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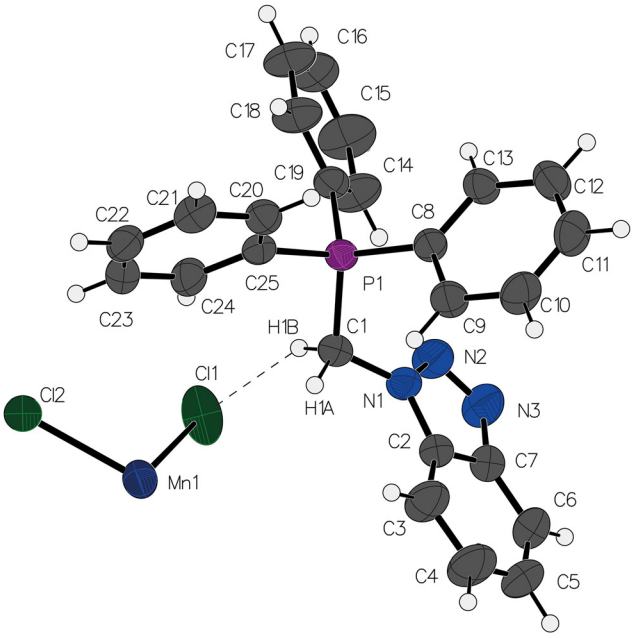
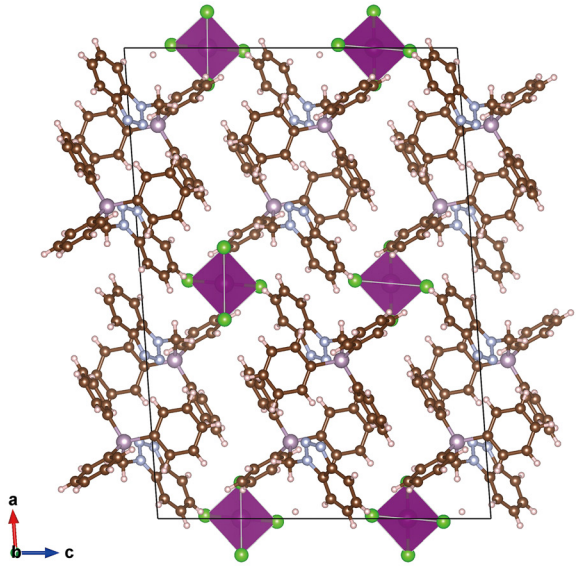
Crystal structure of bis(((3a,7a-dihydro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)methyl) triphenylphosphonium) tetrachloridomanganate(II), $C_{50}H_{42}Cl_4MnN_6P_2$





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Abstract

$C_{50}H_{42}Cl_4MnN_6P_2$, monoclinic, *C*2/*c* (no. 15), a = 26.2608(7) Å, b = 9.7828(2) Å, c = 18.5648(5) Å, β = 94.103(2)°, V = 4757(2) Å^3, Z = 4, $R_{gt}(F)$ = 0.0479 $wR_{ref}(F^2)$ = 0.1046, T = 293 K.

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The molecular structure is shown in the figure. Table 1 contains the crystallographic data and the list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

Table 1: Data collection and handling.

Crystal:	Clear greenish green block
Size:	0.38 × 0.23 × 0.21 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.61 mm^{-1}
Diffractometer, scan mode:	Rigaku, ω scans
θ_{max}, completeness:	29.2°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	11698, 5498, 0.023
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4,069
$N(param)_{refined}$:	285
Programs:	Rigaku,[1] SHELX,[2,3] Olex2[4]

1 Source of materials

The crystalline material was prepared by dissolving ((3a,7a-dihydro-1*H*-benzo [*d*][1,2,3]triazol-1-yl)methyl)triphenylphosphonium chloride (0.05 mmol) and manganese

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dichloride (0.05 mmol) in anhydrous ethanol (4.0 mL) within a 10 mL Schlenk tube. Concentrated hydrochloric acid (37 %, 0.50 mL) was added dropwise with stirring. The homogeneous solution was filtered through a 0.45 μm PTFE syringe filter into a clean 5 mL glass vial, which was subsequently placed inside a larger vessel containing 10 mL of diethyl ether as a reservoir for vapor diffusion. Crystallization occurred over 7 days at room temperature. Crystal dimensions were optimized by adjusting the evaporative flux through controlled needle aperture occlusion.

2 Experimental details

The structure was solved using intrinsic phasing methods within SHELXT.[2] Subsequent anisotropic full-matrix least-squares refinement on all non-hydrogen atoms was conducted using SHELXL[3] within the Olex2 platform.[4] Hydrogen atoms were incorporated at idealized positions employing riding models, with fixed isotropic displacement parameters.

3 Comment

Triphenylphosphonium (TPP) cations constitute a privileged class of supramolecular building blocks in crystal engineering, renowned for their capacity to direct hierarchical assembly through synergistic cation-π interactions, C–H$\cdots\pi$ contacts, and van der Waals forces.[5–8] The steric bulk and electronic anisotropy of TPP systems have been leveraged to construct functional materials with engineered void spaces, tunable luminescence, and proton-conducting behavior, as evidenced by structural studies of tetrafluoroborate and hexafluorophosphate analogues. Our elucidation of the single-crystal structure of ((3a,7a-dihydro-1*H*-benzo[*d*][1, 2,3] triazol-1-yl)methyl)triphenylphosphonium manganese tetrachloride represents the first systematic integration of benzotriazole-functionalized TPP cations with paramagnetic $[MnCl_4]^{2-}$ moieties. The crystalline hybrid material exhibits prospects as a prototype for designing stimuli-responsive magnetic systems.

As illustrated in the Figure, the crystal structure of the title compound reveals a phosphorus atom bonded to four substituents: three phenyl groups and one 3a,7a-dihydro-1H-benzo[*d*][1,2,3]triazolyl group. The observed P–C bond lengths are approximately 1.80 Å, consistent with values reported in the literature for similar systems.[9–12] The interplanar angles between the three phenyl groups are 89.7°, 67.9°, and 87.9°, respectively. The dihedral angles formed between the 3a,7a-dihydro-1*H*-benzo[*d*][1,2,3] triazolyl group and each of the phenyl rings are 70.9°, 19.1°, and 83.6°.

Within the title compound, the $[MnCl_4]^{2-}$ anion interacts with the triphenylphosphonium moiety, forming an organic-inorganic hybrid architecture (right side of the figure). The $[MnCl_4]^{2-}$ anion exhibits a tetrahedral geometry, with Mn–Cl bond lengths averaging approximately 2.38 Å, in agreement with literature precedents.[13–16] The crystal structure features an alternating arrangement of these organic cations and inorganic anions.

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