

Supplementary material

Table S1. Data collection and refinement details for **Cl2**

Chemical formula	H ₄ Cl ₂ EuO ₂
M_r	258.89
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	100
a, b, c (Å)	11.636 (3), 6.358 (2), 6.637 (2)
β (°)	105.81 (3)
V (Å ³)	472.4 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	14.24
Crystal size (mm)	0.21 × 0.12 × 0.06
Diffractometer	Xcalibur, Ruby
T_{\min}, T_{\max}	0.194, 0.541
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3765, 653, 642
R_{int}	0.023
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.701
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.013, 0.033, 1.23
No. of reflections	653
No. of parameters	32
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.44, -1.07

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.35.19 (release 27-10-2011 CrysAlis171 .NET) (compiled Oct 27 2011, 15:02:11), *SHELXS97* (Sheldrick, 1990), *SHELXL97* (Sheldrick, 1997).

Table S2. Data collection and refinement details for **Cl6**

Chemical formula	Cl ₂ EuH ₁₂ O ₆
M_r	330.96
Crystal system, space group	Trigonal, <i>P321</i>
Temperature (K)	80
a, c (Å)	7.923 (2), 4.089 (1)
V (Å ³)	222.29 (10)
Z	1.0
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	7.63
Crystal size (mm)	0.18 × 0.07 × 0.05
Diffractometer	Xcalibur, Ruby, Gemini ultra
T_{\min}, T_{\max}	0.437, 0.752

No. of measured, independent and observed [$F > 6\sigma(F)$] reflections	27961, 2091, 2091
R_{int}	0.039
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	1.186
$R[F > 6\sigma(F)]$, $wR(F^2)$, S	0.009, 0.0223, 0.75
No. of reflections	2091
No. of parameters	66
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e \AA^{-3})	0.72, -2.86
Absolute structure parameter	-0.003 (8)

Computer programs: *CrysAlis PRO* 1.171.42.50a (Rigaku OD, 2022), *SHELXS*, Volkov *et al.*, (2006).

Table S3. Data collection and refinement details for **Br1**

Chemical formula	$\text{Br}_2\text{H}_2\text{EuO}$
M_r	329.80
Crystal system, space group	Orthorhombic, <i>Pnma</i>
Temperature (K)	100
a , b , c (\AA)	11.349 (1), 4.278 (1), 9.144 (1)
V (\AA^3)	443.95 (12)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	31.93
Crystal size (mm)	$0.13 \times 0.08 \times 0.05$
Diffractometer	Xcalibur, Ruby, Gemini ultra
T_{min} , T_{max}	0.122, 0.344
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3250, 667, 632
R_{int}	0.024
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.698
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.012, 0.026, 1.13
No. of reflections	667
No. of parameters	32
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e \AA^{-3})	0.72, -0.57

Computer programs: *CrysAlis PRO* 1.171.41.80a (Rigaku OD, 2020), *SHELXS*, *SHELXL2018/3* (Sheldrick, 2018).

Table S4. Data collection and refinement details for **Br6**

Chemical formula	$\text{Br}_2\text{H}_{12}\text{EuO}_6$
M_r	419.88
Crystal system, space group	Trigonal, <i>P321</i>
Temperature (K)	100

a, c (Å)	8.200 (2), 4.138 (1)
V (Å ³)	240.96 (13)
Z	1
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	14.78
Crystal size (mm)	0.17 × 0.10 × 0.08
Diffractometer	Xcalibur, Ruby, Gemini ultra
T_{\min}, T_{\max}	0.194, 0.434
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3999, 454, 453
R_{int}	0.040
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.702
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.012, 0.029, 1.13
No. of reflections	454
No. of parameters	25
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.46, -0.51
Absolute structure parameter	0.022 (18)
Computer programs: <i>CrysAlis PRO</i> 1.171.41.80a (Rigaku OD, 2020), <i>SHELXS</i> , <i>SHELXL2018/3</i> (Sheldrick, 2018).	

Table S5. Data collection and refinement details for **I6**

Chemical formula	EuH ₁₂ I ₂ O ₆
M_r	513.86
Crystal system, space group	Trigonal, $P321$
Temperature (K)	100
a, c (Å)	8.565 (2), 4.241 (1)
V (Å ³)	269.43 (14)
Z	1
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	11.53
Crystal size (mm)	0.17 × 0.11 × 0.05
Diffractometer	Xcalibur, Ruby, Gemini ultra
T_{\min}, T_{\max}	0.251, 0.603
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5433, 514, 510
R_{int}	0.031
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.699
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.021, 0.051, 1.41
No. of reflections	514

No. of parameters	25
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	2.84, -3.69
Absolute structure parameter	0.027 (14)

Computer programs: *CrysAlis PRO* 1.171.42.50a (Rigaku OD, 2022), *SHELXS*, *SHELXL2018/3* (Sheldrick, 2018).

---Table S6. Hydrogen bonds and interactions.

H-bond	D-H (Å)	H...A (Å)	D...A (Å)	$\angle(\text{D-H}\cdots\text{A})$ (°)
Cl2				
O-H1...Cl ⁱ	0.87(5)	2.22(5)	3.080(3)	170(4)
O-H2...Cl ⁱⁱ	0.77(4)	2.54(4)	2.225(3)	149(4)
Cl6				
O1W-H1W1...Cl ⁱⁱⁱ	0.99	2.21	3.1882(11)	172
O2W-H1W2...Cl ⁱⁱⁱ	0.98	2.65	3.5813(6)	159
Br1				
OW-H1...Br2 ^{iv}	0.70(5)	2.84(5)	3.310(3)	128(5)
OW-H1...Br1 ^v	0.70(5)	2.92(4)	3.383(3)	126.14(2)
OW-H1...Br1 ^{vi}	0.70(5)	2.92(4)	3.383(3)	126.14(2)
OW-H2...Br2 ^{vii}	0.78(6)	2.77(4)	3.298(3)	126.33(2)
OW-H2...Br2 ^{viii}	0.78(6)	2.77(4)	3.298(3)	126.33(2)
Br6				
O1W-H1W1...Br ^{ix}	0.82(4)	2.55(4)	3.3469(18)	165(5)
O2W-H1W2...Br ^x	0.74(4)	2.63(4)	3.3450(12)	165(4)
I6				
O1W-H1W1...I ^{ix}	0.87(13)	2.72(14)	3.564(7)	162(14)
O2W-H1W2...I ^{xi}	0.97(13)	2.89(15)	3.566(5)	127(12)
O2W-H1W2...I ^x	0.97(13)	3.02(15)	3.811(5)	140(13)

Symmetry codes: ⁱ x, 1-y, -1/2+z; ⁱⁱ 1/2-x, 1/2+y, 3/2-z; ⁱⁱⁱ 1+x-y, 1-y, -z; ^{iv} -1/2+x, 3/2-y, 3/2-z; ^v 1/2-x, 1-y, 1/2+z; ^{vi} 1/2-x, 2-y, 1/2+z; ^{vii} 1/2-x, 1-y, -1/2+z; ^{viii} 1/2-x, 2-y, -1/2+z; ^{ix} x-y, -y-z; ^x 1+x, y, z; ^{xi} 1+x, y, 1+z;

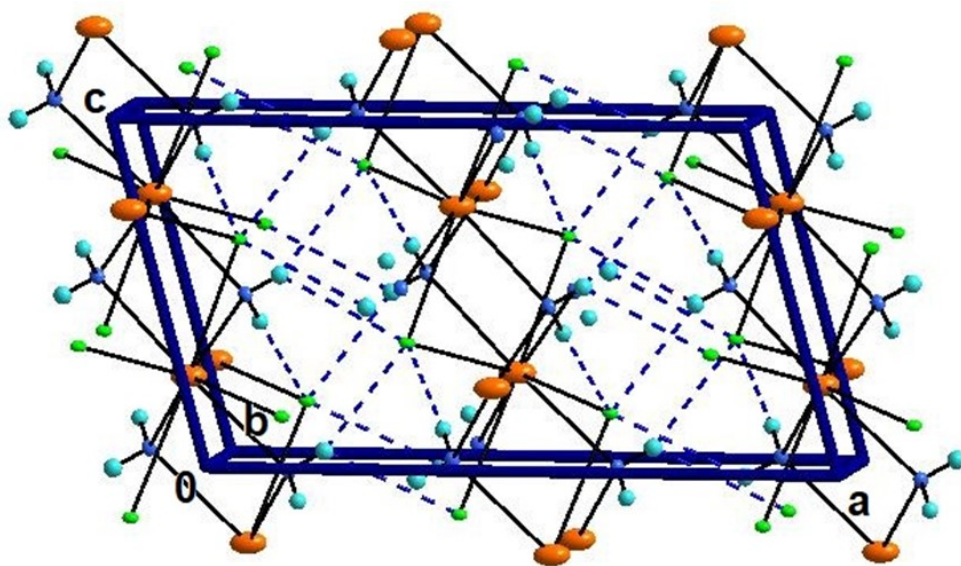


Fig. S1. Packing diagram of **Cl2**. The Eu ellipsoids are drawn at 99 % probability, all others - at 50 %. The hydrogen bonds are dashed blue.

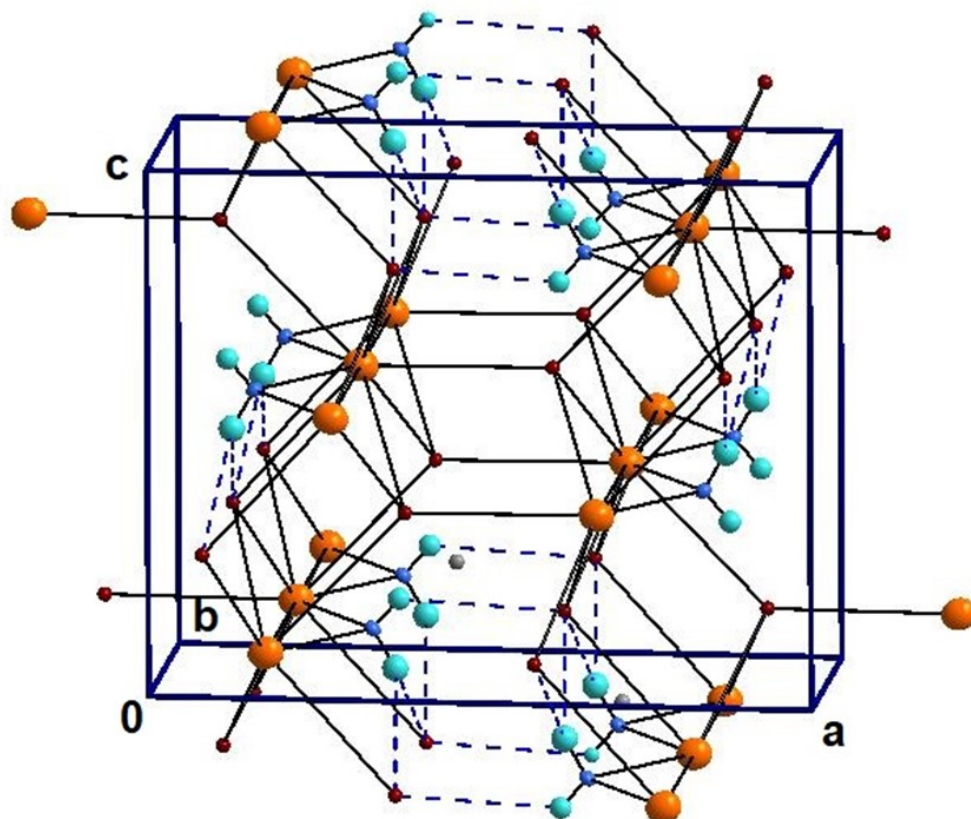


Fig. S2. Packing diagram of **Br1**. The Eu ellipsoids are drawn at 99 % probability, all others - at 50 %. The hydrogen bonds are dashed blue.

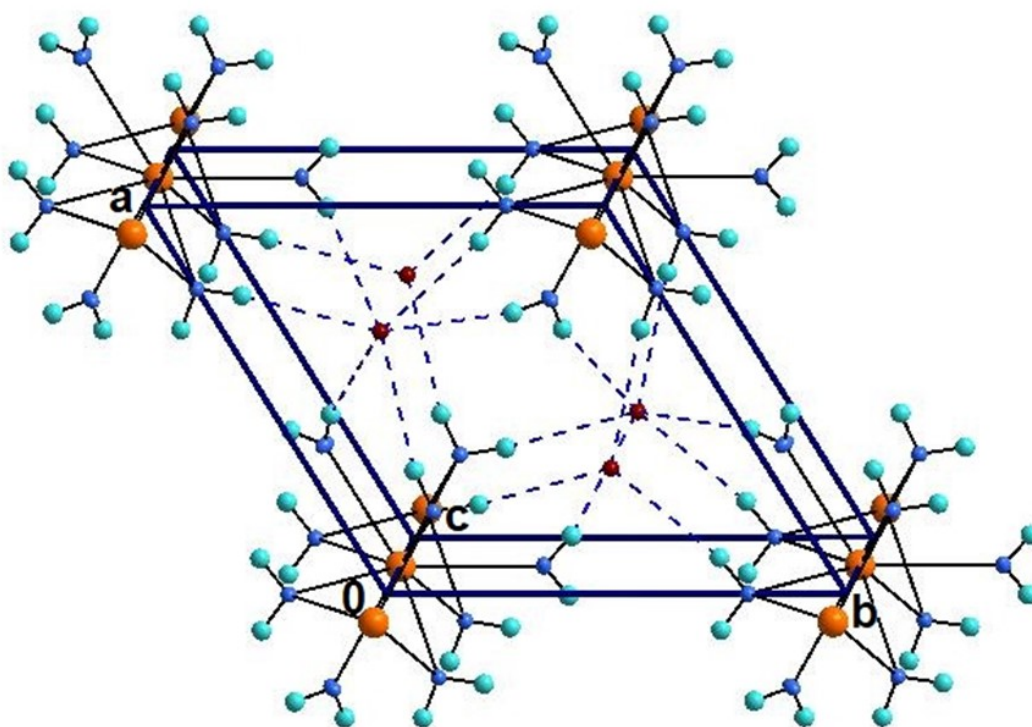


Fig. S3. Packing diagram of **Br6**. The Eu ellipsoids are drawn at 99 % probability, all others - at 50 %. The hydrogen bonds are dashed blue.

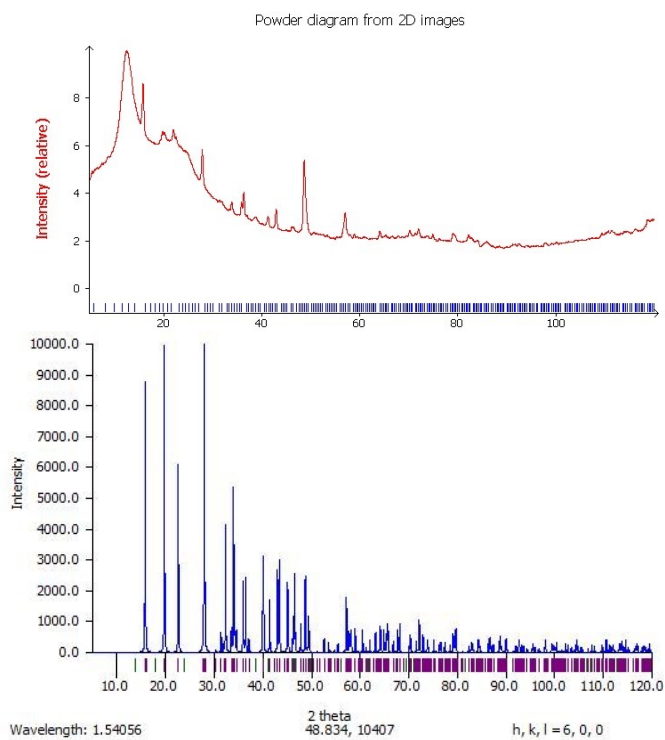


Fig. S4. Experimental¹ (upper diagram) and simulated² (lower diagram) powder diffractogram of **Cl2**.

Powder diagram from 2D images

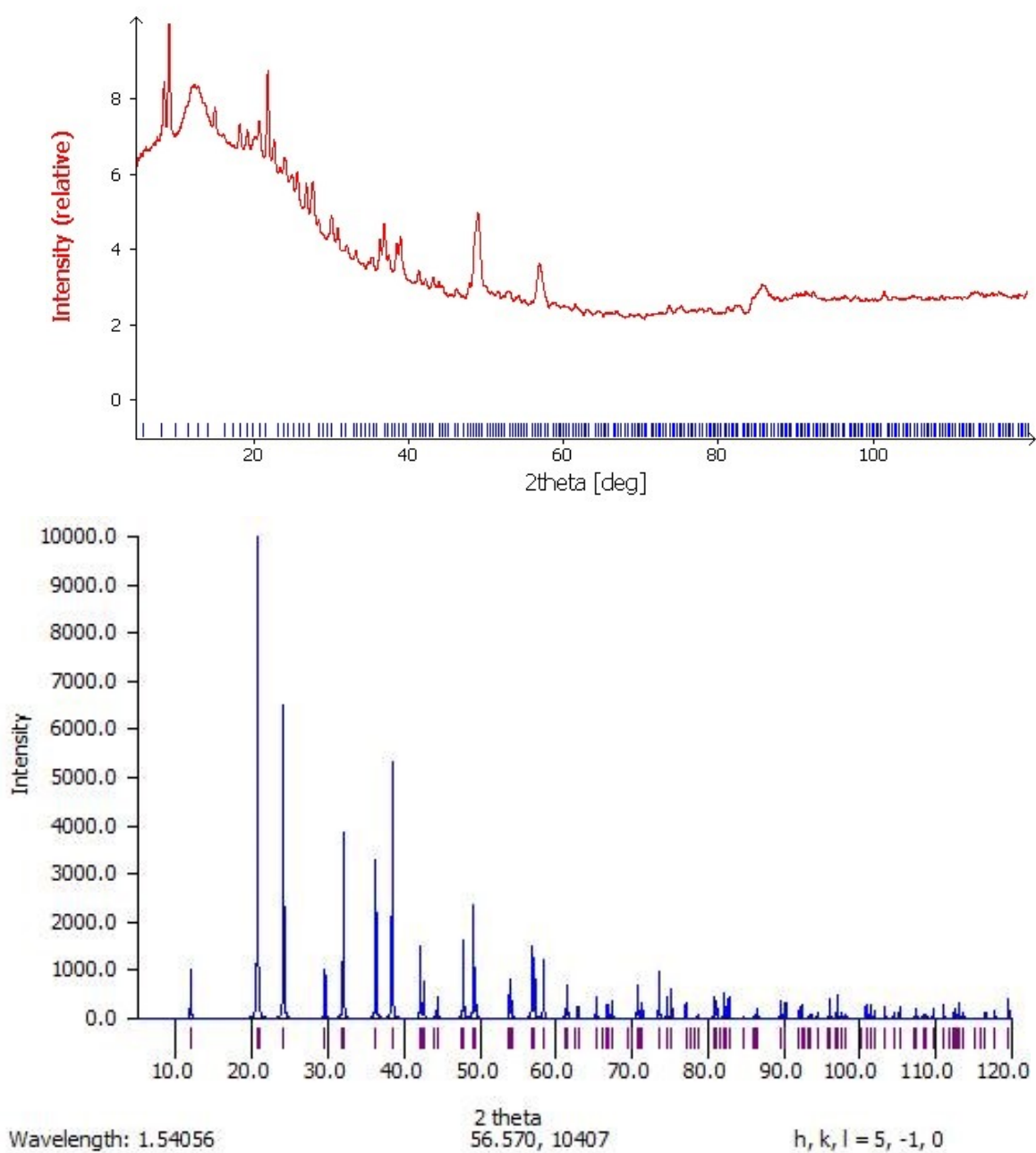


Fig. S5. Experimental¹ (upper diagram) and simulated² (lower diagram) powder diffractogram of **16**.

¹ Rigaku Oxford Diffraction, (2023), CrysAlisPro Software system, version 1.171.42.50a, Rigaku Corporation, Wrocław, Poland.

² Mercury 4.0: from visualization to analysis, design and prediction C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler and P. A. Wood, *J. Appl. Cryst.*, 2020, **53**, 226-235,