Structural Chemistry of $(PPh_4)_2M(WS_4)_2$ Materials

Clare J. Crossland,*[a] Ivana R. Evans[a,b] and John S.O. Evans[b]

Atom	*x/a*	*y/b*	*z/c*	U_{iso} /Å^2
Ni	0.0	0.0	0.0	0.129 (1)
W	−0.0953 (4)	0.2609 (3)	−0.1236 (3)	0.129 (1)
S1	−0.227 (2)	0.142 (1)	−0.057 (1)	0.129 (1)
S2	0.135 (2)	0.130 (1)	−0.085 (1)	0.129 (1)
S3	−0.108 (1)	0.355 (1)	−0.021 (1)	0.129 (1)
S4	−0.137 (1)	0.375 (1)	−0.309 (1)	0.129 (1)
P	0.5782 (6)	0.2443 (5)	0.3395 (5)	0.153 (4)

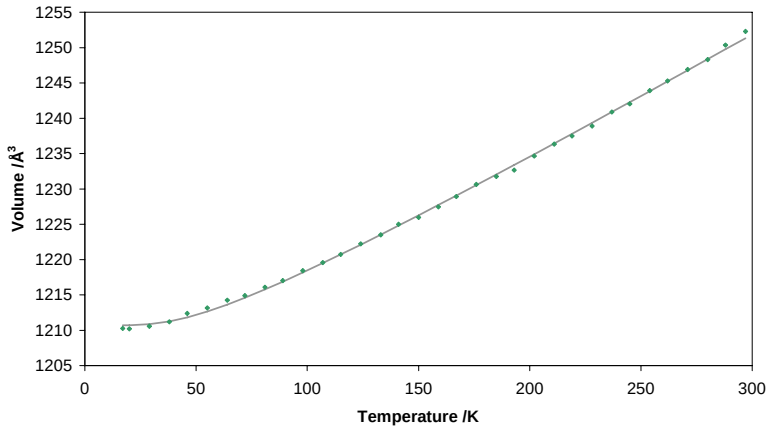
Fractional atomic coordinates and isotropic temperature factors for atoms in $(PPh_4)_2Ni(WS_4)_2$.

x_{rot} /°	16.0 (2)
y_{rot} /°	26.4 (2)
z_{rot} /°	203.0 (2)
torsion 1 /°	17.1 (8)
torsion 2 /°	−67.7 (7)
torsion 3 /°	18.9 (6)
torsion 4 /°	83.2 (7)

Torsion angles and rotations about the axes for the rigid PPh_4^+ cation in $(PPh_4)_2Ni(WS_4)_2$.

Bond Lengths /Å		Bond Angles /°	
Ni – S	2.12 (1)	S– Ni – S	180
	2.25 (2)		83.4 (4)
			96.6 (4)
W – S	2.03 (2)	S– W – S	102.1 (4)
	2.11 (2)		102.3 (3)
	2.16 (1)		110.8 (4)
	2.17 (1)		111.7 (4)
			113.5 (6)
			115.2 (4)

Bond lengths and angles in the anionic units in $(PPh_4)_2Ni(WS_4)_2$.



Change in cell volume of $(PPh_4)_2Ni(WS_4)_2$ on cooling. Data are shown in green, calculated values are shown in grey.

	a	*b*	*c*
a_0 /Å	9.2640 (6)	12.3422 (6)	12.3776 (6)
θ_1 /K	162 (7)	119 (4)	124 (6)
c_1 /K^{-1}	52.2 (7) × 10^{-6}	50.2 (4) × 10^{-6}	45.1 (4) × 10^{-6}
$\alpha_{15K\text{-}300K}$ /K^{-1}	41.6 (8) × 10^{-6}	43.3 (5) × 10^{-6}	38.5 (6) × 10^{-6}

Thermal expansion parameters for $(PPh_4)_2Ni(WS_4)_2$ using the expression: $\ln a_{calc} = \ln a_0 + \sum_0^i \frac{c_i \theta_i}{\exp(\theta_i / T) - 1}$

Bond lengths /Å		Bond angles /°	
Zn1 – S1	2.387 (1)	S1 – Zn1 – S1	116.07 (3)
W1 – S1	2.234 (1)	S1 – Zn1 – S1	96.95 (6)
W1 – S2	2.161 (1)	S1 – W1 – S1	106.20 (7)
P1 – C1	1.791 (3)	S1 – W1 – S2	110.38 (5)
C1 – C2	1.403 (4)	S1 – W1 – S2	110.50 (5)
C1 – C4	1.395 (4)	S2 – W1 – S2	108.88 (8)
C2 – C3	1.385 (4)	C1 – P1 – C1	110.21 (9)
C3 – C5	1.375 (5)	C1 – P1 – C1	107.99 (18)
C4 – C6	1.382 (4)		
C5 – C6	1.402 (5)		

Selected bond lengths and angles for the substructure of the tetragonal polymorph of $(PPh_4)_2Zn(WS_4)_2$ using a subcell model.

Atom	*x/a*	*y/b*	*z/c*	U_{iso} /Å^2
W1	0.1830 (3)	0.0195 (4)	−0.0784 (4)	0.125 (3)
W2	0.2612 (3)	0.3761 (5)	0.0079 (4)	0.125 (3)
Zn1	0.2214 (7)	0.194 (1)	−0.0312 (8)	0.084 (6)
S1	0.286 (1)	0.078 (2)	−0.047 (1)	0.168 (5)
S2	0.168 (1)	−0.030 (2)	−0.190 (2)	0.168 (5)
S3	0.179 (1)	−0.087 (2)	−0.013 (2)	0.168 (5)
S4	0.106 (1)	0.127 (2)	−0.065 (1)	0.168 (5)
S5	0.253 (2)	0.277 (2)	0.083 (2)	0.168 (5)
S6	0.239 (2)	0.320 (2)	−0.100 (2)	0.168 (5)
S7	0.191 (1)	0.459 (2)	0.018 (2)	0.168 (5)
S8	0.382 (1)	0.430 (2)	0.054 (2)	0.168 (5)
P1	0.8851 (5)	0.327 (1)	0.2266 (6)	0.112 (5)
P2	0.5391 (5)	0.092 (1)	0.2111 (6)	0.112 (5)

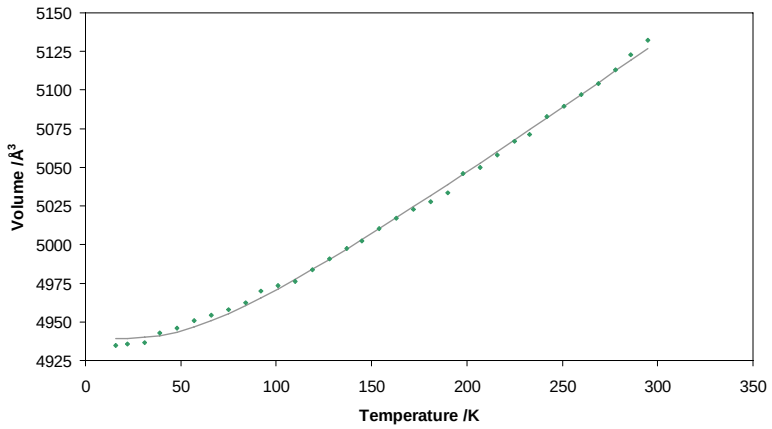
Selected fractional atomic coordinates and isotropic temperature factors for the monoclinic polymorph of $(PPh_4)_2Zn(WS_4)_2$.

	Cation 1	Cation 2
x_{rot} /°	−94.4 (3)	−234.9 (4)
y_{rot} /°	145.9 (2)	−76.5 (2)
z_{rot} /°	−180.1 (2)	27.4 (4)
torsion 1 /°	73 (1)	−67 (1)
torsion 2 /°	−19 (1)	21 (1)
torsion 3 /°	−21 (1)	79 (1)
torsion 4 /°	83 (1)	13 (1)

Angles of rotation about the axis and torsion angles in the two crystallographically independent PPh_4 units in monoclinic $(PPh_4)_2Zn(WS_4)_2$.

Bond lengths /Å		Bond Angles /°	
Zn – S	2.22 (4)	S – Zn – S	91 (1)
	2.28 (3)		96 (1)
	2.42 (4)		113(1)
	2.43 (4)		115 (1)
			120 (1)
			124 (1)
W1 – S	2.03 (3)	S – W1 – S	102 (1)
	2.08 (4)		104 (1)
	2.17 (3)		106 (1)
	2.26 (3)		111 (1)
			113 (1)
			119 (1)
W2 – S	1.89 (3)	S – W2 – S	102 (1)
	2.13 (4)		106 (1)
	2.14(4)		109 (1)
	2.29 (3)		111 (1)
			111 (9)
			117 (1)

Selected Bond lengths and angles in the anion in monoclinic $(PPh_4)_2Zn(WS_4)_2$.



The variation in cell volume with temperature in monoclinic $(PPh_4)_2Zn(WS_4)_2$. Observed data are shown in green calculated values are shown in grey.

	a	*b*	*c*
a_0 /Å	18.4096 (1)	15.077 (3)	18.871 (2)
θ_1 /K	174 (8)	258 (15)	77 (17)
c_1 /K^{-1}	56.5 (8) × 10^{-6}	98 (3) × 10^{-6}	22.6 (5) × 10^{-6}
$\alpha_{15K\text{-}300K}$ /K^{-1}	44 (1) × 10^{-6}	66 (3) × 10^{-6}	21.0 (9) × 10^{-6}

Thermal expansion parameters for the monoclinic form of $(PPh_4)_2Zn(WS_4)_2$.

Atom	*x*	*y*	*z*	Occupancy	U_{iso} /Å^2
Zn(1)	0	0	0	0.64218(3)	0.01281(7)
Zn(2)	-0.5	0	0.25	0.77212(3)	0.01432(7)
Zn(3)	0	0	-0.5	0.35782(3)	0.01317(7)
Zn(4)	-0.5	0	0.75	0.22788(3)	0.09234(7)
W(1)	-0.5	0	0.46551(7)	0.77212(3)	0.01207(6)
W(2)	0	0	-0.21543(8)	0.64218(3)	0.00565(6)
W(3)	-0.5	0	0.53263(9)	0.22788(3)	0.09094(7)
W(4)	0	0	-0.28483(8)	0.35782(3)	0.01015(6)
S(1)	-0.08544(9)	0.04071(9)	0.11658(9)	0.64218(3)	0.01177(3)
S(2)	-0.54765(9)	-0.08338(9)	0.13412(9)	0.77212(3)	0.01177(3)
S(3)	-0.08694(9)	0.04299(9)	-0.30630(9)	0.64218(3)	0.01177(3)
S(4)	-0.54495(9)	-0.07994(9)	0.55987(9)	0.77212(3)	0.01177(3)
S(5)	-0.04500(9)	-0.09043(9)	-0.19568(9)	0.35782(3)	0.01841(3)
S(6)	-0.44359(9)	0.08252(9)	0.63601(9)	0.22788(3)	0.01841(3)
S(7)	-0.57219(9)	0.04651(9)	0.43547(9)	0.22788(3)	0.01841(3)
S(8)	-0.08620(9)	0.03820(9)	-0.38103(9)	0.35782(3)	0.01841(3)
P(1)	-0.25074(9)	0.25342(8)	0.11999(9)		0.01180(7)
C(11)	-0.22890(9)	0.17533(9)	0.04442(9)		0.03111(7)
C(12)	-0.17441(7)	0.18940(7)	-0.02218(7)		0.02881(7)
C(13)	-0.14997(7)	0.13575(7)	-0.08456(7)		0.01132(7)
C(14)	-0.18113(7)	0.06859(7)	-0.08149(7)		0.03125(7)
C(15)	-0.23759(7)	0.05527(7)	-0.01774(7)		0.03197(7)
C(16)	-0.26142(7)	0.10858(7)	0.04535(7)		0.02627(7)
C(21)	-0.31912(9)	0.22617(9)	0.20305(9)		0.00048(7)
C(22)	-0.31067(7)	0.16824(7)	0.26650(7)		0.01690(7)
C(23)	-0.36766(7)	0.14676(7)	0.32504(7)		0.02977(7)
C(24)	-0.42979(7)	0.18752(7)	0.32773(7)		0.01499(7)
C(25)	-0.43812(7)	0.24562(7)	0.26477(7)		0.00894(7)
C(26)	-0.38251(7)	0.26519(7)	0.20258(7)		0.00946(7)
C(31)	-0.27364(9)	0.32894(9)	0.04334(9)		0.02487(7)
C(32)	-0.32879(7)	0.31351(7)	-0.02158(7)		0.04488(7)
C(33)	-0.35324(7)	0.36598(7)	-0.08561(7)		0.01450(7)
C(34)	-0.32602(7)	0.43467(7)	-0.07971(7)		0.03014(7)
C(35)	-0.26979(7)	0.44968(7)	-0.01623(7)		0.02009(7)
C(36)	-0.24276(7)	0.39643(7)	0.04406(7)		0.01674(7)
C(41)	-0.17955(9)	0.27947(9)	0.20288(9)		0.00231(7)
C(42)	-0.11662(7)	0.24041(7)	0.20274(7)		0.01183(7)
C(43)	-0.06024(7)	0.26161(7)	0.26276(7)		0.02218(7)
C(44)	-0.06597(7)	0.32379(7)	0.31881(7)		0.03008(7)
C(45)	-0.12814(7)	0.36422(7)	0.31615(7)		0.01368(7)
C(46)	-0.18601(7)	0.34049(7)	0.26094(7)		0.01135(7)
H(121)	-0.15429(7)	0.23869(7)	-0.02811(7)		0.0441
H(131)	-0.10799(7)	0.14488(7)	-0.12837(7)		0.0493
H(141)	-0.15971(7)	0.02840(7)	-0.12002(7)		0.0525
H(151)	-0.25917(7)	0.00650(7)	-0.01388(7)		0.0559
H(161)	-0.30402(7)	0.09988(7)	0.08817(7)		0.0548
H(221)	-0.26467(7)	0.14118(7)	0.26372(7)		0.0406
H(231)	-0.36042(7)	0.10418(7)	0.36841(7)		0.0394
H(241)	-0.46896(7)	0.17150(7)	0.37271(7)		0.0437
H(251)	-0.48469(7)	0.27177(7)	0.26562(7)		0.0451
H(261)	-0.38875(7)	0.30920(7)	0.16169(7)		0.0457
H(321)	-0.35059(7)	0.26482(7)	-0.02502(7)		0.0525
H(331)	-0.39786(7)	0.35810(7)	-0.12466(7)		0.0478
H(341)	-0.34779(7)	0.47513(7)	-0.11731(7)		0.0486
H(351)	-0.24703(7)	0.49799(7)	-0.01445(7)		0.0514
H(361)	-0.19907(7)	0.40456(7)	0.08496(7)		0.0522
H(421)	-0.11039(7)	0.19736(7)	0.15995(7)		0.0445
H(431)	-0.01466(7)	0.23381(7)	0.26514(7)		0.0458
H(441)	-0.02722(7)	0.33820(7)	0.36549(7)		0.0466
H(451)	-0.13328(7)	0.40891(7)	0.35590(7)		0.0428
H(461)	-0.23190(7)	0.36778(7)	0.25923(7)		0.0436

Table.1 Atomic positions in the superstructure of the tetragonal form of $(PPh_4)_2Zn(WS_4)_2$.

Bond Lengths /Å					
Zn(1) - W(2)	2.9233(13)	W(1) - S(4)	2.1504(15)	P(1) - C(31)	1.824(2)
Zn(1) - W(2)	2.9233(13)	W(1) - S(7)	1.6542(17)	P(1) - C(41)	1.792(2)
Zn(1) - S(1)	2.3835(15)	W(1) - S(7)	1.6542(17)	C(11) - C(12)	1.3876(19)
Zn(1) - S(1)	2.3835(15)	W(2) - W(4)	0.9378(13)	C(11) - C(16)	1.392(2)
Zn(1) - S(1)	2.3835(15)	W(2) - S(1)	2.2201(16)	C(12) - C(13)	1.3909(16)
Zn(1) - S(1)	2.3835(15)	W(2) - S(1)	2.2201(16)	C(13) - C(14)	1.3874(17)
Zn(2) - W(1)	2.9220(12)	W(2) - S(3)	2.1923(16)	C(14) - C(15)	1.3870(16)
Zn(2) - W(1)	2.9220(12)	W(2) - S(3)	2.1923(16)	C(15) - C(16)	1.3894(16)
Zn(2) - S(2)	2.3931(14)	W(2) - S(5)	1.8948(17)	C(21) - C(22)	1.3926(19)
Zn(2) - S(2)	2.3931(14)	W(2) - S(5)	1.8948(17)	C(21) - C(26)	1.397(2)
Zn(2) - S(2)	2.3931(14)	W(3) - S(4)	1.7649(16)	C(22) - C(23)	1.3866(16)
Zn(2) - S(2)	2.3931(14)	W(3) - S(4)	1.7649(16)	C(23) - C(24)	1.3955(17)
Zn(3) - W(4)	2.9206(13)	W(3) - S(6)	2.3413(18)	C(24) - C(25)	1.3926(16)
Zn(3) - W(4)	2.9206(13)	W(3) - S(6)	2.3413(18)	C(25) - C(26)	1.3916(16)
Zn(3) - S(8)	2.3862(16)	W(3) - S(7)	2.0715(18)	C(31) - C(32)	1.3876(19)
Zn(3) - S(8)	2.3862(16)	W(3) - S(7)	2.0715(18)	C(31) - C(36)	1.388(2)
Zn(3) - S(8)	2.3862(16)	W(4) - S(3)	1.8370(16)	C(32) - C(33)	1.3879(16)
Zn(3) - S(8)	2.3862(16)	W(4) - S(3)	1.8370(16)	C(33) - C(34)	1.3863(17)
Zn(4) - W(3)	2.9539(16)	W(4) - S(5)	2.2308(17)	C(34) - C(35)	1.3902(16)
Zn(4) - W(3)	2.9539(16)	W(4) - S(5)	2.2308(17)	C(35) - C(36)	1.3879(16)
Zn(4) - S(6)	2.4327(16)	W(4) - S(8)	2.2059(17)	C(41) - C(42)	1.390(2)
Zn(4) - S(6)	2.4327(16)	W(4) - S(8)	2.2059(17)	C(41) - C(46)	1.3898(19)
Zn(4) - S(6)	2.4327(16)	S(1) - S(5)	1.0680(18)	C(42) - C(43)	1.3943(16)
Zn(4) - S(6)	2.4327(16)	S(2) - S(7)	0.9610(18)	C(43) - C(44)	1.3961(16)
W(1) - W(3)	0.9057(15)	S(3) - S(8)	1.0270(18)	C(44) - C(45)	1.3906(17)
W(1) - S(2)	2.2447(15)	S(4) - S(6)	1.0447(18)	C(45) - C(46)	1.3912(16)
W(1) - S(2)	2.2447(15)	P(1) - C(11)	1.818(2)		
W(1) - S(4)	2.1504(15)	P(1) - C(21)	1.796(2)		

Bond Angles /°			
W(2) - Zn(1) - W(2)	180	Zn(4) - W(3) - S(4)	77.55(6)
W(2) - Zn(1) - S(1)	131.85(3)	W(1) - W(3) - S(4)	102.45(6)
W(2) - Zn(1) - S(1)	48.15(3)	Zn(4) - W(3) - S(4)	77.55(6)
W(2) - Zn(1) - S(1)	48.15(3)	W(1) - W(3) - S(4)	102.45(6)
W(2) - Zn(1) - S(1)	131.85(3)	S(4) - W(3) - S(4)	155.10(11)
S(1) - Zn(1) - S(1)	116.44(4)	Zn(4) - W(3) - S(6)	53.18(4)
W(2) - Zn(1) - S(1)	131.85(3)	W(1) - W(3) - S(6)	126.82(4)
W(2) - Zn(1) - S(1)	48.15(3)	S(4) - W(3) - S(6)	130.53(8)
S(1) - Zn(1) - S(1)	96.29(7)	S(4) - W(3) - S(6)	24.75(6)
S(1) - Zn(1) - S(1)	116.44(4)	Zn(4) - W(3) - S(6)	53.18(4)
W(2) - Zn(1) - S(1)	48.15(3)	W(1) - W(3) - S(6)	126.82(4)
W(2) - Zn(1) - S(1)	131.85(3)	S(4) - W(3) - S(6)	24.75(6)
S(1) - Zn(1) - S(1)	116.44(4)	S(4) - W(3) - S(6)	130.53(8)
S(1) - Zn(1) - S(1)	96.29(7)	S(6) - W(3) - S(6)	106.36(9)
S(1) - Zn(1) - S(1)	116.44(4)	Zn(4) - W(3) - S(7)	129.27(5)
W(1) - Zn(2) - W(1)	180	W(1) - W(3) - S(7)	50.73(5)
W(1) - Zn(2) - S(2)	131.28(3)	S(4) - W(3) - S(7)	100.25(7)
W(1) - Zn(2) - S(2)	48.72(3)	S(4) - W(3) - S(7)	95.45(7)
W(1) - Zn(2) - S(2)	48.72(3)	S(6) - W(3) - S(7)	113.42(6)
W(1) - Zn(2) - S(2)	131.28(3)	Zn(4) - W(3) - S(7)	129.27(5)
S(2) - Zn(2) - S(2)	115.80(4)	W(1) - W(3) - S(7)	50.73(5)
W(1) - Zn(2) - S(2)	131.28(3)	S(4) - W(3) - S(7)	95.45(7)
W(1) - Zn(2) - S(2)	48.72(3)	S(4) - W(3) - S(7)	100.25(7)
S(2) - Zn(2) - S(2)	97.44(7)	S(6) - W(3) - S(7)	111.18(6)
S(2) - Zn(2) - S(2)	115.80(4)	S(6) - W(3) - S(7)	111.18(6)
W(1) - Zn(2) - S(2)	48.72(3)	S(6) - W(3) - S(7)	113.42(6)
W(1) - Zn(2) - S(2)	131.28(3)	S(7) - W(3) - S(7)	101.45(10)
S(2) - Zn(2) - S(2)	115.80(4)	Zn(3) - W(4) - W(2)	179.99
S(2) - Zn(2) - S(2)	97.44(7)	Zn(3) - W(4) - S(3)	80.77(5)
S(2) - Zn(2) - S(2)	115.80(4)	W(2) - W(4) - S(3)	99.23(5)
W(4) - Zn(3) - W(4)	180	Zn(3) - W(4) - S(3)	80.77(5)
W(4) - Zn(3) - S(8)	47.83(4)	W(2) - W(4) - S(3)	99.23(5)
W(4) - Zn(3) - S(8)	132.17(4)	S(3) - W(4) - S(3)	161.55(10)
W(4) - Zn(3) - S(8)	132.17(4)	Zn(3) - W(4) - S(5)	122.78(4)
W(4) - Zn(3) - S(8)	47.83(4)	W(2) - W(4) - S(5)	57.22(4)
S(8) - Zn(3) - S(8)	116.79(4)	S(3) - W(4) - S(5)	94.72(7)
W(4) - Zn(3) - S(8)	47.83(4)	S(3) - W(4) - S(5)	95.24(6)
W(4) - Zn(3) - S(8)	132.17(4)	Zn(3) - W(4) - S(5)	122.78(4)
S(8) - Zn(3) - S(8)	95.66(7)	W(2) - W(4) - S(5)	57.22(4)
S(8) - Zn(3) - S(8)	116.79(4)	S(3) - W(4) - S(5)	95.24(6)
W(4) - Zn(3) - S(8)	132.17(4)	S(3) - W(4) - S(5)	94.72(7)
W(4) - Zn(3) - S(8)	47.83(4)	S(5) - W(4) - S(5)	114.43(9)

S(8) - Zn(3) - S(8)	116.79(4)	Zn(3) - W(4) - S(8)	53.29(4)
S(8) - Zn(3) - S(8)	95.66(7)	W(2) - W(4) - S(8)	126.71(4)
S(8) - Zn(3) - S(8)	116.79(4)	S(3) - W(4) - S(8)	27.54(5)
W(3) - Zn(4) - W(3)	180	S(3) - W(4) - S(8)	134.03(7)
W(3) - Zn(4) - S(6)	50.39(4)	S(5) - W(4) - S(8)	107.20(6)
W(3) - Zn(4) - S(6)	129.61(4)	Zn(3) - W(4) - S(8)	53.29(4)
W(3) - Zn(4) - S(6)	129.61(4)	W(2) - W(4) - S(8)	126.71(4)
W(3) - Zn(4) - S(6)	50.39(4)	S(3) - W(4) - S(8)	134.03(7)
S(6) - Zn(4) - S(6)	113.98(4)	S(3) - W(4) - S(8)	27.55(5)
W(3) - Zn(4) - S(6)	50.39(4)	S(5) - W(4) - S(8)	110.59(6)
W(3) - Zn(4) - S(6)	129.61(4)	S(5) - W(4) - S(8)	110.59(6)
S(6) - Zn(4) - S(6)	100.79(7)	S(5) - W(4) - S(8)	107.20(6)
S(6) - Zn(4) - S(6)	113.98(4)	S(8) - W(4) - S(8)	106.59(9)
W(3) - Zn(4) - S(6)	129.61(4)	Zn(1) - S(1) - W(2)	78.75(6)
W(3) - Zn(4) - S(6)	50.39(4)	Zn(1) - S(1) - S(5)	137.19(15)
S(6) - Zn(4) - S(6)	113.98(4)	W(2) - S(1) - S(5)	58.48(12)
S(6) - Zn(4) - S(6)	100.79(7)	Zn(2) - S(2) - W(1)	78.03(5)
S(6) - Zn(4) - S(6)	113.98(4)	Zn(2) - S(2) - S(7)	119.33(15)
Zn(2) - W(1) - W(3)	179.99	W(1) - S(2) - S(7)	41.60(12)
Zn(2) - W(1) - S(2)	53.24(4)	W(2) - S(3) - W(4)	24.98(4)
W(3) - W(1) - S(2)	126.76(4)	W(2) - S(3) - S(8)	121.57(15)
Zn(2) - W(1) - S(2)	53.24(4)	W(4) - S(3) - S(8)	96.65(14)
W(3) - W(1) - S(2)	126.76(4)	W(1) - S(4) - W(3)	24.28(5)
S(2) - W(1) - S(2)	106.49(8)	W(1) - S(4) - S(6)	134.12(15)
Zn(2) - W(1) - S(4)	126.73(4)	W(3) - S(4) - S(6)	110.23(15)
W(3) - W(1) - S(4)	53.27(4)	W(2) - S(5) - W(4)	24.59(4)
S(2) - W(1) - S(4)	111.27(6)	W(2) - S(5) - S(1)	92.80(14)
S(2) - W(1) - S(4)	110.67(6)	W(4) - S(5) - S(1)	117.38(15)
Zn(2) - W(1) - S(4)	126.73(4)	Zn(4) - S(6) - W(3)	76.42(6)
W(3) - W(1) - S(4)	53.27(4)	Zn(4) - S(6) - S(4)	120.55(15)
S(2) - W(1) - S(4)	110.67(6)	W(3) - S(6) - S(4)	45.02(11)
S(2) - W(1) - S(4)	111.27(6)	W(1) - S(7) - W(3)	25.08(4)
S(4) - W(1) - S(4)	106.54(8)	W(1) - S(7) - S(2)	115.71(16)
Zn(2) - W(1) - S(7)	75.80(5)	W(3) - S(7) - S(2)	140.62(17)
W(3) - W(1) - S(7)	104.20(5)	Zn(3) - S(8) - W(4)	78.88(6)
S(2) - W(1) - S(7)	22.69(6)	Zn(3) - S(8) - S(3)	134.49(15)
S(2) - W(1) - S(7)	128.98(7)	W(4) - S(8) - S(3)	55.81(12)
S(4) - W(1) - S(7)	100.91(7)	C(11) - P(1) - C(21)	106.88(10)
Zn(2) - W(1) - S(7)	75.80(5)	C(11) - P(1) - C(31)	110.58(9)
W(3) - W(1) - S(7)	104.20(5)	C(21) - P(1) - C(31)	113.24(11)
S(2) - W(1) - S(7)	128.98(7)	C(11) - P(1) - C(41)	114.14(11)
S(2) - W(1) - S(7)	22.69(6)	C(21) - P(1) - C(41)	103.29(9)
S(4) - W(1) - S(7)	95.97(7)	C(31) - P(1) - C(41)	108.60(10)
S(4) - W(1) - S(7)	95.97(7)	P(1) - C(11) - C(12)	112.62(12)
S(4) - W(1) - S(7)	100.91(7)	P(1) - C(11) - C(16)	127.55(12)
S(7) - W(1) - S(7)	151.61(10)	C(12) - C(11) - C(16)	119.78(13)
Zn(1) - W(2) - W(4)	179.99	C(11) - C(12) - C(13)	120.10(12)
Zn(1) - W(2) - S(1)	53.10(4)	C(12) - C(13) - C(14)	119.87(10)
W(4) - W(2) - S(1)	126.90(4)	C(13) - C(14) - C(15)	120.20(10)
Zn(1) - W(2) - S(1)	53.10(4)	C(14) - C(15) - C(16)	119.86(11)
W(4) - W(2) - S(1)	126.90(4)	C(11) - C(16) - C(15)	120.07(11)
S(1) - W(2) - S(1)	106.20(8)	P(1) - C(21) - C(22)	121.16(13)
Zn(1) - W(2) - S(3)	124.20(4)	P(1) - C(21) - C(26)	118.10(11)
W(4) - W(2) - S(3)	55.80(4)	C(22) - C(21) - C(26)	120.75(13)
S(1) - W(2) - S(3)	109.24(6)	C(21) - C(22) - C(23)	119.10(12)
S(1) - W(2) - S(3)	110.21(6)	C(22) - C(23) - C(24)	120.16(11)
Zn(1) - W(2) - S(3)	124.20(4)	C(23) - C(24) - C(25)	120.56(10)
W(4) - W(2) - S(3)	55.80(4)	C(24) - C(25) - C(26)	119.25(11)
S(1) - W(2) - S(3)	110.21(6)	C(21) - C(26) - C(25)	119.90(11)
S(1) - W(2) - S(3)	109.24(6)	P(1) - C(31) - C(32)	112.63(12)
S(3) - W(2) - S(3)	111.60(8)	P(1) - C(31) - C(36)	126.87(12)
Zn(1) - W(2) - S(5)	81.80(5)	C(32) - C(31) - C(36)	120.48(13)
W(4) - W(2) - S(5)	98.20(5)	C(31) - C(32) - C(33)	119.46(12)
S(1) - W(2) - S(5)	134.90(7)	C(32) - C(33) - C(34)	120.15(10)
S(1) - W(2) - S(5)	28.72(5)	C(33) - C(34) - C(35)	119.97(10)
S(3) - W(2) - S(5)	94.34(7)	C(34) - C(35) - C(36)	119.86(11)
Zn(1) - W(2) - S(5)	81.80(5)	C(31) - C(36) - C(35)	119.70(11)
W(4) - W(2) - S(5)	98.20(5)	P(1) - C(41) - C(42)	118.64(12)
S(1) - W(2) - S(5)	28.72(5)	P(1) - C(41) - C(46)	120.92(13)
S(1) - W(2) - S(5)	134.90(7)	C(42) - C(41) - C(46)	120.40(13)
S(3) - W(2) - S(5)	94.85(6)	C(41) - C(42) - C(43)	119.62(11)
S(3) - W(2) - S(5)	94.85(6)	C(42) - C(43) - C(44)	119.75(11)

S(3) - W(2) - S(5)	94.34(7)	C(43) - C(44) - C(45)	120.41(10)
S(5) - W(2) - S(5)	163.61(10)	C(44) - C(45) - C(46)	119.47(11)
Zn(4) - W(3) - W(1)	179.99	C(41) - C(46) - C(45)	120.09(12)

Bond lengths and angles in the superstructure of tetragonal form of $(PPh_4)_2Zn(WS_4)_2$.