# Structural chemistry of (PPh<sub>4</sub>)<sub>2</sub>M(WS<sub>4</sub>)<sub>2</sub> materials † \$

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In this paper we discuss the structural chemistry of  $(PPh_4)_2M(WS_4)_2$  (M = Co, Ni, Zn) materials. For M = Ni we and others have been unable to grow single crystals and we report the structure determination from powder diffraction. The material is triclinic ( $P\overline{1}$ , a = 9.3730(2), b = 12.4951(3), c = 12.5189(3) Å, a = 65.814(1),  $\beta = 83.751(1)$ ,  $\gamma = 69.571(1)^{\circ}$  at T = 293 K). It contains square-planar coordination around Ni. For M = Zn we have isolated two polymorphs. We describe new analysis of the complex superstructure and diffuse scattering observed in the tetragonal polymorph ( $I\overline{4}$ , a = 18.723(4), c = 13.563(4) Å at T = 120 K) and the bulk preparation of a monoclinic ( $P2_1/c$ , a = 18.6397(4), b = 15.3693(5), c = 18.9822(5) Å,  $\beta = 109.239(2)^{\circ}$  at T = 293 K) polymorph isostructural with the M = Co material.

# Introduction

The chemistry of transition-metal containing thiometallates has been extensively investigated over many years and a number of reviews of their chemistry are available.1-5 Thiomolybdate and thiotungstate salts have also been investigated as precursor materials to produce nano-structured MoS<sub>2</sub>/WS<sub>2</sub> hydrodesulfurization (HDS) catalysts; Ni/Co promoted systems being of particular interest.<sup>6-11</sup> We have been interested in thiometallates as potential reagents for the low-temperature synthesis of metastable metal chalcogenides, and have successfully prepared a range of ternary  $A_2MX_4$  (A = Cu, Ag; M = Mo, W; X = S, Se) materials.<sup>12,13</sup> During work aimed at preparing transitionmetal doped quaternary chalcogenides we have reinvestigated the structural chemistry of a family of  $(PPh_4)_2M(WS_4)_2$  materials which were first reported for M = Fe, Co, Ni and Zn by Muller, though an improved synthesis was later reported by Callahan.<sup>14</sup> Such materials are potential single-source precursors for HDS catalysts. In our hands the original synthetic route produces only brown X-ray amorphous materials whereas the latter allows isolation of essentially phase-pure (poly)crystalline materials. We report the structure determination of the M = Ni phase by powder diffraction methods, the identification of a new monoclinic polymorph for M = Zn and describe the complex superstructure and origins of diffuse scatter in the tetragonal form of the M = Znmaterial.

## Experimental

## $(NH_4)_2WS_4$

 $(NH_4)_2WS_4$  was prepared according to the method of McDonald.<sup>15</sup> NH<sub>3</sub> (28% w/w aqueous solution, 40 ml) was added to solid H<sub>2</sub>WO<sub>4</sub> (5.0619 g) to form a suspension of white powder in a colourless solution. The suspension was saturated by slow addition of H<sub>2</sub>S (g) for about 20 min at room temperature, then filtered to remove a green solid. The bright yellow filtrate was heated to 60 °C with stirring and a continuous flow of H<sub>2</sub>S (g) bubbling through the solution (rate ~1–2 bubbles s<sup>-1</sup>) for 7 h, resulting in the formation of a yellow solid. The solution was purged with N<sub>2</sub> and cooled; the solid was isolated by filtration and dried under vacuum. Yield 4.14 g, 59%. CHN analysis (%): measured: C: 0, H: 2.32, N 7.90; calc.: C 0, H 2.32, N 8.05. Identity was confirmed by comparison of the PXRD pattern to the PDF<sup>16</sup> (48-1663).

## $(PPh_4)_2Ni(WS_4)_2$

(PPh<sub>4</sub>)<sub>2</sub>Ni(WS<sub>4</sub>)<sub>2</sub> was prepared using the method of Muller/Callahan.<sup>14,17</sup> A solution of NiCl<sub>2</sub> (0.0324 g, 0.25 mmol) in a 1 : 1 (v/v) mixture of H<sub>2</sub>O–CH<sub>3</sub>CN (5 ml), acidified with a few drops of glacial acetic acid, was added to a solution of (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> (0.1758 g, 0.53 mmol) in a 1 : 3 (v/v) mixture of H<sub>2</sub>O–CH<sub>3</sub>CN (5 ml) to give a red solution. A solution of (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>PCl (0.7059 g, 1.88 mmol) in a 1 : 1 (v/v) mixture of H<sub>2</sub>O–CH<sub>3</sub>CN (7 ml) was added to this mixture resulting in the formation of a pale brown solid which showed some long-term instability in air. CHN analysis (%): measured: C 40.16, H 2.84, N 0; calc.: C 42.34, H 2.96, N 0.

## $(PPh_4)_2Zn(WS_4)_2$

 $(PPh_4)_2Zn(WS_4)_2$  was made using the same methodology. The solution (solvents and volumes as above) formed from  $ZnCl_2$  (0.0343 g, 0.25 mmol) and  $(NH_4)_2WS_4$  (0.1749 g, 0.50 mmol) was bright orange. Addition of  $(C_6H_5)_4PCl$  (0.7517 g, 2.01 mmol) resulted in the formation of a bright orange solid which showed

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 $<sup>\</sup>S$  Electronic supplementary information (ESI) available: Tables of bond distances and angles for materials described; thermal expansion data for (PPh\_4)\_2Ni(WS\_4)\_2 and monoclinic (PPh\_4)\_2Zn(WS\_4)\_2. See DOI: 10.1039/b716407f

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some long-term instability in air. CHN analysis (%): measured: C 39.27, H 2.80, N 0; calc.: C 42.13, H 2.95, N 0.

## $(PPh_4)_2Co(WS_4)_2$

Solutions (see above) of  $Co(NO_3)_2 \cdot 6H_2O(0.0728 \text{ g}, 0.25 \text{ mmol})$ and  $(NH_4)_2WS_4$  (0.1747 g, 0.50 mmol) were mixed to give a dark brown solution. Addition of a solution of  $(C_6H_5)_4PCI$  (0.7511 g, 2.0 mmol) gave a dark green solid. The solid showed long-term instability in air. CHN analysis (%): measured: C 40.94, H 2.81, N 0; calc.: C 42.33, H 2.96, N 0.

## Methods

Single-crystal diffraction experiments were performed on a Bruker AXS Smart 6000 diffractometer equipped with a Mo tube on samples cooled to 120 K using an Oxford Cryosystems nitrogen cryostream. Structures were solved using SIR92<sup>18</sup> and refined using the Crystals package.<sup>19</sup> Powder diffraction patterns were collected on a Bruker d8 powder diffractometer equipped with a Cu tube, a Ge(111) incident beam monochromator and a Braun PSD-50M linear position-sensitive detector. Room-temperature measurements were performed on samples mounted on "zero background" Si single-crystal sample holders. Low-temperature measurements were performed on samples sprinkled on an Al plate and mounted in an Oxford Cryosystems pHeniX cryostat. Indexing,<sup>20</sup> simulated annealing<sup>21</sup> and Rietveld refinement were performed using the Topas-Academic software suite.

## **Results and discussion**

## $(PPh_4)_2Ni(WS_4)_2$

To the best of our knowledge the structure of  $(PPh_4)_2Ni(WS_4)_2$  has not been reported. As reported by earlier workers, we were unable to prepare single crystals of this material, but were able to prepare a brown polycrystalline solid which was stable in air for short periods but showed some long-term instability. Powder diffraction data were collected on a sample sprinkled on a Si zero-background sample holder. All but two reflections could be indexed using a triclinic cell of a = 9.3730, b = 12.4951, c = 12.5189 Å, a = $65.814, \beta = 83.751, \gamma = 69.571^{\circ}$ . A structure-independent Pawley<sup>22</sup> refinement gave an excellent fit to the data. The structure could be solved using a real-space simulated annealing protocol in space group P1. PPh<sub>4</sub><sup>+</sup> groups were modelled as rigid bodies with a P-C bond of 1.792 Å (the mean bond length for P–C bonds of PPh<sub>4</sub><sup>+</sup> groups in the CSD<sup>23</sup>) with tetrahedral geometry at P and phenyl groups with C-C and C-H bond lengths of 1.39 and 0.998 Å, respectively. Four torsion angles of Ph groups around P-C bonds were allowed to vary. The anion was originally described using a Ni(WS<sub>4</sub>)<sub>2</sub> rigid body with square-planar Ni and tetrahedral W, though this geometry was allowed to relax in final refinements. Simulated annealing was performed in which PPh<sub>4</sub><sup>+</sup> cations were moved by up to  $\pm 5$  Å, rigid-body rotations by  $\pm 180^{\circ}$  and torsion angles by  $\pm 30^{\circ}$ , followed by full Rietveld refinement. Since P1 has a floating origin the Ni atom was fixed at (0, 0, 0). Using this protocol the same low R-factor solution was found approximately every 4000 cycles of randomisation/refinement to convergence.

Examination of this structural model revealed an approximate centre of symmetry at Ni and final Rietveld refinement using all

 Table 1
 Agreement factors for Rietveld refinement of (PPh<sub>4</sub>)<sub>2</sub>Ni(WS<sub>4</sub>)<sub>2</sub>

Space group	$P\overline{1}$	$2\theta$ range/°	5-70
a/Å	9.3730(2)	$2\theta$ step/°	0.0144
b/Å	12.4951(3)	Time per step/s	27
c/Å	12.5189(3)	$R_{wp}$ (%)	3.92
$a/^{\circ}$	65.814(1)	$R_{\text{Bragg}}$ (%)	1.62
β/°	83.751(1)	$\chi^2$	2.23
γ/°	69.571(1)	No. of refined	74
		parameters	

data was therefore performed in  $P\overline{1}$ . A total of 74 parameters were refined (18 coefficients of a Chebychev polynomial to describe the background, sample displacement, an axial coefficient to describe peak asymmetry, 6 pseudo-Voigt peak shape parameters, 14 coefficients of a spherical harmonic function to describe the preferred orientation, 6 cell parameters, 15 atomic coordinates for the anion, 10 parameters to describe the rigid PPh<sub>4</sub><sup>+</sup> unit and 2 temperature factors, one each for the anion and cation; soft restraints were applied to W-S (2.240 Å) and Ni-S (2.296 Å) bond lengths and to WS<sub>4</sub> tetrahedral angles). Final agreement factors are given in Table 1 and the Rietveld plot in Fig. 1. We note that separate diffraction experiments on these materials confirmed the presence of preferred orientation; the spherical harmonic correction applied led to improvements in the quality of the Rietveld fit but no significant changes in fractional coordinates.  $(PPh_4)_2Ni(WS_4)_2$  is isostructural with  $(AsPh_4)_2Ni(WS_4)_2^{24}$  and (PPh<sub>4</sub>)<sub>2</sub>Ni(WSe<sub>4</sub>)<sub>2</sub><sup>25</sup> materials. Two views of the structure of (PPh<sub>4</sub>)<sub>2</sub>Ni(WS<sub>4</sub>)<sub>2</sub> are shown in Fig. 2. Bond angles around Ni of 2  $\times$  83.4(4)° and 2  $\times$  96.6(4)° reveal an essentially square planar geometry around Ni. Ni-S (2.12(1)-2.25(2) Å) and W-S (2.03(2)-2.17(2) Å) bond lengths are within the range expected



Fig. 1 Observed, calculated and difference (lower curve) plots for the Rietveld refinement of  $(PPh_4)_2Ni(WS_4)_2$ . Tick marks show allowed reflection positions. A zoom of the region between 24 and 40°  $2\theta$  is shown.



**Fig. 2** The structure of  $(PPh_4)_2 Ni(WS_4)_2$  viewed down the *a* axis (left) and down the *b* axis (right). W tetrahedra are shown in green, square-planar Ni ions in red, S in yellow, P in orange, C in blue and H in grey.

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for a structure of this type refined from powder data. The packing of  $PPh_4^+$  and  $Ni(WS_4)_2^{2-}$  anions is discussed in more detail below.

Powder diffraction data were also recorded on cooling  $(PPh_4)_2Ni(WS_4)_2$  from 300 to 16 K. A smooth variation in cell parameters was observed suggesting no phase transitions (see ESI§). Thermal expansion was relatively isotropic with thermal expansion coefficients between 15 and 300 K of  $a_a = 41.6(8) \times 10^{-6}$ ,  $a_b = 43.3(5) \times 10^{-6}$ ,  $a_c = 38.5(6) \times 10^{-6}$  K<sup>-1</sup>.

## (PPh<sub>4</sub>)<sub>2</sub>Zn(WS<sub>4</sub>)<sub>2</sub>: tetragonal polymorph

Orange single crystals of (PPh<sub>4</sub>)<sub>2</sub>Zn(WS<sub>4</sub>)<sub>2</sub> were grown at 4 °C by layering ethanol on a DMF solution of the polycrystalline material. A small number of crystals of sufficient quality for single-crystal structural analysis could be obtained. Fig. 3 shows a typical image collected from such a crystal. The most intense sharp reflections could all be indexed on a tetragonal cell of a =13.2295, c = 6.7770 Å. However between these layers weaker reflections could be observed superimposed on lines of significant diffuse scatter. The supercell reflections could be indexed using a cell of a = b = 18.723, c = 13.563 Å *i.e.*  $a_{sup} \sim \sqrt{2}a_{sub}$ ,  $c_{sup}$  $\sim 2c_{sub}$  (Table 2). Similar observations were made in the original paper on this material, though no attempt was made to refine the superstructure.<sup>26</sup> An excellent fit to the subcell-only data  $(R/R_w =$ 1.76/3.96%) could be obtained using the disordered structural model illustrated in Fig. 4 and final agreement factors are given in Table 2. In this model  $[Zn(WS_4)_2]^{2-}$  anions lie along the 4 axes of the tetragonal unit cell with  $\ensuremath{\mathsf{PPh}_4^+}$  cations interspersed between them. Note that Fig. 4 shows only one of two possible sets of anion positions. An alternative set of sites is located at +c/2 from those

<sup>¶</sup> Diffraction data were collected using a Bruker AXS Smart 6000 diffractometer on a crystal of dimensions  $0.08 \times 0.08 \times 0.3$  mm. Two full spheres of data were collected with a frame width of  $0.3^{\circ}$  and integrated using the SAINT<sup>29</sup> software package to give 20241 reflections for the subcell and 82669 for the supercell. Correction for absorption using SADABS<sup>30</sup> and merging ( $R_{int} = 1.9/3.0\%$ ) resulted in 1292/4564 reflections of which 1175/2471 had  $I > 3\sigma(I)$ . Systematic extinctions were consistent with space group  $I\overline{4}$ .



**Fig. 3** Diffraction data for crystals of  $(PPh_4)_2Zn(WS_4)_2$  with predicted reflections for the subcell overlaid. Predicted reflections are shown by squares for reflections centred on this particular frame, crosses for reflections centred a few frames before this one and circles for reflections centred a few frames after this one.

Table 2 Crystallographic details for sub- and super-structure refinement of  $(PPh_4)_2Zn(WS_4)_2$ 

Formula	$[P(C_6H_5)_4]_2Zn(WS_4)_2$	$[P(C_6H_5)_4]_2Zn(WS_4)_2$
M <sub>r</sub>	1368.38	1368.38
Crystal system	Tetragonal	Tetragonal
Space group	IĀ	IĀ
a/Å	13.2295(3)	18.723(4)
b/Å	13.2295(3)	18.723(4)
c/Å	6.7770(2)	13.563(4)
$V/Å^3$	1186.11(5)	4754(2)
T/K	120	120
$D_{\rm c}/{\rm g~cm^{-3}}$	1.916	1.912
$\mu/\mathrm{mm}^{-1}$	5.793	5.781
Total no. reflections	20241	82669
No. unique reflections	1292	4564
No. observed reflections	1175	2471
No. refined parameters	83	142
$R_{\rm int}$ (%)	1.9	3.0
R(%)	1.76	4.97
$R_{\rm w}$ (%)	3.96	5.94
Twin element parameter (%)	_	24.5(5)

shown. This places the Zn atom at the centre of the anion on the original position occupied by the W atom. As such the S atoms on the "lower half" of the  $ZnS_4$  tetrahedron are superimposed on sites originally on the "upper half" of the WS<sub>4</sub> tetrahedron. The S positions are therefore, to a first approximation, unaffected by this disorder.



**Fig. 4** An ordered view of the substructure of the tetragonal polymorph of  $(PPh_4)_2Zn(WS_4)_2$ , viewed down the *c* axis (left) and perpendicular to the *c* axis (right) with the cations omitted. Note that only half of the anion sites are shown. W is shown in green, Zn in red, S in yellow, P in orange, C in blue and H in grey.

This disorder model is the origin of the supercell reflections and diffuse scatter observed on the X-ray images. The superstructure was solved using SIR92 and refined successfully to  $R/R_w = 4.97/5.94\%$ .\* A twin law of the form (0 1 0; 1 0 0; 0 0 - 1) was applied, as is commonly required for structures in Laue group 4/m. In the superstructure model there are two crystallographically independent chains of  $[Zn(WS_4)_2]^{2-}$  anions in the unit cell. These correspond to the chains at (0, 0, z) and  $(\frac{1}{2}, \frac{1}{2}, z)$  of Fig. 4. Within these chains we refine  $\sim 64 : 36$  and 77 : 23% disorder of anions over two sets of positions related to those refined in the subcell

<sup>\*</sup> For final cycles of refinement an optimal weighting scheme based on a third-order Chebychev polynomial was applied. Soft restraints were applied to maintain the planarity and regularity of phenyl rings. H atoms were added geometrically and refined using the riding model. Isotropic temperature factors were refined for all atoms.

model (where occupancies are fixed at 50 : 50% by symmetry). The two disordered positions and resulting average anion chain structure are shown in Fig. 5. It can be seen from this figure that the superposition of these two disordered sites leads to an approximate superposition of atomic coordinates (*e.g.* metal sites are separated by ~1 Å). If these sites superimpose precisely and the site occupancies were 50 : 50% the tetragonal substructure would result. Presumably within a given anion chain  $[Zn(WS_4)_2]^2$  units are fully ordered. As one moves to adjacent chains the registry is rapidly lost as the sulfur atoms of the anion chains can "lock in" to the PPh<sub>4</sub><sup>+</sup> cations in one of two possible positions along *c*. The length scale of registry is reflected in the ~30% refined occupancy of the minor component of each chain and further manifests itself as the streaks of diffuse scatter on all X-ray images. Full details of the superstructure model have been deposited.



**Fig. 5** Disordered chain in the superstructure of the tetragonal form of  $(PPh_4)_2Zn(WS_4)_2$  viewed down the *b* axis. Major anion sites are shown in red, minor anion sites in blue.

#### (PPh<sub>4</sub>)<sub>2</sub>Zn(WS<sub>4</sub>)<sub>2</sub>: monoclinic polymorph

Powder diffraction measurements on the polycrystalline sample from which the tetragonal single crystal was grown revealed a very different structure to that obtained by single-crystal methods. The powder diffraction pattern could instead be indexed on a monclinic cell of a = 18.6397, b = 15.3693, c = 18.9822 Å,  $\beta =$ 109.239° close to that expected from the single-crystal structure reported for the Co material.27 Rietveld refinement of the powder data was performed using the Co structure as a starting model. A total of 97 parameters were refined: 12 coefficients of a Chebychev polynomial to describe the background, sample displacement, an axial model parameter to describe peak asymmetry, a scale factor, 6 peak shape parameters, 15 coefficients of a spherical harmonic function to describe preferred orientation, 4 cell parameters, 33 coordinates of atoms in the anion, and 4 temperature factors; PPh<sub>4</sub> units were modelled as rigid bodies with P-C distances of 1.79 Å, C-C distances of 1.39 Å and C-H distances of 0.998 Å. Six parameters were refined to describe the rotations and translations of these units relative to the x, y and z axes, 4 torsion angles were also refined for each unit to describe the rotation of the phenyl rings around the P-C bonds. Final agreement factors of  $R_{\rm wp} = 6.38\%$  and  $R_{\rm Bragg} = 1.72\%$  were obtained. The Rietveld plot is shown in Fig. 6 and refinement details in Table 3. A .cif file

Table 3 Agreement factors for Rietveld refinement of  $(PPh_4)_2 Zn(WS_4)_2$ 

Space group	$P2_{1}/c$	$2\theta$ range/°	4.5–70
a/Å	18.6397(4)	$2\theta$ step/°	0.0144
b/Å	15.3693(5)	Time per step/s	90
c/Å	18.9822(5)	$R_{wp}$ (%)	6.38
β/°	109.239(2)	$R_{\text{Bragg}}$ (%)	1.72
No. refined parameters	97	$\chi^2$	10.55



**Fig. 6** Observed, calculated and difference (lower curve) plots for the Rietveld refinement of monoclinic  $(PPh_4)_2Zn(WS_4)_2$ . Tick marks show allowed reflection positions. A zoom of the region between 24 and 40°  $2\theta$  is shown.

has been deposited. Bond lengths and angles of  $Zn(WS_4)_2$  units showed minor distortions from tetrahedral geometry. W–S bond lengths ranged from 1.89(3) to 2.29(3) Å and angles from 102(1) to 119(1)°. ZnS<sub>4</sub> tetrahedra showed more marked distortion with bond lengths from 2.22(4) to 2.43(4) Å and angles from 91(1) to 124(2)°. ZnS<sub>4</sub> tetrahedra are, however, significantly distorted in the tetragonal polymorph (Zn–S 2.387(1), S–Zn–S 96.95(6) and 116.07(3) with the subcell model). CoS<sub>4</sub> polyhedra in the corresponding M = Co phase have bond angles from 101.8 to 116.1°. The significant distortion is presumably caused by repulsion between formally Zn<sup>2+</sup> and W<sup>6+</sup> ions in edge-sharing tetrahedra.

Powder diffraction of the monoclinic material between 15 and 300 K revealed no phase transitions. Thermal expansion coefficients between 15 and 300 K of  $a_a = 44(1) \times 10^{-6}$ ,  $a_b = 66(3) \times 10^{-6}$ ,  $a_c = 21(1) \times 10^{-6}$  K<sup>-1</sup> showed slightly higher anisotropy than the M = Ni material (see ESI<sup>‡</sup>).

#### Conclusions

We have shown that there are three basic structural types available to  $(PPh_4)_2M(WS_4)_2$  materials. The Mn material is reported to have a tetragonal structure.<sup>28</sup> Single crystals of the Co material are monoclinic.<sup>27</sup> We have confirmed that the bulk powder has the same structure as reported for a single crystal. Single crystals of the Zn material are tetragonal yet the bulk polycrystalline phase prepared here is monoclinic and isostructural with M = Co. The M = Ni structure is distinct, driven by the preference of Ni for square-planar geometry. The anion packing arrangements are compared in Fig. 7. The cell volumes per formula unit are given in Table 4. It can be seen that the Ni and monoclinic Zn structures have significantly larger cell volumes than other materials. Since both samples were characterised using powder diffraction we

Metal	Crystal symmetry	Cell volume per $(PPh_4)_2M(WS_4)_2$ unit/Å <sup>3</sup>
Mn	Tetragonal	1210
Co	Monoclinic	1269
Ni	Triclinic	1361
Zn	Monoclinic	1368
Zn	Tetragonal	1186
Mn Co Ni Zn Zn	Tetragonal Monoclinic Triclinic Monoclinic Tetragonal	1210 1269 1361 1368 1186



**Fig. 7** Packing of  $M(WS_4)_2^{2-}$  units in the tetragonal polymorph of  $(PPh_4)_2Zn(WS_4)_2$  (left),  $(PPh_4)_2Co(WS_4)_2$  (middle) and  $(PPh_4)_2Ni(WS_4)_2$  (right). S is shown in yellow, W tetrahedra in green, Zn tetrahedra in orange, Co tetrahedra in red and Ni polyhedra in blue.

can't exclude the possibility of the presence of disordered solvent molecules.

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