

X-Ray crystal structure of [Ag₄(μ-dppm)₂(μ-C₂F₅COO)₄]. Synthesis and spectroscopy of silver(I) perfluorinated carboxylate complexes with bis(diphenylphosphino)methane

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Complexes of Ag(I) carboxylates with dppm = bis(diphenylphosphino)methane of general formula [Ag₂(RCOO)₂(dppm)], where R = CF₃, C₂F₅, C₃F₇, C₄F₉, C₆F₁₃, C₉F₁₉, were obtained and characterized with ¹H, ¹³C, ¹⁹F, ³¹P NMR and IR. The X-ray crystal structure of [Ag₄(μ-dppm)₂(μ-C₂F₅COO)₄] determined at 100(1) K (*R* = 0.0316) revealed a centrosymmetric tetranuclear aggregate with the silver atoms bridged by two dppm and four pentafluoropropionates forming two monoatomic μ₂-(η¹-O) and two triple μ₃-(η²-O, η¹-O') bridges. Of the two crystallographically independent Ag(I) atoms one has distorted tetrahedral geometry with one Ag–P bond and three Ag–O bonds, while the second has trigonal planar geometry with an Ag–P and two Ag–O bonds. The ³¹P CP MAS NMR spectra demonstrate splitting due to ¹*J*(^{107,109}Ag–³¹P) and ²*J*(P–P) coupling between crystallographically inequivalent phosphorus atoms. Variable-temperature ³¹P NMR spectra were recorded between 323 and 223 K and ¹*J*(¹⁰⁷Ag–³¹P), ³*J*(¹⁰⁷Ag–³¹P), ¹*J*(¹⁰⁹Ag–³¹P), ³*J*(¹⁰⁹Ag–³¹P) spin–spin coupling constants calculated. Analysis of coordination shifts and coupling constants is in favor, in solution, of binuclear trigonal Ag(I) complexes with bridging carboxylates and dppm.

Introduction

Coordination compounds of silver(I) have been studied, among others, due to their possible applications as precursors in chemical vapor deposition (CVD) of metallic layers. The volatility of Ag(I) complexes with oxygen bonded ligands (β-diketonates and carboxylates)^{1–5} prompted us to study analogous silver(I) complexes with perfluorinated carboxylates and bis(diphenylphosphino)methane (dppm). Moreover, Ag(I) ions demonstrate a variable nuclearity in their phosphine complexes which makes them an attractive model for structural studies. Diphosphines have been widely used as ligands because they reveal versatile coordination behavior. They can act as bridging or chelating ligands, which stabilize unfavorable coordination bonds between silver and the secondary ligand. In the present paper bis(diphenylphosphino)methane has been chosen to enhance the stability of the Ag–O bond and the complex. Perfluorinated aliphatic carboxylates were chosen as O-donor ligands because fluorine improves the volatility of complexes, which is important for CVD experiments. Moreover, carboxylates are able to bind in mono- or polydentate (chelating or bridging) mode; hence one may expect multinuclear complexes.⁶ The crystal structures of Ag(I) complexes have confirmed the presence of the bridging carboxylates,^{7–10} but in [Ag(HCOO)(PPh₃)₂] the formate appeared to be monodentately bonded,¹¹ while rare chelating carboxylate was found in [Ag(C₁₇H₃₅COO)(PPh₃)₂]¹² and [Ag(C₃H₇COO)(PPh₃)₂].¹³ Some silver complexes with non-fluorinated carboxylates and dppm have also been reported.^{10,14} In these compounds dppm formed bridges but different carboxylate coordination modes and nuclearities were observed. In the case of tetranuclear [Ag₄(CH₃COO)₄(dppm)₂], the acetates formed monoatomic and *syn-anti* bridges, while chelating carboxylates were noted in the binuclear compound [Ag₂(CH₃COO)₂(dppm)₂].^{10,14} However for the similar complexes [Ag₂(RCOO)₂(dppm)], where R = C₂H₅, *i*-C₃H₇, C₆H₅, the carboxylate coordination mode was not determined.¹⁴ In the case of perfluorinated carboxylates, due to the lower basicity of the COO group than for the non-fluorinated analogs, a different coordination mode can be expected. In the present paper we report the synthesis, X-ray diffraction analysis and ¹H, ¹³C, ¹⁹F,

³¹P NMR characterization of new silver(I) complexes of general formula [Ag₂(RCOO)₂(dppm)] where R = CF₃, C₂F₅, C₃F₇, C₄F₉, C₆F₁₃, C₉F₁₉. Detailed analysis of the ¹H, ¹³C, ¹⁹F, ³¹P NMR resonances and the spin–spin coupling patterns will be focused on to elucidate the geometry of the complexes and ligand coordination modes in solution, whereas IR and ³¹P CP MAS NMR spectroscopy will be used for the same purpose in the solid state.

Experimental

¹H, ¹³C, ¹⁹F and ³¹P NMR spectra in CDCl₃ were registered with a Varian Gem. 200 MHz spectrometer, using TMS, CF₃COOH and 85% H₃PO₄ as the standards. Variable-temperature ³¹P NMR spectra (323–223 K) were measured using a Bruker MSL 300 MHz spectrometer with the same standard and solvent. CP-MAS ³¹P-{¹H} NMR spectra were recorded at ambient temperature with an AMX 300 Bruker spectrometer at 121.49 MHz. The samples were spun at 4500 Hz in 5 mm Dual 13 rotors. The chemical shifts were referenced to 85% H₃PO₄. NMR spectra simulations were calculated using the program gNMR 3.6 for Windows. IR spectra were measured with a Perkin–Elmer 2000 FT IR spectrophotometer in the range 4000–400 cm^{–1} in KBr discs, whereas 400–100 cm^{–1} spectra were run in polyethylene discs. Silver was determined argentometrically, after complex mineralization; C, H and P were determined by elemental semi-microanalysis.

Preparation of the complexes

Bis(diphenylphosphino)methane (Aldrich), perfluorinated carboxylic acids (97–99%) (Aldrich) and AgNO₃ (POCh Gliwice) were used without further purification. Perfluorinated carboxylates of silver(I) were obtained as reported.¹⁵ Solvents of analytical grade were purified and dried by standard methods. Sodium carboxylates for IR experiments were obtained as described.¹⁶ The reactions were performed in argon atmosphere using Schlenk techniques. Complexes were prepared in a general procedure in which [RCOOAg] (4 mmol), where R = CF₃, C₂F₅, C₃F₇, C₄F₉, C₆F₁₃, C₉F₁₉, was added to a

Table 1 Crystallographic data for complex **2**

Empirical formula	C ₃₁ H ₂₂ Ag ₂ F ₁₀ O ₄ P ₂
<i>M</i>	926.17
Crystal system	Monoclinic
<i>T</i> / <i>K</i>	100(1)
Space group	<i>C2/c</i>
<i>a</i> /Å	25.079(5)
<i>b</i> /Å	13.725(3)
<i>c</i> /Å	20.382(4)
β /°	108.56(3)
<i>V</i> /Å ³	6651(2)
<i>Z</i>	8
<i>D_c</i> /Mg m ⁻³	1.850
μ /mm ⁻¹	1.366
<i>F</i> (000)	3632
Crystal size/mm	0.15 × 0.20 × 0.20
θ range for data collection/°	3.35–27.0
Index ranges, <i>hkl</i>	–31 to 32, –17 to 17, –26 to 17
Reflections collected	21280
Reflections unique (<i>R</i> _{int})	7170 (0.033)
Goodness-of-fit on <i>F</i> ²	1.152
Data/parameters	7170/548
Final <i>R</i> ₁ , <i>wR</i> ₂ indices [<i>I</i> > 2σ(<i>I</i>)]	0.0316, 0.0729
Final <i>R</i> ₁ , <i>wR</i> ₂ indices (all data)	0.0388, 0.0763
Largest difference peak, hole/e Å ⁻³	0.850, –0.824

solution of dppm (2 mmol) in CH₂Cl₂ (20 cm³) and the resulting suspension was stirred for 4 h (for R = C₆F₁₃, C₉F₁₉, 24 h) at room temperature in the dark, filtered and evaporated to dryness on a vacuum line depositing a microcrystalline material. Recrystallization from CH₂Cl₂ produced white crystals of [Ag₂(RCOO)₂(dppm)]. The results of elemental analyses were as follows (%): C₂₉H₂₂Ag₂F₆O₄P₂ **1**: Calc. C 42.1, H 2.7, P 7.5, Ag 26.2. Found: C 41.1, H 2.9, P 7.2, Ag 25.9. C₃₁H₂₂Ag₂F₁₀O₄P₂ **2**: Calc. C 41.1, H 2.4, P 6.7, Ag 23.3. Found: C 40.0, H 2.3, P 6.2, Ag 23.1. C₃₃H₂₂Ag₂F₁₄O₄P₂ **3**: Calc. C 38.6, H 2.1, P 6.0, Ag 21.1. Found: C 38.3, H 1.9, P 5.9, Ag 20.9. C₃₅H₂₂Ag₂F₁₈O₄P₂ **4**: Calc. C 37.3, H 2.0, P 5.5, Ag 19.2. Found: C 37.8, H 1.8, P 6.0, Ag 18.9. C₃₉H₂₂Ag₂F₂₆O₄P₂ **5**: Calc. C 35.3, H 1.7, P 4.7, Ag 16.3. Found: C 36.0, H 1.6, P 3.9, Ag 16.2. C₄₅H₂₂Ag₂F₃₈O₄P₂ **6**: Calc. C 33.2, H 1.4, P 3.8, Ag 13.3. Found: C 35.4, H 1.7, P 3.4, Ag 13.3.

X-Ray crystallography

X-Ray data for complex **2** were collected with a KUMA KM4CCD κ -axis diffractometer with graphite-monochromated Mo-*K* α radiation, by the ω -2 θ method. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using the SHELXS97 program.¹⁷ SHELXL97¹⁸ was applied for data refinement by full-matrix least-squares methods. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included from the $\Delta\rho$ maps and refined with isotropic thermal parameters. One of the pentafluoropropionates reveals a disorder of the terminal CF₃ group. Final refinement resulted in *R*₁ = 0.0316, *wR*₂ = 0.0729. Other refinement details and crystal data are summarized in Table 1. Bond lengths and angles are given in Table 2. The atomic scattering factors were taken from International Tables for Crystallography.¹⁹ The geometry of the reported complex was compared to other complexes by reference to the Cambridge Structural Database.²⁰

CCDC reference number 208152.

See <http://www.rsc.org/suppdata/dt/b3/b304004f/> for crystallographic data in CIF or other electronic format.

Results and discussion

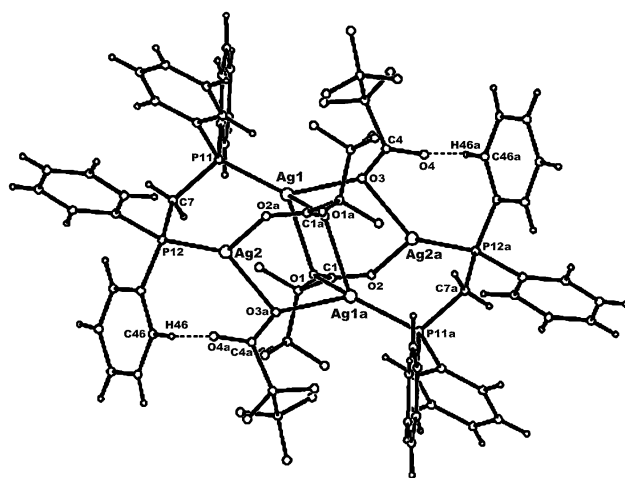
Crystal structure

Single crystal diffraction study of the [Ag₂(μ -dppm)(μ -C₂F₅-COO)₂] **2** reveals a centrosymmetric tetranuclear complex. The molecular structure is shown in Fig. 1 and selected bond

Table 2 Selected interatomic distances and bond angles for complex **2**

Ag(1) ⋯ Ag(1a)	3.8021(6)	Ag(2)–O(3a)	2.336(2)
Ag(1) ⋯ Ag(2)	3.0415(7)	Ag(2)–O(4a)	2.840(2)
Ag(1) ⋯ Ag(2a)	3.9412(7)	Ag(2)–P(12)	2.3498(8)
Ag(2) ⋯ Ag(2a)	5.9251(7)	C(1)–O(1)	1.261(4)
Ag(1)–O(3)	2.356(2)	C(1)–O(2)	1.234(4)
Ag(1)–O(1a)	2.356(2)	C(4)–O(3)	1.267(4)
Ag(1)–O(1)	2.485(2)	C(4)–O(4)	1.228(4)
Ag(1)–P(11)	2.3612(8)	P(11)–C(7)	1.838(3)
Ag(2)–O(2a)	2.308(6)	P(12)–C(7)	1.844(3)
O(3)–Ag(1)–O(1a)	80.92(7)	O(2a)–Ag(2)–P(12)	140.53(6)
O(3)–Ag(1)–P(11)	130.88(5)	O(1)–C(1)–O(2)	129.7(3)
O(1a)–Ag(1)–P(11)	138.16(5)	O(3)–C(4)–O(4)	127.3(3)
O(3)–Ag(1)–O(1)	80.73(8)	Ag(1)–P(11)–C(7)	114.8(1)
O(1a)–Ag(1)–O(1)	76.52(7)	Ag(2)–P(12)–C(7)	113.3(1)
P(11)–Ag(1)–O(1)	127.94(5)	P(11)–C(7)–P(12)	111.7(2)
O(2a)–Ag(2)–O(3a)	83.14(8)		

Symmetry transformation used to generate equivalent atoms: $-x + 1/2, -y + 1/2, -z$.

**Fig. 1** Structure of [Ag₂(μ -dppm)(μ -C₂F₅COO)₂] **2**.

distances and angles are listed in Table 1. Two crystallographically independent Ag(I) atoms are bridged by dppm and pentafluoropropionate ligands. On the other hand these disilver fragments are linked by carboxylate ligands in monoatomic and tridentate bridging modes.

The distances between adjacent Ag(I) ions in the tetranuclear aggregate are: 3.0415(7) [Ag(1)–Ag(2)], 3.8021(6) [Ag(1)–Ag(1a)] and 3.9412(7) Å [Ag(1)–Ag(2a)]. The shortest of these might indicate a weak interaction between metal centers. The independent Ag(I) atoms revealed different environments. The Ag(1) ion is surrounded by P(11), O(1), O(1a) and O(3) in a non-regular tetrahedral arrangement, the corresponding bond distances being 2.3612(8), 2.485(2), 2.356(2) and 2.356(2) Å, respectively. The bond angles on the distorted tetrahedral structure ranged between 76.52(7) [O(1a)–Ag(1)–O(1)] and 138.16(5)° [O(1a)–Ag(1)–P(11)]. The geometry of the Ag(2) ion environment can be considered to be more trigonal planar than tetrahedral. The O(4a) atom position indicates some form of weak interaction between two ions making the assignment of the coordination number and the geometry of the metal center somewhat ambiguous. A distance of 2.840(2) Å (longer than sum of the ionic radii of Ag and O) indicates that this interaction appears to be essentially electrostatic implying a three-coordinated silver atom. In addition the sum of the angles around Ag(2) atom is 359.9° what indicates the planar geometry of silver atom. Ag(2) forms coordination bonds to P(12), O(2a) and O(3a) atoms, the corresponding distances being 2.3498(8), 2.308(2) and 2.336(2) Å, respectively. The “trigonal” angles: P(11)–Ag(1)–O(2a), P(11)–Ag(1)–O(3a) and O(2a)–Ag(1)–O(3a) are 140.53(6) 136.22(6) and 83.14(8)°, respectively. The

Table 3 Structural differences between tetranuclear Ag(I) complexes with phosphines and carboxylates

Ligand	Shortest Ag ··· Ag distance/Å	Ag(I) environment	Modes of RCOO ⁻ coordination	Ref.
PPh ₃ CH ₃ COO ⁻	3.122	Trigonal planar Tetrahedral	μ ₂ -O,O' μ ₃ -O,O,O'	21
dppm CH ₃ COO ⁻	3.077	Trigonal planar	μ ₂ -O μ ₂ -O,O'	10
dppm C ₂ F ₅ COO ⁻	3.041	Trigonal planar Tetrahedral	μ ₂ -O μ ₃ -O,O,O'	This work
dppf ^a CH ₃ COO ⁻	3.104	Tetrahedral	μ ₂ -O,O,O' μ ₃ -O,O,O'	22

^a dppf = 1,1'-bis(diphenylphosphino)ferrocene.

Table 4 ¹³C NMR spectral data (ppm)

Compound	δ _C (COO ⁻)	Δ ₁ ^a	² J(C-F)/Hz	δ(CH ₂)	Δ ₂ ^a	¹ J(C-P)/Hz
[Ag ₂ (CF ₃ COO) ₂ (dppm)] 1	163.1	-0.2	33.9	28.7	3.2	14.7
[Ag ₂ (C ₂ F ₅ COO) ₂ (dppm)] 2	163.1	-0.3	25.4	28.7	3.2	14.9
[Ag ₂ (C ₃ F ₇ COO) ₂ (dppm)] 3	162.9	-0.4	24.8	29.0	3.5	14.0
[Ag ₂ (C ₄ F ₉ COO) ₂ (dppm)] 4	162.8	-0.5	25.2	28.7	3.2	^b
[Ag ₂ (C ₆ F ₁₃ COO) ₂ (dppm)] 5	162.8	-0.4	25.2	28.8	3.3	14.5
[Ag ₂ (C ₉ F ₁₉ COO) ₂ (dppm)] 6	162.8	-0.6	25.6	29.0	3.5	^b

^a Δ₁ = δ_C(COO⁻) - δ_A(COO⁻); C = complex, A = carboxylic acid; Δ₂ = δ_C(CH₂) - δ(CH₂ dppm), δ(CH₂ dppm) = 25.5 ppm. ^b Splitting was not observed.

Ag-P and Ag-O bond lengths are comparable with those found in other tetranuclear silver complexes.^{10,21-23} The pentafluoropropionate ions play two structural roles. Two of the ions formed unsymmetrical bridges *via* a single oxygen atom. The other pentafluoropropionate ions had one of its oxygen atoms bound to one silver atom, while the other is linked to two silver ions. Such a mode has been reported so far for two Ag(I) complexes with phosphine and carboxylates ligands (Table 3).^{14,21}

Table 3 presents the main structural differences between known tetranuclear Ag(I) complexes with phosphines and carboxylate ligands. Careful inspection of Table 3 shows some key features of these structures: a relatively small range of the shortest Ag ··· Ag distance, a variable coordination number (and symmetry) of silver atoms and different ligating forms of carboxylates. Summarizing, it is difficult to predict correctly symmetry for the Ag(I) atom and coordination mode of carboxylate ligands in a given compound: *e.g.* one could expect a similar structure in [Ag₂(CH₃COO)₂(dppm)] and **2**, with the same diphosphine ligand. However, the lower basicity of the oxygen atoms, the hydrogen bond C-H ··· O (2.602 Å, 172.1°) and the perfluorocarbon chain, influence the molecular structure of **2** such that the modes of carboxylate coordination and Ag(I) environments are different.

NMR studies in solution

¹H NMR spectra reveal the dppm methylene group resonances as triplets, due to ³¹P-¹H spin-spin coupling, in the range 3.23–3.27 ppm. The signal was shifted towards higher frequency in relation to free dppm (2.83 ppm), as the result of Ag-P coordination bond formation. Moreover, the coupling constant ²J(¹H-³¹P) increased from 1.6 Hz in free dppm to 9.2–10.8 Hz in the complexes. Similar effects were found in the complexes [Ag₂(RCOO)₂(dppm)] (R = CH₃, C₂H₅, *i*-C₃H₇, C₆H₅) with bridging dppm.¹⁴ The chemical shift of the methylene protons can be used for the evaluation of the charge changes on the coordinating phosphorus atom. The appropriate values were calculated according to Grim and Walton,²⁴ using the empirical equation:

$$\delta_{\text{CH}_2} (\text{ppm}) = 1.57\Sigma q_i + 2.65,$$

where q_i is the charge on the i th phosphorus nucleus). The obtained changes of charge were from +0.18 to +0.20 and well correlate with the observed upper frequency coordination shift of phosphorus nuclei in ³¹P NMR spectra (*vide infra*).

In ¹³C NMR spectra signals of the CH₂ group were detected as a triplet (for **4** and **6** only broad singlets) in the range 28.7–29.0 ppm (25.5 ppm for free dppm), Table 4. Calculated coupling constants ¹J(¹³C-³¹P) = 14.0–14.9 Hz were much lower than for dppm (21.1 Hz), which can be related to the change of the s character of the P-C bond²⁵ and the charge on the phosphorus atom. This effect can be explained by the chain (P-C-P) geometry in the complexes in comparison to free dppm that implicates a decrease of electron density on the carbon. One set of phenyl carbons signals is observed for coordinated dppm, which suggests that the metal atoms possess a symmetrical arrangement with the respect to dppm ligand on the NMR time scale; otherwise the phenyl groups would become diastereotopic. The ¹³C resonances of COO carbon were observed as weak signals shifted towards lower frequency in comparison to the free acids. The magnitude of the COO coordination shift is similar to those observed for Ag(I) complexes with tertiary phosphines and bidentately bonded carboxylates.²⁶ The bands are split due to the heterogeneous C-F spin-spin coupling for **2–6** into triplets, ²J(¹³C-¹⁹F) = 24.8–25.6 Hz, and for **1** into a quartet (33.9 Hz). This shape of COO signal reveals that the carboxylates do not participate in chemical exchange reactions, forming two symmetrical bridges between the silver ions.

Although fluorine atoms are not involved in direct interactions with the central ion, their resonances can be affected by carboxylate coordination to the silver ion. The largest influence should be observed on the signal of C_αF₂ fluorine (C_αF₃ in the case of **1**). Recorded ¹⁹F NMR spectra of **1–6** (Table 5) revealed C_αF₂ signals shifted towards higher frequency upon coordination (Δδ_{F_α} being 3.4–4.9 ppm and 2.2 ppm for C_αF₃ in **1**). The coordination shift of C_αF₂ signals can be taken as an evidence of the carboxylate linkage with the central ion in solution. Analogous effects were observed in ¹⁹F NMR spectra of Cu(I), Ag(I) and Au(I) complexes with perfluorinated carboxylates and tertiary phosphines.^{16,26-28}

Table 5 ^{19}F and ^{31}P NMR spectral data (ppm)

Compound	^{19}F			^{31}P		
	$\delta_{\text{C}}(\text{C}_a\text{F}_2)$	Δ_1^a	$^4J(\text{F}-\text{F})/\text{Hz}$	$\delta(\text{P}_{\text{C}})$	Δ_2^a	$^1J(\text{Ag}-\text{P})/\text{Hz}$
$[\text{Ag}_2(\text{CF}_3\text{COO})_2(\text{dppm})]$ 1	2.2 ^b	2.2 ^b	^c	10.2	32.3	643
$[\text{Ag}_2(\text{C}_2\text{F}_5\text{COO})_2(\text{dppm})]$ 2	-41.5	3.4	^c	9.8	31.9	696
$[\text{Ag}_2(\text{C}_3\text{F}_7\text{COO})_2(\text{dppm})]$ 3	-40.8	3.5	8.8	9.8	31.9	681
$[\text{Ag}_2(\text{C}_4\text{F}_9\text{COO})_2(\text{dppm})]$ 4	-38.5	4.9	11.7	9.8	31.9	692
$[\text{Ag}_2(\text{C}_6\text{F}_{13}\text{COO})_2(\text{dppm})]$ 5	-38.4	4.9	12.2	10.0	32.1	656
$[\text{Ag}_2(\text{C}_9\text{F}_{19}\text{COO})_2(\text{dppm})]$ 6	-38.3	4.7	12.0	10.0	32.0	689

^a $\Delta_1 = \delta_{\text{C}}(\text{C}_a\text{F}_2) - \delta_{\text{A}}(\text{C}_a\text{F}_2)$, C = complex, A = carboxylic acid; $\Delta_2 = \delta(\text{P}_{\text{C}}) - \delta(\text{P}_{\text{dppm}})$. ^b Data for C_aF_3 group. ^c Splitting was not observed; $\delta(^{31}\text{P}_{\text{dppm}}) = -22.1$ ppm.

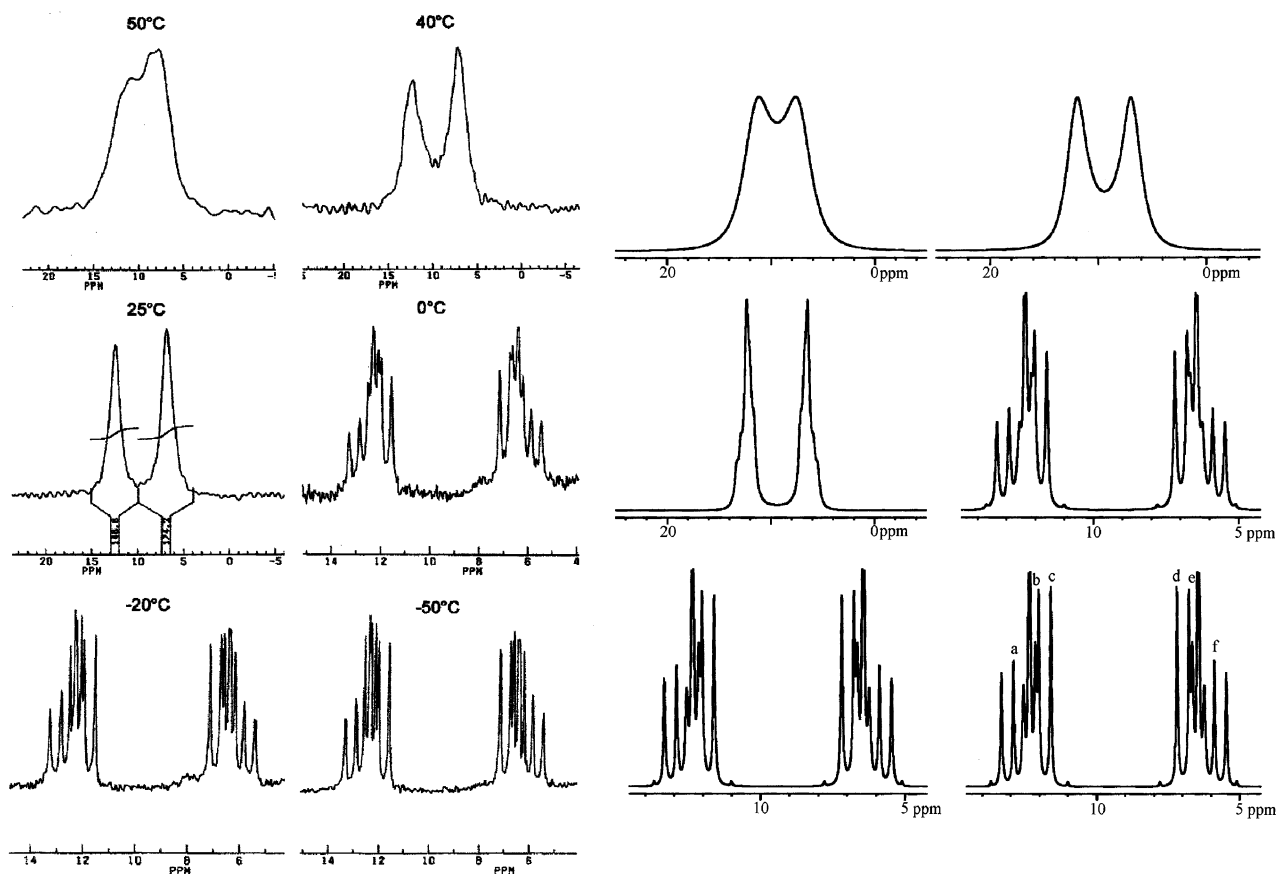


Fig. 2 Variable-temperature ^{31}P NMR spectra of $[\text{Ag}_2(\mu\text{-dppm})(\mu\text{-C}_2\text{F}_5\text{COO})_2]$ (left) **2** and computer simulations using calculated parameters (right).

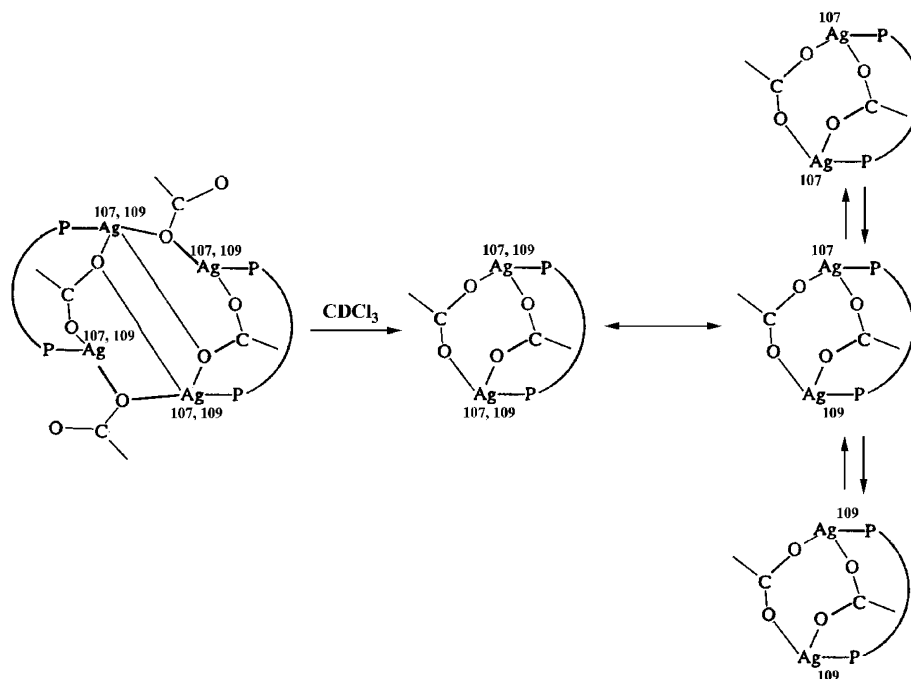
The interpretation of ^{31}P chemical shifts is complicated due to such effects as: the variability of σ - and π -contributions to the metal–phosphorus bond, the influence of other ligands coordinated to the metal, and the geometry of the complex. ^{31}P NMR spectra of the complexes recorded at ambient temperature revealed well-resolved doublets in the range 9.8–10.2 ppm in spite of the fact that the components of the signal had large linewidths. This feature is typical for all studied complexes (**1–6**) and is determined by the value of the coupling constant $^1J(^{107,109}\text{Ag}-\text{P})$ and the fast (in NMR scale) ligand exchange reaction. The ^{31}P signal was significantly shifted towards higher frequency in relation to free dppm (-22.1 ppm) that confirmed diphosphine coordination and the calculated coupling constants $^1J(^{107,109}\text{Ag}-\text{P})$ in the range 643–696 Hz indicated the bridging coordination mode of the ligand.¹⁴ We have noticed some discrepancy between the mean value of the coupling constant $^1J(^{107,109}\text{Ag}-\text{P})$ in solution and the analogous parameter for the planar trigonal Ag environment in the solid state (*vide infra*). Most probably the trigonal structure of Ag in the solid state is different from that in the solution because in the latter

the carboxylate ligands can form two symmetrical bridges. Moreover even in the case of $[\text{Ag}_2(\text{CH}_3\text{COO})_2(\text{dppm})_2]$, where in the solid state all Ag ions exist in tetrahedral form, in solution tribridged binuclear species were suggested with trigonal Ag ions.¹⁰

Variable-temperature ^{31}P NMR spectra (Table 5) were registered for **2** (Fig. 2) and **3** in the range 323–223 K. When the temperature was raised from 298 to 313 K the rate of the ligand chemical exchange reactions increased, the components of doublet began to overlap and at 323 K only one broad band, centred at 9.6 ppm was observed. When the sample was cooled, the exchange processes proceeded slowly, and the components of the multiplets were detectable. Already at 273 K two groups of multiplets centred at 9.4 ppm were observed, and finally at 223 K each multiplet had eight components with different intensities. The observed peak pattern corresponds to the registered sum of the A part of the different AA'XX' patterns resulting from each combination of the silver isotopes ^{107}Ag (51.8%) and ^{109}Ag (48.2%); which implicate bidentate dppm in the complex.^{10,14,23} From the experimental data at 223 K, values

Table 6 Chemical shifts (ppm) and coupling constants (Hz) calculated from variable-temperature ^{31}P NMR spectra

Compound [$\text{Ag}_2(\text{RCOO})_2(\text{dppm})$]	$\delta(\text{P}_i)$	$^1J(^{107}\text{Ag}-\text{P})$	$^3J(^{107}\text{Ag}-\text{P})$	$^1J(^{109}\text{Ag}-\text{P})$	$^3J(^{109}\text{Ag}-\text{P})$	$^2J(\text{P}-\text{P})$
R = C_2F_5 2	9.40	671	-4.5	775	-6.3	159
R = C_3F_7 3	9.28	669	-4.3	773	-6.1	157

**Fig. 3** Proposed exchange reaction equilibria in solution for the studied complexes [$\text{Ag}_2(\mu\text{-dppm})(\mu\text{-RCOO})_2$].

of the coupling constants $^1J(^{107}\text{Ag}-\text{P})$, $^1J(^{109}\text{Ag}-\text{P})$, $^3J(^{107}\text{Ag}-\text{P})$, $^3J(^{109}\text{Ag}-\text{P})$ and $^2J(\text{P}-\text{P})$ were calculated (Table 6) using the following equations (the symbols are indicated on Fig. 2):¹⁴

$$\begin{aligned} \sqrt{(a-f)(c-d)} &= |^1J(^{107}\text{Ag}-\text{P}) - ^3J(^{107}\text{Ag}-\text{P})| \\ |b-e| &= |^1J(^{107}\text{Ag}-\text{P}) + ^3J(^{107}\text{Ag}-\text{P})| \\ |a-c| &= |d-f| = |^2J(\text{P}-\text{P})| \end{aligned}$$

For compound **2** we were able to simulate the ^{31}P NMR variable-temperature spectra using the A part of the sum of AA'XX' spin systems and taking the exchange reactions in solution into account (Fig. 2). Moreover the values of the chemical shifts, the shapes of ^{31}P VT NMR and ^{13}C NMR $\delta_{\text{C}}(\text{COO}^-)$ signals suggested the existence of binuclear species bonded by two carboxylate bridges with participation of $^{107}\text{Ag}^{107}\text{Ag}$ (26.9%), $^{107}\text{Ag}^{109}\text{Ag}$ (49.9%) and $^{109}\text{Ag}^{109}\text{Ag}$ (23.2%). Therefore the intermolecular diphosphine exchange process between these molecules can be proposed (Fig. 3).

Solid-state ^{31}P CP MAS NMR spectroscopy

The ^{31}P CP MAS NMR spectra of studied complexes demonstrate splitting due to $^1J(\text{Ag}-\text{P})$ coupling, although the separate splitting for ^{107}Ag and ^{109}Ag nuclei are not resolved because greater line widths are observed in the solid-state spectra²⁹⁻³² (Fig. 4). The presence of two doublets of doublets in the spectrum of **2** implies two types of magnetically inequivalent phosphorus nuclei (signals at 19.8 and 9.7 ppm, respectively) and two different silver environments in this complex (Table 7).

The calculated $^1J(\text{Ag}-\text{P})$ coupling constants were 751 and 720 Hz. The larger value can be associated with silver in trigonal geometry (Ag-P distance of 2.3498(8) Å) and the smaller one with tetrahedral silver ion (2.3612(8) Å). Bowmaker *et al.*³³ observed decreasing $^1J(\text{Ag}-\text{P})$ value in CP MAS NMR with

increasing of the Ag-P bond length ($J \propto 1/r^3$), which was confirmed by others.³⁴ A computer simulation demonstrates that the 19.8 ppm signal can be attributed to trigonal silver whereas that at 7.8 ppm is attributed to tetrahedral Ag(I). Moreover, smaller splitting is assigned to $^2J(\text{P}-\text{P})$ coupling (185 Hz) between the two inequivalent P atoms. The spectra of **3** and **5** presented a similar pattern of ^{31}P signals and analogous structures are proposed for them. The spectrum of **6** demonstrated an irregular quartet which may be caused by superposition of two doublets (at 11.2 and 20.2 ppm) but the values of $^1J(\text{Ag}-\text{P})$ were difficult to estimate and the separate splitting due to $^2J(\text{P}-\text{P})$ coupling was not registered. The spectrum of **4** is different from the remainder of the studied compounds. It shows only a quasi-triplet centred at 8.0 ppm ($^1J(\text{Ag}-\text{P}) = 705$ Hz). This can be rationalized as the result of magnetically and more probably crystallographic equivalence of the phosphorus atoms after coordination. Moreover, the magnitudes of the chemical shift and the coupling constant were close to that observed for phosphorus in a tetrahedral silver ion environment (Table 7), but presently we do not have more spectral data to propose a detailed structure.

Vibrational spectroscopy

Carboxylates coordinate to metal ions in many ways, such as uni- or polydentate (bridging or chelating). As a criterion of carboxylate binding in the solid state we have applied the parameter $\Delta\nu = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$. The estimation of the carboxylate linkage with a metal ion is based on the relation between $\Delta\nu$ calculated for the considered complex and found in the appropriate sodium carboxylate.

In the spectra of the studied complexes absorption bands of COO vibrations were detected in the ranges $\nu_{\text{as}}(\text{COO}) = 1670\text{--}1673\text{ cm}^{-1}$ and $\nu_{\text{s}}(\text{COO}) = 1396\text{--}1407\text{ cm}^{-1}$ (Table 8). In the case of **2** two different types of pentafluoropropionates were observed (monoatomic bridging and triple bridging). We

Table 7 ^{31}P CP MAS NMR spectral data

Compound	$\delta(\text{P}_1)/\text{ppm}$	$^1J(\text{Ag-P})/\text{Hz}$	$\delta(\text{P}_2)/\text{ppm}$	$^1J(\text{Ag-P})/\text{Hz}$	$^2J(\text{P-P})/\text{Hz}$
$[\text{Ag}_2(\text{C}_2\text{F}_5\text{COO})_2(\text{dppm})]$ 2	9.6	720	19.9	751	186
$[\text{Ag}_2(\text{C}_3\text{F}_7\text{COO})_2(\text{dppm})]$ 3	9.5	739	20.2	766	190
$[\text{Ag}_2(\text{C}_6\text{F}_{13}\text{COO})_2(\text{dppm})]$ 5	9.7	733	19.9	765	196
$[\text{Ag}_2(\text{C}_9\text{F}_{19}\text{COO})_2(\text{dppm})]$ 6	11.2	^a	20.2	^a	^b

$\delta(\text{P dppm}) = -25.1$ ppm. ^a The values of $^1J(\text{Ag-P})$ were difficult to estimate. ^b Splitting was not observed.

Table 8 Characteristic IR spectral frequencies (cm^{-1})

Compound	$\nu_{\text{as}}(\text{COO})$	$\nu_{\text{s}}(\text{COO})$	$\Delta\nu^a$	$\Delta\nu_1^b$	$\nu(\text{Ag-P})$	$\nu(\text{Ag-P})$	$\nu(\text{Ag-O})$	$\nu(\text{Ag-O})$
$[\text{Ag}_2(\text{CF}_3\text{COO})_2(\text{dppm})]$ 1	1670	1407	263	223	247	226	302	279
$[\text{Ag}_2(\text{C}_2\text{F}_5\text{COO})_2(\text{dppm})]$ 2	1672	1406	266	268	249	226	296	279
$[\text{Ag}_2(\text{C}_3\text{F}_7\text{COO})_2(\text{dppm})]$ 3	1670	1396	274	272	244	227	297	264
$[\text{Ag}_2(\text{C}_4\text{F}_9\text{COO})_2(\text{dppm})]$ 4	1672	1398	274	272	252	224	302	264
$[\text{Ag}_2(\text{C}_6\text{F}_{13}\text{COO})_2(\text{dppm})]$ 5	1672	1398	274	272	247	226	303	279
$[\text{Ag}_2(\text{C}_9\text{F}_{19}\text{COO})_2(\text{dppm})]$ 6	1673	1397	276	276	250	226	301	281

^a $\Delta\nu = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$ for the complex. ^b $\Delta\nu_1 = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$ for RCOONa .

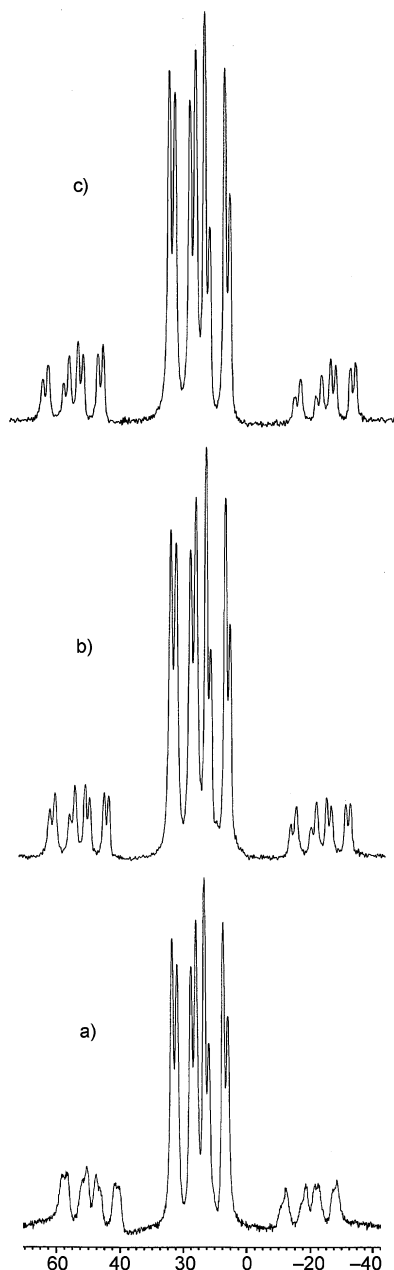


Fig. 4 ^{31}P CP MAS NMR spectra of (a) $[\text{Ag}_2(\text{C}_2\text{F}_5\text{COO})_2(\text{dppm})]$ **2**, (b) $[\text{Ag}_2(\text{C}_3\text{F}_7\text{COO})_2(\text{dppm})]$ **3** and (c) $[\text{Ag}_2(\text{C}_6\text{F}_{13}\text{COO})_2(\text{dppm})]$ **5**.

could expect for **2** that for the monoatomic bridging carboxylate the parameter $\Delta\nu = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$ would approach the value typical for monodentate bonding.^{35,36} However, in the registered spectrum only one set of bands ($\nu_{\text{as}}(\text{COO})$ (1672 cm^{-1}), $\nu_{\text{s}}(\text{COO})$ (1406 cm^{-1})) was observed. The calculated $\Delta\nu$ value (266 cm^{-1}) is close to $\Delta\nu_1$ (268 cm^{-1}) for the sodium pentafluoropropionate and is in favor of a bridging linkage.⁶ The significant deviation from the values for monodentate carboxylate coordination may be rationalized by the presence of the additional weak interaction between the metal and carbonyl oxygen from the carboxylate (Fig. 1). For the remaining complexes (**1**, **3–6**), $\Delta\nu$ parameters varied from 263 to 276 cm^{-1} . These values are similar to $\Delta\nu_1$ for the appropriate sodium carboxylates and are in favor of the bridging linkage.⁶ However, the precise type of bridge cannot be proposed on the grounds of the $\Delta\nu$ parameter.⁶

Spectra in the range of metal–ligand vibrations revealed two bands in the range $297\text{--}303$ and $264\text{--}281\text{ cm}^{-1}$, which can be assigned to $\nu(\text{Ag-O})$ vibrations (Table 8).²⁸ Moreover the absorption bands in the ranges $244\text{--}250$ and $224\text{--}227\text{ cm}^{-1}$ can be most likely assigned to $\nu(\text{Ag-P})$ vibrations (Table 8).^{37,38}

Conclusions

Six new perfluorinated carboxylate complexes of $\text{Ag}(\text{I})$ with dppm have been synthesized and structurally characterized. In spite of different lengths of carbon chain and/or various steric and electronic effects, the majority of the investigated complexes appear to have a tetranuclear structure in the solid state as established for **2** (crystal structure) and suggested for **3**, **5**, **6** on the basis of ^{31}P CP MAS NMR results. However, in solution the complexes revealed spectral properties which are in favor of a binuclear trigonal $\text{Ag}(\text{I})$ geometry with bridging dppm. Carboxylates are bidentately bonded and most probably in bridging positions, rather than chelating. This feature can be related to the lower basicity, compared to aliphatic carboxylates, of COO in perfluorinated carboxylates, consistent with the magnitude of the ^{13}C NMR shift of the COO group.

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