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Synthesis, structures and ^{31}P NMR studies of bis(diphenylphosphino)-methane adducts of copper and silver thiocarboxylates †

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The compounds $[Cu_3(\mu\text{-dppm})_3(SC\{O\}Me)_2][PF_6]$ **1**, $[Cu_3(\mu\text{-dppm})_3(SC\{O\}Ph)_2][X]$ (X = ClO_4 **2** or PF_6 **2a**) were synthesized by treating $Na^+R\{O\}CS^-$ (R = Me or Ph) with a mixture of $[Cu(MeCN)_4]X$ (X = PF_6 or ClO_4) and bis(diphenylphosphino)methane (dppm) in stoichiometric ratios. The structures of **1** and **2** have been determined by single crystal X-ray crystallography. The trinuclear core is held intact by the three bridging dppm ligands and two capping thiocarboxylate anions. One of the thiocarboxylate anions triply bridges to the $Cu_3(\mu\text{-dppm})_3$ core through a μ_3-S and the other by a μ_3-S,O bonding mode. Compounds $[Ag_3(\mu\text{-dppm})_3(SC\{O\}Me)_2][X]$ (X = NO_3 **3** or ClO_4 **3a**) and $[Ag_3(\mu\text{-dppm})_3(SC\{O\}Ph)_2][ClO_4]$ **4** were prepared by treating $Na^+R\{O\}CS^-$ (R = Me or Ph) with dppm and the corresponding silver salt. The structures of **3** and **4** were determined by X-ray crystallography. Both the thiocarboxylate anions bond in μ-*S* fashion, thereby stabilizing the trinuclear core. In all the four crystal structures C–H · · · O hydrogen bonding is present between one of the methylene hydrogen atoms and the carbonyl oxygen of the thiocarboxylate ligand. ^{31}P NMR studies in solution at low temperatures reveal that all the compounds retain their trinuclear core in solution, while intramolecular exchange involving dppm does not cease even at lower temperatures. Attempts to prepare monocapped trinuclear cations, $[M_3(\mu\text{-dppm})_3(SC\{O\}R)]^{2+}$, and binuclear neutral compounds, $[M_2(\mu\text{-dppm})_2(SC\{O\}R)_2]$, yielded only the corresponding bicapped trinuclear compounds.

Introduction

Bis(diphenylphosphino)methane (dppm) is known to form a wide range of polynuclear compounds.[1] Owing to its short bite angle it enforces a short metal–metal contact. Though aurophilic interactions (between gold metal atoms) have been studied and understood by both experimental and theoretical calculations[2] and proven to exist beyond any doubt, similar interactions among other coinage metals, Cu and Ag, are debatable.[3–6] Recently Che *et al.* have reported spectroscopic evidence for the existence of argentophilicity and cuprophilicity in binuclear silver and copper phosphine compounds.[7] The dppm adducts of coinage metal salts are known to exhibit luminescent properties.[8–11] Trinuclear silver(I) clusters of type $[Ag_3(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2(\mu\text{-dppm})_3]Cl$ and $[Ag_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4NO_2\text{-}p)_2(\mu\text{-dppm})_3][PF_6]$, for example, have been reported to be luminescent.[12,13] Samuelson and co-workers have synthesized a series of bicapped trinuclear copper(I) dppm complexes of general formula $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}X)_2]^+$ (X = Cl, Br or I) and $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}X)(\mu_3\text{-}Y)]$ (X = Cl, Y = WO_4).[14,15] The ability of X or Y to bind to the three metals is responsible for the formation of such trinuclear compounds. In the absence of a suitable triply bridging ligand, only dimeric compounds result.[14,15]

Monothiocarboxylates are interesting systems to study both for their usage as "single source precursors"[16–18] and for their versatile co-ordinating behaviour.[19] Our interest in studying the dppm adducts of coinage metal thiocarboxylates stems from the systematic research we have been carrying out on the chemistry of thiocarboxylates.[19–28] We recently revealed the ability of thiocarboxylates to display μ-*S*, μ-*S*, *O*, μ_3-S_2, *O* and μ_3-S_3 bonding modes in triphenylphosphine copper thiocarboxylate compounds.[19] Surprisingly, the chemistry of the triphenylphosphine silver thiocarboxylate compounds is different from that of their copper analogues.[20] Hence it was thought that a study on the reaction between copper and silver thiocarboxylates with dppm could be interesting. In this paper we report the synthesis, structure and the low temperature ^{31}P NMR studies of cationic trinuclear compounds of general formula $[M_3(\mu\text{-dppm})_3(\mu\text{-}SC\{O\}R)_2]^+$ (M = Cu or Ag; R = Me or Ph) in solution.

Experimental

All materials were obtained commercially and used as received. The solvents were dried by allowing them to stand over 3 Å molecular sieves overnight. $[Cu(MeCN)_4]PF_6$ was prepared according to the literature method,[29] $[Cu(MeCN)_4]ClO_4$ by refluxing Cu_2O and $HClO_4$(slight excess) in MeCN for about an hour, layering the colourless clear solution with Et_2O, washing the white precipitate obtained with Et_2O and drying under vacuum. $[Ag_2(dppm)_2(NO_3)_2]$ was prepared by a known method.[30] The preparations were carried out under a nitrogen atmosphere. The yields are reported with respect to the metal salts. The compounds are fairly stable, however they were stored under nitrogen at 5 °C to avoid any decomposition. The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker ACF300 FT-NMR machine using TMS as internal reference at 25 °C in CD_2Cl_2 or $CDCl_3$, IR spectra (KBr pellet) using a Bio-Rad FTIR spectrophotometer. The elemental analyses were performed in the microanalytical laboratory in the Chemistry Department, National University of Singapore. **CAUTION:** Perchlorate metal salts are potentially explosive and were handled in small quantities and under an inert N_2 atmosphere to avoid any untoward incident.

Syntheses

$[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-}SC\{O\}Me\text{-}S)(\mu_3\text{-}SC\{O\}Me\text{-}S,O)][PF_6]$ 1. To an MeCN (15 mL) solution of $[Cu(MeCN)_4]PF_6$ (0.145 g, 0.52 mmol), dppm (0.150 g, 0.52 mmol) was added as a solid,

† Electronic supplementary information (ESI) available: variable temperature ^{31}P NMR spectral data. See http://www.rsc.org/suppdata/dt/b0/b007867k/

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which resulted in a colourless clear solution. To this was added NaSC{O}Me prepared *in situ* by mixing 19 μL (0.35 mmol) of Me{O}CSH and 0.006 g (0.35 mmol) of sodium in 10 mL of MeOH, giving a bright yellow solution. After stirring for about an hour, the solvents were vacuum evaporated. The product was extracted into 15 mL of $CHCl_3$, layered with hexane and left in a refrigerator. The cream coloured precipitate was filtered off, washed with Et_2O and dried in vacuum. Yield 0.16 g (55%). Calc. for (desolvated) $C_{79}H_{72}Cu_3F_6O_2P_7S_2$: C, 57.89; H, 4.43. Found: C, 57.72; H, 4.01%. ^{1}H NMR (CD_2Cl_2): δ 2.47 (s, 6H, $CH_3\{O\}CS^-$), 3.35 (s, 6H, CH_2 of dppm) and 6.96–7.61 (m, 60H, C_6H_5 of dppm). ^{31}P NMR (CD_2Cl_2): δ −11.68s and −144.46 (septet, $^1J(^{31}P–^{19}F) = 710$ Hz). IR: 3051.4m, 1641.4s, 1571.5s, 1480.1s, 1435.3s, 1340.0w, 1097.8s, 947.2m, 836.4s, 735.7s, 692.1s, 619.0m, 554.4s, 511.3s and 468.2m cm^{-1}. Single crystals of complex **1**·2.25$CHCl_3$·H_2O for X-ray diffraction studies were obtained by slow diffusion of light petroleum (bp 35–60 °C) into a $CHCl_3$ solution of the compound.

[Cu_3(μ-dppm)$_3$(μ$_3$-SC{O}Ph-*S*)(μ$_3$-SC{O}Ph-*S*,*O*)][ClO_4] 2. $[Cu(MeCN)_4]ClO_4$ (0.170 g, 0.52 mmol) was dissolved in 10 mL of MeCN and dppm (0.200 g, 0.52 mmol) added as a solid and stirred for about 10 minutes to give a clear colourless solution. To this NaSC{O}Ph, prepared by mixing NaOMe (obtained from 0.008 g (0.35 mmol) of Na in 10 mL MeOH) and 41 μL (0.35 mmol) of thiobenzoic acid in MeOH, was added. The resulting bright yellow solution was stirred for about an hour and then vacuum evaporated. The yellow oil was extracted into 15 mL of $CHCl_3$, layered with hexane and left in a refrigerator. The yellow crystalline compound formed was washed with diethyl ether and dried under vacuum. Yield 0.24 g (82%). Calc. for (desolvated) $C_{89}H_{76}ClCu_3O_6P_6S_2$: C, 62.24; H, 4.46; Cl, 2.06. Found: C, 61.22; H, 4.48; Cl, 2.48%. ^{1}H NMR (CD_2Cl_2): δ 3.35 (s, 6H, CH_2 of dppm) and 6.8–8.2 (m, 70H, C_6H_5 of dppm and Ph{O}CS). ^{31}P NMR (CD_2Cl_2): δ −10.84s. IR: 3056.6w, 1609.1m, 1571.5w, 1544.96m, 1480.1s, 1435.3s, 1340.0w, 1308.1m, 1188.4s, 1159.8s, 1097.8s, 1025.8m, 997.1m, 947.2m, 836.4w, 772.2s, 735.7s, 692.1s, 619.0m, 511.3s and 468.2s cm^{-1}. Single crystals of complex **2**·2$CHCl_3$ were obtained by slow diffusion of hexane into a $CHCl_3$ solution of the compound.

[Cu_3(μ-dppm)$_3$(SC{O}Ph)$_2$][PF_6] 2a. The preparation was essentially the same as above with $[Cu(MeCN)_4]PF_6$ as the starting material. Yield: 65%. Calc. for $C_{89}H_{76}Cu_3F_6O_2P_7S_2$·1.5$CH_2Cl_2$: C, 57.49; H, 4.21; F, 6.46. Found: C, 57.28; H, 4.28; F, 6.43%. ^{1}H NMR (CD_2Cl_2): δ 3.32 (s, 6H, CH_2 of dppm) and 6.8–8.02 (m, 70H, C_6H_5 of dppm and Ph{O}CS). ^{31}P NMR (CD_2Cl_2): δ −10.93s and −144.59 (septet, $^1J(^{31}P–^{19}F) = 710$ Hz). IR: 3051.3w, 1686.8w, 1609.1m, 1571.5m, 1480.1m, 1435.3s, 1308.0w, 1188.4m, 1159.8m, 1097.8m, 1025.8m, 997.1m, 947.2m, 836.4s, 772.2m, 735.7s, 692.1s, 619.0w, 554.4m, 511.3m and 468.2m cm^{-1}.

[Ag_3(μ-dppm)$_3$(μ-SC{O}Me-*S*)$_2$][NO_3] 3. A solution of $AgNO_3$ (0.088 g, 0.52 mmol) in 10 mL of MeCN was mixed with dppm (0.200 g, 0.52 mmol) and the resulting colourless clear solution stirred for 15 minutes. NaSC{O}Me, prepared *in situ* from Me{O}CSH (25 μL, 0.35 mmol) and Na (0.008 g, 0.35 mmol) in 10 mL of MeOH, was added and stirred for about 30 minutes. The resulting colourless solution was subjected to vacuum evaporation. The product was dissolved in 20 mL of CH_2Cl_2, layered with Et_2O. Colourless crystals were obtained the following day, which were collected, washed with Et_2O and dried under vacuum. Yield 0.24 g (82%). Calc. for (desolvated) $C_{79}H_{72}Ag_3NO_5P_6S_2$: C, 56.18; H, 4.30. Found: C, 55.99; H, 4.19%. ^{1}H NMR (CD_2Cl_2): δ 2.40 (s, 6H, $CH_3\{O\}CS$), 3.48 (s, 6H, CH_2 of dppm) and 6.99–7.22 (m, 60H, C_6H_5 of dppm). ^{31}P NMR (CD_2Cl_2, 300 K): δ −0.02 (J(Ag–P) = 376 Hz). Single crystals were obtained by slow diffusion of Et_2O into a solution of the compound in CH_2Cl_2.

[Ag_3(μ-dppm)$_3$(μ-SC{O}Me-*S*)$_2$][ClO_4] 3a. The procedure was essentially the same as above but $AgNO_3$ was replaced with $AgClO_4$. Yield: 56%. Calc. for $C_{79}H_{72}Ag_3ClO_6P_6S_2$·2$CHCl_3$: C, 49.51; H, 3.79; Cl, 12.62; S, 3.26. Found: C, 49.59; H, 3.08; Cl, 12.20; S, 3.26%. ^{1}H NMR (CD_2Cl_2): δ 2.41 (s, 6H, CH_3COS^-), 3.49 (s, 6H, CH_2 of dppm) and 7.00–7.26 (m, 60H, C_6H_5 of dppm). ^{31}P NMR (CD_2Cl_2, 253 K): δ −0.27 (overlapping doublets, $^1J(^{107/109}Ag–P)$ ($^{107}Ag)_3 = 348$, ($^{107}Ag)_2(^{109}Ag) = 375$, ($^{107}Ag)(^{109}Ag)_2 = 395$ and ($^{109}Ag)_3 = 403$ Hz). IR: 3044.0m, 1630s, 1585.7m, 1485.4m, 1437.1s, 1360w, 1311.8w, 1194.1w, 1093.8s, 943.3m, 742.7s, 694.5s, 626.9m, 517.0m and 478.4m.

[Ag_3(dppm)$_3$(μ-SC{O}Ph-*S*)$_2$][ClO_4] 4. The procedure was very similar to the previous one but with thiobenzoic acid in place of thioacetic acid. Yield 73%. Calc. for (desolvated) $C_{89}H_{76}Ag_3ClO_6P_6S_2$: C, 57.76; H, 4.14; Cl, 1.92; S, 3.47. Found: C, 55.81; H, 3.73; Cl, 1.83; S, 3.45%. ^{1}H NMR (CD_2Cl_2): δ 3.53 (s, 6H, CH_2 of dppm) and 6.87–8.10 (m, 70H, C_6H_5 of dppm and Ph{O}CS). ^{31}P NMR (CD_2Cl_2, 273 K): δ 1.57 (overlapping doublets, $^1J(^{107/109}Ag–P)$ ($^{107}Ag)_3 = 364$, ($^{107}Ag)_2(^{109}Ag) = 376$, ($^{107}Ag)(^{109}Ag)_2 = 398$ and ($^{109}Ag)_3 = 416$ Hz). IR: 3046.3 m, 1605.2s, 1570.4s, 1483.6s, 1435.4s, 1196.2s, 1090s, 999.4m, 777.5m, 686.8s, 623.2m and 509.3m cm^{-1}. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a $CHCl_3$ solution of the compound.

Under similar conditions attempts to synthesize [M_2(dppm)$_2$(SCOR)$_2$] and [M_3(μ-dppm)$_3$(SCOR)]$^{2+}$ cations resulted in formation of [M_3(dppm)$_3$(SCOR)$_2$]$^+$ which was confirmed by ^{1}H NMR and elemental analysis.

Crystal structure determinations

The diffraction experiments were carried out on a Bruker SMART CCD diffractometer with a Mo-Kα sealed tube at 20 °C. The program SMART[31] was used for collecting frames of data, indexing reflections and determination of lattice parameters, SAINT[31] for integration of the intensity of reflections and scaling, SADABS[32] for absorption correction and SHELXTL[33] for space group and structure determination and least-squares refinements on F^2. The relevant crystallographic data and refinement details are shown in Table 1. Compound **1** crystallized with 2.25 molecules of $CHCl_3$ and one of H_2O. One of the $CHCl_3$ molecules had occupancy of 0.25 while the other two were disordered. Three models were resolved with occupancies 0.5, 0.25 and 0.25 in one $CHCl_3$ while the other was disordered with occupancies 0.7 and 0.3. The water molecule was also disordered (occupancies 0.5, 0.25 and 0.25). In **2** two molecules of $CHCl_3$ were found, both disordered. Two models were resolved for each solvate molecule with occupancies 0.6 and 0.4. A soft SADI constraint was imposed on Cl–O and O···O distances of the perchlorate anion. In compound **3** one of the methyl groups in the thioacetate ligand was disordered. Three disorder models were resolved with occupancies 0.45, 0.3 and 0.25. One of the phenyl rings in the dppm ligand was disordered with occupancies of 0.55 and 0.45. In compound **4** the chlorine atoms of the CH_2Cl_2 were disordered. The oxygens in the ClO_4^- anion were disordered and two disorder models with 0.5 and 0.5 occupancies each were resolved. The carbonyl group in the thiobenzoate ligand was disordered and 3 models were resolved with occupancies 0.5, 0.25 and 0.25. One of the phenyl rings attached to the dppm ligand was disordered and two models with occupancies 0.7 and 0.3 were resolved.

CCDC reference number 186/2283.

See http://www.rsc.org/suppdata/dt/b0/b007867k/ for crystallographic files in .cif format.

Results and discussion

The compounds **1**–**4** were prepared by treating the appropriate metal salt with dppm and thiocarboxylate anion in 3 : 3 : 2 ratio,

as in eqn. (1) (M = Cu or Ag; R = Me or Ph; X = NO_3, ClO_4 or

$$3MX + 3\ dppm + 2\ R\{O\}CS^- Na^+ \longrightarrow [M_3(\mu\text{-}dppm)_3(SC\{O\}R)_2][X] + 2NaX \quad (1)$$

PF_6). Compound **3** was also obtained when $[Ag_2(\mu\text{-}dppm)_2][NO_3]_2$[30] was treated with 2 mole equivalents of $Me\{O\}CS^-$. Metal halide salts were purposely avoided in order to prevent competition in capping the trimetallic core. Attempts to prepare mono capped trinuclear compounds of general formula $[M_3(dppm)_3(SC\{O\}R)][X]_2$ and the binuclear compound $[M_2(\mu\text{-}dppm)_2(SC\{O\}R)_2]$ resulted in the bicapped trinuclear compounds as shown by ^{31}P NMR studies (see below).

Proton NMR spectra of all the compounds in CD_2Cl_2 solution consisted of broad singlet resonances in the range δ 3.32–3.53 for the methylene protons of the dppm ligand at ambient as well as low temperatures (200 K). This can be explained by assuming that the phosphine ligand undergoes some form of intra-molecular exchange process even at reduced temperatures. However there are examples in the literature where the methylene signals of the dppm[30] and dmpm[34,35] ligands appear as a quintet and septet respectively due to coupling to the phosphorus atoms.

The ^{31}P NMR of compounds **1** and **2a** in CD_2Cl_2 gave broad singlet signals at room temperature (δ −11.68 ($\Delta\nu_{1/2} = 46$) and −10.93 (50 Hz)) respectively for the cations. Cooling the sample to 200 K did not give rise to additional peaks and no couplings were observed for all three compounds (*e.g.* ^2J(P–C–P) or ^2J(P–Cu–P)) at all temperatures. Upon cooling to 223 K the signals appeared at δ −11.43 ($\Delta\nu_{1/2} = 19$) and −11.42 (15 Hz) respectively. It may be noted that the triphenylphosphine adducts of the copper and silver thiocarboxylates show multiple peaks at lower temperatures and have been shown to aggregate or disassociate to form various species in solution.[19,20] Similar observations were made recently for 1,2-bis(diphenylphosphino)ethane and other bisphosphine adducts of copper(I) salts.[36] Harvey *et al.* observed multiple peaks in the ^{31}P NMR at reduced temperatures and this is thought to be due to disassociation of compound $[Cu_2(dppm)_2(O_2CMe)][BF_4]$ into $[Cu_2(dppm)(O_2CMe)][BF_4]$ and free dppm.[37] From the absence of any such observation in our study, it was concluded that the trimetallic cluster remains intact in solution.

In order to find out whether the binuclear compound $[Cu_2(dppm)_2(RC\{O\}S)_2]$ existed in solution, variable temperature ^{31}P NMR experiments were made for a mixture containing one molar equivalent of $Me\{O\}CS^-Na^+$ and **1** in CD_2Cl_2 solution. One strong and one weak signal were observed at temperatures 300 to 223 K as shown in Fig. 1. The major peak at δ −11.68 at 300 K does not change very much upon cooling. In contrast, the chemical shift of the minor signal was found to be sensitive to temperature and varies from δ −5.66 to −14.72. The former signal is attributed to the trinuclear compound **1** as is confirmed by comparing the variable temperature ^{31}P NMR chemical shifts of **1** (see ESI material). The low intensity signal may tentatively be assigned to the existence of the expected binuclear compound $[Cu_2(\mu\text{-}dppm)_2(SC\{O\}Me)_2]$ and this is further supported by comparing the variable temperature ^{31}P NMR spectral data of $[Cu_2(dppm)_2][PF_6]_2$ (see ESI material). The relative intensities of the two signals may indicate stability of the trinuclear compound in solution and its reluctance in reacting with another mol of thioacetate to yield the compound $[Cu_2(\mu\text{-}dppm)_2(\mu\text{-}SC\{O\}Me)_2]$. At present we do not have an explanation for this behaviour as well as the increase of this intensity with decreasing temperature. Further work is necessary to confirm the presence of the binuclear species in solution. However, it may also be noted that attempts to synthesize these binuclear compounds lead to isolation of the trinuclear compounds as the only identifiable product.

The variable temperature ^{31}P NMR spectra of a mixture containing $[Cu(MeCN)_4]PF_6$, dppm and $NaSC\{O\}Me$ in the ratio

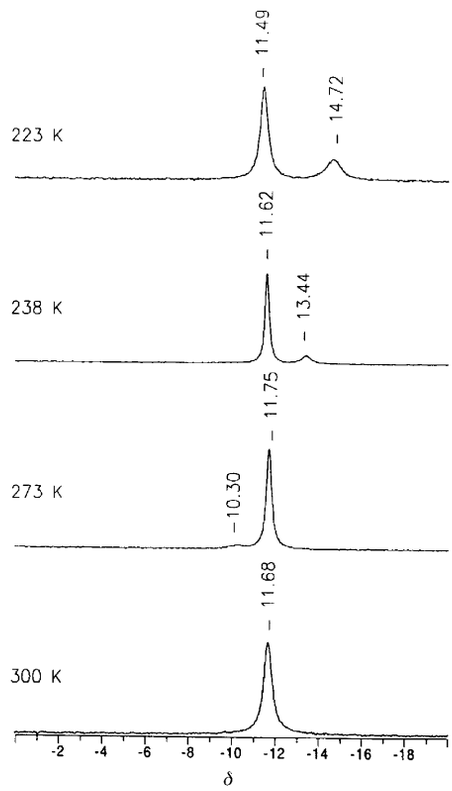

Fig. 1 Variable temperature ^{31}P NMR of complex **1** + $Me\{O\}CS^-Na^+$.

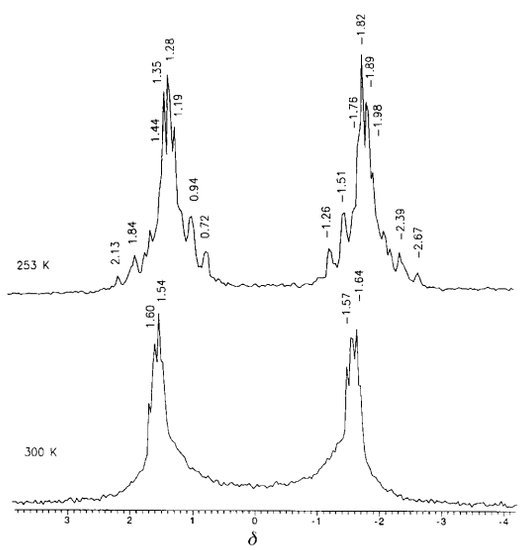

Fig. 2 Variable temperature ^{31}P NMR of complex **3a**.

3:3:1 show a similar pattern (see ESI material). It is evident that the trinuclear core is the major species along with small amounts of binuclear compound in solution.

The ^{31}P NMR of compound **3a**, at ambient temperature, gave a broad doublet resonance with additional peaks. However cooled to 253 K the spectrum was quite well resolved consisting of four major doublets (Fig. 2) with coupling constants of 348, 375, 395 and 403 Hz. The appearance of the four major doublets is due to the existence of isotopomers containing $(^{107}Ag)_3$, $(^{107}Ag)_2(^{109}Ag)$, $(^{107}Ag)(^{109}Ag)_2$ and $(^{109}Ag)_3$ in the trinuclear compound,[34,35,38,39] thus confirming the nuclearity of the cation in solution. The ratio between $^1J(^{109}Ag–^{31}P)$ and $^1J(^{107}Ag–^{31}P)$ was calculated to be 1.158:1. This value is quite close to the ratio of the gyromagnetic constants of ^{109}Ag and ^{107}Ag (1.150:1).[40,41] A similar observation was made for compound **4**. The four major doublet separations were observed at

Table 1 Crystallographic data for compounds **1**, **2**, **3** and **4**

	1	**2**	**3**	**4**
Chemical formula	$C_{79}H_{72}Cu_3F_6O_2P_7S_2\cdot 2.25CHCl_3\cdot H_2O$	$C_{89}H_{76}ClCu_3O_6P_6S_2\cdot 2CHCl_3$	$C_{79}H_{72}Ag_3NO_5P_6S_2$	$C_{89}H_{76}Ag_3ClO_6P_6S_2\cdot CH_2Cl_2$
Formula weight	1925.74	1956.24	1688.93	1935.42
T/K	293(2)	293(2)	293(2)	293(2)
Radiation, λ/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a/Å	35.8440(3)	13.9558(1)	15.2530(2)	19.8545(8)
b/Å	14.3432(3)	15.9713(2)	26.8770(3)	25.3496(10)
c/Å	33.9877(7)	20.6451(3)	19.3100(1)	17.8933(7)
α/°		82.647(1)		
β/°	95.806(1)	85.295(1)	107.455(1)	102.325(1)
γ/°		83.44(1)		
V/Å^3	17384.0(5)	4523.33(9)	7551.71(14)	8798.2(6)
Z	8	2	4	4
μ/mm^{-1}	1.171	1.11	1.003	0.960
Independent reflections	15016	14871	13133	17602
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0866, 0.2054	0.0784, 0.1771	0.0600, 0.1329	0.0863, 0.1998

Table 2 Hydrogen bonding parameters

Compound	O···H/Å	C···O/Å	C–H···O/°
1	2.472 (O1–H5A)	3.254(10) (C5–O1)	137.48 (C5–H5A–O1)
2	2.320 (O1–H15B)	3.096(9) (C15–O1)	136.39 (C15–H15B–O1)
3	2.536 (H5A–O1)	3.182(7) (C5–O1)	124.02 (C5–H5A–O1)
	2.476 (H6B–O2)	3.151(9) (C6–O2)	126.49 (C6–H6B–O2)
4[a]	2.488 (O1–H17B)	3.225(11) (C17–O1)	132.66 (C17–H17B–O1)
	2.344 (O2–H16A)	3.052(20) (C16–O2)	129.30 (C16–H16A–O2)
	2.299 (O2A–H16A)	2.999(38) (C16–O2A)	128.36 (C16–H16A–O2A)
	2.596 (O2B–H16A)	3.263(27) (C16–O2B)	126.14 (C16–H16A–O2B)

[a] The oxygen atom O(2) is disordered.

273 K and the calculated coupling constants are 364, 376, 398, 416 Hz. The ratio between the $^1J(^{109}Ag–^{31}P)$ and $^1J(^{107}Ag–^{31}P)$ was calculated to be 1.143 : 1. Hence it was concluded that the compound had a trinuclear core. The appearance of other long range couplings like ^2J(P–C–P), ^2J(P–Ag–P), ^3J(Ag–P–C–P), ^4J(Ag–P–C–P–Ag) and ^4J(P–Ag–P–C–P) made the NMR spectra too complicated to be interpreted completely. Moreover the ^1J(Ag–P) coupling constant falls within the expected range of 310–600 Hz, which is commonly observed for two phosphorus atoms attached to a silver metal atom.[42] It should be noted that ^1J(Ag–P) depends on the P–Ag–P angle and the Ag–P distance. The greater the P–Ag–P angle the greater will be the J value and a smaller Ag–P bond length would lead to greater J separations.[43]

From the ^{1}H NMR results and the microanalysis data the stoichiometry of the compounds was confirmed. The ^{31}P NMR studies especially for the silver complexes indicated a trinuclear structure but did not yield any additional information regarding the bonding modes of the thiocarboxylate ligand. Hence X-ray diffraction experiments were carried out for selective compounds. The structures are described below.

General structural features

The solid-state structures of compounds **1**, **2**, **3**, **4** consist of discrete cations and anions (ClO_4^-, PF_6^- or NO_3^-) and these are disordered in **2**, **3** and **4**. The three metal atoms form a triangle and the three dppm ligands bridge between two metal atoms in a μ fashion forming a $M_3(\mu\text{-dppm})_3$ core. The M_2P_2 units present in the structure are nearly coplanar. Two of the methylene groups of the dppm ligand are oriented in one direction and one in the opposite direction. These orientations in all these compounds are similar to those of analogous trinuclear compounds reported.[44] The Cu–P and Ag–P distances are normal and fall in a narrow range of 2.220(2)–2.308(2) and 2.437(2)–2.515(2) Å respectively. A CSDS search shows that normal Cu–P, Ag–P bonds in such trinuclear compounds fall within the ranges 2.226–2.319 and 2.413–2.505 Å respectively.[45] In each structure the oxygen atom from one of the thiocarboxylate ligands is involved in intramolecular C–H···O hydrogen bonding with a methylene hydrogen atom. Such hydrogen bonding is now found to be ubiquitous and important in influencing the molecular packing in solid-state structures.[46] The hydrogen bonding parameters are listed in Table 2. The mode of bonding of the capping thiocarboxylate anion and subsequent changes in the structures, including the metal–metal distances, of the compounds, however, differ in each structure. The following sections describe these structural features in detail.

Structure of compound 1

A perspective view of compound **1** can be seen in Fig. 3 and relevant bond distances and angles are shown in Table 3. The three copper metal atoms assume distorted tetrahedral coordination geometry. Cu(1) and Cu(2) have a P_2S_2 environment while Cu(3) maintains a P_2SO environment (ignoring the Cu···Cu interactions). The two thioacetate ligands triply bridge the trinuclear core through μ_3-*S*,*O* and μ_3-*S* linkages. These bonding modes have recently been observed in a few neutral triphenylphosphine adducts of copper thiocarboxylates. The thioacetate ligand (which bridges by a μ_3-*S* bonding mode) is unsymmetrically bonded to the three copper atoms. The distances Cu(1)–S(1), Cu(2)–S(1) and Cu(3)–S(1) are 2.431(2), 2.351(2) and 2.291(2) Å respectively. One of the methylene hydrogens on C(5) is involved in hydrogen bonding with the carbonyl oxygen, O(1). For the thiocarboxylate ligand, which binds through μ_3-*S*,*O* the Cu(1)–S(2) and Cu(2)–S(2) distances are 2.370(2) and 2.392(2) Å respectively and Cu(3)–O(2) is 2.436(6) Å. The Cu–O bond distance is longer than those observed in the compounds $[Cu_4(SC\{O\}Ph)_4(PPh_3)_3]$ and $[Cu_2(SC\{O\}Me)_2(PPh_3)_4]$.[19] Consequently C(3)–

Table 3 Selected bond lengths (Å) and angles (°) for compound **1**

Cu(1)–P(1)	2.245(2)	Cu(1)–P(6)	2.260(2)
Cu(2)–P(2)	2.262(2)	Cu(2)–P(3)	2.245(2)
Cu(3)–P(4)	2.235(2)	Cu(3)–P(5)	2.246(2)
Cu(1)–S(1)	2.431(2)	Cu(1)–S(2)	2.370(2)
Cu(2)–S(1)	2.351(2)	Cu(2)–S(2)	2.392(2)
Cu(3)–S(1)	2.291(2)	Cu(3)–O(2)	2.436(6)
C(1)–S(1)	1.753(8)	C(3)–S(2)	1.722(8)
C(1)–O(1)	1.170(9)	C(3)–O(2)	1.202(9)
C(1)–C(2)	1.467(1)	C(3)–C(4)	1.502(1)
P(1)–C(5)	1.831(7)	P(2)–C(5)	1.817(7)
P(3)–C(6)	1.836(7)	P(4)–C(6)	1.827(7)
P(5)–C(7)	1.831(8)	P(6)–C(7)	1.820(8)
Cu(1)···Cu(2)	2.794(1)	Cu(1)···Cu(3)	3.641(1)
Cu(2)···Cu(3)	3.459(1)		
Cu(1)–S(1)–Cu(2)	71.47(6)	Cu(1)–S(1)–Cu(3)	100.85(8)
Cu(2)–S(1)–Cu(3)	96.36(8)	Cu(1)–S(2)–Cu(2)	71.84(6)
Cu(2)–Cu(1)–S(1)	52.92(5)	Cu(2)–Cu(1)–S(2)	54.44(5)
S(2)–Cu(1)–S(1)	99.37(7)	P(1)–Cu(1)–P(6)	126.62(8)
P(3)–Cu(2)–P(2)	119.06(7)	P(3)–Cu(2)–S(1)	113.04(7)
P(2)–Cu(2)–S(1)	109.53(7)	P(3)–Cu(2)–S(2)	106.70(8)
P(2)–Cu(2)–S(2)	105.52(7)	S(1)–Cu(2)–S(2)	101.08(7)
P(3)–Cu(2)–Cu(1)	146.51(6)	P(2)–Cu(2)–Cu(1)	93.75(5)
S(1)–Cu(2)–Cu(1)	55.61(5)	S(2)–Cu(2)–Cu(1)	53.72(5)
P(4)–Cu(3)–P(5)	134.35(8)	P(4)–Cu(3)–S(1)	114.21(8)
P(5)–Cu(3)–S(1)	111.16(8)	P(4)–Cu(3)–O(2)	89.27(15)
P(5)–Cu(3)–O(2)	85.89(15)	S(1)–Cu(3)–O(2)	102.39(14)
P(1)–Cu(1)–S(1)	104.85(7)	P(1)–Cu(1)–S(2)	108.54(7)
P(6)–Cu(1)–S(1)	107.87(8)	P(6)–Cu(1)–S(2)	106.30(8)
P(1)–Cu(1)–Cu(2)	92.62(5)	P(6)–Cu(1)–Cu(2)	140.74(7)

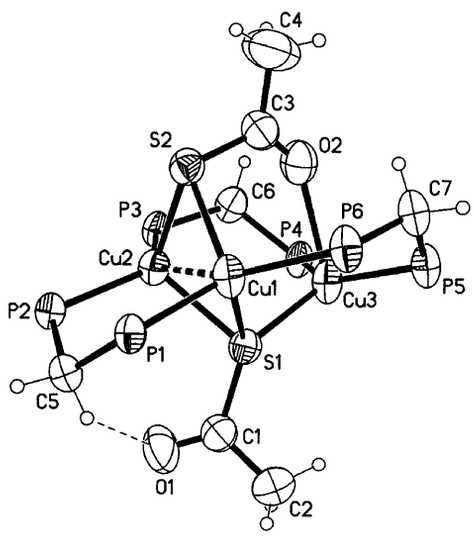

Fig. 3 An ORTEP[47] diagram (with 50% probability thermal ellipsoids) of the cation in complex **1**. The phenyl rings in the cation are omitted for clarity.

O(2) is longer than C(1)–O(1) and C(3)–S(2) is shorter than C(1)–S(1) which are dictated by the charge delocalization of the thioacetate ligand. The distance between Cu(1) and Cu(2), 2.794(1) Å, is slightly shorter than the sum of the van der Waals radii (2.8 Å).[48]

Structure of compound 2

A ball and stick diagram of complex **2** is shown in Fig. 4 and related bond lengths and angles are listed in Table 4. The thiobenzoate anion caps the trinuclear compound in two different ways, namely μ_3-*S* and μ_3-*S*,*O* as in compound **1**, hence the three copper metal atoms are four-coordinated and of these Cu(1) and Cu(3) have a P_2S_2 environment and Cu(2) has a P_2SO environment. Considering the thiocarboxylate that is μ_3-*S* bonding, the three Cu–S distances, 2.381(2), 2.327(2) and 2.589(2) Å for Cu(1)–S(1), Cu(2)–S(1) and Cu(3)–S(1) respectively, are unsymmetrical. The Cu(3)–S(1) bond is longer

Table 4 Selected bond lengths (Å) and angles (°) for compound **2**

Cu(1)–P(1)	2.282(2)	Cu(1)–P(6)	2.308(2)
Cu(2)–P(2)	2.220(2)	Cu(2)–P(3)	2.261(2)
Cu(3)–P(4)	2.262(2)	Cu(3)–P(5)	2.261(2)
Cu(1)–S(1)	2.381(2)	Cu(1)–S(2)	2.423(2)
Cu(2)–S(1)	2.327(2)	Cu(3)–S(1)	2.589(2)
Cu(3)–S(2)	2.350(2)	Cu(2)–O(2)	2.194(5)
C(1)–S(1)	1.757(9)	C(8)–S(2)	1.738(8)
C(1)–O(1)	1.218(9)	O(2)–C(8)	1.231(8)
Cu(1)···Cu(3)	2.990(1)	Cu(1)···Cu(2)	3.133(1)
Cu(2)···Cu(3)	3.464(1)		
P(1)–Cu(1)–P(6)	117.87(7)	P(1)–Cu(1)–S(1)	111.83(7)
P(6)–Cu(1)–S(1)	109.82(7)	P(1)–Cu(1)–S(2)	119.31(7)
P(6)–Cu(1)–S(2)	94.59(7)	S(1)–Cu(1)–S(2)	101.19(7)
P(1)–Cu(1)–Cu(3)	152.18(6)	P(6)–Cu(1)–Cu(3)	89.76(5)
S(1)–Cu(1)–Cu(3)	56.26(5)	S(2)–Cu(1)–Cu(3)	50.12(5)
O(2)–Cu(2)–P(2)	107.87(15)	O(2)–Cu(2)–P(3)	90.63(15)
P(2)–Cu(2)–P(3)	125.11(8)	O(2)–Cu(2)–S(1)	115.01(15)
P(2)–Cu(2)–S(1)	113.30(7)	P(3)–Cu(2)–S(1)	103.33(7)
P(5)–Cu(3)–P(4)	128.12(7)	P(5)–Cu(3)–S(2)	101.02(7)
P(4)–Cu(3)–S(2)	114.46(7)	P(5)–Cu(3)–S(1)	105.04(7)
P(4)–Cu(3)–S(1)	106.42(7)	S(2)–Cu(3)–S(1)	97.37(7)
P(5)–Cu(3)–Cu(1)	92.02(5)	P(4)–Cu(3)–Cu(1)	139.54(6)
S(2)–Cu(3)–Cu(1)	52.32(5)	S(1)–Cu(3)–Cu(1)	49.90(5)
C(1)–S(1)–Cu(2)	112.9(3)	C(1)–S(1)–Cu(1)	107.7(3)
Cu(2)–S(1)–Cu(1)	83.42(7)	C(1)–S(1)–Cu(3)	157.7(3)
Cu(2)–S(1)–Cu(3)	89.43(7)	Cu(1)–S(1)–Cu(3)	73.84(6)
C(8)–S(2)–Cu(3)	104.2(2)	C(8)–S(2)–Cu(1)	107.9(3)
Cu(3)–S(2)–Cu(1)	77.56(6)	C(8)–O(2)–Cu(2)	132.8(5)
O(1)–C(1)–C(2)	118.4(8)	O(1)–C(1)–S(1)	122.8(6)
C(2)–C(1)–S(1)	118.8(6)		

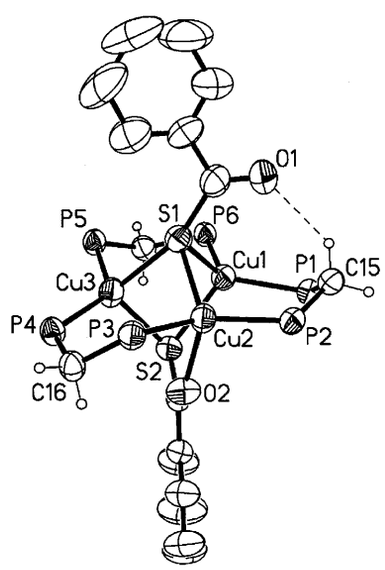

Fig. 4 An ORTEP[47] thermal ellipsoid plot of the cationic core in complex **2** omitting the phenyl rings attached to the phosphorus atoms.

as hydrogen bonding between the carbonyl oxygen of the thiobenzoate anion and one of the hydrogens on the methylene carbon C(15) forces the ligand to orient in such a way that S(1) is inclined more towards Cu(1) and Cu(2). The other thiocarboxylate ligand bridges in a μ_3-*S*,*O* fashion. The sulfur, S(2), is bridging copper atoms Cu(1) and Cu(3) while the oxygen is coordinated to Cu(2). The Cu(1)–S(2) and Cu(3)–S(2) bond distances are 2.423(2) Å and 2.350(2) Å; Cu(2)–O(2) is 2.194(5) Å. These distances are comparable to those found in the compound $[Cu_4(SC\{O\}Ph)_4(PPh_3)_3]$ with similar bonding modes[19] but shorter than the values observed in **1**. The C(1)–S(1) bond distance, 1.757(9) Å, is longer than C(8)–S(2) 1.738(8) Å and C(1)–O(1) 1.218(9) Å is shorter than C(8)–O(2) 1.231(8) Å. This is due to the bonding modes of the corresponding thiocarboxylate anion. A μ_3-*S*,*O* bonding mode, due to the delocalization of the negative charge, shortens the C–S bond

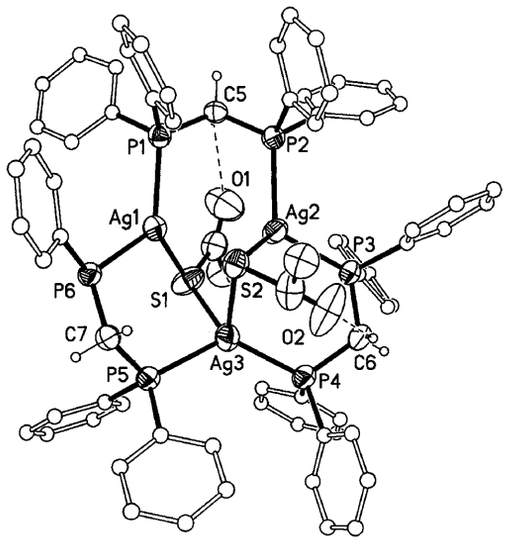

Fig. 5 A perspective view of the cation in complex **3**.

(as it attains partial double bond character) and lengthens the C–O bond. Similar delocalization is absent in the other thiobenzoate ligand as the bonding mode is μ_3-*S*. The Cu···Cu distances fall in the range 2.990(1)–3.464 (1) Å. The shortest, 2.990(1) Å between Cu(1) and Cu(3), is longer than the sum of the van der Waals radii.[48]

Structure of compound 3

A view of compound **3** is shown in Fig. 5 and the bond lengths and angles are listed in Table 5. The two thioacetate anions bridge two silver atoms above and below the Ag_3 triangle through μ-S bonding. Of the sulfur atoms in the thioacetate ligands, S(1) bridges between Ag(1) and Ag(3) while S(2) bridges Ag(2) and Ag(3). Hence Ag(3) assumes a distorted tetrahedral geometry while Ag(1) and Ag(2) have distorted trigonal planar geometry. The Ag–S bond distances are unsymmetrical: Ag(1)–S(1), Ag(3)–S(1), Ag(2)–S(2) and Ag(3)–S(2) are 2.489(2), 2.780(2), 2.593(2) and 2.698(2) Å respectively. Of the three Ag···Ag distances, Ag(1)···Ag(2) and Ag(2)···Ag(3) are 3.2321(6) and 3.0945(7) Å respectively, shorter than the sum of the van der Waals radii, 3.4 Å.[48] The distance between the other two silver metal atoms Ag(1) and Ag(3) is 3.50 Å. The two oxygen atoms of the thioacetate ligands, which are not bonded to silver, are involved in weak C–H···O hydrogen bonding. The details of the hydrogen bonding are shown in Table 2. The C(1)–S(1) and C(1)–O(1) bond distances are 1.748(7) Å and 1.208(9), slightly longer than C(3)–S(2) and C(3)–O(2) which are 1.732(7) and 1.182(9) Å.

Structure of compound 4

Fig. 6 is a perspective view of compound **4** and related bond parameters are listed in Table 6. The structural description and bonding modes are very similar to those of **3**. The silver metal atom Ag(3) is in a distorted tetrahedral geometry while Ag(1) and Ag(2) are in distorted trigonal planar geometry. Hence Ag(1) and Ag(2) have a P_2S environment while Ag(3) has a P_2S_2 environment. The two thiobenzoate ligands, unlike in the copper analogue, anchor the trinuclear core through two μ-*S* bridges. The S(1) atom bridges Ag(1) and Ag(3) while S(2) is used to bridge atoms Ag(2) and Ag(3). The distances Ag(1)–Ag(3) and Ag(2)–Ag(3) are 3.0792(9) and 3.1296(9) Å respectively, shorter than the sum of the van der Waals radii (3.4 Å).[48] These short metal–metal contacts might be due to the conformational differences in the dppm ligands and need not be attributed to argentophilic interactions. However they cannot be neglected.[7] The Ag(3)–S(1) and Ag(3)–S(2) bond distances are 2.730(2) and 2.709(2) Å respectively, while Ag(1)–S(1) and Ag(2)–S(2) are 2.541(2) and 2.542(2) Å respectively. In other words, the Ag–S bond distances at the tetrahedral centre are longer than those found around the trigonal planar metal centre, similar to those found in **3**. The two silver compounds are unique for the reason that the trinuclear $M_3(dppm)_3$ core is sustained by two μ-S bridging ligands. In all previously reported trinuclear compounds the capping ligands are bonded to all three metals.

In conclusion, trinuclear bicapped cations of type $[M_3(dppm)_3(SC\{O\}R)_2]^+$ have been synthesized and characterized. Attempts to synthesize binuclear compounds, $[M_2(dppm)_2(SC\{O\}R)_2]$, or trinuclear monocapped compounds, $[M_3(dppm)_3$-

Table 5 Selected bond lengths (Å) and angles (°) for compound **3**

Ag(1)–P(1)	2.450(2)	Ag(1)–P(6)	2.493(2)
Ag(2)–P(2)	2.494(2)	Ag(2)–P(3)	2.487(2)
Ag(3)–P(4)	2.466(2)	Ag(3)–P(5)	2.492(2)
Ag(1)–S(1)	2.489(2)	Ag(2)–S(2)	2.593(2)
Ag(3)–S(1)	2.780(2)	Ag(3)–S(2)	2.698(2)
C(1)–S(1)	1.748(7)	C(3)–S(2)	1.732(7)
C(1)–O(1)	1.208(9)	C(3)–O(2)	1.182(9)
C(5)–P(2)	1.819(3)	C(5)–P(1)	1.840(3)
C(6)–P(4)	1.840(6)	C(6)–P(3)	1.841(6)
C(7)–P(5)	1.825(5)	C(7)–P(6)	1.849(5)
Ag(1)···Ag(2)	3.232(1)	Ag(2)···Ag(3)	3.095(1)
Ag(1)···Ag(3)	3.500(1)	Ag(1)···S(2)	3.161(2)
Ag(2)···S(1)	3.227(2)		
P(1)–Ag(1)–S(1)	121.38(6)	P(1)–Ag(1)–P(6)	122.59(5)
S(1)–Ag(1)–P(6)	112.81(6)	P(1)–Ag(1)–Ag(2)	88.64(4)
S(1)–Ag(1)–Ag(2)	67.23(5)	P(6)–Ag(1)–Ag(2)	130.90(4)
P(3)–Ag(2)–P(2)	115.61(5)	P(3)–Ag(2)–S(2)	118.28(5)
P(2)–Ag(2)–S(2)	113.19(5)	P(3)–Ag(2)–Ag(3)	88.57(4)
P(2)–Ag(2)–Ag(3)	154.56(4)	S(2)–Ag(2)–Ag(3)	55.80(4)
P(3)–Ag(2)–Ag(1)	148.75(4)	P(2)–Ag(2)–Ag(1)	87.45(4)
S(2)–Ag(2)–Ag(1)	64.66(4)	Ag(3)–Ag(2)–Ag(1)	67.14(2)
P(4)–Ag(3)–P(5)	128.82(5)	P(4)–Ag(3)–S(2)	117.67(5)
P(5)–Ag(3)–S(2)	95.62(5)	P(4)–Ag(3)–S(1)	110.37(6)
P(5)–Ag(3)–S(1)	99.91(6)	S(2)–Ag(3)–S(1)	99.67(5)
P(4)–Ag(3)–Ag(2)	91.75(4)	P(5)–Ag(3)–Ag(2)	138.82(4)
S(2)–Ag(3)–Ag(2)	52.64(4)	S(1)–Ag(3)–Ag(2)	66.39(5)
C(1)–S(1)–Ag(1)	111.3(3)	C(1)–S(1)–Ag(3)	132.0(2)
Ag(1)–S(1)–Ag(3)	83.05(5)	C(3)–S(2)–Ag(2)	103.1(2)
C(3)–S(2)–Ag(3)	97.5(3)	Ag(2)–S(2)–Ag(3)	71.56(4)
Ag(1)···S(2)–C(3)	168.1(3)	Ag(2)···S(1)–C(1)	81.5(3)
Ag(1)···S(2)–Ag(2)	67.51(4)	Ag(1)···S(2)–Ag(3)	72.88(4)
Ag(2)···S(1)–Ag(1)	67.44(5)	Ag(2)···S(1)–Ag(3)	61.48(4)

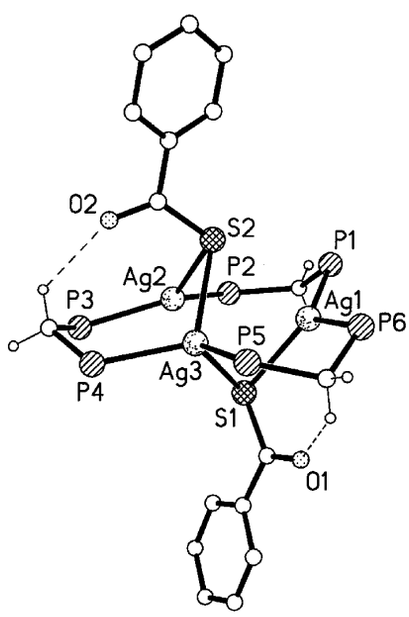

Fig. 6 Ball and stick diagram of the cation core in complex **4**. The phenyl rings are omitted for clarity.

Table 6 Selected bond lengths (Å) and angles (°) for compound **4**

Ag(1)–P(1)	2.463(2)	Ag(1)–P(6)	2.437(2)
Ag(2)–P(2)	2.497(2)	Ag(2)–P(3)	2.462(2)
Ag(3)–P(4)	2.496(2)	Ag(3)–P(5)	2.515(2)
Ag(1)–S(1)	2.541(2)	Ag(2)–S(2)	2.542(2)
Ag(3)–S(1)	2.730(2)	Ag(3)–S(2)	2.709(2)
P(1)–C(15)	1.858(9)	P(2)–C(15)	1.859(9)
P(3)–C(16)	1.840(8)	P(4)–C(16)	1.836(9)
P(5)–C(17)	1.843(8)	P(6)–C(17)	1.838(7)
C(1)–S(1)	1.772(9)	C(1)–O(1)	1.203(1)
C(8)–S(2)	1.739(1)	C(8)–O(2)	1.240(2)
Ag(1)···Ag(3)	3.079(1)	Ag(2)···Ag(3)	3.130(1)
Ag(1)···Ag(2)	3.754(1)	Ag(1)···S(2)	3.041(2)
Ag(2)···S(1)	3.062(2)		
P(6)–Ag(1)–P(1)	128.51(7)	P(6)–Ag(1)–S(1)	120.47(7)
P(1)–Ag(1)–S(1)	107.79(7)	P(6)–Ag(1)–Ag(3)	91.54(5)
P(1)–Ag(1)–Ag(3)	131.74(6)	S(1)–Ag(1)–Ag(3)	57.16(5)
P(3)–Ag(2)–P(2)	129.95(8)	P(3)–Ag(2)–S(2)	117.99(8)
P(2)–Ag(2)–S(2)	109.52(8)	P(3)–Ag(2)–Ag(3)	90.08(6)
P(2)–Ag(2)–Ag(3)	131.26(6)	S(2)–Ag(2)–Ag(3)	55.91(6)
P(4)–Ag(3)–P(5)	110.00(7)	P(4)–Ag(2)–S(2)	110.92(8)
P(5)–Ag(3)–S(2)	113.72(8)	P(4)–Ag(3)–S(1)	114.74(7)
P(5)–Ag(3)–S(1)	112.48(7)	S(2)–Ag(3)–S(1)	94.27(7)
P(4)–Ag(3)–Ag(1)	161.51(6)	P(5)–Ag(3)–Ag(1)	88.00(5)
S(2)–Ag(3)–Ag(1)	63.00(5)	S(1)–Ag(3)–Ag(1)	51.45(5)
P(4)–Ag(3)–Ag(2)	88.29(5)	P(5)–Ag(3)–Ag(2)	160.60(6)
S(2)–Ag(3)–Ag(2)	50.99(5)	S(1)–Ag(3)–Ag(2)	62.57(5)
S(1)–Ag(3)–Ag(2)	62.57(5)	Ag(1)–Ag(3)–Ag(2)	74.40(2)
C(1)–S(1)–Ag(1)	106.8(3)	C(1)–S(1)–Ag(3)	101.9(3)
Ag(1)–S(1)–Ag(3)	71.38(6)	C(8)–S(2)–Ag(3)	101.4(3)
Ag(2)–S(2)–Ag(3)	73.09(6)	Ag(1)···S(2)–C(8)	159.8(4)
Ag(2)···S(1)–C(1)	160.5(3)	Ag(1)···S(2)–Ag(2)	84.01(7)
Ag(1)···S(2)–Ag(3)	64.46(5)	Ag(2)···S(1)–Ag(1)	83.58(6)
Ag(2)···S(1)–Ag(3)	65.12(5)		

$(SC\{O\}R)][X]_2$, resulted in formation of trinuclear bicapped compounds. ^{31}P NMR studies show that the compounds retain their trinuclear core in solution. Hence it may be concluded that the trinuclear bicapped compounds are the most stable and their formation is favoured both in the solid-state and in solution. Owing to the presence of a soft sulfur donor and a hard oxygen donor in the thiocarboxylate ligand it is expected to form diverse bonding modes to various metal atoms similar to monothiocarbamates or monothioxanthates. The present study clearly illustrates the diversified bonding nature of the thiocarboxylate ligand. In the silver compounds the trinuclear core is held intact by two μ-*S* bridges. However a review of the existing literature suggests that strong triply bridging ligands (*e.g.* halides) are needed to form a trinuclear core with silver(I) ions. There are short Ag···Ag non-bonding distances, which could be attributed to either the bite angle of the dppm ligand or the argentophilicity.

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