

Supplementary Material
Structural And Magnetic Properties Of Some Vacancy Ordered Osmium Halide
Perovskites

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Table S 1. Refined structural parameters for K_2OsCl_6 $T = 90$ K based on SXRD data. Space Group $Fm\bar{3}m$ $a = 9.703218(22)$ Å Cell volume = $913.582(4)$ Å³ R_{wp} 0.042 $R(F^2)$ 0.048 χ^2 11.44

Atom	Site	x	y	z	Ui/Ue*100 (Å ²)
K	8c	0.25	0.25	0.25	1.30*
Os	4a	0	0	0	0.65*
Cl	24e	0.23970(7)	0	0	1.36*
	U ¹¹	U ²²	U ³³	U ¹²	U ¹³ = U ²³
K	1.301(16)	= U ¹¹	= U ¹¹	0	0
Os	0.648(5)	= U ¹¹	= U ¹¹	0	0
Cl	1.06(4)	1.514(22)	= U ²²	0	0

* Refined using anisotropic APDs. See ESI for the corresponding CIF.

Table S2. Summary of the mode decomposition (with respect to their Group $Fm\bar{3}m$ parent structure) of the $P2_1/n$ structures of in K_2OsBr_6 and Na_2OsBr_6 at the indicated temperatures. In K_2OsBr_6 the X_3^+ mode associated with the in-phase tilts has a larger amplitude than the GM_4^+ mode suggesting it would be lost first, resulting in the $P4/mnc$ structure. Conversely in Na_2OsBr_6 the GM_4^+ mode is larger suggesting the X_3^+ in-phase tilts will be lost first resulting in the $I4/mcm$ structure. They are followed in magnitude by two modes of the GM_5^+ irreducible representation related to octahedra distortion and an X_5^+ mode related to displacement of Na or K atoms in ab -plane

K-Vector	Irrep	Direction	Dimension	Amplitude (Å)			
				K_2OsBr_6		Na_2OsBr_6	
				90K	300 K	90 K	480 K
(0 ,0, 0)	Gm_1^+	(a)	1	0.028	0.038	0.002	0.062
(0 ,0, 0)	Gm_3^+	(a,0)	1	0.045	0.062	0.007	0.028
(0 ,0, 0)	Gm_4^+	(a,a,0)	1	0.470	0.283	1.514	1.417
(0 ,0, 0)	Gm_5^+	(-b, a, -a)	4	0.131	0.354	0.355	0.315
(0 ,1, 0)	X_2^+	(0, a, 0)	1	0.023	0.056	0.067	0.043
(0 ,1, 0)	X_3^+	(0, a, 0)	1	0.653	0.531	1.125	1.082
(0 ,1, 0)	X_5^+	(a, a, 0, 0, a, a)	3	0.274	0.157	0.880	0.802

Table S3. Refined structural parameters for Na₂OsBr₆ at 90 K. The structure was refined in SG *P2₁/n* with *a* = 6.83374(7) *b* = 7.16183(6) *c* = 9.90163(10) Å β = 91.1282(7)° Vol = 484.512(8) Å³. χ^2 = 42.7 R_p = 0.049 WR_p = 0.073

Name	Site	x	y	z	Ui/Ue*100 (Å ²)
Os	2 <i>a</i>	0	0	0	0.93(4)
Na	4 <i>e</i>	0.5297(12)	0.0864(9)	0.2367(8)	1.26(25)
Br1	4 <i>e</i>	0.2962(3)	0.18681(29)	0.94472(22)	1.07*
Br2	4 <i>e</i>	0.1115(3)	0.9798(3)	0.23890(21)	0.90*
Br3	4 <i>e</i>	0.67601(32)	0.79384(29)	0.45060(21)	1.16*

* Refined using anisotropic APDs. See ESI for the corresponding CIF.

Table S 4. Refined structural parameters for K₂OsCl₆ T = 3 K based on NPD data. Space Group *I4/m* *a* = 6.83383(9) *c* = 9.72742(17) Å Cell volume = 454.283(15) Å³ R_{wp} 0.049 R(F²) 0.038 χ^2 3.58

Name	Site	x	y	z	Ui/Ue*100 (Å ²)
K	4 <i>d</i>	0	0.5	0.25	0.35(8)
Os	2 <i>a</i>	0	0	0	0.04(5)
Cl1	4 <i>e</i>	0	0	0.24029(21)	0.39*
Cl2	8 <i>h</i>	0.22750(19)	0.25367(22)	0	0.44*
	U ¹¹	U ²²	U ³³	U ¹²	U ¹³ = U ²³
Cl1	0.48(7)	0.48(7)	0.22(10)	0	0
Cl2	0.26(7)	0.13(11)	0.91(8)	-0.36(6)	0

Table S5. Refined structural parameters for Na₂OsBr₆·6H₂O at 300 K. The structure was refined in SG $P\bar{1}$ $a = 7.051419(20)$ $b = 7.287631(21)$ $c = 8.581013(24)$ Å $\alpha = 78.49110(20)$ $\beta = 97.88580(20)$ $\gamma = 72.56320(20)^\circ$ Vol = 402.9851(21) Å³ $\chi^2 = 37.5$ $R_p = 0.038$ $WR_p = 0.063$

Name	Site	x	y	z	Ui/Ue*100 (Å ²)
Os	1a	0	0	0	2.89(5)
Na	2i	0.5498(12)	0.7306(12)	0.5225(9)	6.54(29)
Br1	2i	0.23268(30)	0.19561(30)	-0.01527(25)	4.05(8)
Br2	2i	0.08900(31)	0.91432(29)	0.30390(24)	4.12(8)
Br3	2i	0.27750(30)	0.69832(30)	-0.00162(26)	4.17(8)
O1	2i	0.1046(17)	0.3915(16)	0.3270(13)	6.05(25)*
O2	2i	0.4100(16)	-0.0091(16)	0.6558(13)	6.05(25)*
O3	2i	0.6396(15)	0.4956(15)	0.3584(12)	6.05(25)*

* The isotropic displacement parameters for the three oxygen atoms were constrained to be equal. The hydrogen atoms were not located.

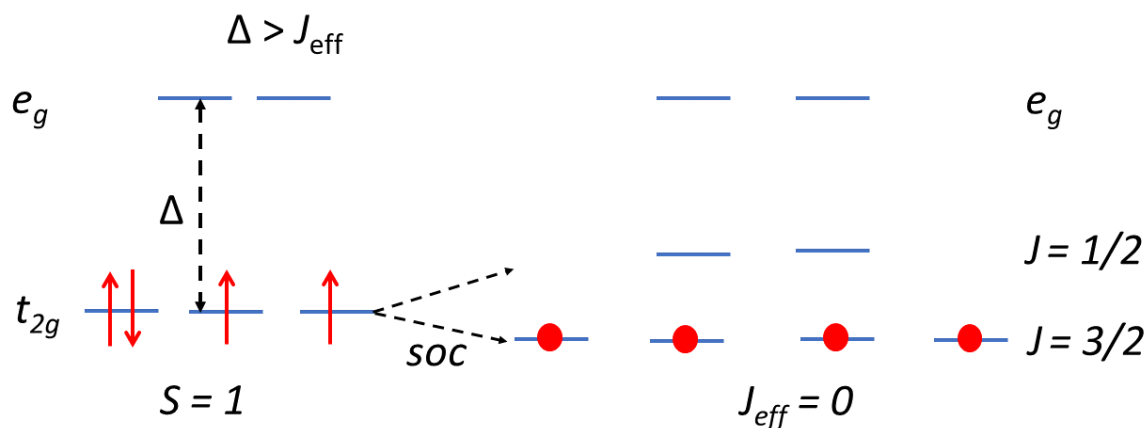


Figure S1 Impact of Hund's coupling J_H , Spin orbit coupling (SOC) λ , and crystal field splitting Δ on the energy and occupancy of the 5d orbitals for an Os(IV) d^4 cation in an octahedral field. When $\Delta > J_H$ the four spins occupy the t_{2g} orbitals. For large SOC the $J = 3/2$ level is fully occupied giving $J_{eff} = 0$.

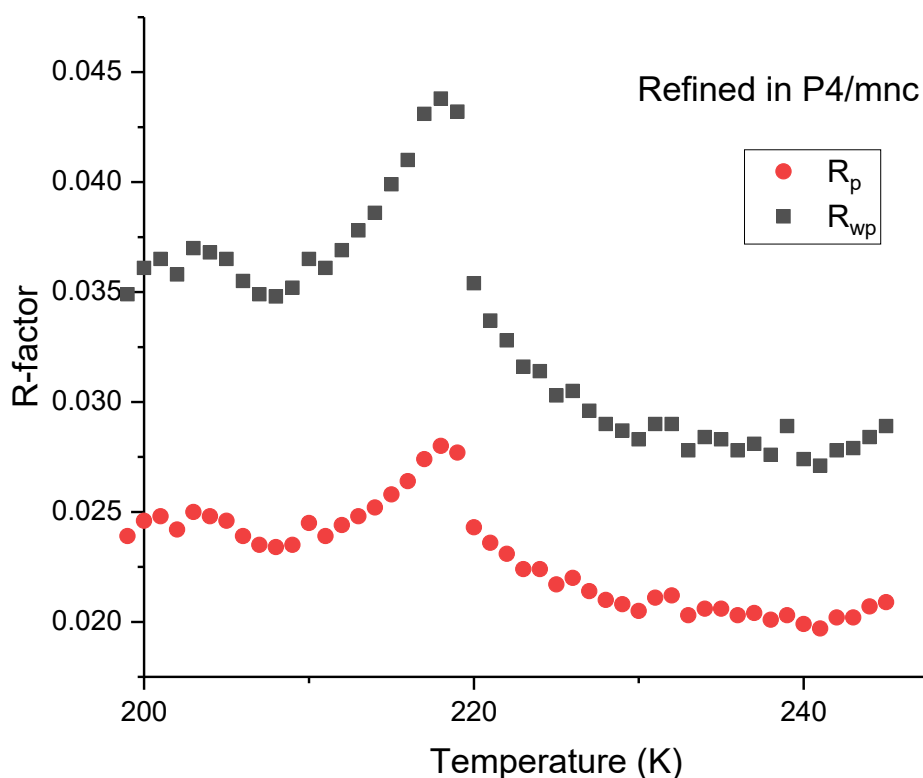


Figure S2. Temperature dependence of the R_p and R_{wp} values for profiles measured between 200 and 250 K and modeled using a single phase $P4/mnc$ model for K_2OsBr_6 . Around 220 K there is a small, but discernable, increase in the Rietveld R-factors indicating that the transition to the cubic structure involves a small two-phase region (~ 10 K). Since the cell

metric of the two phases are essentially identical quantification of the two phases was not possible

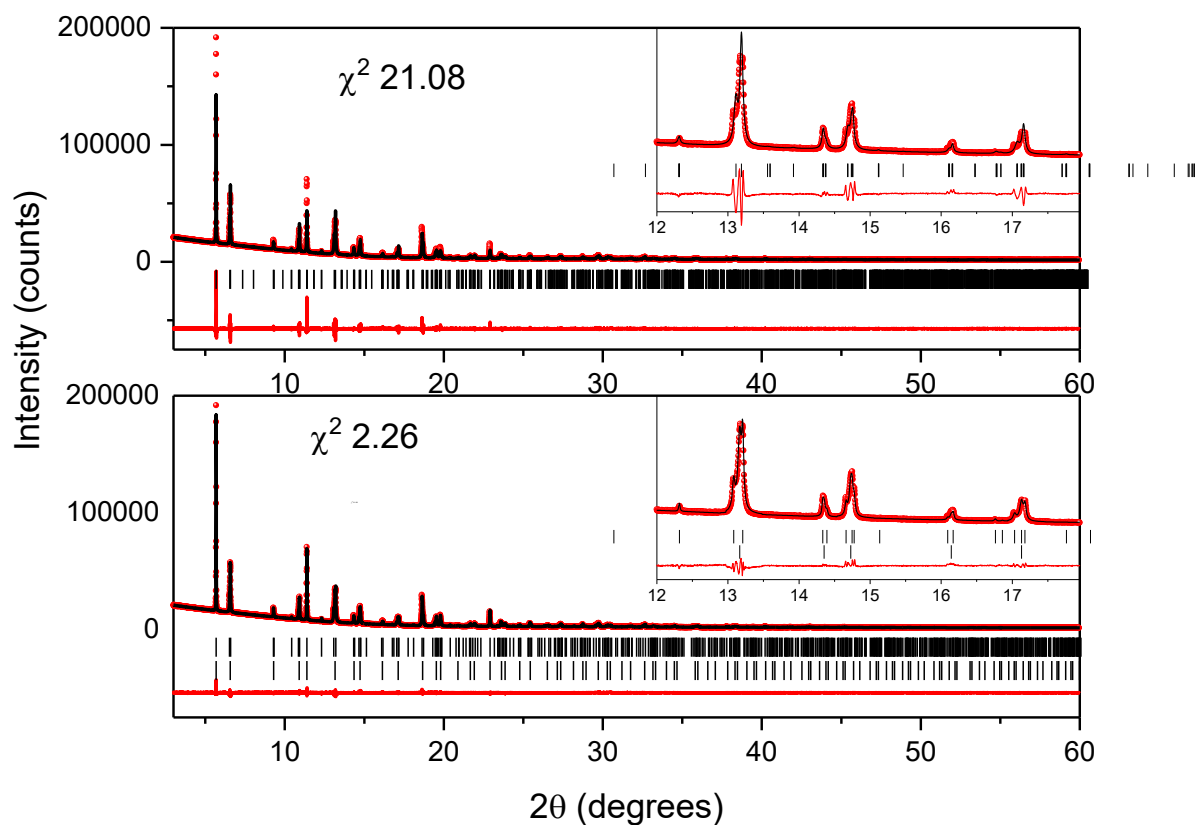


Figure S3. Illustration of the Rietveld profiles for K_2OsBr_6 at 218 K. The top profile was analysed as a single phase $P4/mnc$ model and had $\chi^2 = 21.08$. The bottom profile was analysed using a two phase $Fm\bar{3}m$ and $P4/mnc$ model and had $\chi^2 = 2.26$.

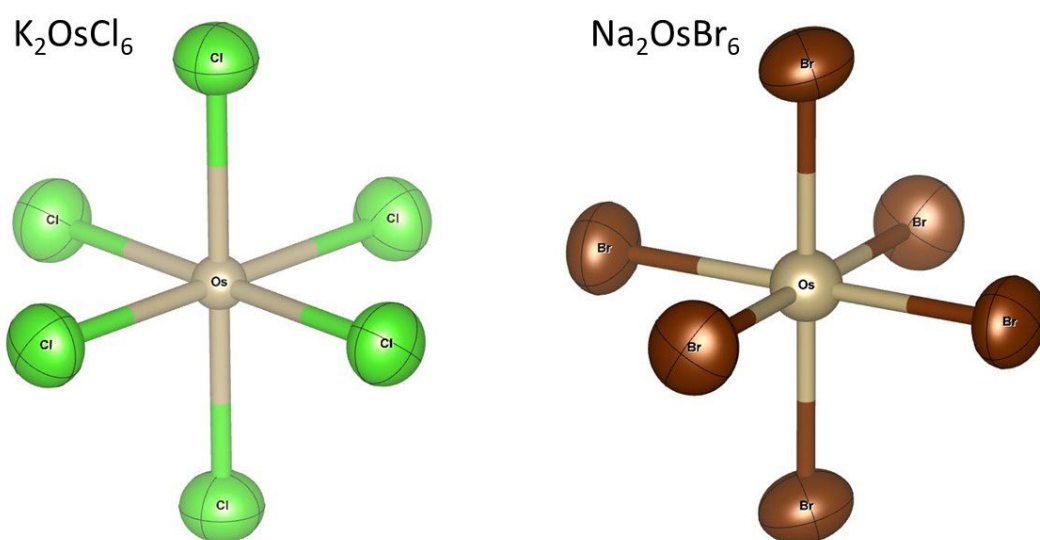


Figure S4. Representation of the octahedral units in cubic ($Fm\bar{3}m$) K_2OsCl_6 and monoclinic ($P2_1/n$) structured Na_2OsBr_6 illustrating the inhibition of the displacement along the Os-X bonds.

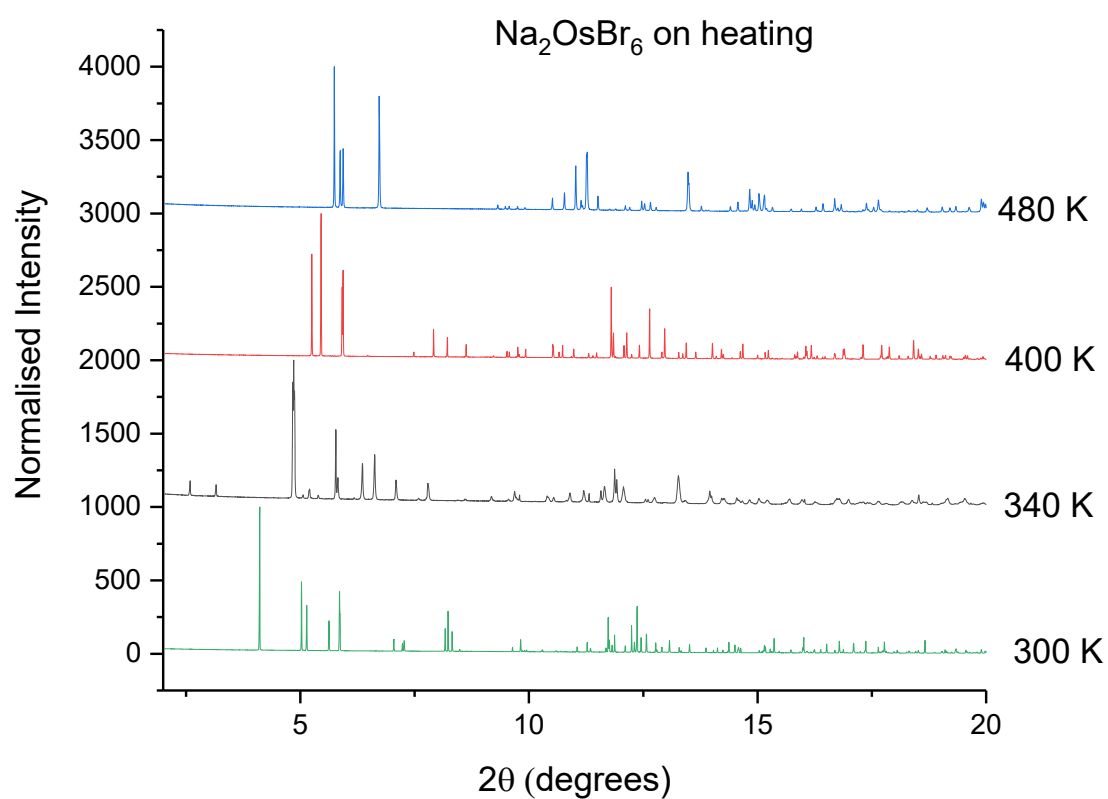


Figure S5. Representative examples of the diffraction profiles for the four phases seen during the in-situ dehydration of $\text{Na}_2\text{OsBr}_6 \cdot 6\text{H}_2\text{O}$. The peaks in the profile at 340 K are broader than those at other temperatures.

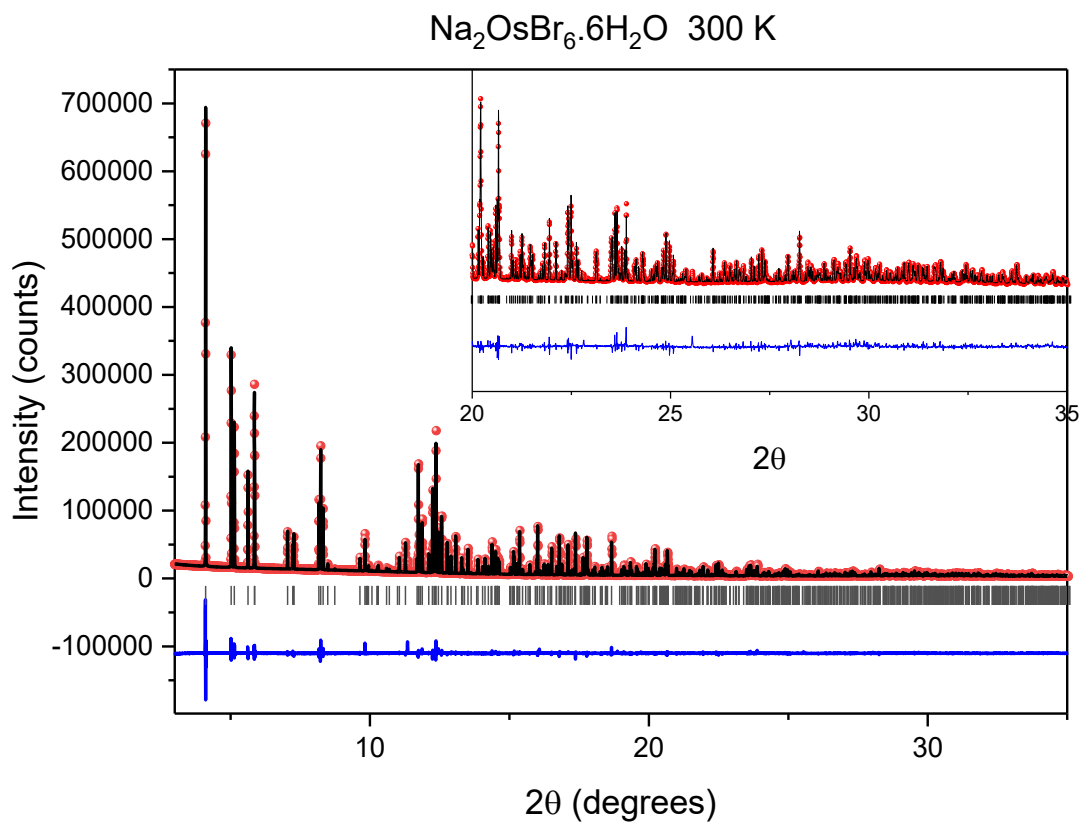


Figure S6. Rietveld refinement profiles for $\text{Na}_2\text{OsBr}_6 \cdot 6\text{H}_2\text{O}$ obtained at 300 K. The experimental (●) and calculated (black) profiles are shown together with the difference curve (blue line). The vertical tickmarks show the positions of the space group allowed Bragg reflections. The inset highlights the quality of the data and fit at higher angles.

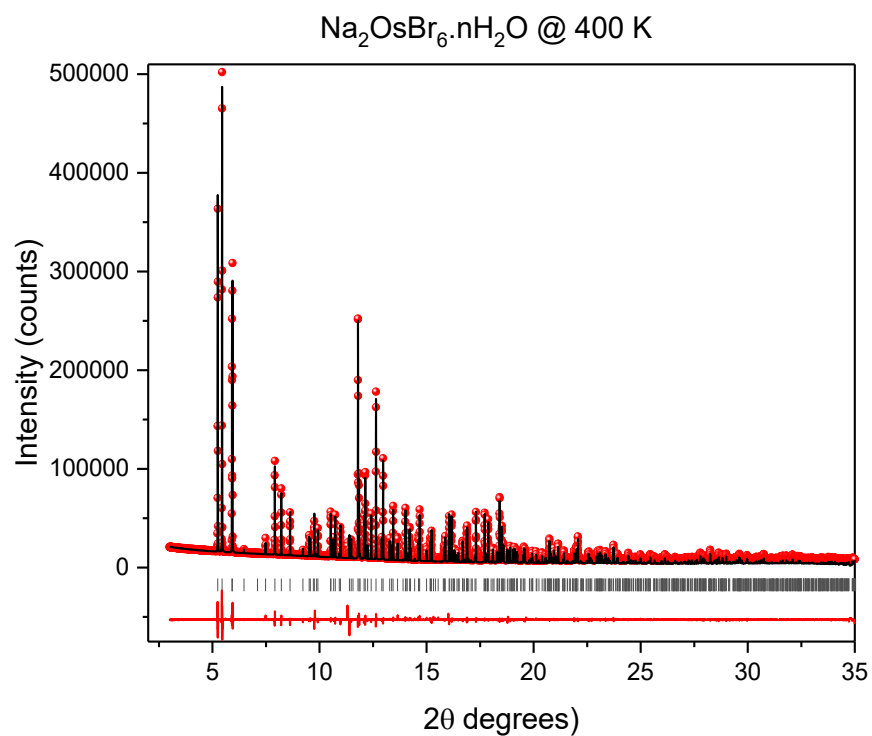


Figure S7 LeBail fit for $\text{Na}_2\text{OsBr}_6 \cdot n\text{H}_2\text{O}$ at 400 K. The experimental (●) and calculated (black) profiles are shown together with the difference curve (blue line). The vertical tick marks show the positions of the allowed Bragg reflections. The data was obtained *in-situ* by dehydration of $\text{Na}_2\text{OsBr}_6 \cdot 6\text{H}_2\text{O}$ at 400 K.

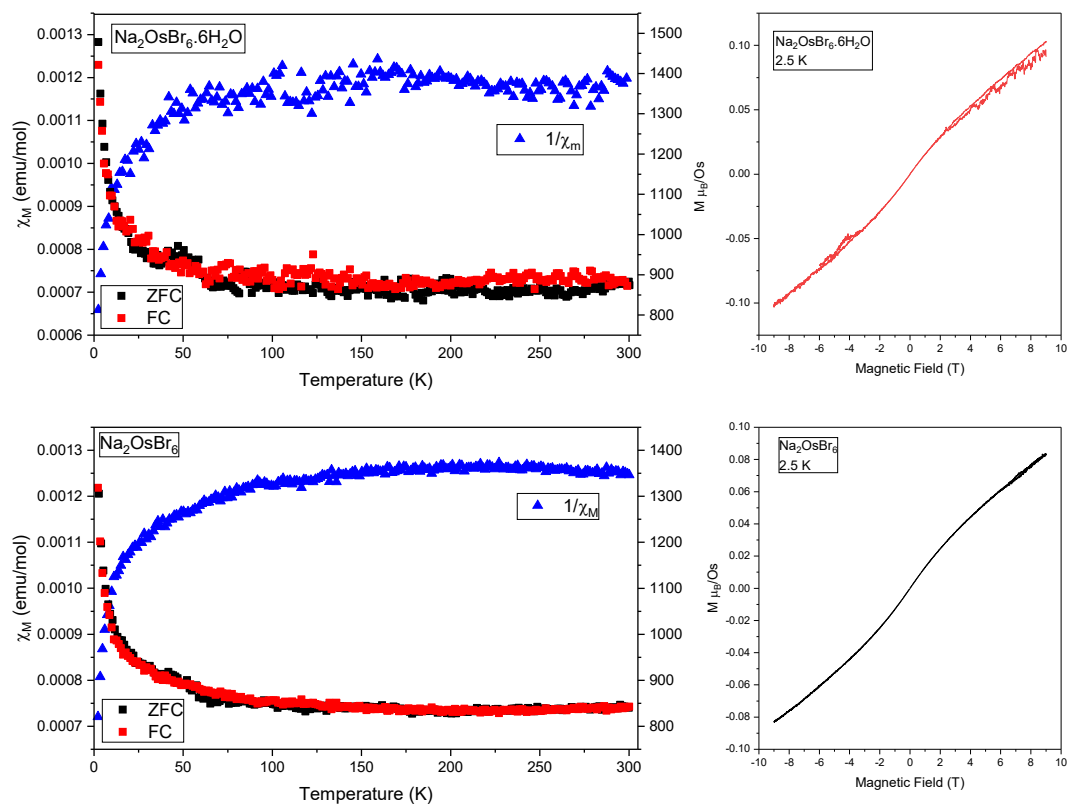


Figure S8. Temperature dependence of the field cooled and zero field cooled magnetic susceptibility for $\text{Na}_2\text{OsBr}_6 \cdot 6\text{H}_2\text{O}$ and Na_2OsBr_6 measured with an applied field of 1.0 T. The inverse of the ZFC susceptibility is also shown. The scatter in the data reflects the low measured susceptibilities. The right-hand panels show the field dependence of the magnetisation of the two compounds at 2.5 K.

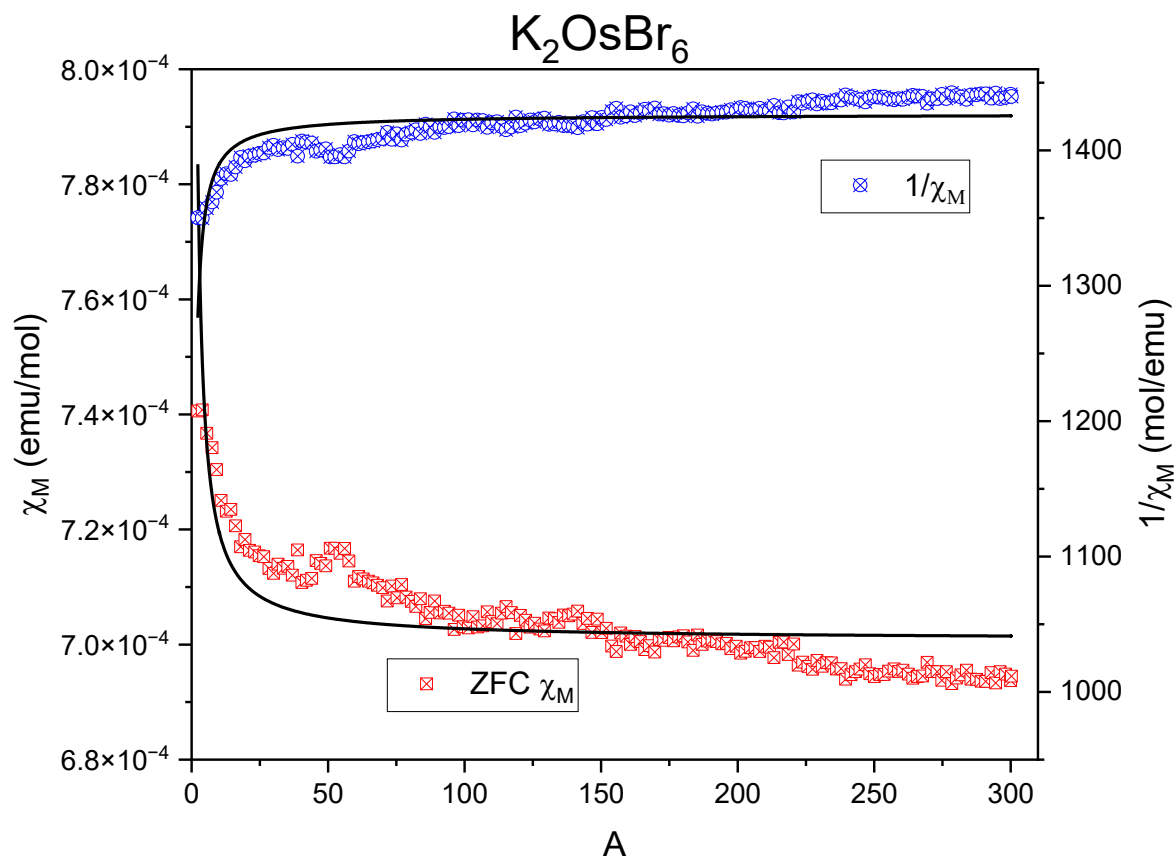


Figure S9. Temperature dependence of the magnetic susceptibilities (red squares lines) and inverse susceptibilities (blue circles) for K_2OsBr_6 . The solid lines are the best fit to the CW expression $\chi_{cal} = \left[(1 - d) * \frac{C}{T - \theta} + TIP \right] + d * \left(\frac{0.375}{T} \right)$ where d indicates the amount of paramagnetic impurity, TIP is a temperature independent contribution to the magnetic susceptibility and C and θ are Curie and Weiss constants respectively. The fitting suggested θ was ~ 0 K and that the TIP term was non-trivial $\sim 7.7 \times 10^{-4}$ emu mol $^{-1}$ with 0.1% of a $S = 1$ impurity.

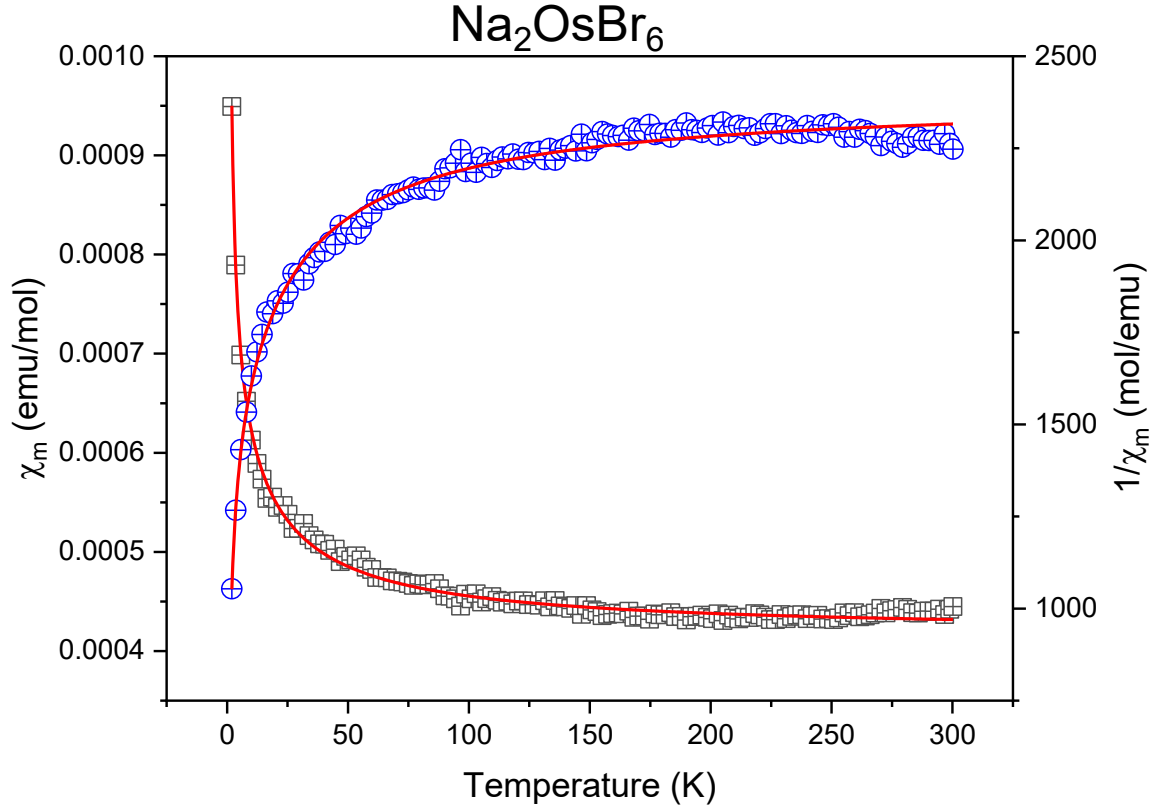


Figure S10 Temperature dependence of the magnetic susceptibilities (black squares) and inverse susceptibilities (blue circles) for Na_2OsBr_6 . The solid lines are the best fit to the CW expression $\chi_{cal} = \left[(1 - d) * \frac{C}{T - \theta} + TIP \right] + d * \left(\frac{0.375}{T} \right)$ where d indicates the amount of paramagnetic impurity, TIP is a temperature independent contribution to the magnetic susceptibility and C and θ are Curie and Weiss constants respectively. The fitting suggested θ was -15 K and that the TIP term was non-trivial $\sim 4.2 \times 10^{-04} \text{ emu mol}^{-1}$ with 0.5% of a $S = 1$ impurity.

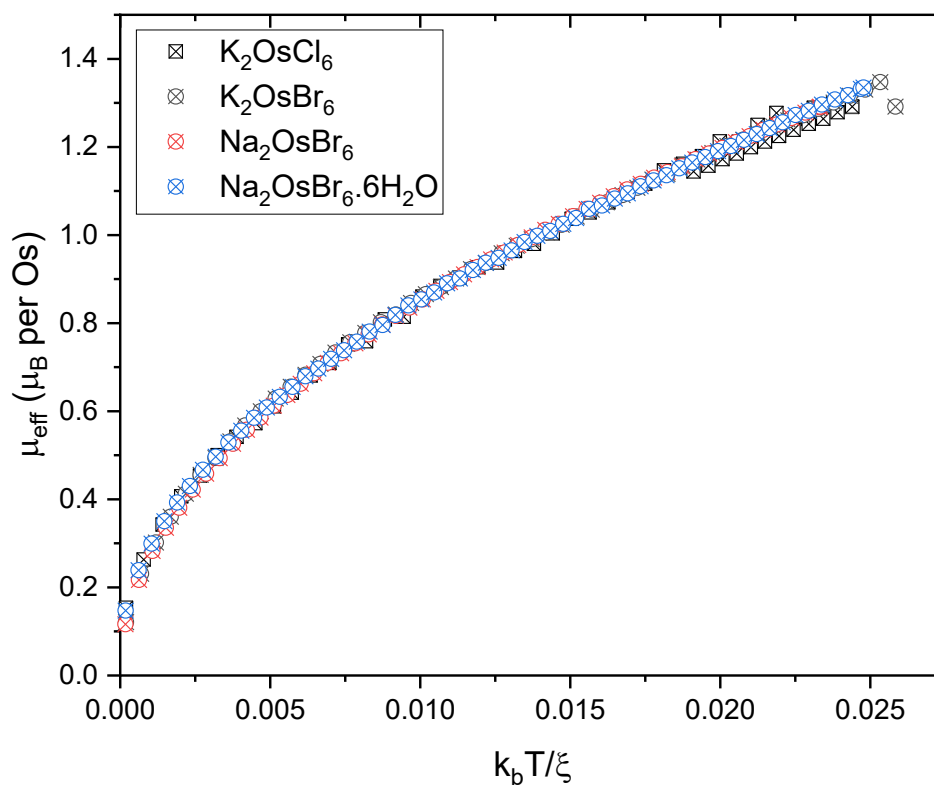


Figure S11 Kotani plots for the four $\text{Os}^{4+} 5d^4$ halides K_2OsCl_6 , K_2OsBr_6 , Na_2OsBr_6 and $\text{Na}_2\text{OsBr}_6 \cdot 6\text{H}_2\text{O}$. The values of the spin orbit coupling constants used are 8077, 8946, 8442 and 8553 cm^{-1} respectively.