Syntheses and Structures of Trinuclear Trigonal-bipyramidal Silver(I) Complexes with Bis(diphenylphosphino)amide Ligands

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Treatment of Ag(CF_3CO_2) with an equivalent of bis(diphenylphosphino)amide (dppa) gave a trinuclear trigonal-bipyramidal silver(I) complex $[Ag_3(\mu_3\text{-Cl})_2(\mu\text{-dppa})_3][CF_3CO_2]\cdot CH_2Cl_2\cdot H_2O$ ([**1**] $[CF_3CO_2]\cdot CH_2Cl_2\cdot H_2O$). Reaction of $AgNO_3$ with an equivalent of dppa in the presence of $[NH_4][GaCl_4]$ and $[Et_4N][FeCl_4]$ afforded the corresponding complexes $[Ag_3(\mu_3\text{-Cl})_2(\mu\text{-dppa})_3][GaCl_4]\cdot 2THF\cdot MeOH\cdot H_2O$, ([**1**]$[GaCl_4]\cdot 2THF\cdot MeOH\cdot H_2O$) and $[Ag_3(\mu\text{-Cl})(\mu_3\text{-Cl})(\mu\text{-dppa})_3][FeCl_4]$, ([**2**]$[FeCl_4]$), respectively. Complexes **1** and **2** contain trigonal-bipyramidal $[Ag_3(\mu_3\text{-Cl})_2]^+$ and $[Ag_3(\mu\text{-Cl})(\mu_3\text{-Cl})]^+$ cores, respectively, surrounded by three bridging μ-dppa ligands.

Key words: Synthesis, Crystal Structure, Silver(I) Complex, Bis(diphenylphosphino)amide

Introduction

There has been an extensive interest in polynuclear d^{10} metal complexes with phosphine ligands due to their potential application in intense and long-lived luminescence [1 – 3]. The diverse photophysical and photochemical properties are related to metal-metal interactions in these complexes [4, 5]. Recently, the notable studies of Fenske, Yam and Liu have revealed polynucluear copper or silver complexes supported by tertiary phosphine ligands containing triangular M_3 (M = Cu or Ag) units to be capped by the bridging anions such as halides and chalcogenides [6 – 8]. Structural features of trinuclear halogen-capped complexes with bidentate bis(diphenylphosphino)methane (dppm) $[M_3(\mu_3\text{-}X)_2(\mu\text{-dppm})_3]X$ (M = Cu, Ag; X = Cl, Br, I) were found to be related to properties of metal-phosphorus coordination and metal-metal interactions [7 – 15]. As an analogous ligand, neutral bidentate bis(diphenylphosphino)amide (dppa) shows a relatively high solubility as compared to dppm. Although the trinuclear halogen-capped trigonal-bipyramidal complexes $[M_3(\mu_3\text{-}X)_2(\mu\text{-dppm})_3]X$ (M = Cu, Ag; X = Cl, Br, I) have been well documented, few analogous complexes with dppa ligands have been reported so far [16]. Silver(I) salts are often used in forming polynuclear complexes because silver(I) can easily form complexes with coordination numbers of two, three or four as needed to form many different conformations. For the understanding of reactive properties and structural features of silver complexes with dppa ligands, we set out to study the reactions of different silver(I) species with dppa ligands and describe syntheses and structures of a series of trinuclear trigonal-bipyramidal silver(I) complexes with dppa ligands in this paper.

Experimental Section

General

All syntheses were performed in oven-dried glassware under a purified nitrogen atmosphere using standard Schlenk techniques. All reagents, unless otherwise stated, were purchased as analysis grade and were used without further purification. Bis(diphenylphosphino)amine (dppa) was synthesized from the reaction of Ph_2PCl with $(Me_3Si)NH(SiMe_3)$ in toluene [17]. $[NH_4][GaCl_4]$ [18] and $[Et_4N][FeCl_4]$ [19] were prepared according to procedures described in the literature. CF_3COOAg and $AgNO_3$ were purchased from Alfa Ltd. Infrared spectra were recorded on a Digilab FTS-40 spectrophotometer with use of pressed KBr pellets. Electronic spectra were performed on a Hitachi U-3410 spectrophotometer. Microanalytical (C, H, N) data were obtained using a Perkin-Elmer 2400 elemental analyzer.

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Table 1. Crystal data, data collection parameters and details of the structure refinement.

Complex	[**1**][CF_3CO_2]·CH_2Cl_2·H_2O	[**1**][$GaCl_4$]·2THF·MeOH·H_2O	[**2**][$FeCl_4$]
Empirical formula	$C_{75}H_{67}Ag_3Cl_4F_3N_3O_3P_6$	$C_{81}H_{85}Ag_3Cl_6GaN_3O_4P_6$	$C_{72}H_{63}Ag_3Cl_6FeN_3P_6$
Formula weight	1766.55	1956.37	1748.23
Color, habit	colorless, block	colorless, bar	orange, block
Crystal size, mm^3	0.26 × 0.22 × 0.20	0.42 × 0.28 × 0.16	0.25 × 0.21 × 0.07
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	13.8005(1)	12.1698(2)	17.8118(3)
b, Å	14.8396(1)	19.7025(4)	14.8811(3)
c, Å	20.3722(2)	19.8566(4)	28.4645(5)
α, deg	73.949(1)	81.415(1)	90
β, deg	73.175(1)	80.504(1)	96.040(1)
γ, deg	85.099(1)	82.696(1)	90
Volume, Å^3	3837.76(5)	4617.55(15)	7502.9(2)
Z	2	2	4
Density (calcd.), g cm^{-3}	1.53	1.41	1.55
Absorption coefficient, mm^{-1}	1.08	1.24	1.34
Temperature, K	296(2)	296(2)	296(2)
$F(000)$ e	1776	1976	3500
Radiation	Mo$K\alpha$ (λ = 0.71073 Å)	Mo$K\alpha$ (λ = 0.71073 Å)	Mo$K\alpha$ (λ = 0.71073 Å)
Reflections coll./indep.	71853/17545	85842/21110	73888/17081
R_{int}	0.042	0.038	0.056
Reflections with $[I \geq 2\sigma(I)]$	12083	14235	10651
Parameters refined	859	902	820
Final $R1/wR2$ (all data)[a]	0.073/0.122	0.101/0.236	0.083/0.092
Weighting scheme; param. a/b	0.0562/2.1176	0.1420/5.1046	0.0338/0.8581
Goodness of fit (GoF)[b]	1.03	1.05	1.02
$\Delta\rho_{\text{fin}}$ (max/min), e Å^{-3}	+0.79/−1.01	+2.46/−1.67	+0.46/−0.48

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$, where $P = (F_o{}^2 + 2F_c{}^2)/3$; [b] GoF = $[\Sigma w(F_o{}^2 - F_c{}^2)^2/(N_{\text{obs}} - N_{\text{param}})]^{1/2}$.

Syntheses

[$Ag_3(\mu_3$-$Cl)_2(\mu$-dppa$)_3$][CF_3CO_2]·CH_2Cl_2·H_2O ([1][CF_3CO_2]·CH_2Cl_2·H_2O)

A mixture of CF_3COOAg (33 mg, 0.15 mmol) and dppa (578 mg, 0.15 mmol) dissolved in THF/CH_2Cl_2 (40 mL, 1 : 1) was stirred overnight at r. t. The resulting colorless solution was filtered, and the volume of the filtrate was reduced to *ca.* 20 mL. Colorless block-shaped crystals of [$Ag_3(\mu_3$-$Cl)_2$ (μ-dppa$)_3$][CF_3CO_2]· CH_2Cl_2·H_2O, ([**1**][CF_3CO_2]·CH_2Cl_2 ·H_2O), were obtained by layering with hexane at r. t. Yield: 541 mg (89 %). – IR (KBr): $\nu(H_2O)$ = 3541 (br), ν(O–H) = 3342 (br), ν(N–H) = 3335 (br), ν(C–O) = 1474 (vs) and 1439 (vs), ν(P–C) = 521 (s), 513 (s) and 479 (m) cm^{-1}. – UV/Vis (CH_2Cl_2): λ = 365 (s) nm. – Anal. for $C_{74}H_{63}Ag_3Cl_2F_3N_3O_2P_6$·($CH_2Cl_2$)·($H_2O$): calcd. C 51.0, H 3.82, N 2.38; found C 50.4, H 3.75, N 2.35.

[$Ag_3(\mu_3$-$Cl)_2(\mu$-dppa$)_3$] [$GaCl_4$]·2THF·MeOH·H_2O ([1][$GaCl_4$]·2THF·MeOH·H_2O)

A mixture of $AgNO_3$ (26 mg, 0.15 mmol), [NH_4][$GaCl_4$] (35 mg, 0.15 mmol) and dppa (578 mg, 0.15 mmol) dissolved in THF/MeOH (40 mL, 3 : 1) was stirred overnight at r. t. The resulting colorless solution was filtered, and the volume of the filtrate was reduced to *ca.* 20 mL. Colorless bar-shaped crystals of [$Ag_3(\mu_3$-$Cl)_2(\mu$-dppa$)_3$][$GaCl_4$]· 2THF·MeOH, ([**1**][$GaCl_4$]·2THF·MeOH), were obtained by layering with diethyl ether at r. t. Yield: 453 mg (71 %). – IR (KBr): ν(N–H) = 3328 (br), ν(P–C) = 525 (s), 501 (s) and 484 (m) cm^{-1}. – UV/Vis (CH_2Cl_2): λ = 364 (s) nm. – Anal. for $C_{72}H_{73}Ag_3Cl_6Ga\,N_3P_6$·2($C_4H_8O$)·($CH_4O$) ·($H_2O$): calcd. C 49.7, H 4.38, N 2.15; found C 50.0, H 4.27, N 2.15.

[$Ag_3(\mu$-$Cl)(\mu_3$-$Cl)(\mu$-dppa$)_3$][$FeCl_4$] ([2][$FeCl_4$])

Complex [**2**][$FeCl_4$] was prepared similarly as described for [**1**][$GaCl_4$] using [Et_4N][$FeCl_4$] (54 mg, 0.2 mmol) instead of [NH_4][$GaCl_4$]. Orange block-shaped crystals were obtained in a yield of 59.2 % (635 mg). – IR (KBr): ν(N–H) = 3325 (br), ν(P–C) = 526 (s), 504 (s) and 489 (m) cm^{-1}. – UV/Vis (CH_2Cl_2): λ = 364 (s) nm. – Anal. for $C_{72}H_{63}Ag_3Cl_6Fe\,N_3P_6$: calcd. C 49.5, H 3.63, N 2.40; found C 49.2, H, 3.59, N 2.37.

Crystal structure determination

Single crystals of [**1**][CF_3CO_2]·CH_2Cl_2·H_2O (0.26 × 0.22 × 0.20 mm^3), [**1**][$GaCl_4$]·2THF·MeOH (0.42 × 0.28 × 0.16 mm^3) and [**2**][$FeCl_4$] (0.25 × 0.21 × 0.07 mm^3) were

Table 2. Selected bond lengths (Å) and bond angles (deg) for complexes [**1**][CF_3CO_2]·CH_2Cl_2·H_2O, [**1**][$GaCl_4$]·2THF·MeOH·H_2O and [**2**][$FeCl_4$].

Complexes	[**1**][CF_3CO_2]·CH_2Cl_2·H_2O	[**1**][$GaCl_4$]·2THF ·MeOH·H_2O	[**2**][$FeCl_4$]
Ag(1)–P(1)	2.451(1)	2.442(2)	2.442(1)
Ag(2)–P(2)	2.447(1)	2.460(1)	2.431(1)
Ag(2)–P(3)	2.444(1)	2.461(1)	2.445(1)
Ag(3)–P(4)	2.434(1)	2.452(1)	2.431(1)
Ag(3)–P(5)	2.426(1)	2.455(2)	2.426(1)
Ag(1)–P(6)	2.453(1)	2.442(2)	2.439(1)
Ag(1)–Cl(1)	2.703(1)	2.761(1)	2.749(1)
Ag(1)–Cl(2)	2.730(1)	2.708(1)	2.641(1)
Ag(2)–Cl(1)	2.740(1)	2.777(1)	2.620(1)
Ag(2)–Cl(2)	2.654(1)	2.759(1)	
Ag(3)–Cl(1)	2.661(1)	2.738(1)	2.779(1)
Ag(3)–Cl(2)	2.743(1)	2.796(1)	2.644(1)
Ag(1)–Ag(2)	3.188(1)	3.222(1)	3.337(1)
Ag(2)–Ag(3)	3.185(1)	3.200(1)	3.075(1)
Ag(1)–Ag(3)	3.149(1)	3.226(1)	3.196(1)
P(1)–Ag(1)–P(6)	126.32(3)	123.49(5)	128.92(3)
P(3)–Ag(2)–P(2)	124.60(3)	128.16(5)	127.85(3)
P(5)–Ag(3)–P(4)	123.73(3)	125.10(5)	124.32(3)
P(1)–Ag(1)–Cl(1)	112.67(3)	101.89(5)	102.97(3)
P(6)–Ag(1)–Cl(1)	106.48(3)	110.11(5)	102.25(3)
P(1)–Ag(1)–Cl(2)	103.57(3)	114.58(5)	108.23(3)
P(6)–Ag(1)–Cl(2)	108.73(3)	106.84(5)	112.33(3)
P(3)–Ag(2)–Cl(2)	112.48(3)	104.96(4)	
P(2)–Ag(2)–Cl(2)	109.27(3)	110.29(4)	
P(3)–Ag(2)–Cl(1)	104.54(3)	109.71(4)	102.18(3)
P(2)–Ag(2)–Cl(1)	106.31(3)	103.95(4)	115.85(3)
P(5)–Ag(3)–Cl(1)	108.98(3)	116.77(5)	101.03(3)
P(4)–Ag(3)–Cl(1)	112.27(3)	105.63(5)	112.33(3)
P(5)–Ag(3)–Cl(2)	112.21(3)	97.86(5)	112.30(3)
P(4)–Ag(3)–Cl(2)	100.69(3)	112.13(4)	107.63(3)
Cl(1)–Ag(1)–Cl(2)	94.20(3)	96.31(4)	96.08(3)
Cl(2)–Ag(2)–Cl(1)	95.08(3)	94.80(4)	
Cl(1)–Ag(3)–Cl(2)	94.87(3)	94.84(4)	95.27(3)
Ag(3)–Cl(1)–Ag(1)	71.89(2)	71.16(3)	74.41(3)
Ag(3)–Cl(1)–Ag(2)	72.26(3)	71.61(3)	69.36(2)
Ag(1)–Cl(1)–Ag(2)	71.71(2)	71.15(3)	76.82(2)
Ag(2)–Cl(2)–Ag(1)	72.60(3)	72.20(3)	70.64(2)
Ag(2)–Cl(2)–Ag(3)	72.31(2)	71.02(3)	
Ag(1)–Cl(2)–Ag(3)	70.24(3)	71.07(3)	
Ag(1)–Ag(3)–Ag(2)	60.44(1)	60.17(1)	59.63(1)
Ag(3)–Ag(1)–Ag(2)	60.34(1)	60.33(1)	56.11(1)
Ag(3)–Ag(2)–Ag(1)	59.21(1)	59.50(1)	64.27(1)

mounted in random orientation on glass fibers. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with MoK_α radiation (λ = 0.71073 Å) at 296 K using an ω scan mode. The collected frames were processed with the software SAINT [20]. The data were corrected for absorption using the program SADABS [21]. Structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [22]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp^3}–H = 0.96, C_{sp^2}–H = 0.93 and O–H = 0.82 Å) and included in the structure factor calculations with assigned isotropic displacement parameters but were not refined. One of the phenyl rings of [**1**][CF_3CO_2]·CH_2Cl_2·H_2O, was geometrically constrained and refined with isotropic displacement parameters. The CH_2Cl_2 solvent molecule in [**1**][CF_3CO_2]·CH_2Cl_2·H_2O was refined isotropically. The hydrogen atoms of the interstitial water molecules were also excluded in [**1**][CF_3CO_2]·CH_2Cl_2·H_2O and [**1**][$GaCl_4$]·2THF·MeOH·H_2O. The four chlorine atoms in the [$GaCl_4$]$^-$ anion were treated for disorder and refined isotropically. Their site occupancies were each initially set to 0.5, but they were then refined with the restriction that their sum should add up to unity, which resulted in different site occupancy values. The largest peak in the final difference map had a height of 2.46 e Å^{-3} for [**1**][$GaCl_4$]·2THF·MeOH·H_2O and is in the vicinity of the gallium atom. Crystal data, data collection parameters and details of the structure refinement are given in Table 1.

CCDC 703021/703022/703023 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

We previously reported the isolation of a tetranuclear silver(I) complex [$Ag_4(\mu$-dppa$)_2(\mu_4$-$O_2PPh_2)_2$ $(\mu$-$CF_3CO_2)_2$] from the reaction of Ag(CF_3CO_2) with two equivalents of bis(diphenylphosphino) amine (dppa) in THF [23]. The reaction involved P–N bond cleavage of dppa by hydrolysis in the presence of moist air, resulting in oxidation and formation of the [Ph_2PO_2]$^-$ ligand. However, the interaction of Ag(CF_3CO_2) with one equivalent of dppa in a mixed THF/CH_2Cl_2 solvent affords the trinuclear trigonal-bipyramidal complex [$Ag_3(\mu_3$-Cl$)_2$ $(\mu$-dppa$)_3$][CF_3CO_2]· CH_2Cl_2·H_2O, ([**1**][CF_3CO_2]·CH_2Cl_2·H_2O), in a yield of 69 %. Similar trinuclear complexes [$Ag_3(\mu_3$-$X)_2(\mu$-dppm$)_3$]·X (X = Cl, Br, I) were prepared *via* the reactions of $AgNO_3$ and bis (diphenylphosphino)methane (dppm) in the presence of the corresponding halides. Because of the similar character of the bridging ligands dppa and dppm, the formation of analogous complexes like [$Ag_3(\mu_3$-I$)_2(\mu$-dppa$)_3$]·I in the presence of iodine ion is not surprising [11–15]. The chloride ions in complex [**1**][CF_3CO_2]·CH_2Cl_2·H_2O is due to the dechlorination of CH_2Cl_2 as a chloride source. For a better understanding of the underlying processes, the reactions of $AgNO_3$ and dppa were carried out in the presence of [NH_4]

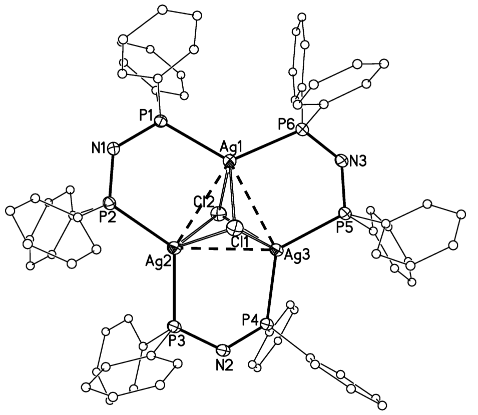

Fig. 1. Molecular structure of the cation $[Ag_3(\mu_3\text{-}Cl)_2(\mu\text{-}dppa)_3]^+$ [**1**] (hydrogen atoms omitted for clarity).

$[GaCl_4]$ and $[Et_4N][FeCl_4]$ in non-halide solvents to give the trinuclear trigonal-bipyramidal silver(I) complexes $[Ag_3(\mu_3\text{-}Cl)_2(\mu\text{-}dppa)_3][GaCl_4]\cdot 2THF\cdot MeOH\cdot H_2O$, ([**1**]$[GaCl_4]\cdot 2THF\cdot MeOH\cdot H_2O$), and $[Ag_3(\mu\text{-}Cl)(\mu_3\text{-}Cl)(\mu\text{-}dppa)_3][FeCl_4]$, ([**2**]$[FeCl_4]$), respectively. The chloride ions in the complexes [**1**]$[GaCl_4]\cdot 2THF\cdot MeOH$ and [**2**]$[FeCl_4]$ obviously came from the species $[GaCl_4]^-$ and $[FeCl_4]^-$ as the chloride sources.

The broad peaks at *ca.* 3330 cm^{-1} for $\nu(N-H)$ and three peaks in the range of 480 – 530 cm^{-1} for $\nu(P-C)$ in the IR spectra indicate the presence of dppa ligands in all three complexes. Two strong peaks at 1474 and 1439 cm^{-1} can be assigned to the $\nu(C\text{–}O)$ vibrations of the free $[CF_3CO_2]^-$ anion in complex [**1**]$[CF_3CO_2]\cdot CH_2Cl_2\cdot H_2O$. Also present are strong broad peaks at 3541 and 3537 cm^{-1} indicative of the water molecules in [**1**]$[CF_3CO_2]\cdot CH_2Cl_2\cdot H_2O$ and [**1**]$[GaCl_4]\cdot 2THF\cdot MeOH\cdot H_2O$. Each of the electronic absorption spectra of the three complexes shows one intense peak at about 365 nm. A comparison with that of the free dppa ligand suggests that the high-energy absorptions for the three complexes are obviously shifted toward higher wavelengths, thereby indicating a strong metal-to-ligand charge transfer (MLCT) interaction between silver atoms and dppa ligands [24].

The structures of three complexes [**1**]$[CF_3CO_2]\cdot CH_2Cl_2\cdot H_2O$, [**1**]$[GaCl_4]\cdot 2THF\cdot MeOH\cdot H_2O$ and [**2**]$[FeCl_4]$ were determined by r. t. single-crystal X-ray diffraction. The structures of the cationic species **1** and **2** are shown in Figs. 1 and 2, respectively. Selected bond lengths and angles of the three complexes are compiled in Table 2 for comparison. Both complexes [**1**]$[CF_3CO_2]\cdot CH_2Cl_2\cdot H_2O$ and [**1**]$[GaCl_4]\cdot 2THF\cdot MeOH\cdot H_2O$ crystallize in the triclinic space group $P\bar{1}$ with well separated cations and anions along with the lattice solvate molecules in the cells, while complex [**2**]$[FeCl_4]$ crystallizes in the monoclinic space group $P2_1/c$ with well separated four $[\mathbf{2}]^+$ cations and four $[FeCl_4]^-$ anions in the cell. Similar to the structures of $[Ag_3(\mu_3\text{-}X)_2(\mu\text{-}dppm)_3]^+$ (X = Cl, Br, I) [11, 13, 14], both chloride atoms in **1** tri-cap the Ag_3 triangle from both sides, forming a $[Ag_3(\mu_3\text{-}Cl)_2]$ trigonal bypyramid; however, one chloride atom tri-caps three silver atoms from one side and the other bridges two silver atoms only from the opposite side in **2**, forming an asymmetric $[Ag_3(\mu\text{-}Cl)(\mu_3\text{-}Cl)]$ unit. The Ag–μ_3-Cl–Ag bridges in **1** have bond lengths of 2.661(1), 2.703(1) and 2.740(1) Å for Ag(3)–Cl(1), Ag(1)–Cl(1) and Ag(2)–Cl(1), respectively, and 2.654(1), 2.730(1) and 2.743(1) Å for Ag(2)–Cl(2), Ag(3)–Cl(1) and Ag(1)–Cl(2), respectively. Essentially the same data are also found in complex [**1**]$[GaCl_4]\cdot 2THF\cdot MeOH\cdot H_2O$ (see Table 2). The tricoordinate chloride atoms are at the apex of a trigonal pyramid with a sum of cone angles of *ca.* 215°. All silver atoms in **1** display a distorted tetrahedral surrounding with the P–Ag–P angles (av. 124.9(1)° for [**1**]$[CF_3CO_2]\cdot CH_2Cl_2\cdot H_2O$ and av. 125.6(1)° for [**1**]$[GaCl_4]\cdot 2THF\cdot MeOH\cdot H_2O$) being *ca.* 30° larger than the Cl–Ag–Cl angles (av. 94.7(1)° for [**1**]$[CF_3CO_2]\cdot CH_2Cl_2\cdot H_2O$ and av. 95.3(1)° for [**1**]$[GaCl_4]\cdot 2THF\cdot MeOH\cdot H_2O$). Similarly, the Ag–$\mu_3$-Cl–Ag bridges in **2** are also different with bond lengths 2.620(1), 2.749(1) and 2.779(1) Å for Ag(2)–Cl(1), Ag(1)–Cl(1) and Ag(3)–Cl(1), re-

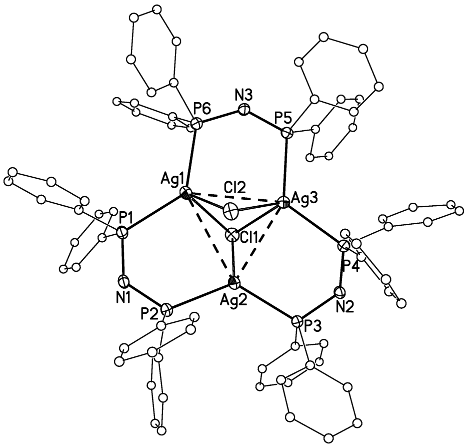

Fig. 2. Molecular structure of the cation $[Ag_3(\mu\text{-}Cl)(\mu_3\text{-}Cl)(\mu\text{-}dppa)_3]^+$ [**2**] (hydrogen atoms omitted for clarity).

spectively; however, the Ag–μ-Cl–Ag bridge in **2** is almost symmetrical with bond lengths of 2.641(1) Å for Ag(1)–Cl(2) and 2.644(1) Å for Ag(3)–Cl(2) along with a Ag(1)–Cl(2)–Ag(2) angle of 70.6(1)°. No reason can be given at this point for the different coordination modes of the two Cl atoms in **2** (μ *vs.* μ_3) which also distinguishes complexes **1** and **2**. Although there are two kinds of silver atoms, tetrahedral geometry for Ag(1) and Ag(3) and trigonal geometry for Ag(2) in **2**, the bond parameters seem to be less influenced by the different silver coordination geometries by comparison with **1** (see Table 2).

Each dppa bidentate ligand bridges one Ag$\cdots$Ag edge, resulting in chair-type six-membered NP_2Ag_2Cl rings for **1** and **2**, respectively, to construct a roughly planar $[Ag_3P_6]$ structure. The average Ag$\cdots$Ag distances are 3.174(1), 3.216(1) and 3.203(1) Å for [**1**]$[CF_3CO_2]\cdot CH_2Cl_2\cdot H_2O$, [**1**]$[GaCl_4]\cdot$2THF$\cdot$MeOH$\cdot H_2O$ and [**2**]$[FeCl_4]$, respectively, which are slightly shorter than those observed in $[Ag_3(\mu_3\text{-}X)_2(\mu\text{-dppm})_3]^+$ cations (X = Cl: 3.372(2) Å [12], Br: 3.303(3) Å [13] and I: 3.236(1) Å [14]) and comparable to that in $[Ag_3(\mu_3\text{-Cl})_2(\mu\text{-dppa})_3][PF_6]$ (3.228(2) Å [15]), possibly due to the relatively stronger phosphorus σ donor capacity of dppa (amine) *versus* dppm (methane). The three Ag$\cdots$Ag$\cdots$Ag angles in **1** are close to the standard 60° of the equilateral triangle, however, the Ag(1)$\cdots$Ag(2)$\cdots$Ag(3) angle of 64.3(1)° at the trigonal silver atom is obviously larger than the Ag(2)$\cdots$Ag(1)$\cdots$Ag(3) and Ag(1)$\cdots$Ag(3)$\cdots$Ag(2) angles of 56.1(1)° and 59.6(1)°, respectively, at the tetrahedral silver atoms. The Ag–P bond lengths in the three complexes are normal, and compare well with those in related silver-dppa complexes. The average Ga–Cl bond length in the $[GaCl_4]^-$ anion is 2.147(1) Å, and the average Fe–Cl bond length in the $[FeCl_4]^-$ anion is 2.189(1) Å. These values are typical for this type of anions.

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