Electronic Supplementary Material (ESI) for Dalton Transactions.

A journey through ternary lead chlorido tungstates by thermal scanning

Supporting Information

Table of contents:

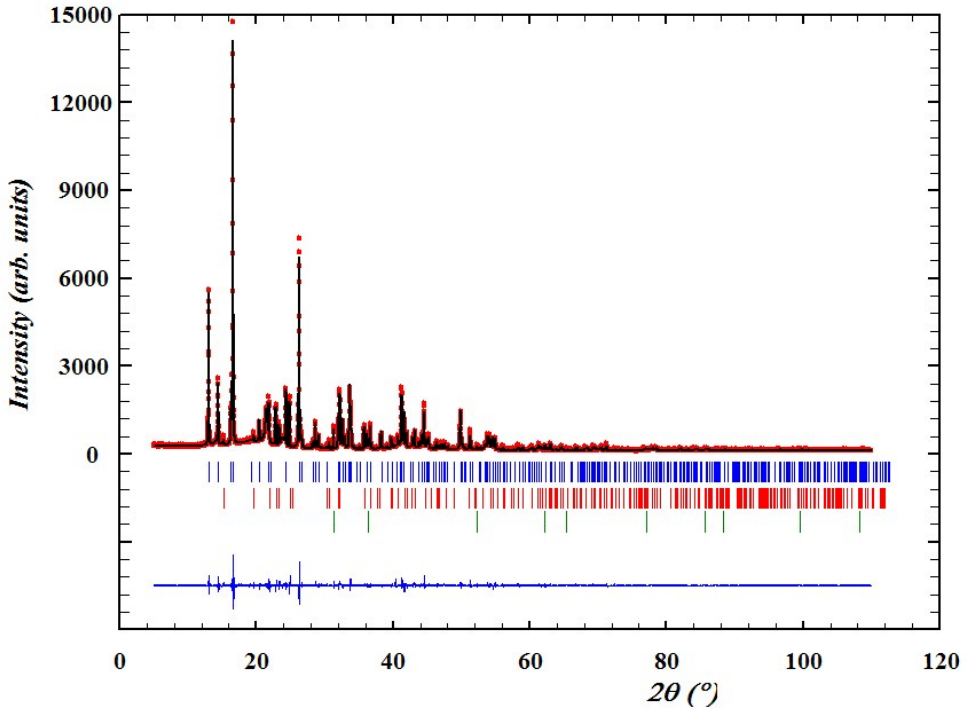

Figure S1. Powder XRD refinement pattern of $Pb_{0.5}WCl_6$.

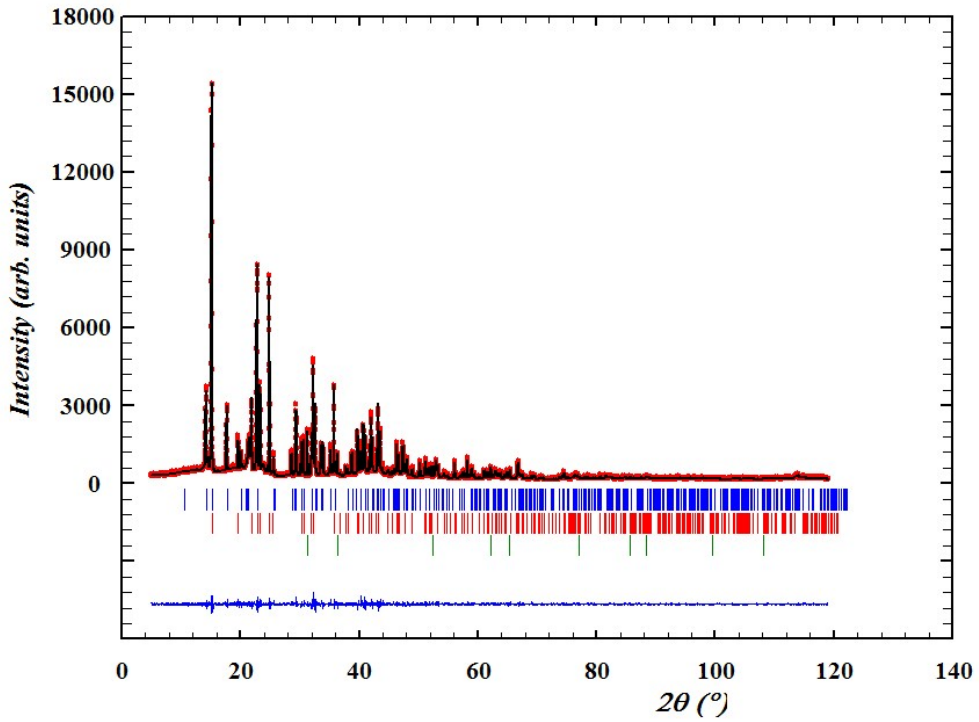

Figure S2. Powder XRD refinement pattern of PbW_2Cl_{10}.

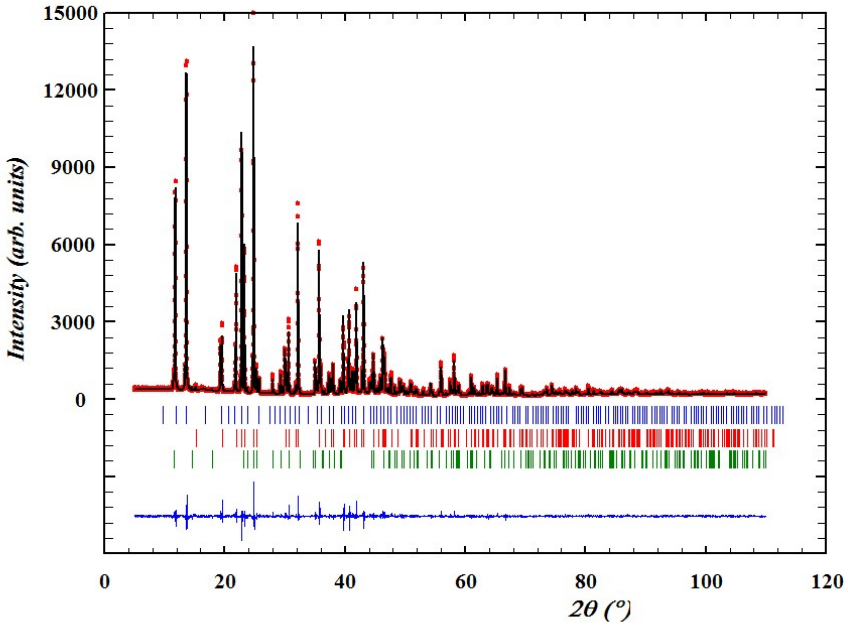

Figure S3. Powder XRD refinement pattern of PbW_6Cl_{14}.

Table S1. Crystal data and structure refinement data for $Pb_{0.5}WCl_6$.

Empirical formula	$Pb_{0.5}WCl_6$
ICSD No	432 728
Formula weight	500.168 g/mol
Temperature	298(2) K
Wavelength	1.54060 Å
Crystal system	Tetragonal
Space group	P 4_2/n (No. 86)
Unit cell dimensions	a = b = 8.67052(9) Å
	c = 10.8489(2) Å
Volume	815.67(2) $Å^3$
Z	4
μ (CuKa)	63.084 mm^{-1}
Density (calculated)	4.0727 gcm^{-3}
Theta range for data collection	2.5 to 55 °
Total number of reflections	540
Refined parameters	43
Refined structure parameters	22
R_p, R_{wp}	5.3961, 7.0788
R_{Bragg}	3.2977
χ^2	1.4295

Table S2. Crystal data and structure refinement for PbW_2Cl_{10}.

Empirical formula	PbW_2Cl_{10}
ICSD No	432 730
Formula weight	929.38 g/mol
Temperature	298(2) K
Wavelength	1.54060 Å
Crystal system	Tetragonal
Space group	P 4_2/m (No. 86)
Unit cell dimensions	a = b = 6.2222(1) Å
	c = 16.7414(3) Å
Volume	648.16(2) $Å^3$
Z	2
μ (CuKa)	73.537 mm^{-1}
Density (calculated)	4.7634 gcm^{-3}
Theta range for data collection	2.5 to 59.5 °
Total number of reflections	521
Refined parameters	59
Refined structure parameters	36
R_p, R_{wp}	4.61, 5.93
R_{Bragg}	2.2656
χ^2	1.4979

Table S3. Crystal data and structure refinement for $Pb_{1.5}W_3Cl_{13}$.

Empirical formula	$Pb_{1.5}W_3Cl_{13}$	
ICSD No	432 729	
Formula weight	1323.19	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$P4_2/m$	
Unit cell dimensions	a = 13.4831(10) Å	α= 90°.
	b = 13.4831(10) Å	β= 90°.
	c = 9.8247(7) Å	γ = 90°.
Volume	1786.1(3) $Å^3$	
Z	2	
Density (calculated)	4.921 g/cm^3	
Absorption coefficient	35.265 mm^{-1}	
F(000)	2264	
Crystal size	0.1 x 0.02 x 0.02 mm^3	
Theta range for data collection	2.565 to 25.022°.	
Index ranges	$-16 \le h \le 16$, $-16 \le k \le 16$, $-10 \le l \le 11$	
Reflections collected	17310	
Independent reflections	1680 [R(int) = 0.0852]	
Completeness to theta = 25.022°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1680 / 0 / 87	
Goodness-of-fit on F^2	1.226	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0565, wR2 = 0.0776	
R indices (all data)	R1 = 0.0757, wR2 = 0.0818	
Largest diff. peak and hole	1.971 and -1.707 $e.Å^{-3}$	

Table S4. Crystal data and structure refinement for $Pb_2W_3Cl_{14}$.

Empirical formula	$Pb_2W_3Cl_{14}$	
ICSD No	432 780	
Formula weight	1462.23	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.5253(5) Å	α= 111.752(5)°.
	b = 10.7498(7) Å	β= 98.044(5)°.
	c = 12.5959(8) Å	γ = 96.224(5)°.
Volume	922.75(11) $Å^3$	
Z	2	
Density (calculated)	5.263 g/cm^3	
Absorption coefficient	38.817 mm^{-1}	
F(000)	1248	
Crystal size	0.3 x 0.3 x 0.1 mm^3	
Theta range for data collection	2.776 to 25.350°.	
Index ranges	$-8 \le h \le 9$, $-12 \le k \le 12$, $-15 \le l \le 14$	
Reflections collected	5793	
Independent reflections	3164 [R(int) = 0.0362]	
Completeness to theta = 25.242°	93.9 %	
Max. and min. transmission	0.5596 and 0.2017	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3164 / 0 / 173	
Goodness-of-fit on F^2	1.043	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0320, wR2 = 0.0602	
R indices (all data)	R1 = 0.0471, wR2 = 0.0638	
Largest diff. peak and hole	1.462 and -1.229 $e.Å^{-3}$	

Table S5. Crystal data and structure refinement for PbW_6Cl_{14}.

Empirical formula	PbW_6Cl_{14}
ICSD No	432 731
Formula weight	1806.58 g/mol
Temperature	298(2) K
Wavelength	1.54060 Å
Crystal system	Cubic
Space group	*Pn-3* (No. 14)
Unit cell dimensions	a = 12.9540(2) Å
Volume	2173.77(6) $Å^3$
Z	4
μ (CuKa)	87.401 mm^{-1}
Density (calculated)	5.5212 gcm^{-3}
Theta range for data collection	2.5 to 55 °
Total number of reflections	488
Refined parameters	51
R_p, R_{wp}	0.0551, 0.0707
R_{Bragg}	2.4660
χ^2	1.9680

Table S6. Atomic coordinates and equivalent isotropic displacement parameters (pm^2) for $Pb_{0.5}WCl_6$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
W1	½	½	0	0.0533(6)
Pb1	¼	¼	¼	0.0586(8)
Cl1	0.6916(8)	0.4425(7)	0.8636(6)	0.053(3)
Cl2	0.4653(7)	0.2371(7)	0.0372(5)	0.061(3)
Cl3	0.6758(8)	0.5116(7)	0.1560(6)	0.071(3)

Table S7. Atomic coordinates and equivalent isotropic displacement parameters (pm^2) for PbW_2Cl_{10}. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
W1	½	0	0.0808(1)	0.046(2)
Pb1	½	½	¼	0.052(2)
Cl1	0.2823(6)	0.1422(7)	0.1893(3)	0.074(2)
Cl2	0.7622(7)	-0.1790(9)	0	0.040(2)
Cl3	0.6969(5)	0.3128(5)	0.0887(3)	0.071(2)

Table S8. Atomic coordinates and equivalent isotropic displacement parameters (pm^2) for $Pb_{1,5}W_3Cl_{13}$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pb(1)	½	½	-¼	0.028(1)
Pb(2)	651(1)	1796(1)	½	0.034(1)
W(1)	1186(1)	2898(1)	1383(1)	0.021(1)
W(2)	2733(1)	3733(1)	0	0.019(1)
Cl(1)	2333(5)	2007(5)	0	0.023(1)
Cl(2)	1735(4)	4572(3)	1662(5)	0.027(1)
Cl(3)	3637(5)	5328(5)	0	0.026(2)
Cl(4)	-100(5)	3571(5)	0	0.025(1)
Cl(5)	54(4)	3388(4)	3227(5)	0.036(1)
Cl(6)	2198(4)	2334(4)	3262(5)	0.034(1)
Cl(7)	359(4)	1358(4)	1581(5)	0.034(1)
Cl(8)	3950(4)	3256(4)	1637(5)	0.032(1)

Table S9. Atomic coordinates and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for $Pb_2W_3Cl_{14}$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
W(6)	2112(1)	7355(1)	9066(1)	0.016(1)
W(7)	3698(1)	6890(1)	7176(1)	0.017(1)
W(8)	2194(1)	4738(1)	7602(1)	0.017(1)
Pb(1)	-61(1)	1212(1)	7910(1)	0.027(1)
Pb(2)	5194(1)	7862(1)	4771(1)	0.031(1)
Cl(1)	509(4)	6262(3)	7077(3)	0.020(1)
Cl(2)	-705(4)	3773(3)	7824(3)	0.025(1)
Cl(3)	3272(4)	5686(3)	9662(3)	0.024(1)
Cl(4)	5302(4)	5186(3)	7440(3)	0.023(1)
Cl(5)	5178(4)	8239(3)	9135(3)	0.023(1)
Cl(6)	3146(4)	8724(3)	11178(3)	0.026(1)
Cl(7)	1328(4)	3203(3)	5604(3)	0.026(1)
Cl(8)	1197(5)	9364(3)	9017(3)	0.026(1)
Cl(9)	-725(4)	6887(3)	9595(3)	0.025(1)
Cl(10)	6697(4)	7693(3)	6848(3)	0.025(1)
Cl(11)	2924(5)	8774(3)	6746(3)	0.027(1)
Cl(12)	3315(5)	2738(3)	7798(3)	0.030(1)
Cl(13)	2994(4)	5688(3)	5111(3)	0.026(1)
Cl(14)	7422(5)	10360(4)	5745(3)	0.036(1)

Table S10. Atomic coordinates and equivalent isotropic displacement parameters (pm^2) for PbW_6Cl_{14}. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
W1	0.86532(15)	0.0293(3)	0.9638(3)	0.0342(5)
Pb1	½	½	½	0.0332(9)
Cl1	0.1346(5)	0.1346(5)	0.1346(5)	0.038(6)
Cl2	0.3791(4)	0.6903(4)	0.9343(4)	0.033(3)
Cl3	0.5875(6)	0.8135(4)	0.0715(6)	0.090(3)

Table S11. Selected Bond lengths [Å] for $Pb_{0.5}WCl_6$.

W1	Cl1	2.280(7)
W1	Cl1	2.280(7)
W1	Cl2	2.334(6)
W1	Cl2	2.334(6)
W1	Cl3	2.280(7)
W1	Cl3	2.280(7)
Pb1	Cl1	2.981(6)
Pb1	Cl1	2.981(6)
Pb1	Cl1	2.981(7)
Pb1	Cl1	2.981(7)
Pb1	Cl2	2.971(6)
Pb1	Cl2	2.971(6)
Pb1	Cl2	2.971(6)
Pb1	Cl2	2.971(6)

Table S12. Selected Bond lengths [Å] for PbW_2Cl_{10}.

W1	W1	2.706(2)
W1	Cl1	2.432(5)
W1	Cl1	2.432(5)
W1	Cl2	2.394(4)
W1	Cl2	2.394(4)
W1	Cl3	2.304(3)
W1	Cl3	2.304(3)
Pb1	Cl1	2.797(4)
Pb1	Cl1	2.797(4)
Pb1	Cl1	2.797(4)
Pb1	Cl1	2.797(4)
Pb1	Cl3	3.186(5)
Pb1	Cl3	3.186(5)
Pb1	Cl3	3.186(5)
Pb1	Cl3	3.186(5)

Table S13. Bond lengths [pm] and angles [°] for $Pb_{1.5}W_3Cl_{13}$.

Pb(1)-Cl(8)#1	2.873(5)
Pb(1)-Cl(8)#2	2.873(5)
Pb(1)-Cl(8)#3	2.873(5)
Pb(1)-Cl(8)#4	2.873(5)
Pb(2)-Cl(6)#5	2.792(5)
Pb(2)-Cl(6)	2.792(5)
Pb(2)-Cl(5)#5	2.879(5)
Pb(2)-Cl(5)	2.879(5)
W(1)-Cl(7)	2.365(5)
W(1)-Cl(4)	2.382(6)
W(1)-Cl(1)	2.383(5)
W(1)-Cl(2)	2.391(5)
W(1)-Cl(6)	2.419(5)
W(1)-Cl(5)	2.460(5)
W(1)-W(1)#2	2.717(2)
W(1)-W(2)	2.732(1)
W(2)-Cl(8)	2.386(5)
W(2)-Cl(8)#2	2.386(5)
W(2)-Cl(1)	2.390(6)
W(2)-Cl(2)#2	2.399(5)
W(2)-Cl(2)	2.399(5)
W(2)-Cl(3)	2.471(6)
W(2)-W(1)#2	2.732(1)

Cl(8)#1-Pb(1)-Cl(8)#2	145.7(2)
Cl(8)#1-Pb(1)-Cl(8)#3	94.99(6)
Cl(8)#2-Pb(1)-Cl(8)#3	94.99(6)
Cl(8)#1-Pb(1)-Cl(8)#4	94.99(6)
Cl(8)#2-Pb(1)-Cl(8)#4	94.99(6)
Cl(8)#3-Pb(1)-Cl(8)#4	145.7(2)
Cl(6)#5-Pb(2)-Cl(6)	75.4(2)
Cl(6)#5-Pb(2)-Cl(5)#5	69.23(14)
Cl(6)-Pb(2)-Cl(5)#5	112.67(17)
Cl(6)#5-Pb(2)-Cl(5)	112.67(17)
Cl(6)-Pb(2)-Cl(5)	69.23(14)
Cl(5)#5-Pb(2)-Cl(5)	74.5(2)
Cl(7)-W(1)-Cl(4)	92.2(2)
Cl(7)-W(1)-Cl(1)	84.8(2)

Cl(4)-W(1)-Cl(1)	109.83(13)
Cl(7)-W(1)-Cl(2)	164.86(17)
Cl(4)-W(1)-Cl(2)	86.0(2)
Cl(1)-W(1)-Cl(2)	109.91(19)
Cl(7)-W(1)-Cl(6)	85.84(18)
Cl(4)-W(1)-Cl(6)	164.97(16)
Cl(1)-W(1)-Cl(6)	84.87(16)
Cl(2)-W(1)-Cl(6)	91.95(18)
Cl(7)-W(1)-Cl(5)	83.26(19)
Cl(4)-W(1)-Cl(5)	82.30(16)
Cl(1)-W(1)-Cl(5)	163.33(17)
Cl(2)-W(1)-Cl(5)	81.60(18)
Cl(6)-W(1)-Cl(5)	82.67(17)
Cl(7)-W(1)-W(1)#2	94.72(13)
Cl(4)-W(1)-W(1)#2	55.23(9)
Cl(1)-W(1)-W(1)#2	55.25(9)
Cl(2)-W(1)-W(1)#2	96.60(11)
Cl(6)-W(1)-W(1)#2	139.76(13)
Cl(5)-W(1)-W(1)#2	137.44(13)
Cl(7)-W(1)-W(2)	139.72(14)
Cl(4)-W(1)-W(2)	96.59(13)
Cl(1)-W(1)-W(2)	55.20(15)
Cl(2)-W(1)-W(2)	55.36(11)
Cl(6)-W(1)-W(2)	94.49(13)
Cl(5)-W(1)-W(2)	136.82(14)
W(1)#2-W(1)-W(2)	60.188(19)
Cl(8)-W(2)-Cl(8)#2	84.8(3)
Cl(8)-W(2)-Cl(1)	83.81(17)
Cl(8)#2-W(2)-Cl(1)	83.81(17)
Cl(8)-W(2)-Cl(2)#2	166.35(17)
Cl(8)#2-W(2)-Cl(2)#2	93.09(17)
Cl(1)-W(2)-Cl(2)#2	109.40(16)
Cl(8)-W(2)-Cl(2)	93.09(17)
Cl(8)#2-W(2)-Cl(2)	166.35(17)
Cl(1)-W(2)-Cl(2)	109.40(15)
Cl(2)#2-W(2)-Cl(2)	85.8(2)
Cl(8)-W(2)-Cl(3)	84.01(17)
Cl(8)#2-W(2)-Cl(3)	84.01(17)
Cl(1)-W(2)-Cl(3)	163.5(2)
Cl(2)#2-W(2)-Cl(3)	82.36(16)
Cl(2)-W(2)-Cl(3)	82.35(16)

Cl(8)-W(2)-W(1)	94.50(12)
Cl(8)#2-W(2)-W(1)	138.48(13)
Cl(1)-W(2)-W(1)	54.96(12)
Cl(2)#2-W(2)-W(1)	96.00(12)
Cl(2)-W(2)-W(1)	55.08(11)
Cl(3)-W(2)-W(1)	137.33(12)
Cl(8)-W(2)-W(1)#2	138.47(13)
Cl(8)#2-W(2)-W(1)#2	94.50(12)
Cl(1)-W(2)-W(1)#2	54.96(12)
Cl(2)#2-W(2)-W(1)#2	55.08(11)
Cl(2)-W(2)-W(1)#2	96.00(12)
Cl(3)-W(2)-W(1)#2	137.33(12)
W(1)-W(2)-W(1)#2	59.62(4)
W(1)-Cl(1)-W(1)#2	69.50(18)
W(1)-Cl(1)-W(2)	69.84(17)
W(1)#2-Cl(1)-W(2)	69.84(17)
W(1)-Cl(2)-W(2)	69.56(12)
W(1)#2-Cl(4)-W(1)	69.54(19)
W(1)-Cl(5)-Pb(2)	94.12(17)
W(1)-Cl(6)-Pb(2)	97.28(17)
W(2)-Cl(8)-Pb(1)#1	108.47(18)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z #2 x,y,-z #3 y,-x+1,z-1/2

#4 -y+1,x,z-1/2 #5 x,y,-z+1

Table S14. Bond lengths [Å] and angles [°] for $Pb_2W_3Cl_{14}$.

W(6)-Cl(8)	2.355(3)
W(6)-Cl(5)	2.376(3)
W(6)-Cl(9)	2.381(3)
W(6)-Cl(3)	2.388(3)
W(6)-Cl(1)	2.403(3)
W(6)-Cl(6)	2.474(3)
W(6)-W(7)	2.7174(7)
W(6)-W(8)	2.7472(7)
W(7)-Cl(5)	2.379(3)
W(7)-Cl(13)	2.386(3)
W(7)-Cl(11)	2.391(3)
W(7)-Cl(1)	2.395(3)
W(7)-Cl(4)	2.396(3)
W(7)-Cl(10)	2.472(3)
W(7)-W(8)	2.7290(7)
W(8)-Cl(3)	2.387(3)
W(8)-Cl(4)	2.389(3)
W(8)-Cl(7)	2.390(3)
W(8)-Cl(1)	2.398(3)
W(8)-Cl(2)	2.409(3)
W(8)-Cl(12)	2.474(3)
Pb(1)-Cl(6)#1	2.728(3)
Pb(1)-Cl(14)#2	2.862(4)
Pb(1)-Cl(2)	2.885(3)
Pb(1)-Cl(12)	2.921(3)
Pb(1)-Cl(9)#1	2.977(3)
Pb(1)-Cl(8)#3	2.980(3)
Pb(2)-Cl(14)	2.745(4)
Pb(2)-Cl(10)	2.779(3)
Pb(2)-Cl(13)	2.912(3)
Pb(2)-Cl(7)#4	2.996(3)
Pb(2)-Cl(14)#5	3.054(4)
Cl(8)-W(6)-Cl(5)	90.33(11)
Cl(8)-W(6)-Cl(9)	86.90(11)
Cl(5)-W(6)-Cl(9)	162.99(11)
Cl(8)-W(6)-Cl(3)	164.61(12)
Cl(5)-W(6)-Cl(3)	87.22(11)
Cl(9)-W(6)-Cl(3)	91.02(11)
Cl(8)-W(6)-Cl(1)	86.27(11)

Cl(5)-W(6)-Cl(1)	110.03(10)
Cl(9)-W(6)-Cl(1)	86.54(10)
Cl(3)-W(6)-Cl(1)	108.84(11)
Cl(8)-W(6)-Cl(6)	84.39(12)
Cl(5)-W(6)-Cl(6)	78.97(10)
Cl(9)-W(6)-Cl(6)	84.06(11)
Cl(3)-W(6)-Cl(6)	80.23(11)
Cl(1)-W(6)-Cl(6)	167.08(11)
Cl(8)-W(6)-W(7)	93.56(7)
Cl(5)-W(6)-W(7)	55.19(8)
Cl(9)-W(6)-W(7)	141.71(8)
Cl(3)-W(6)-W(7)	97.48(8)
Cl(1)-W(6)-W(7)	55.36(7)
Cl(6)-W(6)-W(7)	134.14(7)
Cl(8)-W(6)-W(8)	140.53(9)
Cl(5)-W(6)-W(8)	95.79(8)
Cl(9)-W(6)-W(8)	97.00(8)
Cl(3)-W(6)-W(8)	54.87(8)
Cl(1)-W(6)-W(8)	55.00(7)
Cl(6)-W(6)-W(8)	135.07(8)
W(7)-W(6)-W(8)	59.918(18)
Cl(5)-W(7)-Cl(13)	164.72(10)
Cl(5)-W(7)-Cl(11)	94.82(12)
Cl(13)-W(7)-Cl(11)	84.19(12)
Cl(5)-W(7)-Cl(1)	110.21(10)
Cl(13)-W(7)-Cl(1)	84.98(11)
Cl(11)-W(7)-Cl(1)	86.52(11)
Cl(5)-W(7)-Cl(4)	84.28(11)
Cl(13)-W(7)-Cl(4)	92.18(11)
Cl(11)-W(7)-Cl(4)	162.82(11)
Cl(1)-W(7)-Cl(4)	109.95(10)
Cl(5)-W(7)-Cl(10)	80.16(10)
Cl(13)-W(7)-Cl(10)	84.61(11)
Cl(11)-W(7)-Cl(10)	81.86(11)
Cl(1)-W(7)-Cl(10)	165.11(11)
Cl(4)-W(7)-Cl(10)	81.08(10)
Cl(5)-W(7)-W(6)	55.09(7)
Cl(13)-W(7)-W(6)	140.19(8)
Cl(11)-W(7)-W(6)	97.71(8)
Cl(1)-W(7)-W(6)	55.64(7)
Cl(4)-W(7)-W(6)	95.81(7)

Cl(10)-W(7)-W(6)	135.15(8)
Cl(5)-W(7)-W(8)	96.20(7)
Cl(13)-W(7)-W(8)	93.90(8)
Cl(11)-W(7)-W(8)	141.77(8)
Cl(1)-W(7)-W(8)	55.34(7)
Cl(4)-W(7)-W(8)	55.10(7)
Cl(10)-W(7)-W(8)	136.12(8)
W(6)-W(7)-W(8)	60.583(18)
Cl(3)-W(8)-Cl(4)	86.49(11)
Cl(3)-W(8)-Cl(7)	163.26(11)
Cl(4)-W(8)-Cl(7)	92.25(11)
Cl(3)-W(8)-Cl(1)	109.04(11)
Cl(4)-W(8)-Cl(1)	110.09(10)
Cl(7)-W(8)-Cl(1)	87.08(11)
Cl(3)-W(8)-Cl(2)	91.19(11)
Cl(4)-W(8)-Cl(2)	165.17(11)
Cl(7)-W(8)-Cl(2)	85.76(11)
Cl(1)-W(8)-Cl(2)	84.52(10)
Cl(3)-W(8)-Cl(12)	81.54(12)
Cl(4)-W(8)-Cl(12)	79.03(11)
Cl(7)-W(8)-Cl(12)	81.83(12)
Cl(1)-W(8)-Cl(12)	165.99(12)
Cl(2)-W(8)-Cl(12)	86.14(11)
Cl(3)-W(8)-W(7)	97.18(8)
Cl(4)-W(8)-W(7)	55.35(7)
Cl(7)-W(8)-W(7)	95.80(8)
Cl(1)-W(8)-W(7)	55.24(7)
Cl(2)-W(8)-W(7)	139.46(8)
Cl(12)-W(8)-W(7)	134.28(8)
Cl(3)-W(8)-W(6)	54.89(8)
Cl(4)-W(8)-W(6)	95.20(8)
Cl(7)-W(8)-W(6)	141.77(8)
Cl(1)-W(8)-W(6)	55.18(8)
Cl(2)-W(8)-W(6)	95.43(8)
Cl(12)-W(8)-W(6)	136.40(9)
W(7)-W(8)-W(6)	59.499(17)
Cl(6)#1-Pb(1)-Cl(14)#2	83.65(11)
Cl(6)#1-Pb(1)-Cl(2)	84.45(9)
Cl(14)#2-Pb(1)-Cl(2)	77.82(10)
Cl(6)#1-Pb(1)-Cl(12)	147.27(10)
Cl(14)#2-Pb(1)-Cl(12)	109.56(10)

Cl(2)-Pb(1)-Cl(12)	70.10(9)
Cl(6)#1-Pb(1)-Cl(9)#1	69.34(9)
Cl(14)#2-Pb(1)-Cl(9)#1	144.00(11)
Cl(2)-Pb(1)-Cl(9)#1	76.33(9)
Cl(12)-Pb(1)-Cl(9)#1	84.49(9)
Cl(6)#1-Pb(1)-Cl(8)#3	90.91(9)
Cl(14)#2-Pb(1)-Cl(8)#3	125.02(10)
Cl(2)-Pb(1)-Cl(8)#3	156.12(10)
Cl(12)-Pb(1)-Cl(8)#3	103.97(9)
Cl(9)#1-Pb(1)-Cl(8)#3	80.11(9)
Cl(14)-Pb(2)-Cl(10)	82.53(10)
Cl(14)-Pb(2)-Cl(13)	148.28(10)
Cl(10)-Pb(2)-Cl(13)	70.09(9)
Cl(14)-Pb(2)-Cl(7)#4	84.18(11)
Cl(10)-Pb(2)-Cl(7)#4	73.84(9)
Cl(13)-Pb(2)-Cl(7)#4	102.55(9)
Cl(14)-Pb(2)-Cl(14)#5	79.49(12)
Cl(10)-Pb(2)-Cl(14)#5	131.46(10)
Cl(13)-Pb(2)-Cl(14)#5	106.59(10)
Cl(7)#4-Pb(2)-Cl(14)#5	146.73(9)
W(7)-Cl(1)-W(8)	69.42(8)
W(7)-Cl(1)-W(6)	69.00(8)
W(8)-Cl(1)-W(6)	69.82(8)
W(8)-Cl(2)-Pb(1)	103.06(11)
W(8)-Cl(3)-W(6)	70.24(9)
W(8)-Cl(4)-W(7)	69.55(8)
W(6)-Cl(5)-W(7)	69.72(9)
W(6)-Cl(6)-Pb(1)#1	105.12(12)
W(8)-Cl(7)-Pb(2)#4	100.32(11)
W(6)-Cl(8)-Pb(1)#6	156.08(14)
W(6)-Cl(9)-Pb(1)#1	100.36(11)
W(7)-Cl(10)-Pb(2)	93.10(10)
W(8)-Cl(12)-Pb(1)	100.43(11)
W(7)-Cl(13)-Pb(2)	91.65(10)
Pb(2)-Cl(14)-Pb(1)#7	122.02(12)
Pb(2)-Cl(14)-Pb(2)#5	100.51(12)
Pb(1)#7-Cl(14)-Pb(2)#5	122.81(13)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+2 #2 x-1,y-1,z #3 x,y-1,z #4 -x+1,-y+1,-z+1

#5 -x+1,-y+2,-z+1 #6 x,y+1,z #7 x+1,y+1,z

Table S15. Selected Bond lengths [Å] for PbW_6Cl_{14}.

W1	W1	2.619(4)
W1	W1	2.619(5)
W1	W1	3.692(3)
W1	W1	2.602(5)
W1	W1	2.602(4)
W1	Cl1	4.350(7)
W1	Cl1	2.476(8)
W1	Cl2	4.382(6)
W1	Cl2	2.485(6)
W1	Cl2	2.488(6)
W1	Cl2	2.475(6)
W1	Cl2	4.376(6)
W1	Cl2	4.374(6)
W1	Cl3	2.471(8)
Pb1	Cl2	4.390(5)
Pb1	Cl2	4.390(5)
Pb1	Cl2	4.390(5)
Pb1	Cl2	4.390(5)
Pb1	Cl2	4.390(5)
Pb1	Cl2	4.390(5)
Pb1	Cl3	2.825(6)
Pb1	Cl3	2.825(8)
Pb1	Cl3	2.825(7)
Pb1	Cl3	2.825(6)
Pb1	Cl3	2.825(8)
Pb1	Cl3	2.825(7)

Table S16. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $Pb_{1.5}W_3Cl_{13}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pb(1)	29(1)	29(1)	25(1)	0	0	0
Pb(2)	35(1)	39(1)	28(1)	0	0	-6(1)
W(1)	23(1)	24(1)	15(1)	2(1)	1(1)	0(1)
W(2)	21(1)	22(1)	15(1)	0	0	-2(1)
Cl(1)	22(3)	23(3)	23(3)	0	0	-2(3)
Cl(2)	33(3)	24(2)	23(3)	-7(2)	2(2)	-2(2)
Cl(3)	33(4)	20(3)	25(3)	0	0	-8(3)
Cl(4)	24(3)	34(4)	16(3)	0	0	1(3)
Cl(5)	37(3)	49(3)	23(3)	4(2)	11(2)	9(2)
Cl(6)	36(3)	46(3)	19(3)	10(2)	-4(2)	3(2)
Cl(7)	37(3)	35(3)	32(3)	11(2)	-2(2)	-8(2)
Cl(8)	32(3)	32(3)	33(3)	5(2)	-8(2)	-2(2)

Table S17. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $Pb_2W_3Cl_{14}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
W(6)	16(1)	16(1)	15(1)	5(1)	0(1)	3(1)
W(7)	16(1)	19(1)	15(1)	5(1)	1(1)	2(1)
W(8)	17(1)	16(1)	17(1)	4(1)	0(1)	4(1)
Pb(1)	28(1)	26(1)	27(1)	12(1)	5(1)	7(1)
Pb(2)	38(1)	25(1)	27(1)	9(1)	2(1)	3(1)
Cl(1)	16(1)	22(2)	19(2)	7(1)	-1(1)	2(1)
Cl(2)	23(2)	20(2)	33(2)	12(1)	7(2)	4(1)
Cl(3)	28(2)	24(2)	19(2)	8(1)	-3(1)	7(1)
Cl(4)	18(2)	23(2)	25(2)	6(1)	2(1)	7(1)
Cl(5)	18(2)	24(2)	19(2)	4(1)	0(1)	-1(1)
Cl(6)	25(2)	27(2)	18(2)	2(1)	1(1)	2(1)
Cl(7)	24(2)	26(2)	20(2)	1(1)	1(1)	4(1)
Cl(8)	36(2)	22(2)	24(2)	9(1)	10(2)	13(1)
Cl(9)	20(2)	28(2)	22(2)	4(1)	5(1)	3(1)
Cl(10)	18(2)	30(2)	22(2)	6(1)	5(1)	0(1)
Cl(11)	30(2)	26(2)	31(2)	15(2)	5(2)	11(1)
Cl(12)	28(2)	23(2)	40(2)	14(2)	2(2)	7(1)
Cl(13)	27(2)	28(2)	16(2)	5(1)	1(1)	2(1)
Cl(14)	42(2)	27(2)	33(2)	12(2)	-9(2)	-2(2)