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Crystal structure of a new polymorph of bis[μ -1,3-bis(diphenylphosphino)propane- $\kappa^2P:P'$ -disilver(I)] bis(tetrafluoroborate), [Ag(dppp)]₂(BF₄)₂, C₅₄H₅₂Ag₂B₂F₈P₄

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.43 × 0.40 × 0.38 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.96 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART, φ and ω -scans
$\theta_{\max}$, completeness:	25°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	16198, 9051, 0.019
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 7937
$N(\text{param})_{\text{refined}}$:	631
Programs:	Bruker programs [1], SHELX [2]

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ag1	0.38326(2)	−0.14484(2)	0.05264(2)	0.01712(6)
Ag2	0.37532(2)	0.34918(2)	0.54432(2)	0.01759(6)
F1	0.61249(15)	0.95548(13)	0.01256(8)	0.0292(4)
F2	0.75579(17)	0.95568(18)	0.11149(9)	0.0496(5)
F3	0.76073(18)	0.88128(17)	−0.00083(9)	0.0478(5)
F4	0.59187(17)	0.78949(15)	0.03978(11)	0.0503(5)
F5	0.42260(16)	0.74094(14)	0.49485(10)	0.0411(4)
F6	0.38281(17)	0.55591(14)	0.49048(9)	0.0394(4)
F7	0.21642(16)	0.60629(16)	0.44633(10)	0.0489(5)
F8	0.31553(19)	0.65901(19)	0.56727(10)	0.0554(6)
P1	0.42184(6)	−0.01546(5)	0.16703(3)	0.01442(13)
P2	0.73604(6)	0.29339(5)	0.05995(3)	0.01371(13)
P3	0.24449(6)	0.21244(5)	0.42887(3)	0.01350(13)
P4	0.55174(6)	0.54181(5)	0.33084(3)	0.01443(13)
B1	0.6826(3)	0.8955(3)	0.04083(16)	0.0238(7)
B2	0.3316(3)	0.6396(3)	0.49932(16)	0.0238(6)
C1	0.4879(2)	0.1364(2)	0.16801(13)	0.0170(5)
H1A	0.4212	0.1516	0.1375	0.020*
H1B	0.5114	0.1848	0.2170	0.020*
C2	0.6071(2)	0.1674(2)	0.14119(13)	0.0171(5)
H2A	0.5893	0.1088	0.0970	0.021*
H2B	0.6798	0.1684	0.1773	0.021*
C3	0.6449(2)	0.2855(2)	0.12630(13)	0.0175(5)
H3A	0.6980	0.3460	0.1711	0.021*
H3B	0.5669	0.2976	0.1079	0.021*
C4	0.2655(2)	−0.0368(2)	0.18321(12)	0.0154(5)
C5	0.2296(2)	−0.0793(2)	0.23894(12)	0.0177(5)
H5	0.2894	−0.0920	0.2726	0.021*
C6	0.1052(2)	−0.1028(2)	0.24456(13)	0.0203(5)
H6	0.0821	−0.1312	0.2820	0.024*
C7	0.0157(2)	−0.0844(2)	0.19508(13)	0.0210(5)
H7	−0.0680	−0.1014	0.1987	0.025*
C8	0.0507(2)	−0.0403(2)	0.13950(14)	0.0223(6)

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Abstract

C₅₄H₅₂Ag₂B₂F₈P₄, triclinic, $P\bar{1}$ $a = 11.4869(4)$ Å, $b = 12.9118(5)$ Å, $c = 19.6858(6)$ Å, $\alpha = 100.8240(10)^\circ$, $\beta = 102.185(2)^\circ$, $\gamma = 110.470(3)^\circ$, $V = 2562.31(15)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0263$, $wR_{\text{ref}}(F^2) = 0.0666$, $T = 293(2)$ K.

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Only one of the two crystallographically independent dinuclear complexes of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was obtained by the reaction of silver(I) tetrafluoroborate (0.0584 g, 0.3 mmol) and 1,3-bis(diphenylphosphino)propane (0.1237 g, 0.3 mmol) in the mixed solution of CH₃OH (5 mL) and CH₂Cl₂ (5 mL) for 6 h

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Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H8	−0.0089	−0.0260	0.1067	0.027*
C9	0.1739(2)	−0.0178(2)	0.13314(13)	0.0202(5)
H9	0.1964	0.0101	0.0954	0.024*
C10	0.5254(2)	−0.0234(2)	0.24735(12)	0.0168(5)
C11	0.5841(2)	−0.1017(2)	0.24111(14)	0.0224(6)
H11	0.5700	−0.1495	0.1958	0.027*
C12	0.6634(3)	−0.1079(2)	0.30258(15)	0.0284(6)
H12	0.7030	−0.1595	0.2983	0.034*
C13	0.6840(3)	−0.0377(2)	0.37047(14)	0.0290(6)
H13	0.7358	−0.0435	0.4116	0.035*
C14	0.6277(3)	0.0406(3)	0.37694(14)	0.0291(6)
H14	0.6423	0.0883	0.4224	0.035*
C15	0.5495(2)	0.0482(2)	0.31591(13)	0.0231(6)
H15	0.5125	0.1018	0.3206	0.028*
C16	0.7784(2)	0.4398(2)	0.05292(12)	0.0171(5)
C17	0.9053(2)	0.5151(2)	0.06265(13)	0.0202(5)
H17	0.9733	0.4921	0.0745	0.024*
C18	0.9309(3)	0.6245(2)	0.05468(13)	0.0235(6)
H18	1.0161	0.6745	0.0612	0.028*
C19	0.8313(3)	0.6600(2)	0.03716(14)	0.0265(6)
H19	0.8492	0.7338	0.0322	0.032*
C20	0.7051(3)	0.5856(2)	0.02699(17)	0.0352(7)
H20	0.6377	0.6093	0.0151	0.042*
C21	0.6781(3)	0.4760(2)	0.03427(16)	0.0314(7)
H21	0.5924	0.4260	0.0267	0.038*
C22	0.8882(2)	0.2873(2)	0.10408(13)	0.0163(5)
C23	0.9350(2)	0.2182(2)	0.06524(14)	0.0214(6)
H23	0.8883	0.1750	0.0174	0.026*
C24	1.0522(3)	0.2135(2)	0.09802(16)	0.0298(7)
H24	1.0847	0.1684	0.0718	0.036*
C25	1.1199(3)	0.2752(2)	0.16885(16)	0.0325(7)
H25	1.1977	0.2711	0.1906	0.039*
C26	1.0735(3)	0.3436(2)	0.20832(16)	0.0342(7)
H26	1.1197	0.3850	0.2565	0.041*
C27	0.9586(3)	0.3501(2)	0.17610(14)	0.0249(6)
H27	0.9277	0.3965	0.2025	0.030*
C28	0.3278(2)	0.2303(2)	0.35919(12)	0.0160(5)
H28A	0.4023	0.2105	0.3704	0.019*
H28B	0.2689	0.1790	0.3123	0.019*
C29	0.3733(2)	0.3556(2)	0.35626(13)	0.0161(5)
H29A	0.4114	0.4068	0.4053	0.019*
H29B	0.2984	0.3687	0.3332	0.019*
C30	0.4737(2)	0.3855(2)	0.31466(12)	0.0162(5)
H30A	0.4308	0.3485	0.2632	0.019*
H30B	0.5393	0.3568	0.3302	0.019*
C31	0.1989(2)	0.0616(2)	0.42733(12)	0.0152(5)
C32	0.2952(3)	0.0181(2)	0.43240(12)	0.0200(5)
H32	0.3795	0.0651	0.4349	0.024*
C33	0.2648(3)	−0.0954(2)	0.43374(13)	0.0244(6)
H33	0.3283	−0.1248	0.4358	0.029*
C34	0.1411(3)	−0.1649(2)	0.43210(13)	0.0284(6)
H34	0.1217	−0.2404	0.4338	0.034*
C35	0.0456(3)	−0.1220(2)	0.42792(14)	0.0291(6)
H35	−0.0380	−0.1688	0.4266	0.035*
C36	0.0749(3)	−0.0086(2)	0.42577(13)	0.0219(6)
H36	0.0107	0.0201	0.4233	0.026*

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C37	0.0937(2)	0.2266(2)	0.39349(13)	0.0164(5)
C38	0.0089(2)	0.1593(2)	0.32467(14)	0.0234(6)
H38	0.0294	0.1057	0.2966	0.028*
C39	−0.1052(3)	0.1718(2)	0.29788(16)	0.0309(7)
H39	−0.1614	0.1267	0.2520	0.037*
C40	−0.1354(3)	0.2514(3)	0.33947(17)	0.0335(7)
H40	−0.2121	0.2598	0.3215	0.040*
C41	−0.0527(3)	0.3185(3)	0.40751(17)	0.0351(7)
H41	−0.0740	0.3718	0.4353	0.042*
C42	0.0620(3)	0.3067(2)	0.43446(15)	0.0258(6)
H42	0.1181	0.3526	0.4802	0.031*
C43	0.6915(2)	0.5632(2)	0.29675(12)	0.0175(5)
C44	0.7877(2)	0.5332(2)	0.33311(14)	0.0237(6)
H44	0.7744	0.4984	0.3697	0.028*
C45	0.9021(3)	0.5547(2)	0.31525(15)	0.0290(6)
H45	0.9654	0.5340	0.3394	0.035*
C46	0.9219(3)	0.6075(2)	0.26094(16)	0.0334(7)
H46	0.9995	0.6235	0.2493	0.040*
C47	0.8280(3)	0.6364(2)	0.22436(15)	0.0299(6)
H47	0.8415	0.6703	0.1874	0.036*
C48	0.7127(3)	0.6152(2)	0.24211(13)	0.0221(6)
H48	0.6497	0.6358	0.2174	0.027*
C49	0.4351(2)	0.5789(2)	0.27357(13)	0.0192(5)
C50	0.3919(3)	0.5376(2)	0.19812(14)	0.0263(6)
H50	0.4233	0.4889	0.1743	0.032*
C51	0.3007(3)	0.5700(3)	0.15848(15)	0.0365(7)
H51	0.2728	0.5441	0.1081	0.044*
C52	0.2522(3)	0.6404(3)	0.19427(17)	0.0360(7)
H52	0.1923	0.6624	0.1678	0.043*
C53	0.2919(3)	0.6780(2)	0.26855(16)	0.0312(7)
H53	0.2569	0.7234	0.2922	0.037*
C54	0.3838(2)	0.6487(2)	0.30852(14)	0.0239(6)
H54	0.4115	0.6758	0.3589	0.029*

at room temperature. The insoluble residues were removed by filtration, and the filtrate was evaporated slowly for about 1 week to yield transparent and colorless crystals. Crystals suitable for single-crystal X-ray diffraction were selected directly.

Experimental details

Semi-empirical absorption corrections were applied using SABABS program [1]. All the structures were solved by Direct Methods using SHELXS program of the SHELXTL-2014/6 package and refined with SHELXL-2014/6 [2]. The hydrogen atoms were generated geometrically and refined with fixed displacement parameters riding on the concerned atoms. The crystallization solvent was lost from the crystal and could not be resolved unambiguously.

Discussion

In the past years, studies have been concerned with the metal silver(I) complexes with nitrogen-heterocycle and diphosphine ligands for their various structures and their potential

applications [3, 4]. The diphosphine groups adopt different coordination modes, such as monodentate, chelating and bridging. The 1,3-bis(diphenylphosphino)propane (*dppp*) ligand which contains diphosphonic groups is widely noticed because of its variety of coordination modes [5]. Many model complexes have been synthesized and characterized by X-ray crystallography to establish the diphosphine chelating behavior [6]. Also, the diphosphine ligands can be used to control the formation of ring or polymeric structures in gold(I) complexes [7].

As know to all, silver(I), a kind of soft acid, is easy to coordinate with P-donor ligands according to the Hard-Soft-Acid-Base (HSAB) theory. In this study, a silver(I) complex $C_{54}H_{52}Ag_2B_2F_8P_4$ with *dppp* ligand has been synthesized and characterized. The most interesting thing in the title crystal structure is a polymorph of a structure reported in the literature [8], which has similar molecular structure.

This compound crystallizes in the triclinic system with space group $P\bar{1}$. The asymmetric unit of the crystal structure is comprised of two Ag(I) atoms and two 1,3-bis(diphenylphosphino)propane ligands. Each Ag(I) is bridged by two *dppp* ligands to form a dinuclear structure. The Ag–P distances are in the range of 2.3887(6)–2.3984(6) Å, which are similar to those in its polymorph $[Ag_2(C_{27}H_{26}P_2)_2](BF_4)_2$. The two Ag–P distances in the second crystallographically independent complex are in the range of 2.3935(7)–2.4016(7) Å. The two angles of Ag–P–Ag in the title crystal structure are 158.75(2)° and 162.77(2)° respectively, while the two identical Ag–P–Ag angles in its polymorph are 159.66(3)°, which is between the two corresponding angles in the title crystal structure. Symmetry codes: $1 - x, 1 - y, 1 - z$; $1 - x, -y, -z$ respectively.

It's a very interesting phenomenon that polymorphisms may be synthesized because of the different molar ratio, different solvent and different crystallization condition. And

we will pay more attention to the different physical properties of the polymorphisms.

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