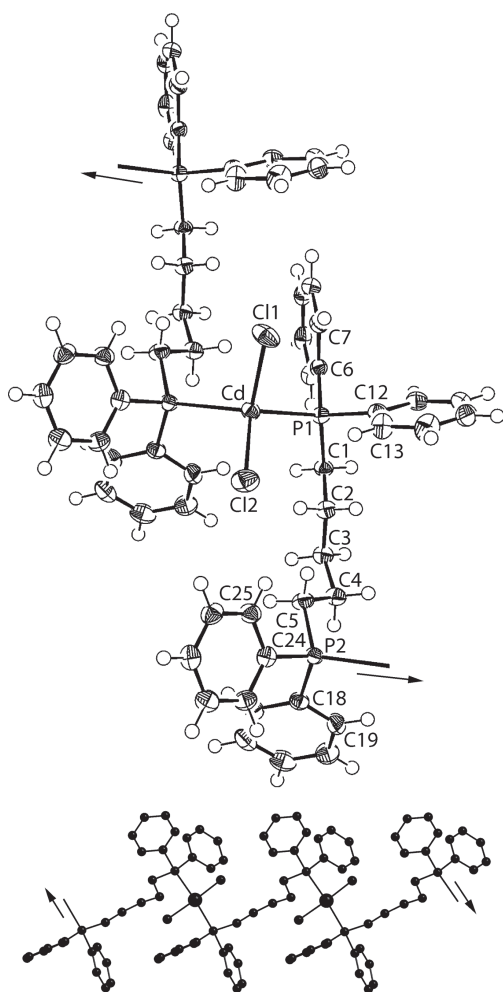


Yee Seng Tan and Edward R.T. Tiekink*

Crystal structure of *catena*-poly[$\{\mu_2$ -1,5-bis(diphenylphosphanyl)pentane- $\kappa^2 P:P'$ dichloridocadmium(II)], $C_{29}H_{30}CdCl_2P_2$



Abstract

$C_{29}H_{30}CdCl_2P_2$, orthorhombic, $Pna2_1$ (no. 33), $a = 15.84368(4)$ Å, $b = 8.46281(2)$ Å, $c = 20.88054(8)$ Å, $V = 2799.705(14)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0275$, $wR_{ref}(F^2) = 0.0719$, $T = 100(2)$ K.

CCDC no.: 1957381

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.19 × 0.17 × 0.13 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	9.20 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	125730, 4962, 0.036
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 4959
$N(param)_{refined}$:	307
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

The title compound was prepared by using a layering method. 1,5-Bis(diphenylphosphino)pentane (Sigma-Aldrich; 0.0660 g, 0.015 mmol) was dissolved in chloroform (Merck; 5 mL) and transferred to a 14 mL test tube. This was followed by careful layering of a buffer solution (Merck; 2 mL 1:1 v/v mixture of chloroform and ethanol). An ethanol solution (5 mL) of cadmium (II) chloride (Acros Organic; 0.0275 g, 0.015 mmol) was prepared and carefully layered upon the buffer solution. The test tube was screwed with a cap and allowed to stand under ambient conditions. Colourless block crystals were formed after one week. Yield: 0.074 g (78.6%). **M.pt** (Stuart SMP30 Melting Point apparatus): 515.0–516.5 K. **IR** (Bruker Vertex 70 V equipped with Platinum ATR from 400 to 80 cm⁻¹): 1433 (m) $\nu(P-CH_2)$; 1101 (w) $\nu(P-C_{aromatic})$; 149 (w) $\nu(Cd-Cl)$; 203 (w) $\nu(Cd-P)$.

<https://doi.org/10.1515/ncrs-2019-0595>

Received August 16, 2019; accepted October 3, 2019; available online October 25, 2019

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

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Cd	0.43651(2)	0.14468(3)	0.49853(2)	0.01744(11)
Cl1	0.35253(6)	−0.00992(14)	0.42354(6)	0.0336(3)
Cl2	0.36351(7)	0.36939(12)	0.54656(6)	0.0327(3)
P1	0.56331(5)	0.23049(12)	0.42723(5)	0.0160(2)
P2	0.47101(6)	0.95645(11)	0.59335(5)	0.0168(2)
C1	0.6389(3)	0.3642(4)	0.4655(2)	0.0176(8)
H1A	0.6663	0.3108	0.5023	0.021*
H1B	0.6833	0.3949	0.4346	0.021*
C2	0.5913(2)	0.5108(4)	0.4886(2)	0.0205(8)
H2A	0.5424	0.4771	0.5148	0.025*
H2B	0.5693	0.5688	0.4509	0.025*
C3	0.6465(3)	0.6218(5)	0.5282(2)	0.0209(8)
H3A	0.7009	0.6386	0.5058	0.025*
H3B	0.6586	0.5727	0.5702	0.025*
C4	0.6025(2)	0.7818(4)	0.53841(19)	0.0211(8)
H4A	0.5927	0.8324	0.4963	0.025*
H4B	0.6401	0.8518	0.5635	0.025*
C5	0.5177(2)	0.7647(5)	0.5737(2)	0.0215(8)
H5A	0.5265	0.7039	0.6136	0.026*
H5B	0.4779	0.7045	0.5464	0.026*
C6	0.6214(2)	0.0589(4)	0.39951(19)	0.0171(7)
C7	0.5763(3)	−0.0547(5)	0.3653(2)	0.0195(8)
H7	0.5199	−0.0339	0.3524	0.023*
C8	0.6139(3)	−0.1987(5)	0.3501(2)	0.0226(8)
H8	0.5837	−0.2756	0.3262	0.027*
C9	0.6964(3)	−0.2290(5)	0.3702(2)	0.0229(8)
H9	0.7219	−0.3279	0.3607	0.027*
C10	0.7411(3)	−0.1157(5)	0.4040(2)	0.0229(8)
H10	0.7972	−0.1370	0.4173	0.028*
C11	0.7042(3)	0.0299(5)	0.4186(2)	0.0216(8)
H11	0.7352	0.1080	0.4412	0.026*
C12	0.5308(3)	0.3377(4)	0.3556(2)	0.0190(8)
C13	0.4531(3)	0.4168(6)	0.3557(2)	0.0261(9)
H13	0.4161	0.4069	0.3913	0.031*
C14	0.4303(3)	0.5092(7)	0.3039(3)	0.0324(11)
H14	0.3780	0.5641	0.3042	0.039*
C15	0.4832(3)	0.5218(5)	0.2518(2)	0.0300(10)
H15	0.4667	0.5840	0.2160	0.036*
C16	0.5602(3)	0.4448(6)	0.2510(3)	0.0307(11)
H16	0.5962	0.4541	0.2149	0.037*
C17	0.5849(4)	0.3536(4)	0.3032(2)	0.0251(9)
H17	0.6382	0.3025	0.3032	0.030*
C18	0.5473(3)	1.0401(5)	0.6490(2)	0.0184(7)
C19	0.6010(3)	1.1573(5)	0.6257(2)	0.0248(9)
H19	0.5920	1.2002	0.5842	0.030*
C20	0.6679(3)	1.2116(5)	0.6631(2)	0.0304(9)
H20	0.7057	1.2889	0.6469	0.036*
C21	0.6785(3)	1.1523(5)	0.7238(3)	0.0294(10)
H21	0.7241	1.1892	0.7493	0.035*
C22	0.6238(3)	1.0392(5)	0.7486(2)	0.0268(9)
H22	0.6308	1.0018	0.7911	0.032*
C23	0.5590(2)	0.9816(6)	0.7106(2)	0.0218(9)
H23	0.5225	0.9019	0.7267	0.026*
C24	0.3785(2)	0.9049(5)	0.64060(19)	0.0191(8)

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C25	0.3324(3)	0.7688(5)	0.6260(2)	0.0222(8)
H25	0.3487	0.7040	0.5909	0.027*
C26	0.2624(3)	0.7283(5)	0.6628(2)	0.0241(8)
H26	0.2314	0.6352	0.6530	0.029*
C27	0.2377(3)	0.8230(5)	0.7136(2)	0.0238(8)
H27	0.1899	0.7950	0.7386	0.029*
C28	0.2828(3)	0.9580(5)	0.7278(2)	0.0247(9)
H28	0.2660	1.0225	0.7627	0.030*
C29	0.3527(3)	1.0004(5)	0.6913(2)	0.0217(8)
H29	0.3828	1.0946	0.7009	0.026*

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The absolute structure was determined based on Friedel pairs included in the whole data set (classical method: Flack parameter: 0.004(7)).

Comment

Recently, the crystal structure determination of [CdCl₂(dppe)]_n, where dppe is 1,2-bis(diphenylphosphino)ethane, was described [5]. The dppe ligands were found to be μ₂-bridging with the outcome being a one-dimensional coordination polymer with a zig-zag topology. A survey of the literature showed that there were in fact several structural motifs for related phosphane adducts of cadmium (II) chloride, all of which featured tetrahedrally coordinated cadmium within Cl₂P₂ donor sets. There are mononuclear structures with mono- and bi-functional phosphane ligands, as exemplified by CdCl₂(PPh₃)₂ [6] and CdCl₂(dppf) [7], respectively; dppf is 1,1'-bis(diphenylphosphanyl)ferrocene. Prior to the most recent study [5], the only other polymeric structure was that formed between CdCl₂ and (*R,R*)-*trans*-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxalane [8]. The title one-dimensional coordination polymer [CdCl₂(dppp)]_n, (I), where dppp is 1,5-bis(diphenylphosphino)propane, was determined in continuation of on-going studies of cadmium coordination polymers [5, 9–11].

The asymmetric unit of (I) is shown in the top view of the figure (70% probability displacement ellipsoids; the unlabelled dppp molecule is related by the symmetry operation (i) *x*, −1 + *y*, *z*) and comprises a cadmium(II), two chlorido ligands and a full dppp ligand. As anticipated, the cadmium atom is tetrahedrally coordinated within a Cl₂P₂ donor set. The Cd–Cl1, Cl2 bond lengths of 2.4359(10) and 2.4412(10) Å, respectively, are experimentally equivalent to each other as are the Cd–P1, P2ⁱ bond lengths of 2.6038(10) and 2.5994(10) Å, respectively. The tetrahedral

angles around the cadmium atom span a relatively narrow range, i.e. $101.76(4)^\circ$, for $Cl1-Cd-P1$, to $116.37(3)^\circ$, for $P1-Cd-P2^i$. The *n*-propanyl link has a curved shape as seen in the sequence of torsion angles (*cf.* upper view of the figure): $P1-C1-C2-C3$ [$173.3(3)^\circ$], $C1-C2-C3-C4$ [$168.2(3)^\circ$], $C2-C3-C4-C5$ [$59.8(5)^\circ$] and $C3-C4-C5-P2$ [$173.9(3)^\circ$], i.e. there is a + syn-clinal conformation about the $C3-C4$ bond. As indicated in the figure, the dppp ligands are μ_2 -bridging so that a one-dimensional coordination polymer results. The chain is propagated by translational symmetry along the *b*-axis so that a linear topology, as shown in the lower view of the figure (all hydrogen atoms have been omitted). When viewed down the *b*-axis, the chain maybe described as having the $CdCl_2$ residues residing in a bay defined by the dppp molecules, indicating the chloride atoms are available to form intermolecular interactions.

In the crystal, the connections between the chains leading to a three-dimensional architecture are of the type phenyl- $C-H \cdots Cl$, involving the same chloride atom [$C9-H9 \cdots Cl1^{ii}$: $H9 \cdots Cl1^{ii} = 2.81 \text{ \AA}$, $C9 \cdots Cl1^{ii} = 3.499(5) \text{ \AA}$ with angle at $H9 = 130^\circ$ and $C22-H22 \cdots Cl1^{iii}$: $H22 \cdots Cl1^{iii} = 2.78 \text{ \AA}$, $C22-H22 \cdots Cl1^{iii} = 3.680(4) \text{ \AA}$ with angle at $H22 = 159^\circ$ for symmetry operations (ii) $1/2 + x, -1/2 - y, z$ and (iii) $1 - x, 1 - y, 1/2 + z$] and phenyl- $C-H \cdots \pi(\text{phenyl})$ interactions [$C26-H26 \cdots Cg(18-C23)^{iv}$: $H26 \cdots Cg(18-C23)^{iv} = 2.81 \text{ \AA}$, $C26 \cdots Cg(18-C23)^{iv} = 3.666(5) \text{ \AA}$ with angle at $H26 = 151^\circ$ and $C28-H28 \cdots Cg(C6-C11)^v$: $H28 \cdots Cg(C6-C11)^v = 2.86 \text{ \AA}$, $C28 \cdots Cg(C6-C11)^v = 3.568(5) \text{ \AA}$ with angle at $H28 = 132^\circ$ for (iv) $-1/2 + x, 3/2 - y, z$ and (v) $1 - x, 1 - y, 1/2 + z$].

Acknowledgements: Sunway University Sdn Bhd is thanked for financial support of this work through Grant no. STR-RCTR-RCCM-001-2019.

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