{1}H NMR Spectra of synthesised compounds


10.14
7.48
7.26
4.46
4.44
4.41
4.39
1.45
1.43
1.40
0.00
COOEt
OH
HO
COOEt
2.00
2.07
4.64
7.00
f1 (ppm)


7.41
7.28
7.28
6.14
6.12
6.11
6.09
6.08
6.07
6.07
6.05
6.03
6.01
5.54
5.54
5.53
5.53
5.49
5.48
5.47
5.47
5.34
5.34
5.33
5.33
5.31
5.30
5.30
5.29
4.63
4.62
4.62
4.61
4.61
4.60
4.44
4.43
4.41
4.39
4.38
4.37
1.59
1.44
1.41
1.41
1.39
COOEt
O
O
COOEt
2.00
2.12
2.22
2.19
4.26
4.17
6.14
f1 (ppm)



Crystal synthesis

20 mg of 2,5-bis(allyloxy)terephthalic acid and 1.2 equivalent of lanthanide nitrate was added to 2 mL of diethylformamide (DEF) and heated in a sealed vial for 3 days at 80 °C, crystals were subsequently washed with fresh DEF and stored in solvent.

$Ce_2(L)_2(DEF)_2(NO_3)_2$ (1): Complex **1** was synthesised following the general procedure above using $Ce(NO_3)_3.xH_2O$ yielding colourless plate crystals after 3 days. $Ce_2C_{44}H_{46}O_{20}N_4$ Mw = 1159.02 g/mol. Selected FTIR: 2976 (w) 1602 (m) 1418 (m) 1285 (m) 1208 (m).

$Pr_2(L)_4(DEF)_2(NO_3)_2$ (2): Complex **2** was synthesised following the general procedure above using $Pr(NO_3)_3.xH_2O$ yielding pale yellow plate crystals after 3 days. $Pr_2C_{44}H_{46}O_{20}N_4$ Mw = 1160.60 g/mol. Selected FTIR: 2975 (w) 1600 (m) 1418 (s) 1287 (m) 1208 (m).

$Nd_2(L)_4(DEF)_2(NO_3)_2$ (3): Complex **3** was synthesised following the general procedure above using $Nd(NO_3)_3.xH_2O$ yielding pale pink plate crystals after 3 days. $Nd_2C_{44}H_{46}O_{20}N_4$ Mw = 1167.26 g/mol. Selected FTIR: 2981 (w) 1603 (m) 1418 (m) 1292 (m) 1211 (m).

$Eu_2(L)_4(DEF)_2(NO_3)_2$ (4): Complex **4** was synthesised following the general procedure above using $Eu(NO_3)_3.xH_2O$ yielding colourless plate crystals after 3 days. $Eu_2C_{44}H_{46}O_{20}N_4$ Mw = 1182.71 g/mol. Selected FTIR: 2986 (w) 1634 (m) 1412 (m) 1281 (m) 1208 (m).

$Gd_2(L)_4(DEF)_2(NO_3)_2$ (5): Complex **5** was synthesised following the general procedure above using $Gd(NO_3)_3.xH_2O$ white colourless plate crystals after 3 days. $Gd_2C_{44}H_{46}O_{20}N_4$ Mw = 1193.28 g/mol. Selected FTIR: 2985 (w) 1609 (m) 1411 (m) 1285 (m) 1213 (m).

$Tb_2(L)_4(DEF)_2(NO_3)_2$ (6): Complex **6** was synthesised following the general procedure above using $Tb(NO_3)_3.xH_2O$ yielding white plate crystals after 3 days. $Tb_2C_{44}H_{46}O_{20}N_4$ Mw = 1196.64 g/mol. Selected FTIR: 2984 (w) 1631 (m) 1417 (m) 1286 (m) 1214 (m).

$Dy_2(L)_4(DEF)_2(NO_3)_2$ (7): Complex **7** was synthesised following the general procedure above using $Dy(NO_3)_3.xH_2O$ yielding pale yellow plate crystals after 3 days. $Dy_2C_{44}H_{46}O_{20}N_4$ = 1203.78 g/mol.

Single crystal X-ray Diffraction

Suitable single crystals of frameworks **1-7** were analysed using a Bruker D8 Venture diffractometer using a CuKα IμS X-radiation source (λ = 1.5406 Å), and a Photon II detector. The single crystals were maintained at 150 K during data collections using an Oxford Cryosystems cryostream. Data collection and reduction were carried out using APEX III software interface, before final post processing and absorption scaling with SADABS.[2] Structures were solved and refined using the Olex2 interface[3] to the ShelX suite of programs, XT for structure solution and XL for structure refinement.[4,5]

Table 1: Summary of unit cell parameters for complexes 1-7 at 150 K

Complex	a (σ)	b	c	α	β	γ	Volume (Å^3)
1 (Ce)	9.9080(16)	11.1776(18)	13.939(2)	109.534(4)	95.570(4)	96.701(5)	1429.6(4)
2 (Pr)	9.8826(9)	11.1554(10)	13.9347(12)	109.747(3)	95.520(2)	96.847(2)	1420.2(2)
3 (Nd)	9.9056(10)	11.1381(11)	13.9162(14)	109.803(3)	95.425(3)	96.535(4)	1429.6(2)
4 (Eu)	10.381(7)	10.4095(7)	13.861(10)	81.397(4)	70.936(4)	89.265(4)	1399.02(17)
5 (Gd)	10.3633(8)	10.4061(8)	13.8433(10)	81.375(3)	70.977(3)	89.188(3)	1394.43(18)
6 (Tb)	10.3607(8)	10.4017(8)	13.8104(10)	81.551(3)	71.010(4)	89.160(3)	1391.18(19)
7 (Dy)	10.3582(8)	10.4047(8)	13.7990(11)	91.692(3)	71.113(3)	89.156(3)	1391.51(19)

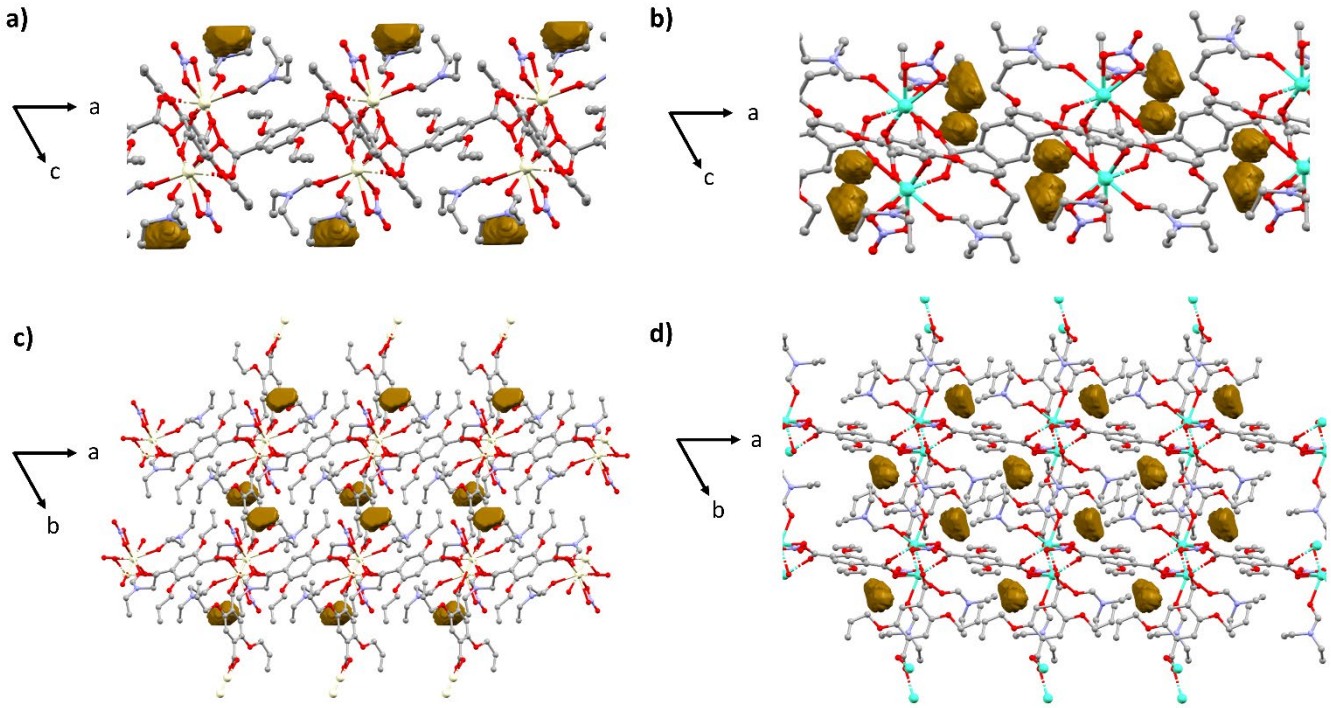


Figure S1: Contact surface void space plots of complexes 1-3 (a and c) and complexes 4-7 (b and d). For complexes 1-3 a probe radius of 1.0 Å is shown, for complexes 4-7 a smaller probe radius of 0.8 Å is shown. Analysis shows that the largest accessible void for complexes 1-3 sits in a pocket of the edge of the network sheet. Whereas for complex 4-7 the largest void space penetrates the framework down the c axis. C- grey, O- red, N-blue, Ln- cream/green. Hydrogen atoms omitted for clarity.

High pressure

A crystal was placed in a diamond anvil cell containing a 1:1 pentane/isopentane mixture with diamond culets of 0.8 mm. The crystal occupies a sample chamber created by a steel gasket of 0.25 mm thickness, pre-indented to 0.15 mm with a precision drilled hole of 300 µm. A ruby sphere was introduced to the sample chamber for pressure determination. To begin the pressure was increased from ambient in 5 kbar increments until there was a notable change in unit cell parameters. Then the diamond anvil cell (DAC) was mounted directly onto the goniometer of XIPHOS II, a four circle Huber diffractometer with Ag–Kα IµS generator.[6] High pressure data were handled using the Bruker APEX2 software suite, which incorporates SAINT and SADABS for integration, cell refinement, and scaling [2,7,8] The SHELX program suite was used for structure solution and refinement of all structures within the OLEX2 interface.[3]

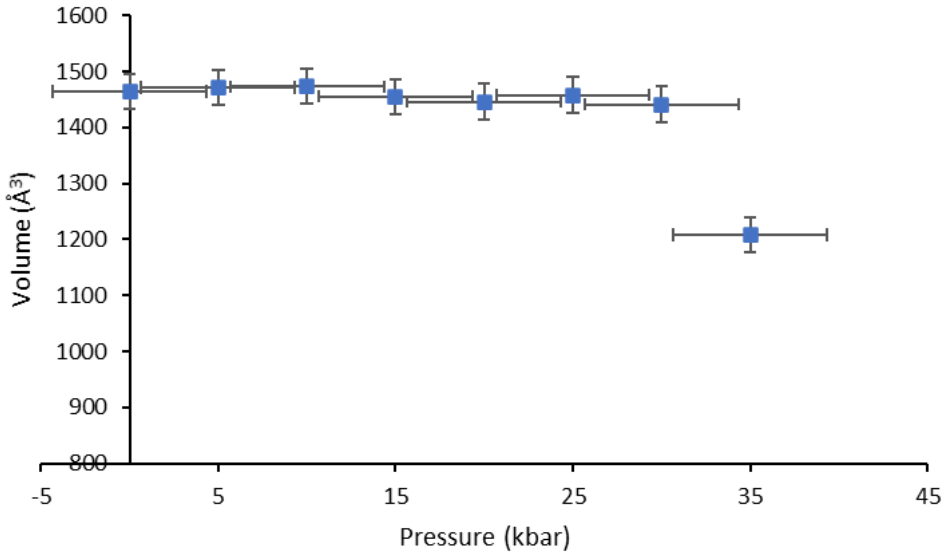


Figure S2: A scatter graph showing the unit cell volume deviation from the ambient pressure structure solution for complex 2 over the pressure range of 0-35 kbar. The complex exhibits a first order phase transition between 30 and 35 kbar.

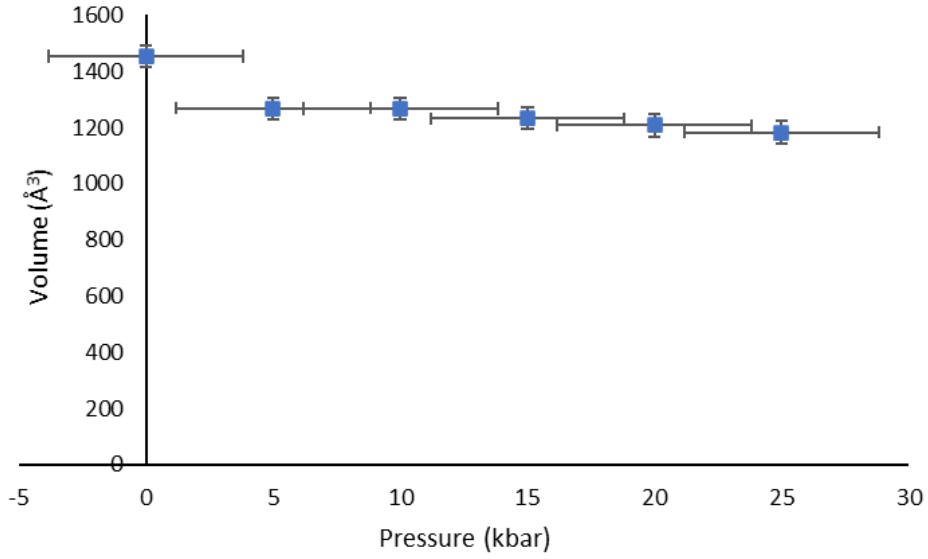


Figure S3: A scatter graph showing the unit cell volume deviation from the ambient pressure structure solution for complex 6 over the pressure range of 0-25 kbar. The complex exhibits an initial compression at 5 kbar resulting in a volume decrease of approximately 185 Å³.

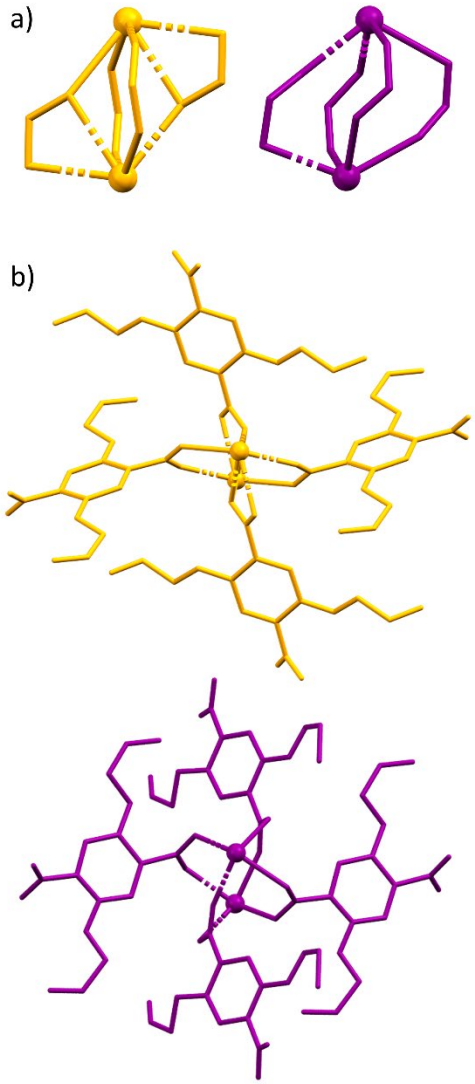
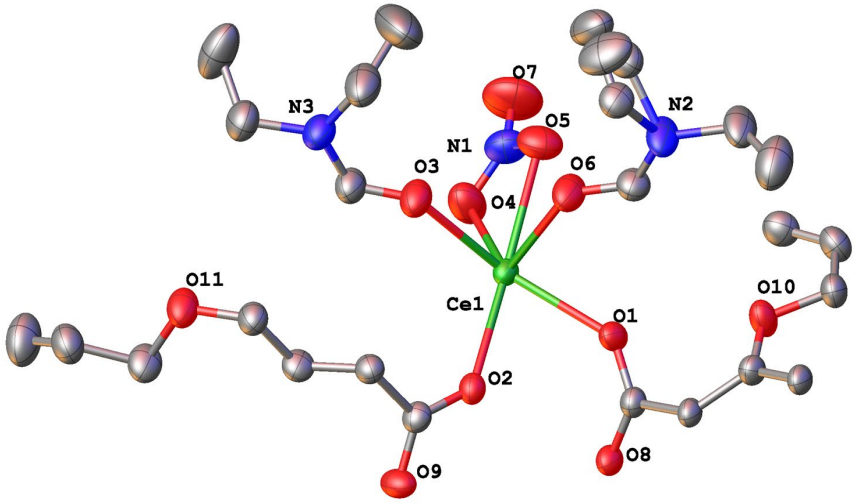


Figure S4: Depicts individual representations of complex 2 at ambient pressure (orange) and at 35 kbar (purple). a) shows a closer inspection of the secondary building unit, highlighting the breaking of a bond. b) highlights the change in the organic allyloxy groups from staggered to eclipsed.

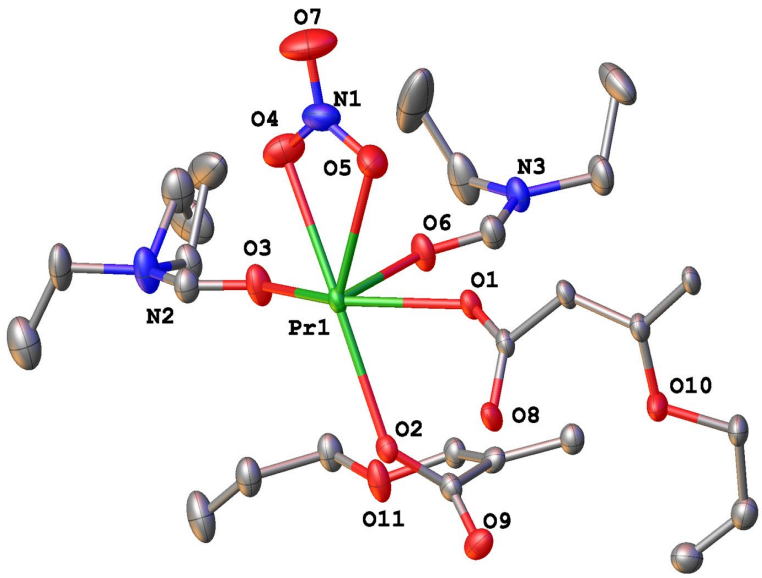
Crystallographic data

1 - Ce, 2 – Pr, 3 – Nd, 4 -Eu, 5 – Gd, 6 – Tb, 7 -Dy



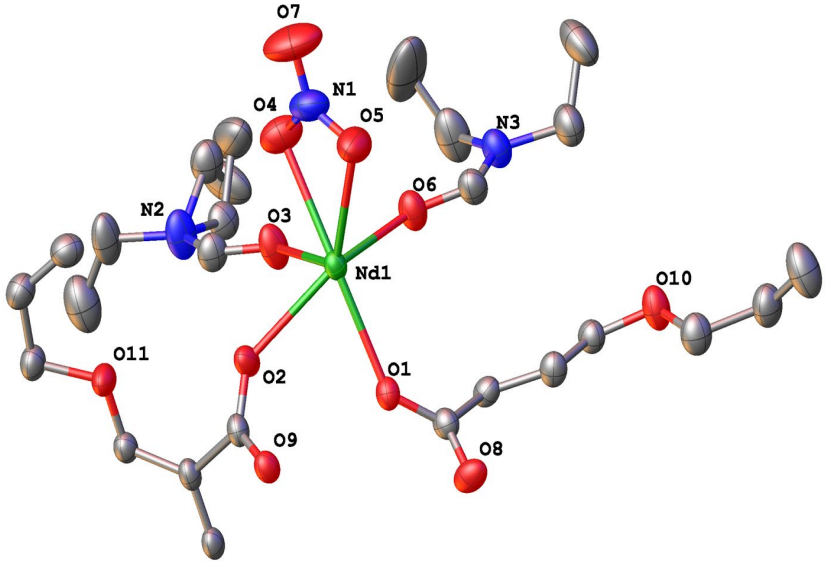
Crystal data and structure refinement for 1.

Identification code	022_R34
Empirical formula	C24H34CeN3O11
Formula weight	680.66
Temperature/K	150.0
Crystal system	triclinic
Space group	P-1
a/Å	9.9080(16)
b/Å	11.1776(18)
c/Å	13.939(2)
α/°	109.534(4)
β/°	95.570(4)
γ/°	96.701(5)
Volume/Å3	1429.6(4)
Z	2
ρcalcg/cm3	1.581
μ/mm 1	12.835
F(000)	690.0
Crystal size/mm3	0.2 × 0.07 × 0.04
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.8 to 135.666
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16
Reflections collected	42338
Independent reflections	5030 [Rint = 0.0680, Rsigma = 0.0332]
Data/restraints/parameters	5030/318/375
Goodness-of-fit on F2	1.039
Final R indexes [I>=2σ (I)]	R1 = 0.0391, wR2 = 0.1092
Final R indexes [all data]	R1 = 0.0398, wR2 = 0.1099
Largest diff. peak/hole / e Å-3	1.53/-0.78



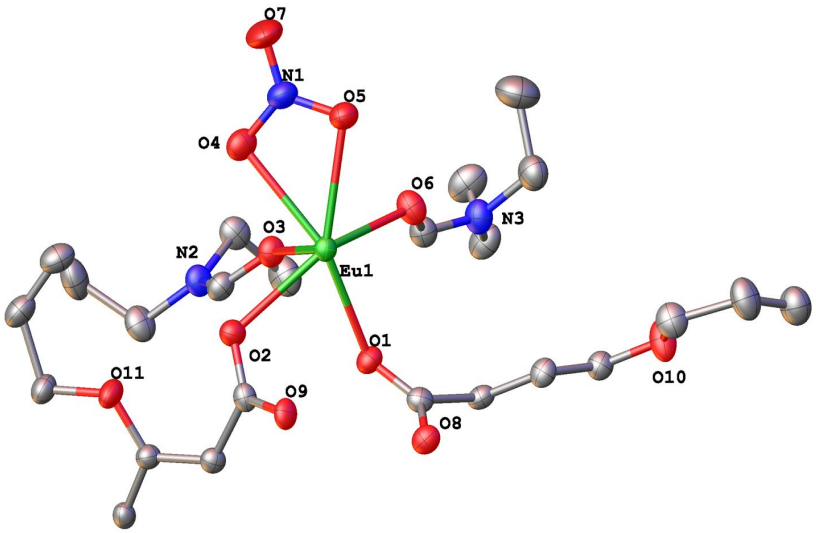
Crystal data and structure refinement for 2

Identification code	lrh_022_r35
Empirical formula	C24H34N3O11Pr
Formula weight	681.45
Temperature/K	150.0
Crystal system	triclinic
Space group	P-1
a/Å	9.8826(9)
b/Å	11.1554(10)
c/Å	13.9347(12)
α/°	109.747(3)
β/°	95.520(2)
γ/°	96.847(2)
Volume/Å3	1420.2(2)
Z	2
ρcalcg/cm3	1.594
μ/mm 1	13.694
F(000)	692.0
Crystal size/mm3	0.1 × 0.06 × 0.03
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	10.554 to 133.188
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16
Reflections collected	58828
Independent reflections	4970 [Rint = 0.0548, Rsigma = 0.0232]
Data/restraints/parameters	4970/296/376
Goodness-of-fit on F2	1.044
Final R indexes [I>=2σ (I)]	R1 = 0.0306, wR2 = 0.0818
Final R indexes [all data]	R1 = 0.0307, wR2 = 0.0819
Largest diff. peak/hole / e Å-3	1.70/-1.47



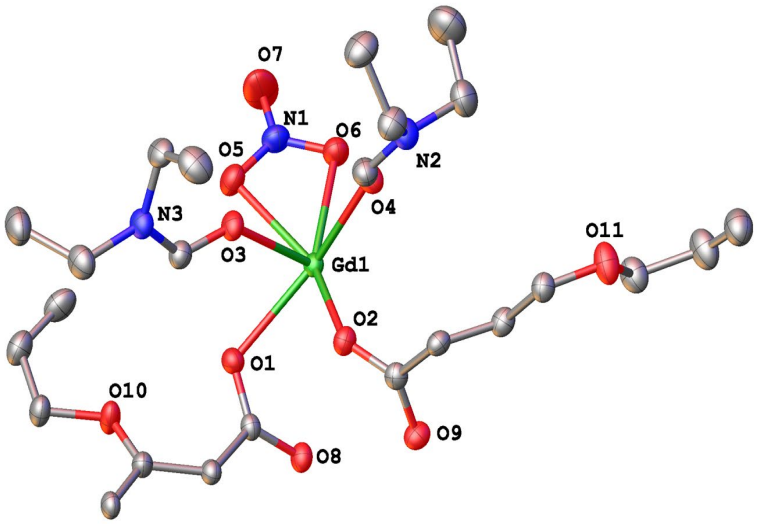
Crystal data and structure refinement for 3

Identification code	lrh_022_r36
Empirical formula	C24H34N3NdO11
Formula weight	684.78
Temperature/K	150.0
Crystal system	triclinic
Space group	P-1
a/Å	9.9056(10)
b/Å	11.1381(11)
c/Å	13.9162(14)
α/°	109.803(3)
β/°	95.425(3)
γ/°	96.535(4)
Volume/Å3	1420.6(2)
Z	2
ρcalcg/cm3	1.601
μ/mm 1	14.479
F(000)	694.0
Crystal size/mm3	0.08 × 0.03 × 0.01
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.82 to 134.222
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16
Reflections collected	54599
Independent reflections	4998 [Rint = 0.0623, Rsigma = 0.0271]
Data/restraints/parameters	4998/294/376
Goodness-of-fit on F2	1.107
Final R indexes [I>=2σ (I)]	R1 = 0.0376, wR2 = 0.1043
Final R indexes [all data]	R1 = 0.0385, wR2 = 0.1054
Largest diff. peak/hole / e Å-3	1.77/-0.77



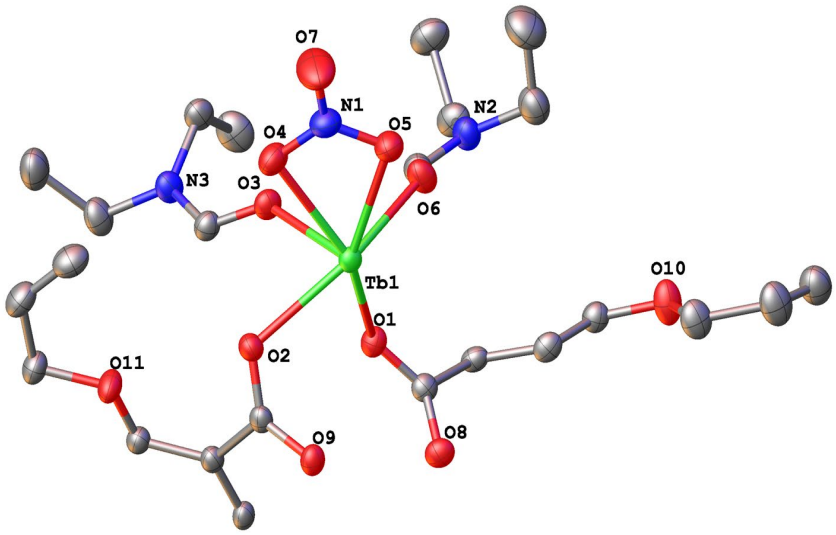
Crystal data and structure refinement for 4

Identification code	022_R37
Empirical formula	C24H34EuN3O11
Formula weight	692.50
Temperature/K	150.0
Crystal system	triclinic
Space group	P-1
a/Å	10.3817(7)
b/Å	10.4095(7)
c/Å	13.8631(10)
α/°	81.397(4)
β/°	70.936(4)
γ/°	89.265(4)
Volume/Å3	1399.02(17)
Z	2
ρcalcg/cm3	1.644
μ/mm 1	16.589
F(000)	700.0
Crystal size/mm3	0.08 × 0.02 × 0.01
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.598 to 145.534
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -16 ≤ l ≤ 16
Reflections collected	35592
Independent reflections	5429 [Rint = 0.0999, Rsigma = 0.0524]
Data/restraints/parameters	5429/265/356
Goodness-of-fit on F2	1.090
Final R indexes [I>=2σ (I)]	R1 = 0.0467, wR2 = 0.1251
Final R indexes [all data]	R1 = 0.0516, wR2 = 0.1289
Largest diff. peak/hole / e Å-3	1.88/-0.74



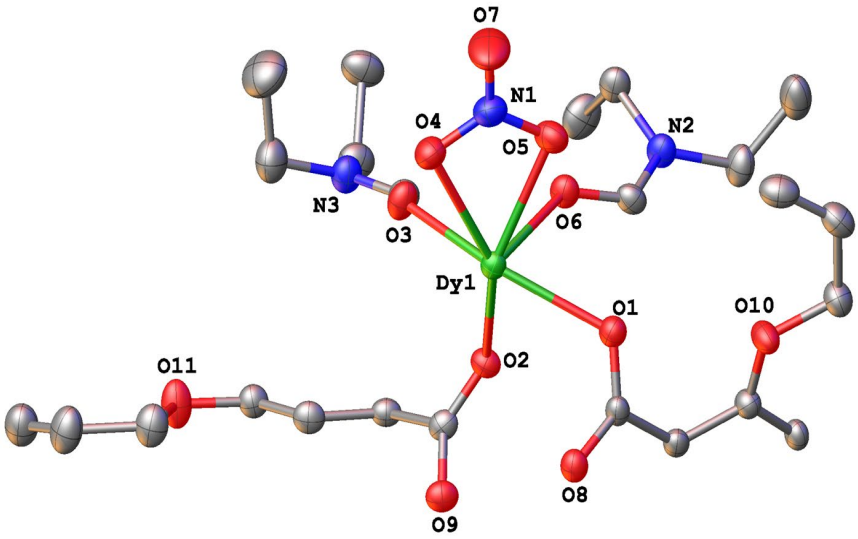
Crystal data and structure refinement for 5

Identification code	lrh_022_r38
Empirical formula	C24H34GdN3O11
Formula weight	697.79
Temperature/K	150.0
Crystal system	triclinic
Space group	P-1
a/Å	10.3633(8)
b/Å	10.4061(8)
c/Å	13.8433(10)
α/°	81.375(3)
β/°	70.977(3)
γ/°	89.188(3)
Volume/Å3	1394.43(18)
Z	2
ρcalcg/cm3	1.662
μ/mm 1	15.927
F(000)	702.0
Crystal size/mm3	0.06 × 0.02 × 0.01
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.836 to 134.368
Index ranges	-12 ≤ h ≤ 11, -12 ≤ k ≤ 12, -16 ≤ l ≤ 16
Reflections collected	53274
Independent reflections	4904 [Rint = 0.0629, Rsigma = 0.0271]
Data/restraints/parameters	4904/265/357
Goodness-of-fit on F2	1.081
Final R indexes [I>=2σ (I)]	R1 = 0.0222, wR2 = 0.0593
Final R indexes [all data]	R1 = 0.0231, wR2 = 0.0598
Largest diff. peak/hole / e Å-3	0.42/-0.55



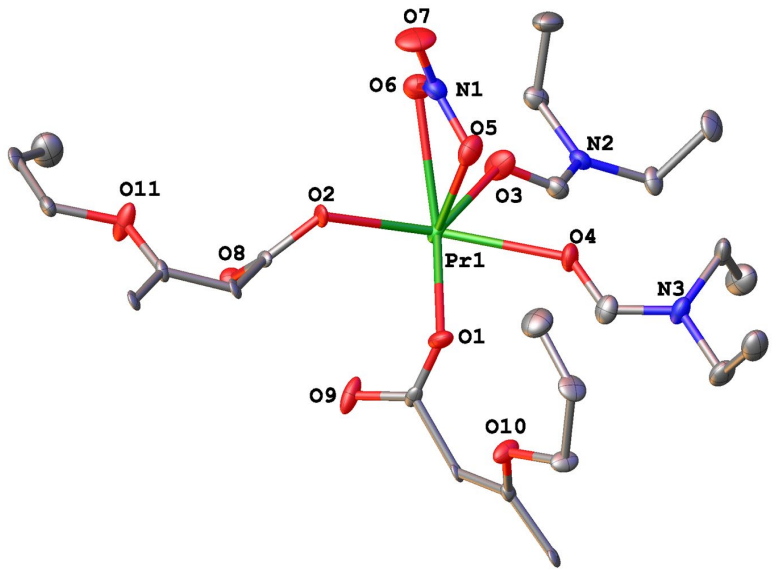
Crystal data and structure refinement for 6

Identification code	LRH_022_R39_0m
Empirical formula	C24H34N3O11Tb
Formula weight	699.46
Temperature/K	150.00
Crystal system	triclinic
Space group	P-1
a/Å	10.3607(8)
b/Å	10.4017(8)
c/Å	13.8104(10)
α/°	81.551(3)
β/°	71.010(4)
γ/°	89.160(3)
Volume/Å3	1391.18(19)
Z	2
ρcalcg/cm3	1.670
μ/mm 1	13.045
F(000)	704.0
Crystal size/mm3	0.07 × 0.03 × 0.02
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.846 to 134.008
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -16 ≤ l ≤ 16
Reflections collected	61503
Independent reflections	4892 [Rint = 0.0662, Rsigma = 0.0259]
Data/restraints/parameters	4892/265/356
Goodness-of-fit on F2	1.116
Final R indexes [I>=2σ (I)]	R1 = 0.0265, wR2 = 0.0719
Final R indexes [all data]	R1 = 0.0281, wR2 = 0.0728
Largest diff. peak/hole / e Å-3	0.66/-0.47



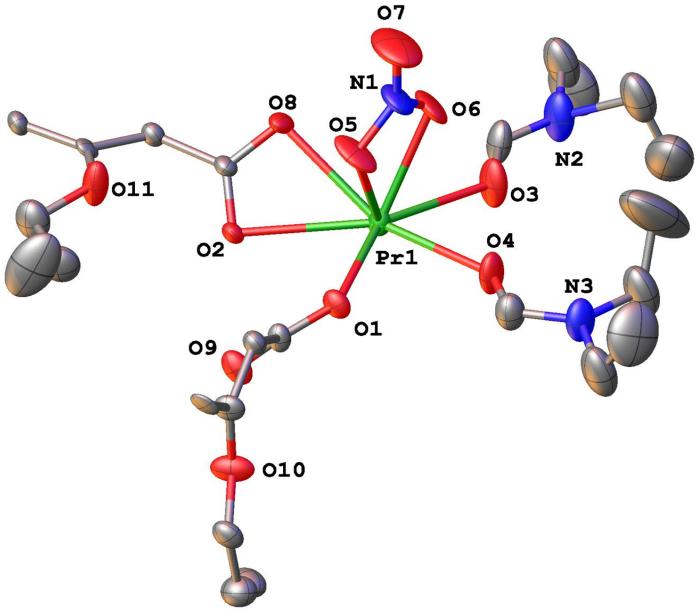
Crystal data and structure refinement for 7

Identification code	LRH_022_R40
Empirical formula	C24H34DyN3O11
Formula weight	703.04
Temperature/K	150.00
Crystal system	triclinic
Space group	P-1
a/Å	10.3582(8)
b/Å	10.4047(8)
c/Å	13.7990(11)
α/°	81.692(3)
β/°	71.113(3)
γ/°	89.156(3)
Volume/Å3	1391.52(19)
Z	2
ρcalcg/cm3	1.678
μ/mm 1	14.911
F(000)	706.0
Crystal size/mm3	0.07 × 0.04 × 0.02
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.594 to 144.876
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -16 ≤ l ≤ 15
Reflections collected	20691
Independent reflections	5362 [Rint = 0.0598, Rsigma = 0.0509]
Data/restraints/parameters	5362/0/357
Goodness-of-fit on F2	1.072
Final R indexes [I>=2σ (I)]	R1 = 0.0401, wR2 = 0.1080
Final R indexes [all data]	R1 = 0.0415, wR2 = 0.1091
Largest diff. peak/hole / e Å-3	1.38/-1.24



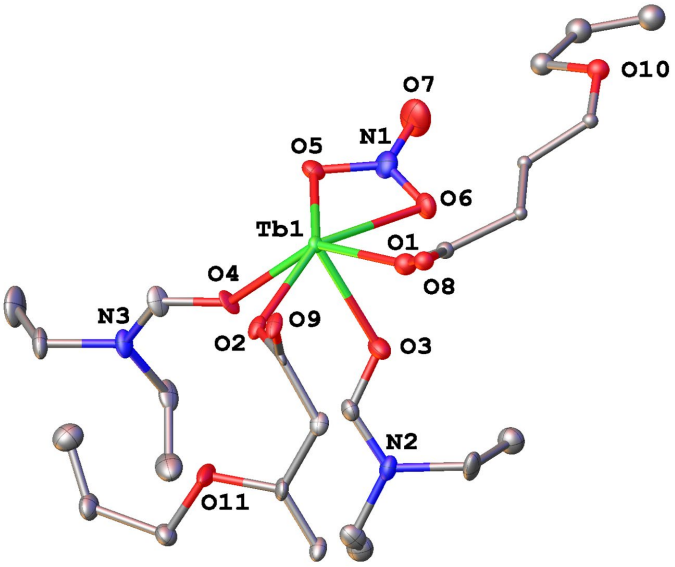
Crystal data and structure refinement for 022_R35_35kbar

Identification code	022_R35_35kbar
Empirical formula	C24H34N3O11Pr
Formula weight	681.45
Temperature/K	293.0
Crystal system	triclinic
Space group	P-1
a/Å	9.8824(4)
b/Å	10.0039(4)
c/Å	13.3049(9)
α/°	98.203(4)
β/°	111.376(4)
γ/°	91.257(2)
Volume/Å3	1208.43(11)
Z	2
ρcalcg/cm3	1.873
μ/mm 1	1.107
F(000)	692.0
Crystal size/mm3	0.06 × 0.03 × 0.02
Radiation	AgKα (λ = 0.56086)
2Θ range for data collection/°	3.256 to 39.304
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -9 ≤ l ≤ 10
Reflections collected	21137
Independent reflections	1688 [Rint = 0.0449, Rsigma = 0.0225]
Data/restraints/parameters	1688/268/338
Goodness-of-fit on F2	1.074
Final R indexes [I>=2σ (I)]	R1 = 0.0216, wR2 = 0.0502
Final R indexes [all data]	R1 = 0.0244, wR2 = 0.0513
Largest diff. peak/hole / e Å-3	0.46/-0.32



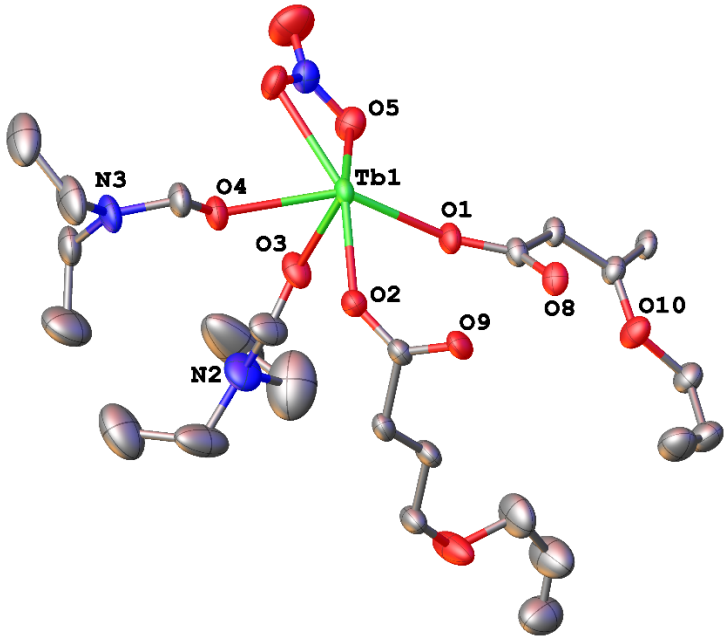
Crystal data and structure refinement for 022_R35_25kbar

Identification code	022_R35_25kbar
Empirical formula	C24H34N3O11Pr
Formula weight	681.45
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	10.0371(3)
b/Å	11.1440(3)
c/Å	14.0248(8)
α/°	109.464(3)
β/°	94.951(3)
γ/°	96.1010(10)
Volume/Å3	1458.25(11)
Z	2
ρcalcg/cm3	1.552
μ/mm 1	0.917
F(000)	692.0
Crystal size/mm3	0.06 × 0.03 × 0.02
Radiation	AgKα (λ = 0.56086)
2Θ range for data collection/°	3.09 to 39.232
Index ranges	-11 ≤ h ≤ 12, -13 ≤ k ≤ 13, -10 ≤ l ≤ 10
Reflections collected	26704
Independent reflections	2021 [Rint = 0.0466, Rsigma = 0.0233]
Data/restraints/parameters	2021/292/332
Goodness-of-fit on F2	1.019
Final R indexes [I>=2σ (I)]	R1 = 0.0324, wR2 = 0.0804
Final R indexes [all data]	R1 = 0.0363, wR2 = 0.0833
Largest diff. peak/hole / e Å-3	0.62/-0.74



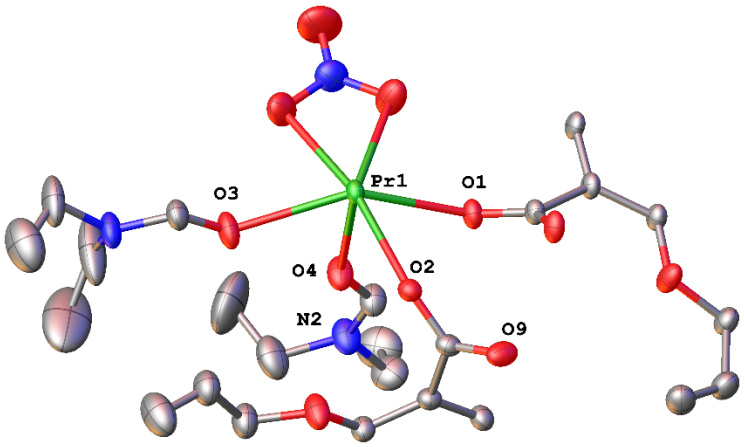
Crystal data and structure refinement for 022_R39_HP

Identification code	022_R39_25kbar
Empirical formula	C24H34N3O11Tb
Formula weight	699.46
Temperature/K	298.0
Crystal system	triclinic
Space group	P-1
a/Å	9.8113(6)
b/Å	9.9140(10)
c/Å	13.2568(8)
α/°	81.104(7)
β/°	68.313(3)
γ/°	88.342(7)
Volume/Å3	1183.23(16)
Z	2
ρcalcg/cm3	1.963
μ/mm 1	1.630
F(000)	704.0
Crystal size/mm3	0.07 × 0.03 × 0.02
Radiation	AgKα (λ = 0.56086)
2Θ range for data collection/°	2.64 to 39.17
Index ranges	-11 ≤ h ≤ 11, -6 ≤ k ≤ 5, -15 ≤ l ≤ 15
Reflections collected	22945
Independent reflections	1625 [Rint = 0.0862, Rsigma = 0.0438]
Data/restraints/parameters	1625/192/300
Goodness-of-fit on F2	1.041
Final R indexes [I>=2σ (I)]	R1 = 0.0303, wR2 = 0.0589
Final R indexes [all data]	R1 = 0.0396, wR2 = 0.0620
Largest diff. peak/hole / e Å-3	0.55/-0.38



Crystal data and structure refinement for 022_R39_rt (Complex 6)

Identification code	022_R39_rt
Empirical formula	$C_{24}H_{34}N_3O_{11}Tb$
Formula weight	699.46
Temperature/K	290.0
Crystal system	triclinic
Space group	P-1
a/Å	10.4991(13)
b/Å	10.5703(13)
c/Å	13.8816(17)
α/°	83.999(5)
β/°	71.592(6)
γ/°	89.746(5)
Volume/Å^3	1453.1(3)
Z	2
ρ_{calc}g/cm^3	1.599
μ/mm^{-1}	12.490
F(000)	704.0
Crystal size/mm^3	0.145 × 0.075 × 0.052
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.298 to 134.434
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -16 ≤ l ≤ 16
Reflections collected	15951
Independent reflections	5063 [R_{int} = 0.0637, R_{sigma} = 0.0569]
Data/restraints/parameters	5063/273/355
Goodness-of-fit on F^2	1.111
Final R indexes [I>=2σ (I)]	R_1 = 0.0535, wR_2 = 0.1506
Final R indexes [all data]	R_1 = 0.0567, wR_2 = 0.1533
Largest diff. peak/hole / e Å^{-3}	1.44/-0.87



Crystal data and structure refinement for 022_R35_rt (Complex 2)

Identification code	022_R35_rt
Empirical formula	$C_{24}H_{34}N_3O_{11}Pr$
Formula weight	681.45
Temperature/K	290.0
Crystal system	triclinic
Space group	P-1
a/Å	10.0678(11)
b/Å	11.1512(12)
c/Å	14.0297(15)
α/°	109.416(3)
β/°	95.138(3)
γ/°	95.947(3)
Volume/Å^3	1464.6(3)
Z	2
ρ_{calc}g/cm^3	1.545
μ/mm^{-1}	13.280
F(000)	692.0
Crystal size/mm^3	0.16 × 0.16 × 0.13
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	10.442 to 141.198
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -16 ≤ l ≤ 17
Reflections collected	21987
Independent reflections	5455 [R_{int} = 0.0571, R_{sigma} = 0.0479]
Data/restraints/parameters	5455/272/355
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0411, wR_2 = 0.1136
Final R indexes [all data]	R_1 = 0.0420, wR_2 = 0.1146
Largest diff. peak/hole / e Å^{-3}	1.17/-0.79

References

1. S. Du, W. Wang, J. Zhang and X. Wan, *Chem. Commun*., 2014,**50**, 9929-9931
2. SADABS, Bruker AXS INC., Madison, WI, 2001.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. J. Puschmann*, J. Appl. Crystallogr*., 2009, **42**, 339–341.
4. G. M. Sheldrick, Acta Crystallogr. *Sect. C Struct. Chem*., 2015, **71**, 3–8.
5. G. M. Sheldrick, Acta Crystallogr. *Sect. A Found. Crystallogr*., 2008, **64**, 112–122.
6. M. R. Probert, J. A. Coome, A. E. Goeta and J. A. K. Howard*, Sect. A: Found. Crystallogr.,* 2011, **67**, 528.
7. T. Schulz, K. Meindl, D. Leusser, D. Stern, J. Graf, C. Michaelsen, M. Ruf, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr*., 2009, **42**, 885–891.
8. APEX2, version 1.08, Bruker AXS Inc., Madison, WI, 2004.
9. SAINT, Bruker AXS Inc., Madison, WI, 2007.