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The crystal structure of tris(6-methylpyridin-2-yl) phosphine selenide, $C_{18}H_{18}N_3PSe$

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Abstract

$C_{18}H_{18}N_3PSe$, monoclinic, $P2_1/n$ (no. 14), $a = 9.3064$ (9) Å, $b = 17.7311$ (18) Å, $c = 11.0556$ (11) Å, $\beta = 105.317(1)^\circ$, $V = 1759.5$ Å³, $Z = 4$, $R_{gt}(F) = 0.0365$, $wR_{ref}(F^2) = 0.0919$, $T = 296(2)$ K.

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The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The 2-bromo-6-methylpyridine (30 mmol), red phosphorus (30 mmol) and powdered KOH (30 mmol) were

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.20 \times 0.15 \times 0.10$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	2.23 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	32.2° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	27,083, 5848, 0.029
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5031
$N(\text{param})_{\text{refined}}$:	211
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

dissolved in 20 mL DMSO and 1 mL H₂O. The solution was stirred for 1 h at 120 °C under dry argon and cooled to room temperature. Then 40 mL H₂O was added and the mixture was extracted with CHCl₃ (3 × 20 mL). The solvent was removed under reduced pressure and the residue washed with diethyl ether (10 mL) and dried in vacuo to afford the phosphine product as a microcrystalline powder. Powdered gray selenium (10 mmol) and degassed toluene (20 mL) were added to the above solids, and the suspension was refluxed for 3 h. After cooling to room temperature the excess selenium was filtered off. The filtrate was evaporated to dryness under vacuum and a beige-colored powder was obtained. Crystals were obtained by slow evaporation in CHCl₃ and CH₃OH within 7 days.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C1	0.30290 (18)	0.81857 (9)	0.01628 (14)	0.0313 (3)
C2	0.1945 (2)	0.83306 (12)	−0.09355 (16)	0.0439 (4)
H2	0.125608	0.871717	−0.098819	0.053*
C3	0.1933 (3)	0.78685 (15)	−0.19646 (18)	0.0591 (6)
H3	0.121651	0.793598	−0.272171	0.071*
C4	0.2988 (3)	0.73171 (14)	−0.18430 (19)	0.0560 (6)
H4	0.299159	0.700769	−0.252133	0.067*
C5	0.4047 (2)	0.72180 (11)	−0.07161 (18)	0.0437 (4)
C6	0.5213 (3)	0.66142 (13)	−0.0543 (2)	0.0602 (6)
H6A	0.617716	0.683062	−0.018597	0.090*
H6B	0.518845	0.639329	−0.134092	0.090*
H6C	0.501844	0.623220	0.000868	0.090*
C7	0.30510 (16)	0.79401 (8)	0.27103 (13)	0.0276 (3)
C8	0.39940 (19)	0.78926 (11)	0.39083 (15)	0.0367 (3)
H8	0.470297	0.826288	0.421962	0.044*
C9	0.3840 (2)	0.72680 (12)	0.46297 (17)	0.0436 (4)
H9	0.445226	0.721146	0.543816	0.052*
C10	0.2779 (2)	0.67407 (11)	0.41359 (18)	0.0436 (4)
H10	0.268310	0.631456	0.459869	0.052*
C11	0.18340 (19)	0.68429 (9)	0.29284 (17)	0.0358 (3)
C12	0.0634 (3)	0.62842 (11)	0.2377 (2)	0.0524 (5)
H12A	−0.009056	0.628384	0.285495	0.079*
H12B	0.106214	0.579029	0.239832	0.079*
H12C	0.015987	0.642028	0.152447	0.079*
C13	0.49402 (16)	0.91372 (8)	0.20445 (13)	0.0274 (3)
C14	0.5695 (2)	0.92949 (10)	0.11526 (16)	0.0355 (3)
H14	0.531612	0.914503	0.032324	0.043*
C15	0.7036 (2)	0.96841 (11)	0.15303 (18)	0.0413 (4)
H15	0.756904	0.980683	0.095488	0.050*
C16	0.7559 (2)	0.98838 (10)	0.27697 (18)	0.0409 (4)
H16	0.845887	1.013950	0.304219	0.049*
C17	0.6743 (2)	0.97040 (10)	0.36155 (16)	0.0377 (3)
C18	0.7271 (3)	0.99008 (18)	0.4985 (2)	0.0662 (7)
H18A	0.650679	1.017716	0.523034	0.099*
H18B	0.815408	1.020443	0.512744	0.099*
H18C	0.748947	0.944638	0.547102	0.099*
N1	0.40678 (17)	0.76489 (8)	0.02889 (13)	0.0355 (3)
N2	0.19774 (15)	0.74375 (8)	0.22234 (13)	0.0319 (3)
N3	0.54352 (16)	0.93426 (8)	0.32509 (13)	0.0330 (3)
P1	0.30913 (4)	0.87031 (2)	0.16087 (3)	0.02617 (8)
Se1	0.13816 (2)	0.95049 (2)	0.14172 (2)	0.04267 (7)

Comment

Pyridyl-substituted phosphines have been extensively used in metal ion coordination chemistry due to their fundamental importance and prospective applications [5–7]. Tris(2-pyridyl)phosphine exhibits rich coordination capabilities owing to its structure. On the other hand, there are many studies on the substitution of pyridine-4-yl substituents in the substituents of pyridine [8, 9]. However, the pyridine-6-yl substituents are less investigated.

The asymmetric unit contains one independent molecule. The nitrogen atoms (N2, N3) are almost form a plane with P1 and C1, while the remaining nitrogen atom (N1) forms a plane with C1, P1 and Se1 (see the figure). This type of arrangement is different from previously seen ones in the structure of tris(2-pyridyl)phosphine oxide and tris(2-pyridyl)phosphine sulphide. However, in the reported tris(2-pyridyl)phosphine selenide structure [10], all nitrogen atoms point in the same direction (towards Se), which can be related to the steric requirement bearing a methyl group at the 6-position of the pyridyl ring. The P=Se bond distance of 2.1022(4) Å is comparable with similar structures found in the literature showing typical double bond character [8–10]. The pyridine ring (N1/C1–C5) makes dihedral angles of 70.97(11)° and 72.42(11)° with the other two pyridine rings (N2/C7–C11 and N3/C13–C17), respectively. In addition, the crystal structure exhibits weak C–H⋯π interactions. [C(6)–H(6A)⋯Cg2'] = 2.94 (4)° Å; Cg2 is the centroid of pyridine ring (N2, C6, C7, C8, C9, C10); ' = $x-1/2, -y+1/2, z+1/2$. The stability of crystal structure can be accounted by this interaction. Furthermore, there are no other obvious π⋯π stacking interactions, as the centroid to centroid distance between the two nearest rings is greater than 4.5 Å.

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References

1. Bruker. *APEX2, SAINT—Plus, XPRED*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2008.
2. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, 42, 339–341.
3. Sheldrick G. M. *SHELXTL* – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, A71, 3–8.
4. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, C71, 3–8.
5. Newkome G. R. Pyridylphosphines. *Chem. Rev.* 1993, 93, 2067–2089.
6. Zhang Z. Z., Cheng H. Chemistry of 2-(diphenylphosphino) pyridine. *Coord. Chem. Rev.* 1996, 147, 1–39.
7. Nippe M., Khayzer R. S., Panetier J. A., Zee D. Z., Olaiya B. S., Head-Gordon M., Chang C. J., Castellano F. N., Long J. R.

- Catalytic proton reduction with transition metal complexes of the redox-active ligand bpy_2PYMe . *Chem. Sci.* 2013, 4, 3934–3945.
8. Hu X. C., Sun T. Q., Zheng C. Y. Synthesis, crystal structures and magnetic properties of two iron (II) tris(pyridyl)phosphine selenides complexes. *Phosphorus, Sulfur Silicon Relat. Elem* 2018, 193, 300–305.
 9. Wang H. Q., Wu N., Zheng J., Zheng C. Y., Wang D. J. Synthesis and structures of two mononuclear iron(II) complexes derived from polypyridine ligands. *Mendeleev Commun.* 2020, 30, 100–102.
 10. Kharat A. N., Bakhoda A., Hajiashrafi T., Abbasi A. Synthesis, characterization, and crystal structures of tris(2-pyridyl) phosphine sulfide and selenide. *Phosphorus, Sulfur Silicon Relat. Elem.* 2010, 185, 2341–2347.