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Synthesis and structural characterization of adducts of silver (I) diethyldithiocarbamate with P-donor ligands

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Abstract

Adducts of triorganophosphines PR₃, and diphosphines $R_2P(CH_2)_nPR_2$ with silver(I) diethyldithiocarbamate Ag(dtc) have been synthesized and characterized both in solution (¹H, ³¹P NMR) and in the solid state (IR, single-crystal X-ray structure analysis). The topology of the structures in the solid state was found to depend on the nature of the P-donor and on the Ag(dtc):P-donor stoichiometric ratio. In the mononuclear [(Ph₂MeP)₂Ag(dtc)] and [{(:CHPPh₂)₂}Ag(dtc)], four-coordinate P₂AgS₂ environments are found, as also in [(dtc)Ag(*P'*-dppm-*P'*)₂Ag(dtc)] where the two Ag(dtc) moieties are linked by the pair of bidentate, bridging, dppm ligands; by contrast the dppp adduct Ag(dtc):dpp (1:1) is an infinite one-dimensional polymer. In the other complexes [(R₃P)Ag(dtc)]₂ structurally defined, the silver environment is PAgS₃, two of the sulfur atoms drawn from the same dtc, now an unsymmetrical chelate, and one of the sulfur atoms bridged to the second silver atom.

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1. Introduction

Dithiocarbamate-containing coordination compounds have been extensively studied, being of interest because of the ability of dithiocarbamates to coordinate different metals in different bonding modes [1]. Copper and silver in wastewater have been simultaneously determined with diethyldithiocarbamates ('dtc') [2]. The Ag-diethyldithiocarbamate method is also commonly used in environmental monitoring and is very effective in the determination of arsenic in water [3], so that a correct knowledge of the coordinating behaviour of silver(I) diethyldithiocarbamates could be useful in the determination and speciation of pollutants derived from group 15 elements. However, with exception of a limited number of papers describing the interaction between triphenylphosphine [4], diferrocenylphenylphosphine [5], and 1,2-bis(diphenylphosphino)ethane [6], and silver(I) dithiocarbamates, the literature is very restricted in defining the spectroscopic and structural features of species derived from the interaction of silver(I) dithiocarbamate salts with mono- or bi-dentate phosphine ligands. For this reason we have decided to systematically investigate the interaction between Ag(diethyldithiocarbamate) and PR₃ (R₃ = Ph₃, Bn₃, MePh₂, *o*-, *m*- and *p*-tolyl₃) or R₂P–X–PR₂ (R = Ph, X = CH₂, C₂H₄, C₃H₆ or C₄H₈ or HC = CH; R = cy, X = CH₂) systems, recording the results hereunder.

2. Experimental

2.1. Materials and methods

All reactions were carried out under an atmosphere of dry oxygen-free dinitrogen, using standard Schlenk tech-

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niques, and protected from light. Solvents were used as supplied or distilled using standard methods. All chemicals were purchased from Aldrich (Milwaukee) and used as received. Elemental analyses (C, H, N, S) were performed with a Fisons Instruments 1108 CHNS-O elemental analyzer. IR spectra were recorded from 4000 to 100 cm⁻¹ with a Perkin–Elmer System 2000 FT-IR instrument. ¹H and ³¹P NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ¹H, and 121.4 MHz for ³¹P). Proton chemical shifts are reported in parts per million versus Me₄Si, while phosphorus chemical shifts are reported in parts per million vs 85% H₃PO₄. The electrical conductances of the CH₂Cl₂ solutions were measured with a Crison CDTM 522 conductimeter at room temperature.

2.2. Syntheses

2.2.1. Synthesis of $[Ag(dtc)(PPh_3)]$ (1)

Silver(I) diethyldithiocarbamate (Ag(dtc)) (0.254 g, 1 mmol) was added to an ethanol solution (30 mL) of PPh₃ (0.262 g, 1 mmol) at 25 °C. After the addition, the solution was stirred during 24 h at room temperature. The colorless precipitate formed was filtered off and washed with ethanol (3×5 mL). Recrystallization from ethanol gave complex 1 as a microcrystalline solid in 80% yield. M.p.: 162–165 °C. IR data (Nujol, cm⁻¹): 3040sh (CH), 995m, 988m, 974m (CS), 518s, 501s, 428 (PPh₃), 396w, 363w, 345w, 317w, 278w, 226w. ¹H NMR (CDCl₃, 293 K): 1.32 (t, 6H, CH_{3dtc}), 4.00 (q, 4H, CH_{2dtc}), 7.2–7.5 (m, 15H, CH_{Ph}). ³¹P{¹H} NMR (CDCl₃, 293 K): δ 12.5. A_{mol} (CH₂Cl₂, conc. = 1.00×10^{-3} M): 0.1 Ω^{-1} cm² mol⁻¹. *Anal.* Calc. for C₂₃H₂₅AgNPS₂: C, 53.29; H, 4.86; N, 2.70; S, 12.37. Found: C, 53.08; H, 4.72; N, 2.35, S, 12.45%.

2.2.2. Synthesis of $[Ag(dtc)(P-p-tolyl_3)]$ (2)

Silver(I) diethyldithiocarbamate (Ag(dtc)) (0.254 g, 1 mmol) was added to an ethanol solution (30 mL) of *p*tolyl₃P (0.304 g, 1 mmol) at 25 °C. After the addition, the solution was stirred during 24 h at room temperature. The colorless precipitate formed was filtered off and washed with ethanol (3×5 mL). Recrystallization from ethanol gave complex **2** as a microcrystalline solid in 80% yield. M.p.: 154–157 °C. IR data (Nujol, cm⁻¹): 3060br, 985 (CS), 552m, 545m, 459s, 449m, 430w, 382w, 357w, 316w. ¹H NMR (CDCl₃, 293 K): 1.30 (t, 6H, CH_{3dtc}), 2.29 (s, 9H, CH_{3tol}), 3.97 (q, 4H, CH_{2dtc}), 7.2–7.5 (m, 12H, CH_{tol}). ³¹P{¹H} NMR (CDCl₃, 293 K): δ 14.8. A_{mol} (CH₂Cl₂, conc. = 1.00×10^{-3} M): 0.1 Ω^{-1} cm² mol⁻¹. *Anal.* Calc. for C₂₆H₃₁AgNPS₂: C, 55.71; H, 5.57; N, 2.50; S, 11.44. Found: C, 55.51; H, 5.42; N, 2.43; S, 11.41%.

2.2.3. Synthesis of $[Ag(dtc)(P-m-tolyl_3)]$ (3)

Silver(I) diethyldithiocarbamate (Ag(dtc)) (0.160 g, 0.62 mmol) was added to an ethanol solution (30 mL) of m-tolyl₃P (0.30 g, 1 mmol) at 25 °C. After the addition, the solution was stirred for 24 h at room temperature. A

colorless precipitate was formed which was filtered off and washed with ethanol (3 × 5 mL). Recrystallization from ethanol gave complex **3** as a microcrystalline solid in 63% yield. M.p.: 158–159 °C. IR data (Nujol, cm⁻¹): 1461w, 1413s, 1373m, 1304ss, 1260m, 1204m, 1168s, 1132s, 1104s, 1071s, 983m, 907s, 835s, 778m, 726s, 694m, 565m, 545, 5353s, 458m, 448m, 430s, 382m, 358s, 316m, 279s, 246s, 228s. ¹H NMR (CDCl₃, 293 K): 1.32 (t, 6H, CH_{3dtc}), 2.31 (s, 9H, CH_{3tol}), 4.0 (q, 4H, CH_{2dtc}), 7.1–7.5 (m, 12H, CH_{tol}). ³¹P{¹H} NMR (CDCl₃, 293 K): δ 14.8. {¹H} NMR (CDCl₃, 223 K): δ 13.6 d br (¹*J*(Ag⁻³¹P): 570 Hz). *A*_{mol} (CH₂Cl₂, conc. = 1.00×10^{-3} M): 0.2 Ω⁻¹ cm² mol⁻¹. *Anal.* Calc. for C₂₆H₃₁AgNPS₂: C, 55.71; H, 5.57; N, 2.50; S, 11.44. Found: C, 55.45; H, 5.37; N, 2.23; S, 11.14%.

2.2.4. Synthesis of $[Ag(dtc)(P-o-tolyl_3)]$ (4)

Silver(I) diethyldithiocarbamate Ag(dtc) (0.254 g, 1 mmol) was added to an ethanol solution (30 mL) of o-tolyl₃P (0.304 g, 1 mmol). After the addition, the solution was stirred for 24 h at room temperature. A colorless precipitate was formed which was filtered off and washed with ethanol $(3 \times 5 \text{ mL})$. Re-crystallization from ethanol gave complex 4 as a microcrystalline solid in 72% yield. M.p.: 161–163 °C. IR data (Nujol, cm⁻¹): 3060br (CH), 1585w, 1486s (CC), 976 (CS), 679w, 665w, 606w, 558s, 514m, 456s, 429m, 399m, 392m, 359w, 325w, 260w, 228w. ¹H NMR (CDCl₃, 293 K): 1.32 (t, 6H, CH_{3dtc}), 2.44 (s, 9H, CH_{3tol}), 3.99 (q, 4H, CH_{2dtc}), 6.75 (m, 3H, C-6 CH_{tol}), 7.09 (m, 3H, CH_{tol}), 7.25–7.30 (m, 6H, CH_{tol}). ³¹P{¹H} NMR (CDCl₃, 293 K): δ -24.6 (s, br).³¹P{¹H} NMR (CDCl₃, 223 K): δ -12.5 (d br, ${}^{1}J({}^{31}P,Ag) = 582$ Hz), -28.1 (s br). Λ_{mol} (CH₂Cl₂, conc. = 1.00×10^{-3} M): $0.2 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1}$. Anal. Calc. for $C_{26}H_{31}AgNPS_2$: C, 55.71; H, 5.57; N, 2.50; S, 11.44. Found: C, 55.46; H, 5.63; N, 2.48; S, 11.22%.

2.2.5. Synthesis of $[Ag(dtc)(PBn_3)]$ (5)

Silver(I) diethyldithiocarbamate (Ag(dtc)) (0.110 g, 0.43 mmol) was added to an ethanol solution (30 mL) of Bn_3P (0.25 g, 0.82 mmol). After the addition, the solution was stirred for 24 h at room temperature. A colorless precipitate was formed which was filtered off and washed with ethanol (3 × 5 mL). Recrystallization from ethanol gave complex **5** as a microcrystalline solid in 52% yield. M.p.: 159–160 °C. IR data (Nujol, cm⁻¹): 1458w, 1411s, 1377m, 1357s, 1303s, 1263w, 1206m, 1168s, 1135s, 1108m, 1067s, 983m, 909s, 841s, 781m, 720s, 693m, 565s, 552m, 546m, 535s, 512s, 459w, 449w, 316s, 280m, 253s. ¹H NMR (CDCl₃, 293 K): 1.33 (t, 6H, CH_{2Bn}), 7.2–7.4 (m, 15H, CH_{Bn}). A_{mol} (CH₂Cl₂, conc. = 1.00×10^{-3} M): $0.2 \Omega^{-1}$ cm² mol⁻¹. *Anal.* Calc. for C₂₆H₃₁AgNPS₂: C, 55.71; H, 5.57; N, 2.50; S, 11.44. Found: C, 55.43; H, 5.58; N, 2.43; S, 11.38%.

2.2.6. Synthesis of $[Ag(dtc)(PMePh_2)]$ (6)

Silver(I) diethyldithiocarbamate (Ag(dtc)) (0.254 g, 1 mmol) was added to an ethanol solution (30 mL) of

MePh₂P (0.200 g, 1 mmol). After the addition, the solution was stirred for 24 h at room temperature. A colorless precipitate was formed which was filtered off and washed with ethanol $(3 \times 5 \text{ mL})$. Recrystallization from ethanol gave complex **6** as a microcrystalline solid in 81% yield. M.p.: 106–108 °C. IR data (Nujol, cm^{-1}): 3060br (CH), 1481s (CC), 985 (CS), 694s, 617w, 604w, 595w, 562m, 508s, 477w, 465m, 430m, 417w, 393w, 361w, 347w, 321w. ¹H NMR (CDCl₃, 293 K): 1.32 (t, 6H, CH_{3dtc}), 1.94 (d, 3H, CH_{3PMePh₂}), 3.97 (q, 4H, CH_{2dtc}), 7.38–7.62 (m, 10H, CH_{PMePh_2}). ³¹P{¹H} NMR (CDCl₃, 293 K): δ -5.5 (s).³¹P{¹H} NMR (CDCl₃, 223 K): δ -5.9 (s br). Λ_{mol} conc. = 1.00×10^{-3} M): $0.2 \Omega^{-1}$ cm² mol⁻¹. (CH₂Cl₂, Anal. Calc. for C18H23AgNPS2: C, 47.38; H, 5.08; N, 3.07; S, 14.05. Found: C, 46.98; H, 5.30; N, 3.36; S, 14.25%.

2.2.7. Synthesis of $[Ag(dtc)(PMePh_2)_2]$ (7)

Silver(I) diethyldithiocarbamate (Ag(dtc)) (0.254 g, 1 mmol) was added to an ethanol solution (30 mL) of MePh₂P (0.500 g, 2.5 mmol). After the addition, the solution was stirred for 24 h at room temperature. A colorless precipitate was formed which was filtered off and washed with ethanol $(3 \times 5 \text{ mL})$. Recrystallization from ethanol gave complex 7 as a microcrystalline solid in 87% yield. M.p.: 119-122 °C. IR data (Nujol, cm⁻¹): 3060br (CH), 1481s (CC), 985 (CS), 694s, 616w, 605w, 564w, 506s, 477m, 466m, 432m, 412w, 395w, 545w. ¹H NMR (CDCl₃, 293 K): 1.24 (t, 6H, CH_{3dtc}), 1.74 (d, 6H, CH_{3PMePh_2}), 3.93 (q, 4H, CH_{2dtc}), 7.22–7.50 (m, 20H, CH_{PMePh_2}). ³¹P{¹H} NMR (CDCl₃, 293 K): δ -12.8 (s br). ³¹P{¹H} NMR (CDCl₃, 223 K): δ -11.6 (s br). Λ_{mol} (CH₂Cl₂, conc. $= 1.00 \times 10^{-3}$ M): $0.3 \Omega^{-1}$ cm² mol⁻¹. Anal. Calc. for C₃₁H₃₆AgNP₂S₂: C, 56.71; H, 5.53; N, 2.13; S, 9.77. Found: C, 56.45; H, 5.82; N, 2.27; S, 10.02%.

2.2.8. Synthesis of [Ag(dtc)(dppm)] (8)

Silver(I) diethyldithiocarbamate (Ag(dtc)) (0.254 g, 1 mmol) was added to an ethanol solution (30 mL) of dppm (0.384 g, 1 mmol). After the addition, the solution was stirred for 24 h at room temperature. A colorless precipitate formed which was filtered off and washed with ethanol $(3 \times 5 \text{ mL})$. Recrystallization from ethanol gave complex 8 as a microcrystalline solid in 80% yield. M.p.: 95–98 °C dec. IR data (Nujol, cm⁻¹): 3060w (CH), 997w, 987m (CS), 5151s, 505s, 471s, 444w, 430w, 409w, 385w, 351w, 279w, 248w. ¹H NMR (CDCl₃, 293 K): 1.21 (t, 6H, CH_{3dtc}), 3.10 (br, 2H, CH_{2dppm}), 3.92 (q, 4H, CH_{2dtc}), 7.1–7.5 (m, 20H, CH_{2dppm}). ³¹P{¹H} NMR (CDCl₃, 293 K): δ -7.9 br. ³¹P{¹H} NMR (CDCl₃, 223 K): δ -5.1 (br, ${}^{1}J(\text{Ag}-{}^{31}\text{P})$: 259 Hz). Λ_{mol} (CH₂Cl₂, conc. = 1.03×10^{-3} M): $1.3 \Omega^{-1}$ cm² mol⁻¹. Anal. Calc. for C₃₀H₃₂AgNP₂S₂: C, 56.25; H, 5.04; N, 2.19; S, 10.01. Found: C, 55.98; H, 5.02; N, 2.13; S, 9.85%.

2.2.9. Synthesis of [Ag(dtc)(dppe)] (9)

Silver(I) diethyldithiocarbamate (Ag(dtc)) (0.254 g, 1 mmol) was added to an ethanol solution (30 mL) of

dppe (0.400 g, 1 mmol). After the addition, the solution was stirred for 24 h at room temperature. A colorless precipitate was formed which was filtered off and washed with ethanol (3×5 mL). Recrystallization from ethanol gave complex **9** as a microcrystalline solid in 82% yield. M.p.: 238–241 °C. IR data (Nujol, cm⁻¹): 1468w, 1455m, 1431m, 1404m, 1374m, 1354s, 1301s, 1261m, 1207m, 1131m, 1094s, 1064s, 1024s, 984s, 907m, 837m, 777s, 747m, 723m, 693m, 563s, 511m, 476m, 417s, 347s, 280s, 246s, 227. ¹H NMR (CDCl₃, 293 K): 1.35 (t, 6H, CH_{3dtc}), 2.36 (m, 4H, CH_{2dppe}), 4.06 (q, 4H, CH_{2dtc}), 7.3–7.7 (m, 20H, CH_{2dppe}). ³¹P{¹H} NMR (CDCl₃, 293 K): δ –1.5br. A_{mol} (CH₂Cl₂, conc. = 1.03 × 10⁻³ M): 0.6 Ω⁻¹ cm² mol⁻¹. Anal. Calc. for C₃₁H₃₄AgNP₂S₂: C, 56.88; H, 5.24; N, 2.14; S, 9.80. Found: C, 57.12; H, 5.11; N, 2.15; S, 9.63%.

2.2.10. Synthesis of [Ag(dtc)(dppp)] (10)

Silver(I) diethyldithiocarbamate (Ag(dtc)) (0.254 g, 1 mmol) was added to an ethanol solution (30 mL) of dppp (0.412 g, 1 mmol). After the addition, the solution was stirred for 24 h at room temperature. The colorless precipitate formed was filtered off and washed with ethanol (3×5 mL). Recrystallization from ethanol gave complex **10** as a microcrystalline solid in 50% yield. M.p.: 163–164 °C. IR data (Nujol, cm⁻¹): 992w (CS), 518m, 509s, 496m, 473m, 432m, 385w, 321w, 296w, 24w. ¹H NMR (CDCl₃, 293 K): 1.30 (t, 6H, CH_{3dtc}), 1.78m, 2.30s (6H, CH_{2dppp}), 4.01 (q, 4H, CH_{2dtc}), 7.1–7.5 (m, 20H, CH_{2dppm}). ³¹P{¹H} NMR (CDCl₃, 293 K): δ –3.1s. ³¹P{¹H} NMR (CDCl₃, 223 K): δ –3.6 (dd, ¹J(¹⁰⁷Ag-³¹P): 346 Hz; dd, ¹J(¹⁰⁹Ag-³¹P): 398 Hz). A_{mol} (CH₂Cl₂, conc. = 1.03×10^{-3} M): $0.4 \Omega^{-1}$ cm² mol⁻¹. *Anal.* Calc. for C₃₂H₃₆AgNP₂S₂: C, 57.49; H, 5.43; N, 2.09; S, 9.59. Found: C, 57.30; H, 5.71; N, 2.13; S, 9.41%.

2.2.11. Synthesis of [Ag(dtc)(dppb)] (11)

Silver(I) diethyldithiocarbamate (Ag(dtc)) (0.254 g, 1 mmol) was added to an ethanol solution (30 mL) of dppb (0.425 g, 1 mmol). After the addition, the solution was stirred during 24 h at room temperature. A colorless precipitate was formed which was filtered off and washed with ethanol $(3 \times 5 \text{ mL})$. Recrystallization from ethanol gave complex 11 as a microcrystalline solid in 92% yield. M.p. > 200 °C. IR data (Nujol, cm⁻¹): 3060sh, 1569w, 1558w, 1420s, 1406m, 1352m, 992w, 617w, 599w, 570w, 518m, 508s, 488s, 455w, 440w, 414w, 398w, 364w, 315w, 301w, 279w, 247w. ¹H NMR (CDCl₃, 293 K): 1.29 (t, 6H, CH3dtc), 1.60 br, 2.05 br (8H, CH2dppb), 4.01 (q, 4H, CH_{2dtc}), 7.2–7.5 (m, 20H, CH_{2dppb}). ³¹P{¹H} NMR (CDCl₃, 293 K): δ -2.2br. ³¹P{^TH} NMR (CDCl₃, 293 K): $\delta -2.6$ (dd, ${}^{1}J({}^{109}\text{Ag}{-}^{31}\text{P})$: 396 Hz; ${}^{1}J({}^{107}\text{Ag}{-}^{31}\text{P})$: 346 Hz). Λ_{mol} (CH₂Cl₂, conc. = 1.03×10^{-3} M): 0.4 Ω^{-1} cm² mol⁻¹. Anal. Calc. for C₃₃H₃₈AgNP₂S₂: C, 58.07; H, 5.61; N, 2.05; S, 9.39. Found: C, 58.02; H, 5.68; N, 2.00; S, 9.53%.

2.2.12. Synthesis of [Ag(dtc)(dcpm)] (12)

Silver(I) diethyldithiocarbamate (Ag(dtc)) (0.254 g, 1 mmol) was added to an ethanol solution (30 mL) of dcpm (0.408 g, 1 mmol). After the addition, the solution was stirred for 24 h at room temperature. A colorless precipitate was formed which was filtered off and washed with ethanol (3×5 mL). Recrystallization from ethanol gave complex **12** as a microcrystalline solid in 42% yield. M.p.: 167–168 °C. IR data (Nujol, cm⁻¹): 1459m, 1376m, 1256s, 685m, 669m, 419s, 398s, 352s, 328s, 305s, 248m. ¹H NMR (CDCl₃, 293 K): 1.27 (t, 6H, CH_{2dcpm}), 4.01 (q, 4H, CH_{2dtc}). A_{mol} (CH₂Cl₂, conc. = 1.03×10^{-3} M): 0.4 Ω^{-1} cm² mol⁻¹. Anal. Calc. for C₃₀H₅₆AgNP₂S₂: C, 54.21; H, 8.49; N, 2.11; S, 9.65. Found: C, 54.11; H, 8.71; N, 2.03; S, 9.37%.

2.2.13. Synthesis of [Ag(dtc)(dppet)] (13)

Silver(I) diethyldithiocarbamate (Ag(dtc)) (0.254 g, 1 mmol) was added to an ethanol solution (30 mL) of dppet (0.397 g, 1 mmol). After the addition, the solution was stirred for 24 h at room temperature. A colorless precipitate was formed which was filtered off and washed with ethanol (3 × 5 mL). Recrystallization from ethanol gave complex **13** as a microcrystalline solid in 47% yield. M.p.: 156–167 °C. IR data (Nujol, cm⁻¹): 1461w, 1434m, 1413s, 1376m, 1352s, 1296s, 1260m, 1205s, 1137m, 1089s, 1071s, 996s, 980m, 906s, 840s, 816m, 749m, 737m, 644s, 600s, 566m, 548s, 521m, 504w, 455w, 443m, 424m, 396m, 321m, 303s, 279m, 255s, 247s. ¹H NMR (CDCl₃, 293 K): 1.34 (t, 6H, CH_{3dtc}), 4.01 (q, 4H, CH_{2dtc}), 7.2–7.6 (m, 22H, CH_{dppet}). ³¹P{¹H} NMR (CDCl₃, 293 K): δ 11.5br, 22.0s. A_{mol} (CH₂Cl₂, conc. = 1.03 × 10⁻³ M): 0.5 Ω^{-1} cm² mol⁻¹.



Table 1
Crystal/refinement data

L	PPh ₃	P(m-tol) ₃	PMePh ₂	PMePh ₂	$CH_2(PPh_2)_2$	CH ₂ (CH ₂ PPh ₂) ₂	(HCPPh ₂) ₂
Cpd	$[LAg(dtc)]_2(1)$	$[LAg(dtc)]_2$ (3)	$[LAg(dtc)]_{(\infty \infty)}$ (6)	$[L_2Ag(dtc)](7)$	$[{(L/2)_2(Ag(dtc))_2)](8)$	$[(L/2)_2(Ag(dtc)]_{(\infty \infty)})$ (10)	LAg(dtc) (13)
Formula	$C_{46}H_{50}Ag_2N_2P_2S_4$	$C_{52}H_{62}Ag_2N_2P_2S_4$	C ₁₈ H ₂₃ AgNPS ₂	C31H36AgNP2S2	$C_{60}H_{64}Ag_2N_2P_4S_4$	C ₃₂ H ₃₆ AgNP ₂ S ₂	C ₃₁ H ₃₂ AgNP ₂ S ₂
$M_{\rm r}$ (dalton)	1036.9	1121.0	456.4	656.6	1281.1	668.6	652.6
Crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P1 (#2)	$P\overline{1}$ (#2)	$P2_1/n$ (#14)	$P2_1/c$ (#14)	$C2_1/c$ (#15)	$P2_1/c$ (#14)	$P2_1/n$ (#14)
a (Å)	10.410(1)	10.373(1)	13.041(1)	10.2830(8)	24.022(6)	14.880(2)	9.9615(9)
b (Å)	10.641(1)	11.441(1)	7.4238(6)	30.099(2)	10.234(2)	12.035(2)	17.923(2)
<i>c</i> (Å)	10.867(1)	12.275(2)	19.892(2)	10.8760(8)	27.114(4)	18.025(2)	16.932(2)
α (°)	92.523(3)	71.407(2)					
β (°)	93.573(3)	68.949(2)	93.237(2)	115.990(2)	118.37(2)	101.09(1)	95.235(2)
γ (°)	109.409(3)	84.512(2)					
$V(\text{\AA}^3)$	1130	1288	1923	3026	5865	3168	3010
Z (f.u.)	1 (dimer)	1 (dimer)	4	4	4 (dimers)	4	4
$D_c ({ m g}{ m cm}^{-3})$	1.52 ₃	1.445	1.576	1.441	1.451	1.402	1.440
$\mu_{\rm Mo}~({\rm mm}^{-1})$	1.16	1.02	1.35	0.93	0.96	0.89	0.94
Specimen (mm)	$0.16\times0.15\times0.06$	$0.38 \times 0.24 \times 0.14$	$0.48 \times 0.07 \times 0.06$	$0.29 \times 0.06 \times 0.04$	$0.90 \times 0.38 \times 0.28$	$0.46 \times 0.23 \times 0.10$	$0.18 \times 0.18 \times 0.13$
$T_{\min/\max}$	0.89	0.80	0.84	0.89	0.89	0.85	0.91
$2\theta_{\max}$ (°)	75	58	75	60	55	50	75
$N_{\rm t}$	23266	15018	39725	55918	13114	7566	62882
$N(R_{\rm int})$	11535 (0.020)	6306 (0.017)	10082 (0.033)	8675 (0.049)	6718 (0.034)	5577 (0.023)	15823 (0.032)
No	10050	5610	7925	6784	5154	3682	11 548
R	0.029	0.025	0.034	0.037	0.044	0.047	0.030
$R_{\rm w}$	0.038	0.033	0.041	0.048	0.056	0.053	0.031
$T(\mathbf{K})$	ca. 153	ca. 153	ca. 153	ca. 153	ca. 295	ca. 295	ca. 153
$ \Delta \rho_{\rm max} $ (e Å ⁻³)	1.40(5)	0.91(4)	1.61(7)	0.76(5)	0.88(4)	0.65(8)	0.78(8)

Anal. Calc. for $C_{31}H_{32}AgNP_2S_2$: C, 57.06; H, 4.94; N, 2.15; S, 9.83. Found: C, 56.95; H, 5.01; N, 2.23; S, 9.65%.

2.3. Structure determinations

Full spheres of 'low'-temperature CCD area detector diffractometer data were measured (Bruker AXS instrument, ω -scans; monochromatic Mo K α radiation, $\lambda = 0.7107_3$ Å; T ca. 153 K) yielding $N_{t(otal)}$ reflections, these merging to N unique (R_{int} cited) after 'empirical'/ multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being considered 'observed' and used



Fig. 1. Single molecules of (a) $[(MePh_2P)_2Ag(S_2CNEt_2)]$ (7) projected normal to the AgP₂ plane and (b) $[\{(:CHPPh_2)_2\}Ag(S_2CNEt_2)]$ (13) projected normal to the AgS₂ plane.

in the full matrix least squares refinements, refining anisotropic displacement parameter forms for the nonhydrogen atoms, $(x, y, z, U_{iso})_{H}$ being constrained at estimated values. Conventional residuals R, R_w (weights: $(\sigma^2(F) + 0.0004F^2)^{-1})$ on |F| are cited at convergence. Neutral atom complex scattering factors were employed within the XTAL 3.7 program system [7]. Results are given below and in the Tables and Figures, the latter showing 50% probability amplitude displacement ellipsoids for the nonhydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

Variata. $[(Ph_2MeP)_2Ag(dtc)](7)$. One of the ethyl groups of the dtc ligand was modelled as disordered over two sets of sites, occupancies refining to 0.642(9) and complement.

 $[CH_2((CH_2)PPh_2)_2Ag(dtc)]_{2,(\infty|\infty)}$ (8, 10). Data sets were measured using a single counter instrument $(2\theta/\theta \text{ scan} \text{ mode})$ at ca. 295 K, a hemisphere for the $CH_2(PPh_2)_2$ adduct, (8) and a second quadrant to $2\theta_{\text{max}}$ 40° for the $CH_2(CH_2PPh_2)_2$ adduct (10). Gaussian absorption corrections were applied.

 $[(m-tol_3P)Ag(dtc)]_2$ (3), and $[(Ph_2PCH=CHPPh_2)-Ag(dtc)]$ (13), $(x, y, z, U_{iso})_H$ were refined.

3. Discussion

From the interaction of 1 equivalent of Ag(dtc) with 1 equivalent of tertiary monophosphine: Ph_3P , $(o-tolyl)_3P$, $(m-tolyl)_3P$, $(p-tolyl)_3P$, Bn_3P or $MePh_2P$ in ethanol at room temperature, complexes **1–6** have been respectively obtained in high yield (Chart 1).

The 1:2 adduct 7 was obtained when the reaction was conducted in excess of the P-donor (>2 equivalents). However, when a large excess of o-tolyl₃P or Bn₃P was employed, the 1:1 adducts were always recovered.



Fig. 2. The dimer of $[(Ph_2PCH_2PPh_2)Ag(S_2CNEt_2)]_2$ (8) projected oblique to the centrosymmetric macrocycle, showing the conformation of the latter.



Fig. 3. A single strand of [(Ph₂P(CH₂)₃PPh₂)Ag(S₂CNEt₂)]_∞ (10), b horizontal in the page.

All derivatives 1–7 show good solubility in chlorinated solvents, acetonitrile, acetone, and dimethyl sulfoxide (DMSO), but are insoluble in diethyl ether, alcohols, aliphatic and aromatic hydrocarbons. They are non-electrolytes in CH₂Cl₂ solution, the Λ_{mol} values being always lower than 2 Ω^{-1} cm² mol⁻¹.

Similarly the chelating P_2 -donors interact with Ag(dtc) to always yield the 1:1 adducts 8–13 (Chart 1).

The infrared spectra of derivatives 1-13 (see Section 2) are consistent with the formulations proposed, showing all of the bands required by the presence of the diet-hyldithiocarbamate group and of the phosphorus donor [8,9], the phosphine ligand absorptions being only slightly shifted with respect to those of the free donors. In the far-IR spectra of all derivatives 1-13 we assigned, on the basis of a previous report on phosphino silver(I) derivatives

Table 2 Comparative P_2AgS_2 core geometries $[(R_3P)_2Ag(S_2CNR'_2)]$

$\frac{1}{(R_3P)_2/R_2'}$	$(Ph_2MeP)_2/Et_2^a$ (7)	$[(\text{HCPPh}_2)_2]/\text{Et}_2^{\text{a}}$ (13)	$[CH_2(CH_2PPh_2)_2]/Et_2^{a}$ (10)	$[CH_2(PPh_2)_2]/Et_2^{a,b}$ (8)	$(Ph_3P)_2/(CH_2)_4^{\ c}$	Fc ₂ PhP/Et ₂ ^d
Distances (Å)						
Ag–P	2.4525(7)	2.5008(4)	2.445(2)	2.406(8)	2.4647(8)	2.500(2)
C	2.3980(9)	2.4735(4)	2.477(1)	2.458(1)	2.4756(8)	2.528(2)
Ag–S	2.6505(8)	2.6047(4)	2.656(2)	2.650(7)	2.5689(9)	2.605(2)
-	2.6449(8)	2.5652(4)	2.621(2)	2.676(2)	2.7082(11)	2.739(2)
S–C	1.716(3)	1.726(1)	1.724(6)	1.716(5)	1.695(4)	1.733(8)
	1.717(3)	1.736(1)	1.682(6)	1.711(6)	1.701(4)	1.721(8)
S(1)S(2)	2.9611(9)	2.9710(5)	2.953(3)	2.966(3)	2.959(2)	2.967(4)
Angles (°)						
P–Ag–P	132.84(3)	86.13(1)	116.16(5)	137.58(9)	124.43(3)	115.95(7)
S-Ag-S	68.00(2)	70.15(1)	68.05(5)	67.69(6)	68.15(4)	67.40(6)
P-Ag-S	106.35(3)	117.60(1)	104.38(5)	90.52(8)	107.23(3)	103.06(7)
-	-127.92(3)	-132.92(1)	-129.54(4)	-128.19(5)	-117.85(3)	-131.73(7)
Ag–S–C	86.3(1)	85.24(4)	85.3(2)	86.1(2)	83.1(1)	89.1(3)
	86.5(1)	86.29(4)	87.0(2)	85.4(2)	87.5(1)	85.0(3)
S-C-S	119.2(2)	118.25(7)	119.6(3)	119.9(3)	121.2(2)	118.4(4)
Interplanar dih	edral angles (°)					
P_2Ag/S_2CNC_2	76.68(4)	87.02(8)	45.4(1)	38.6(1)	88.29(4)	66.10(8)
Silver deviation	(\mathring{A}) from S_2CNC_2 pla	ane				
δAg	0.036(3)	0.076(5)	0.140(4)	0.568(5)	0.165(3)	0.082(5)

^a This work.

^b Ag...Ag' is 4.027(1)Å.

^c Ref. [4].

^d Ref. [5].

[10], the broad absorptions near 500 cm^{-1} and those at $400-450 \text{ cm}^{-1}$ to Whiffen's y and t vibrations, respectively.

The ³¹P NMR spectra at room temperature of complexes 6 and 7 consist of broad singlets, presumably due to rapid exchange equilibria, also unresolved in the spectra recorded at 218 K. By contrast for derivatives 4 and 5, for which, at room temperature, only broad singlets were observed, exchange is quenched at lower temperature, and one and/or two unresolved doublets or resolved pairs of doublets, arising from coupling between the phosphorus and silver atoms, are observed in the accessible temperature range. In particular, in the spectra of derivative 4, typical pairs of doublets, due to ${}^{1}J({}^{31}P-{}^{107}Ag)$ and ${}^{1}J({}^{31}P-{}^{109}Ag)$ coupling, are resolved at 218 K and the observed ${}^{1}J({}^{107}\text{Ag})/{}^{1}J({}^{109}\text{Ag})$ ratio is in good agreement with that calculated from the gyromagnetic ratio of the Ag nuclei $\gamma(^{107}\text{Ag})/\gamma(^{109}\text{Ag})$ [11]. The signal due to each free phosphine ligand is upfield with respect to the corresponding silver(I) complex. The magnitudes of $\Delta (\Delta = \delta^{31} P_{complex})$ $-\delta^{31}P_{\text{free phosphine}}$) that decrease with the decreasing basicity and correlate with steric bulk of the ligands strongly support also P-coordination in solution.

The chemical shifts of the CH_2 and CH_3 protons of the dtc groups do not change noticeably on changing the P-donor and show very little change in the concentration

Table 3 Comparative PAgS_3 core geometries $[(R_3P)_2Ag(dtc)]_{2,(\infty|\infty)}$

PR ₃ (Cpd)	PPh ₃ (1)	$P(m-tolyl)_2$ (3)	$PMePh_2$ (6)
Distances (Å)			
Ag–P	2.4125(4)	2.4034(5)	2.4097(4)
Ag-S(1)	2.7608(4)	2.6516(6)	2.7536(5)
Ag-S(2)	2.5940(4)	2.6540(5)	2.5704(4)
Ag-S(1')	2.5471(4)	2.6120(6)	2.5687(4)
AgAg	3.0312(3)	3.2558(3)	4.3410(3)
S(1)S(1')	4.3625(6)	4.1361(9)	
S(1)–C	1.740(2)	1.740(1)	1.739(1)
S(2)–C	1.709(1)	1.717(2)	1.725(2)
S(1)S(2)	2.9885(6)	2.9833(6)	2.9856(6)
Angles (°)			
P-Ag-S(1)	117.60(1)	123.37(2)	111.46(1)
P-Ag-S(2)	115.64(2)	126.68(2)	136.20(1)
P-Ag-S(1')	120.31(1)	119.26(2)	115.10(1)
S(1)-Ag-S(2)	67.77(1)	68.43(2)	68.12(1)
S(1)-Ag-S(1')	110.48(1)	103.58(2)	116.30(1)
S(2)-Ag-S(1')	113.84(1)	103.94(2)	101.76(1)
Ag-S(1)-C	82.67(5)	85.97(2)	83.25(5)
Ag-S(2)-C	88.55(5)	86.34(6)	89.33(5)
Ag'-S(1)-C	109.30(4)	98.91(7)	106.18(5)
Ag'-S(1)-Ag	69.52(1)	76.42(2)	109.25(1)
S(1)-C-S(2)	120.11(7)	119.3(1)	119.06(8)
Interplanar dihedi	ral angles (S_2CNC)	$_2/Ag_2S_2) (\theta^\circ)$	
θ	63.63(4)	79.45(4)	
Ag-P-C(n1)-C(n1)	n2/6) (ortho) torsi	on angles (°)	
n = 1	52.6(1)	27.8(2)	-71.1(2)
2	28.0(2)	31.6(2)	-21.8(2)
3	38.6(1)	62.8(2)	

Primed atoms are related by the inversion centre or 21 screw.

ranges 2.0×10^{-4} - 1.0×10^{-2} molar, suggesting a strong coordination of dtc to occur also in solution [12].

The results of the single crystal X-ray structure determinations (Table 1) are consistent with the formulations given above: in all cases, one mononuclear formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure, although in a number of cases the structural unit is of higher nuclearity. In all cases the silver atom is four-coordinate. In the four cases, where the silver environments are four-coordinate P₂AgS₂, the diethyldithiocarbamate ligand ('dtc') behaves as a simple quasi-symmetrical chelate. In $[(Ph_2MeP)_2Ag(dtc)]$ (7) and [{(:CHPPh₂)₂}Ag(dtc)] (13) (Fig. 1), discrete mononuclear complexes are found, similar to the arrays found in the only other phosphine ligand/silver dithiocarbamate complexes previously described, namely [(Ph₃P)₂Ag(dtc)] [4] and $[(Fc_2PhP)_2Ag(dtc)]$ [5]; $[(dtc)Ag(P'-dppmP')_2Ag(dtc)]$ (8), may be considered as a pair of such units linked by the two bidentate ligands which are bridging, rather than chelating, ligands, resulting in a centrosymmetric dimer dppm adduct, with an eight-membered for the Ag(Ph₂PCH₂PPh₂)₂Ag ring (Fig. 2). The dppp adduct of the same stoichiometry, i.e. Agdtc : Ph₂P(CH₂)₃PPh₂ (1:1), is an infinite one-dimensional polymer (Fig. 3). The silver environments in these species are tabulated comparatively in Table 2. While the 'bites' of the chelating ligands are, unsurprisingly, effectively constant, associated Ag-S distances and deviations δAg from the conjugated dtc plane vary rather widely, presumably in response to the other parameters of the metal environment. Most notable among the latter is the P-Ag-P angle, presumably a reflection of the effective bulk of strain in the phosphine ligands as they pack around the silver, Ag-P generally shorter for large P-Ag-P, and vice versa.

In all other complexes structurally defined, the silver environment is $PAgS_3$, two of the sulfur atoms being drawn from the same dtc, now an unsymmetrical chelate, and one



Fig. 4. The dimer of $[(Ph_3P)Ag(S_2CNEt_2)]_2$ (1) projected normal to the centrosymmetric Ag_2S_2 core plane.



Fig. 5. A single strand of $[(MePh_2P)Ag(S_2CNEt_2)]_{\infty}$ (6), b horizontal in the page.

of the sulfur atoms bridged to the second silver atom. Different topologies are found. The adducts of Agdtc with PR₃, R = Ph (1), *m*-tolyl (2), might be expected to be similar and indeed they are, both being binuclear/dimers; their geometries are given comparatively in Table 3. Despite the similarity of the ligands and of the binuclear structures, considerable differences are found between 'equivalent' parameters, presumably consequent on 'packing forces', since the substituents are relatively 'benign' and well removed from the cores of the dimers. Of particular interest is the fact that the chelating S(1)-Ag distance in the PPh₃ adduct is longer than the bridging distance by an appreciable amount, less pronounced in the P(*m*-tolyl)₃ adduct; note also the large (and variable) dihedral angle between the dtc plane and the Ag₂S₂ core (see Fig. 4).

The remaining adduct also $Ag(dtc):MePh_2P$ (1:1), **6**, (Fig. 5), has $PAgS_3$ environments, similarly derived but now extended to yield an infinite one-dimensional polymer, rather than closing to form the dimer, perhaps also consequent on change in the effective bulk of the phosphine. In

the polymer, the generator of which is a 2_1 screw axis, the dtc ligand planes form a series of *quasi*-parallel 'castellated' steps in sequence, the phosphine ligands being pendant to either side.

Appendix A. Supplementary material

CCDC 626478–626484 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.02.016.

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