DALTON
FULL PAPER

Comparative structural studies on silver(I) complexes with tripodal polyphosphines. Crystallographic characterisation of the first infinite chain structures in 2 : 1 adducts of silver(I) halides with 1,1,1-tris(diphenylphosphinomethyl)ethane †

José A. Montes,[a] Susana Rodríguez,[a] Damián Fernández,[a] M. Inés García-Seijo,[a] Robert O. Gould[b] and M. Esther García-Fernández *[a]

[a] *Department of Inorganic Chemistry, University of Santiago de Compostela, E-15782 Santiago de Compostela, Spain. E-mail: qiegfq@usc.es*
[b] *Department of Chemistry, University of Edinburgh, King's Buildings, West Mains Road, Edinburgh, UK EH 93 JJ*

Received 9th July 2001, Accepted 19th November 2001
First published as an Advance Article on the web 7th February 2002

The AgX salts [X = Cl, Br, I, NO_3] react with CP_3 [$MeC(CH_2PPh_2)_3$], PP_3 [$P(CH_2CH_2PPh_2)_3$] and NP_3 [$N(CH_2CH_2PPh_2)_3$] in 1 : 1 stoichiometric ratio to afford complexes $Ag(CP_3)X$ [X = Cl (**1**), Br (**2**), I (**3**)], $Ag(PP_3)Cl$ (**4**), $Ag(NP_3)Cl$ (**6**) and $Ag(NP_3)(NO_3)$ (**7**) where Ag(I) is bound to three P atoms of the ligand. The X-ray crystal structure of complex **6** consists of a mononuclear compound with absence of the N atom of NP_3 in the coordination to the metal. The 1 : 1 complex obtained by reaction of $AgNO_3$ with PP_3 was shown by conductivity measurements, mass spectrometry, infrared and NMR spectroscopy to be a dinuclear ionic complex $[Ag_2(PP_3)_2](NO_3)_2$ (**5**) where Ag(I) shows three- and four-coordination. The interaction of AgX halides with CP_3 in 2 : 1 stoichiometric ratio leads to complexes $Ag_2(CP_3)X_2$ [X = Cl (**8**), Br (**9**), I (**10**)] which were shown by X-ray crystallography to consist of infinite zigzag (X = Cl, I) or linear (X = Br) chains containing three- and four-coordinate Ag(I) and constituting the first examples of such complexes with CP_3. These polymeric chains did not give reaction with another equivalent of AgX to form the $Ag_3(CP_3)X_3$ [X = Cl, Br, I] complexes. The 2 : 1 and 3 : 1 nitrate derivatives $Ag_2(PP_3)(NO_3)_2$ (**11**), $Ag_2(NP_3)(NO_3)_2$ (**12**), $Ag_3(PP_3)(NO_3)_3$ (**13**) and $Ag_3(NP_3)(NO_3)_3$ (**14**) show participation of the nitrate anion as ligand finding for **13** two different geometries about Ag(I) in solution. Complexes **13** and **14** react with the corresponding phosphines PP_3 and NP_3 to form complexes **5** and **7**, respectively involving ring-closure reactions.

Introduction

The affinity of Ag(I) for N-donor ligands especially pyridine and its derivatives is well known.[1] However, thermodynamic and spectroscopic studies demonstrate that the silver(I) complexes with phosphorus donor ligands are far more stable than with nitrogen donor ligands.[2] Depending on the phosphine ligand used a wide variety of silver-coordination numbers from two to the unusual five were found in complexes with different Ag : ligand stoichiometric ratios. Thus, complexes formed from silver(I) salts with monodentate tertiary phosphines in 1 : 1 ratio can exist as tetrameric,[3–5] trimeric[5] or dimeric[6] systems of general formula $[\{AgX(PR_3)\}_n]$ (n = 4–2) where the metal achieves coordination numbers four or three. Reactions of silver(I) salts with these ligands in a 1 : 2 ratio generally resulted in the formation of either monomeric $[AgX(PR_3)_2]/[Ag(PR_3)_2]^+X^-$,[5,7–10] or dimeric $[\{AgX(PR_3)\}_2]$ complexes[5,10,11] with four-coordinate Ag(I) in the majority of the neutral compounds and two- or three-coordinate found only when the anion is a weak donor and/or the substituents on the ligand are bulky.[12,13] By complexation of Ag(I) with diphosphines as $Ph_2P(CH_2)_{n'}PPh_2$ (n' = 2–3) in 1 : 2 ratios, ionic and neutral compounds of the types $[Ag(P–P)_2]^+$ [2,14] and $[AgX(P–P)_2]$,[15] respectively, were formed, the metal being in a tetrahedral environment. The neutral complexes (X = Cl, Br, I, CN; n' = 3) exist in solid state as mononuclear systems with both uni- and bidentate diphosphines and coordinated anion. The aminophosphines [L^1 = 3,6-bis(diphenylphosphino)pyridazine, L^2 = 2,6-bis(diphenylphosphino)pyridine, L^3 = (2-diphenylphosphino-6-pyrazol-1-yl)pyridine] form 3 : 2 and 2 : 2 complexes with $AgNO_3$ or $AgClO_4$ of the types $[Ag_2(\mu\text{-}L^1)_3(O_2NO)_2]$, $[Ag_2(\mu\text{-}L^2)_3](ClO_4)_2$ and $[Ag_2(\mu\text{-}L^3)_2(\mu\text{-dppm})](ClO_4)_2$ containing five-(AgP_3O_2), three-(AgP_3) and five-(AgN_2P_2Ag) coordinate silver(I) centres, respectively.[16] Upon reaction of the tripodal triphosphine, $HC(PPh_2)_3$ with $Ag(CF_3SO_3)$ in the presence of $LiClO_4$, a triangular silver(I) complex $[Ag_3\{HC(PPh_2)_3\}_2](ClO_4)_3$ was obtained, with each silver atom being essentially in a linear two-coordinate geometry.[17] Ligands of higher denticity as the linear polyphosphine $Ph_2P(CH_2)_2PPh(CH_2)_2PPh(CH_2)_2PPh_2$ (tetraphos) spontaneously self-assemble into a homochiral double-stranded disilver(I) helicate of the type $[Ag_2(tetraphos)_2]X_2$ upon reaction with appropriate silver(I) salts, where the metal is four-coordinate.[18]

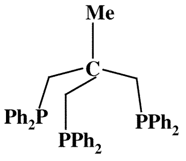
The silver(I) preference for linear two-coordinate and tetrahedral geometries can serve to link bridging ligands[19] to form polymeric chains of unusual and desirable properties and with new coordination modes.[20–22] Thus, Fenske and coworkers reported in 1997 the crystal structure[23] of the polymeric chain complex, $[Ag_{10}(\mu_3\text{-TePh})_{10}(PMe_3)_2]_\infty$, with tetrahedral coordination geometry for the phosphorus-bonded silver(I) centre ($AgPTe_3$) and three-coordination geometry for the remaining ones ($AgTe_3$). However, little work has been directed toward the comparative studies of silver(I) complexes with pendant

---

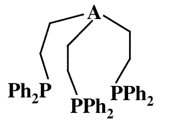
† Electronic supplementary information (ESI) available: $^{31}P\text{-}\{^1H\}$ NMR spectrum of **13**; far-IR spectra of **1** and **8**; view along the *c* axis of the unit cell of **8**; fragment of an infinite chain for **8**, **9** and **10**. See http://www.rsc.org/suppdata/dt/b1/b106021j/

DOI: 10.1039/b106021j

polyphosphines as 1,1,1-tris(diphenylphosphinomethyl)ethane (CP_3),[24,25] tris[2-(diphenylphosphino)ethyl]phosphine (PP_3) and tris[2-(diphenylphosphino)ethyl]amine (NP_3).[26]



CP_3



A = P (PP_3), N (NP_3)

In this work we report the synthesis, structural characterisation and reactivity of 1 : 1, 2 : 1 and 3 : 1 adducts of AgX salts (X = Cl, Br, I, NO_3) with CP_3, PP_3 and NP_3.

The nitrato complexes containing the ligands CP_3 or NP_3 and prepared in 1 : 1 stoichiometric ratio showed different structures in solution from the analogous complexes prepared from AgX salts (X = Cl, Br, I).[27] The structure determination by X-ray diffraction of $Ag(NP_3)Cl$, here reported, shows that the ligand is bound to the metal in a tridentate chelating mode through the three P atoms in a mononuclear complex where silver(I) achieves the four-coordination with participation of Cl as ligand. To our knowledge, except for the reported complex, $Ag_3(CP_3)(NO_3)_3$,[28] no chemistry of Ag(I) with CP_3, PP_3 or NP_3 in 2 : 1 and 3 : 1 ratios has been previously described. The reactions of nitrate complexes 2 : 1 and 3 : 1 with phosphine, carried out in solution, reveal the formation of the corresponding 1 : 1 compounds.

Finally, the crystalline structures of the 2 : 1 adducts, $Ag_2(CP_3)X_2$ [X = Cl, Br, I] consist of infinite zigzag (X = Cl, I) or linear (X = Br) chains, where Ag(I) achieves simultaneously and alternatively the four (AgP_2X_2)- and three (AgX_2P)-coordination, the crystal packing being a function of the bridging ligand X.

Experimental

General procedures and instrumentation

Solvents were dried by conventional methods, distilled and kept under argon. CP_3 and PP_3 were purchased from Strem Chemicals and Aldrich, respectively. Other reagents were available of the highest commercial grade and were used as received. Solvent evaporations were always carried out under vacuum using a rotary evaporator and a vacuum line. Microanalyses (C, H, N) were performed at the University of Santiago de Compostela. Fast Atom Bombardment (FAB) spectra were obtained on a KRATOS MS 50 spectrometer using 3-nitrobenzyl alcohol as the matrix. Electrospray Mass Spectrometry (ESMS) spectrum was recorded at the University of Barcelona on a MICROMASS VG-QUATTRO spectrometer using CH_3CN/H_2O/formic acid 1% as the mobile phase. Infrared spectra were recorded at ambient temperature as KBr pellets (4000–500 cm^{-1}) and Nujol mulls (500–100 cm^{-1}) on a Mattson Cygnus 100 spectrophotometer. The bands are reported as: vs = very strong, s = strong, m = medium, w = weak and sh = shoulder. ^{31}P-{^1H} NMR spectra were recorded on a Bruker AMX-500 spectrometer at 202.46 MHz. ^{109}Ag NMR spectrum was recorded on a Bruker AMX-500 spectrometer at 23.31 MHz. Chemical shifts are reported relative to external standard 85% H_3PO_4 (^{31}P) and a saturated solution of $AgNO_3$ in D_2O (^{109}Ag); δ = chemical shift in ppm; s = singlet, d = doublet, t = triplet, dt = doublet of triplets, m = multiplet, br = broad signal, J = coupling constant in Hz. Conductivities were obtained at 25 °C from 10^{-3} M solutions in DMF or CH_3CN on a WTW model LF-3 instrument.

Synthesis of NP_3

Tris(2-diphenylphosphinoethyl)amine (NP_3) was prepared using a modification of a literature method.[29,30] Diphenylphosphine (11 ml, 11.8 g, 62.9 mmol) was added to a suspension of potassium *tert*-butoxide (18.1 g, 160.9 mmol) in dry and freshly distilled THF (250 ml) under argon. The resulting deep red solution was stirred for 15 min and tris(2-chloroethyl)amine hydrochloride (5.0 g, 20.8 mmol) was added as a powder. The mixture was refluxed for 20 h at 80 °C, poured into 700 ml of water and cooled in an ice bath. The ligand precipitated and was filtered off, recrystallizated from DMF/H_2O and washed with EtOH. Yield: 78%, mp 102 °C. Found: C, 77.1; H, 6.9; N, 2.1. Calc. for $C_{42}H_{42}NP_3$: C, 77.1; H, 6.5; N, 2.1%. $\delta_P(CDCl_3)$: -22.7 (s).

Synthesis of complexes

AgLX. 1 : 1 Complexes were prepared with L = CP_3, X = Cl (**1**), Br (**2**), I (**3**); L = PP_3, X = Cl (**4**), NO_3 (**5**); L = NP_3, X = Cl (**6**), NO_3 (**7**). In each case the reaction involves addition of the silver(I) salt to the appropriate ligand using 1 mol equiv. of AgX per mol of L. Compounds **1**–**7** were obtained by reaction of AgX (0.20–0.50 mmol) as a solid when X = Cl, Br, I and in methanolic solution (10–15 ml) when X = NO_3 to a solution of the ligand (0.20–0.50 mmol) in CH_2Cl_2 (10–15 ml; L = PP_3, NP_3) or $CHCl_3$ (25 ml; L = CP_3). The complexes were precipitated with Et_2O, filtered off and then dried *in vacuo*. **1**: Yield 68%, white solid, mp 175 °C. Found: C, 58.0; H, 5.1. $C_{46}H_{50}OP_3Cl_4Ag$ ($Ag(CP_3)Cl\cdot Et_2O\cdot CHCl_3$) requires: C, 57.5; H, 5.2%. IR ν_{max}/cm^{-1} 204vs (Ag–Cl). $\delta_P(CDCl_3)$: See Table 1. Λ(DMF): 12.7 ohm^{-1} cm^2 mol^{-1}. **2**: Yield 86%, white solid, mp 170 °C. Found: C, 56.9; H, 5.4. $C_{41}H_{45}O_3P_2BrAg$ ($Ag(CP_3)Br\cdot 3H_2O$) requires: C, 56.8; H, 5.2%. IR ν_{max}/cm^{-1} 133vs (Ag–Br). $\delta_P(CDCl_3)$: -21.3 [3P, br]. Λ(DMF): 12.0 ohm^{-1} cm^2 mol^{-1}. **3**: Yield 53%, white solid, mp 160 °C. Found: C, 51.6; H, 4.7. $C_{46}H_{50}OP_3Cl_3IAg$ ($Ag(CP_3)I\cdot Et_2O\cdot CHCl_3$) requires: C, 52.4; H, 4.8%. IR ν_{max}/cm^{-1} 118m (Ag–I). $\delta_P(CDCl_3)$: -24.7 [3P, br]. Λ(DMF): 6.7 ohm^{-1} cm^2 mol^{-1}. **4**: Yield 84%, white solid, mp 230 °C. Found: C, 60.1; H, 5.2. $C_{42.5}H_{43}P_4Cl_2Ag$ ($Ag(PP_3)Cl\cdot 1/2CH_2Cl_2$) requires: C, 59.6; H, 5.0%. IR ν_{max}/cm^{-1} 185s (Ag–Cl). $\delta_P(CDCl_3, CD_2Cl_2)$: See Table 1. Λ(DMF): 87.0 ohm^{-1} cm^2 mol^{-1}. MS (FAB): *m*/*z* 779 ($[M - Cl]^+$, 12%). **5**: Yield 86%, white solid, mp 170 °C. Found: C, 58.1; H, 4.8; N, 1.7. $C_{85}H_{86}P_8N_2O_6Cl_2Ag$ ($[Ag_2(PP_3)_2](NO_3)_2\cdot CH_2Cl_2$) requires: C, 57.8; H, 5.0; N, 1.6%. IR ν_{max}/cm^{-1} 1383vs asym. (N–O). $\delta_P(CD_2Cl_2)$: See Table 1. $\delta_{Ag}(CD_2Cl_2)$: 1376 [2Ag, m, $^1J(^{107/109}AgP)$ 170, 270]. $\Lambda(DMF/CH_3CN)$: 165.7/273.0 ohm^{-1} cm^2 mol^{-1}. MS (FAB): *m*/*z* 1344 ($[M - 2NO_3 - P]^{2+}$, 30%); 779 ($[M - 2NO_3 - L - Ag]^+$, 100%). ESI-MS (+): *m*/*z* 779 ($[M - 2NO_3]^{2+}$, 100%). **6**: Yield 82%, white solid, mp >250 °C. Found: C, 63.0; H, 5.8; N, 1.9. $C_{42}H_{42}NP_3ClAg$ ($Ag(NP_3)Cl$) requires: C, 63.3; H, 5.3; N,1.8%. IR ν_{max}/cm^{-1} 181m (Ag–Cl). $\delta_P(CDCl_3)$: See Table 1. $\Lambda(DMF/CH_3CN)$: 10.9/8.2 ohm^{-1} cm^2 mol^{-1}. MS (FAB): *m*/*z* 762 ($[M - Cl]^+$, 100%). **7**: Yield 63%, white solid, mp >250 °C. Found: C, 61.2; H, 5.3; N, 3.4. $C_{42}H_{42}N_2P_3O_3Ag$ ($Ag(NP_3)NO_3$) requires: C, 61.2; H, 5.1; N, 3.4%. IR ν_{max}/cm^{-1} 1484vs, 1316s (N–O). $\delta_P(DMSO-d_6)$: See Table 1. Λ(DMF): 35.6 ohm^{-1} cm^2 mol^{-1}. MS (FAB): *m*/*z* 762 ($[M - NO_3]^+$, 100%).

Ag_2LX_2. These complexes were isolated with L = CP_3, X = Cl (**8**), Br (**9**), I (**10**); L = PP_3, X = NO_3 (**11**); L = NP_3, X = NO_3 (**12**). The silver(I) salts were added to the appropriate ligand using 2 mol equiv. of AgX per mol of L. AgX (0.30–1.00 mmol) was added as a solid (X = Cl, Br, I) or dissolved in methanol (15–20 ml; X = NO_3) to solutions of L (0.15–0.50 mmol) in CH_2Cl_2 (10 ml; L = PP_3, NP_3) or in $CHCl_3$ (25 ml; L = CP_3). The mixtures were stirred for 24 hours and the solids precipitated by addition of ether. After filtration the solids were dried *in vacuo*. **8**: Yield 59%, white solid, mp >250 °C. Found: C, 53.9; H, 5.1. $C_{45}H_{51}P_3O_2Cl_2Ag_2$ ($Ag_2(CP_3)Cl_2\cdot Et_2O\cdot H_2O$): C, 53.9; H, 5.1%. IR ν_{max}/cm^{-1} 211vs, 190sh, 171sh (Ag–Cl). $\delta_P(CDCl_3)$: See Table 1. **9**: Yield 80%, white solid, mp >250 °C. Found: C, 49.1; H,

Table 1 ^{31}P-{^{1}H} NMR data (r.t.) for complexes **1**, **4**–**8**, **11**–**14** and titrations with ligand of **12**, **13** and **14**

Compound	δ(^{31}P)	^1J($^{107/109}$Ag^{31}P)/Hz	AgP$_x$	Solvent
Ag(CP$_3$)Cl (**1**)	−19.8br			CDCl$_3$
Ag$_2$(CP$_3$)Cl$_2$ (**8**)	−20.3br			CDCl$_3$
Ag(PP$_3$)Cl (**4**)	−3.8br			CDCl$_3$
Ag(PP$_3$)Cl (**4**)[a]	−0.5br, 10.0d,[b] 15.9d[b]	395,[b] 402[b]	AgP$_3$	CD$_2$Cl$_2$
[Ag$_2$(PP$_3$)$_2$](NO$_3$)$_2$ (**5**)	−4.7br d, −0.2dm,[b] 8.0br dd,[b] 15.2br dd[b]	261/176,[b] 376/433,[b] 355/420[b]	AgP$_4$ AgP$_3$	CD$_2$Cl$_2$
[Ag$_2$(PP$_3$)$_2$](NO$_3$)$_2$ (**5**)	1.0dm, 15.1br dd	175/263, 355/395	AgP$_4$, AgP$_3$	CDCl$_3$ + CD$_3$OD
Ag$_2$(PP$_3$)(NO$_3$)$_2$ (**11**)	10.0br, 12.6br, 49.4br			CDCl$_3$
Ag$_3$(PP$_3$)(NO$_3$)$_3$ (**13**)	7.4br			CDCl$_3$ + DMF
Ag$_3$(PP$_3$)(NO$_3$)$_3$ (**13**)[a]	7.6br d, 10.4br d	512, 752	AgP$_2$, AgP	CD$_2$Cl$_2$ + DMF
13 + 1.0 eq. PP$_3$	−3.2br, 7.6br			CDCl$_3$ + DMF
13 + 2.0 eq. PP$_3$	−3.1m, 12.4br dd	230, 356/414	AgP$_4$, AgP$_3$	
13 + 3.0 eq. PP$_3$	−14.9br, −10.7br, −2.6br d, 12.4br d	191, 442	AgP$_4$, AgP$_3$	
Ag(NP$_3$)Cl (**6**)	−19.7dd	277/318	AgP$_3$	CDCl$_3$
Ag(NP$_3$)(NO$_3$) (**7**)	−8.5d	344	AgP$_3$	CDCl$_3$
Ag(NP$_3$)(NO$_3$) (**7**)	−4.3dd	351/274	AgP$_3$	DMSO-d$_6$
Ag$_2$(NP$_3$)(NO$_3$)$_2$ (**12**)	−2.9s			CDCl$_3$
12 + 1.0 eq. NP$_3$	−8.5d	343	AgP$_3$	CDCl$_3$
12 + 2.0 eq. NP$_3$	−18.4br, −11.1d	273	AgP$_3$	
12 + 3.0 eq. NP$_3$	−18.7br, −11.6d	255	AgP$_4$	
12 + 4.0 eq. NP$_3$	−19.9br, −11.8d	243	AgP$_4$	
Ag$_3$(NP$_3$)(NO$_3$)$_3$ (**14**)	0.6s			DMSO-d$_6$
14 + 1.0 eq. NP$_3$	−2.5s			DMSO + CDCl$_3$
14 + 2.0 eq. NP$_3$	−4.1d	336	AgP$_3$	
14 + 3.0 eq. NP$_3$	−11.0br, −5.4d	304	AgP$_3$	

[a] **4** (233 K), **13** (253 K). [b] Signals with coupling constants.

4.7. $C_{45}H_{51}P_3O_2Br_2Ag_2$ ($Ag_2(CP_3)Br_2\cdot Et_2O\cdot H_2O$) requires: C, 49.5; H, 4.7%. IR ν_{max}/cm^{-1} 148sh, 122s (Ag–Br). δ_P(CDCl$_3$): −15.0 [3P, br]. **10**: Yield 91%, white solid, mp 190 °C (decomp.). Found: C, 43.9; H, 3.9. $C_{41}H_{46}P_3O_2Cl_2Ag_2$ ($Ag_2(CP_3)I_2\cdot 2H_2O$) requires: C, 43.6; H, 3.8%. IR ν_{max}/cm^{-1} 133w, 116s (Ag–I). δ_P(DMSO-d$_6$): −13.0 [3P, br]. Λ(DMF): 12.1 ohm^{-1} cm^2 mol^{-1}. **11**: Yield 94%, grey solid, mp 215 °C (decomp.). Found: C, 49.2; H, 4.9; N, 2.8. $C_{42}H_{42}P_4N_2O_6Ag_2$ ($Ag_2(PP_3)(NO_3)_2$) requires: C, 49.9; H, 4.9; N, 2.8%. IR ν_{max}/cm^{-1} 1384vs, 1304s asym. (N–O). δ_P(CDCl$_3$): See Table 1. Λ(DMF): 9.7 ohm^{-1} cm^2 mol^{-1}. MS (FAB): *m*/*z* 950 ([M − NO$_3$]$^+$, 34%); 888 ([M − 2NO$_3$]$^{2+}$, 9%); 779 ([M − 2NO$_3$ − Ag]$^+$, 4%). **12**: Yield 51%, brown solid, mp 138 °C (decomp.). Found: C, 48.6; H, 4.6; N, 4.2. $C_{42.5}H_{43}N_2P_3O_6ClAg_2$ ($Ag_2(NP_3)(NO_3)_2\cdot 1/2CH_2Cl_2$) requires: C, 49.2; H, 4.2; N, 4.0%. IR ν_{max}/cm^{-1} 1384vs, 1296s, 1293s asym. (N–O). δ_P(CDCl$_3$): See Table 1. Λ(DMF): 140.8 ohm^{-1} cm^2 mol^{-1}. MS (FAB): *m*/*z* 933 ([M − NO$_3$]$^+$, 10%); 871 ([M − 2NO$_3$]$^{2+}$, 1%); 762 ([M − 2NO$_3$ − Ag]$^+$, 92%).

Ag_3LX_3. Adducts in 3 : 1 metal : ligand ratio were synthesised with L = PP$_3$, X = NO$_3$ (**13**) and L = NP$_3$, X = NO$_3$ (**14**). **13**: A solution of AgNO$_3$ (1.35 mmol) in methanol (45 ml) was added dropwise to a solution of PP$_3$ (0.34 mmol) in dry CH$_2$Cl$_2$ (15 ml). After stirring the final solution for 24 hours, a solid precipitated which was filtered off and dried *in vacuo*. Yield 73%, white solid, mp 215 °C (decomp.). Found: C, 42.0; H, 3.6; N, 3.6. $C_{42}H_{42}P_4N_3O_9Ag_3$ ($Ag_3(PP_3)(NO_3)_3$) requires: C, 42.7; H, 3.6; N, 3.6%. IR ν_{max}/cm^{-1} 1384vs, 1280s asym. (N–O). δ_P(CD$_2$Cl$_2$ + DMF): See Table 1. Λ(DMF): 101.1 ohm^{-1} cm^2 mol^{-1}. MS (FAB): *m*/*z* 950 ([M − 2NO$_3$ − Ag]$^+$, 26%); 888 ([M − 3NO$_3$ − Ag]$^{2+}$, 7%); 779 ([M − 3NO$_3$ − 2Ag]$^+$, 100%). **14**: A solution of AgNO$_3$ (0.69 mmol) in methanol (28 ml) was added slowly to a solution of NP$_3$ (0.23 mmol) in dry CH$_2$Cl$_2$ (10 ml). After stirring for 24 hours, the final solution was filtered off and solvents were removed *in vacuo*. The solid formed was recrystallised from CH$_2$Cl$_2$/Et$_2$O and dried *in vacuo*. Yield 65%, white solid, mp 104 °C (decomp.). Found: C, 42.3; H, 3.9; N, 4.8. $C_{42.5}H_{43}N_4P_3O_9ClAg_3$ ($Ag_3(NP_3)(NO_3)_3\cdot 1/2CH_2Cl_2$) requires: C, 42.3; H, 3.6; N, 4.6%. IR ν_{max}/cm^{-1} 1384vs, 1292vs asym. (N–O). δ_P(DMSO-d$_6$): See Table 1. Λ(DMF): 182.3 ohm^{-1} cm^2 mol^{-1}. MS (FAB): *m*/*z* 1104 ([M − NO$_3$]$^+$, 6%); 931 ([M − 2NO$_3$ − Ag]$^+$, 16%); 762 ([M − 3NO$_3$ − 2Ag]$^+$, 100%).

Titration of complexes with ligand

$Ag_2(NP_3)(NO_3)_2$. To a solution of $Ag_2(NP_3)(NO_3)_2$ (**12**) in CDCl$_3$, solutions containing 1 and 2 molar equivalents of the ligand in CDCl$_3$ were added. ^{31}P-{^{1}H} NMR spectra were recorded after additions.

$Ag_3L(NO_3)_3$. Solutions of 1, 2 and 3 molar equivalents of the ligand in CDCl$_3$ were added to solutions of $Ag_3(PP_3)(NO_3)_3$ (**13**) in DMF and $Ag_3(NP_3)(NO_3)_3$ (**14**) in DMSO-d$_6$. ^{31}P-{^{1}H} NMR spectra were recorded after additions.

X-Ray crystallography

Colourless crystals of **6**, **8**·2DMF, **9** and **10**·3DMSO were mounted on glass fibers and used for data collection. Crystals data were collected at 291(2) K, using a Bruker SMART CCD 1000 diffractometer (**8**·2DMF, **9** and **10**·3DMSO) and a Stoe Stadi4 four-circle diffractometer (**6**). Crystals of **10**·3DMSO were of a lower quality than those of **8**·2DMF and **9**. This lowered the precision of the crystal structure which can be taken to establish chemical connectivity. Graphite monochromated MoKα radiation (λ = 0.71073 Å) was used throughout. The data were processed with SAINT[31] and empirical absorption correction was made for **8**·2DMF, **9** and **10**·3DMSO using SADABS.[32] No absorption correction was made for **6**. The structures were solved by direct methods using the program SHELXS-97[33] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97.[34] Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed geometrically and positional parameters were refined using a riding model. Atomic scattering factors were obtained with the use of ref. 35. Molecular graphics were obtained from ORTEP-3 for Windows.[36]

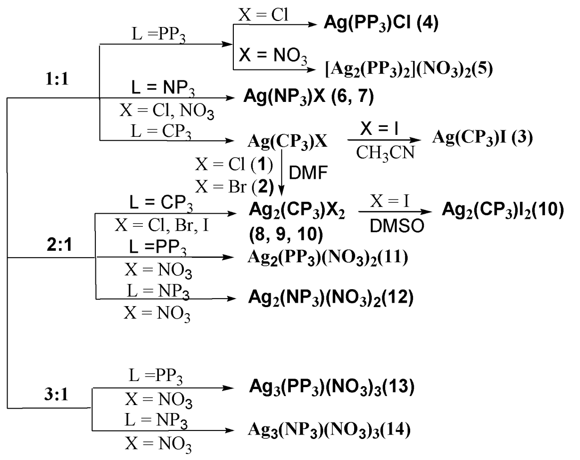
CCDC reference numbers 173819–173822.

See http://www.rsc.org/suppdata/dt/b1/b106021j/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis

The silver(I) complexes prepared with ligands CP$_3$, PP$_3$ and NP$_3$ are shown in Scheme 1. Except for Ag(NP$_3$)X [X = Cl (**6**), NO$_3$



Scheme 1 Silver(I) complexes prepared with tripodal polyphosphine ligands.

(7)], $Ag_2(PP_3)(NO_3)_2$ (**11**) and $Ag_3(PP_3)(NO_3)_3$ (**13**) the other complexes were obtained as dichloromethane (PP_3, NP_3), ether and/or water (CP_3) solvates.

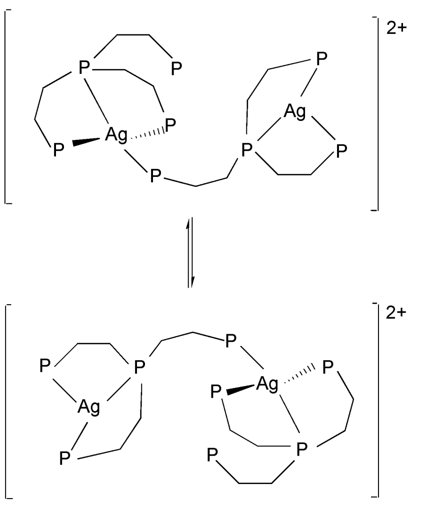
Complexes with 1 : 1 metal : ligand ratios were prepared as chloride (**1**, **4**, **6**) or nitrate ($Ag(CP_3)(NO_3)$,[28] **5**, **7**) systems with CP_3, PP_3 and NP_3. The crystallographic characterisation of complex **6** was done using crystals obtained by recrystallization of $Ag(NP_3)Cl$ in CH_2Cl_2/CH_3CN. Crystals suitable for X-ray diffraction studies of $Ag_2(CP_3)Cl_2$ (**8**·2DMF) and $Ag_2(CP_3)Br_2$ (**9**) were obtained from DMF solutions of $Ag(CP_3)Cl·Et_2O·CHCl_3$ (**1**·$Et_2O·CHCl_3$) and $Ag(CP_3)Br·3H_2O$ (**2**·$3H_2O$) respectively. However, the X-ray structure of complex $Ag_2(CP_3)I_2·3DMSO$ (**10**·3DMSO) was determined using crystals grown (size: 0.34 × 0.17 × 0.07 mm) from DMSO solutions of $Ag_2(CP_3)I_2·2H_2O$ (**10**·$2H_2O$). The reaction of $AgNO_3$ in methanol with PP_3 and NP_3 in dichlorometane using a 2 : 1 stoichiometric ratio led to the formation of complexes **11** and **12**, respectively. By interaction of $AgNO_3$ with CP_3, PP_3 and NP_3 in 3 :1 ratio, all three complexes $Ag_3(CP_3)(NO_3)_3$,[28] $Ag_3(PP_3)(NO_3)_3$ (**13**) and $Ag_3(NP_3)(NO_3)_3$ (**14**) can be prepared. However the complexes $Ag_4L(NO_3)_4$ were not achieved by reaction of PP_3 or NP_3 with $AgNO_3$ in 1 : 4 ratio. While Au(I) forms complexes, $Au_3(CP_3)X_3$,[28] $Au_4(PP_3)X_4$[37] and $Au_3(NP_3)X_3$[38] (X = Cl, Br, I), the reaction between AgCl and CP_3, PP_3 or NP_3 in 3 : 1 and even 4 : 1 ratios led to the formation of the corresponding 2 : 1 adducts. Likewise all attempts to prepare $Ag_3(CP_3)X_3$ (X = Br, I) complexes by addition of AgX to the 2 : 1 adducts were unsuccessful.

All complexes were obtained in acceptable yields, the highest values being for PP_3 and NP_3 derivatives.

Solution studies

1 : 1 Complexes. Fig. 1 shows the $^{31}P-\{^1H\}$ NMR spectra for complexes $Ag(CP_3)Cl$ (**1**), $Ag(PP_3)Cl$ (**4**), $[Ag_2(PP_3)_2](NO_3)_2$ (**5**), $Ag(NP_3)Cl$ (**6**), $Ag(NP_3)(NO_3)$ (**7**)[26] and $Ag(CP_3)(NO_3)$ (*).[28]

Complexes $Ag(CP_3)Cl$ (**1**) and $Ag(PP_3)Cl$ (**4**) are fluxional at room temperature and only broad resonances are observed which can be attributed to exchange processes involving the phosphine ligands. For complex $Ag(PP_3)Cl$ (**4**) this broad resonance undergoes splitting into three broad doublets when the spectrum is recorded in CD_2Cl_2 at 233 K obtaining an "average" $^1J(AgP)$ coupling to the two silver isotopes (^{107}Ag, 51.82% and ^{109}Ag, 48.18%) of *ca.* 400 Hz (Table 1) characteristic of silver bound to three ^{31}P atoms.[39] Likewise the $^1J(AgP)$ values at room temperature for $Ag(NP_3)Cl$ (**6**) and $Ag(NP_3)(NO_3)$ (**7**) of 277/318 and 344 Hz, respectively, are indicative of a tridentate chelating mode of coordination through the P atoms for NP_3. The doublet of doublets at δ 7.0 for complex $Ag(CP_3)(NO_3)$[28] shows $^1J(^{107/109}Ag^{31}P)$ of 487/558 Hz corresponding to Ag(I) coordinated to two ^{31}P atoms and suggesting a bidentate chelating mode of coordination for CP_3 together with the nitrate anion. The nitrate derivative with PP_3 (**5**) shows a more complicated $^{31}P-\{^1H\}$ NMR spectrum (Fig. 1). The doublets at δ −4.7 and 8.0 with integration ratio 1 : 1 in CD_2Cl_2, disappear when the spectrum is recorded in $CDCl_3 + CD_3OD$ (Table 1) and this is attributable to a coordinating behaviour of CD_3OD. The $^1J(AgP)$ coupling constants obtained from the pair of signals at δ −0.2 and 15.2 with integration ratio 4 : 2 in CD_2Cl_2 are 261/176 and 355/420 Hz, respectively, in agreement with silver(I) bound to four and three ^{31}P atoms, respectively.[15,39] On the other hand, the ^{109}Ag NMR spectrum of 5 in CD_2Cl_2 (Fig. 2) shows a multiplet centred at δ 1376[40a] analysable as overlapped multiplets (dt, ddt) with $^1J(AgP)$ values of 170 and 270 Hz also in accordance with AgP_4 and AgP_3 environments, respectively. These results are consistent with the presence of dinuclear species, $[Ag_2(PP_3)_2](NO_3)_2$ where one phosphine PP_3 can act as tridentate and bridging ligand and the other as tridentate ligand with an uncoordinated phosphorus undergoing exchange processes with the bridging one (Scheme 2). Thus while in the $^{31}P-\{^1H\}$ NMR spectrum of **5**, the resonances at δ −4.7 and 8.0 are assignable to an uncoordinated and bridging P, respectively, of the ligands, the resonances at δ −0.2 and 15.2 can be assigned to the two terminal and the apical coordinated P respectively of PP_3. A similar behaviour of PP_3, although without exchange processes was found in its chlorocomplex with gold(I) which exists as a dinuclear ionic compound $[Au_2(PP_3)_2]Cl_2$[37] both in solution and the solid state, with four-coordinate Au(I). The potential argentophilicity in the disilver complex **5** could generate a luminescent behaviour[40b] that will be investigated subsequently.



Scheme 2 Structural equilibrium proposed for $[Ag_2(PP_3)_2](NO_3)_2$ (**5**) in solution.

On the other hand, while the DMF solutions of 1 : 1 complexes $Ag(CP_3)X$ (**1**–**3**), $Ag(NP_3)X$ (**6**) and $Ag(NP_3)(NO_3)$ (**7**) behave as non conductors[41] in agreement with the presence of mononuclear compounds, the solutions of $Ag(PP_3)Cl$ (**4**) and $[Ag_2(PP_3)_2](NO_3)_2$ (**5**) behave as 1 : 1 and 2 : 1 electrolytes, respectively. The conductivity measurement of **5** in a less coordinating solvent as CH_3CN (273 ohm^{-1} m^2 mol^{-1} for 10^{-3} M solutions) is also in accordance with a behaviour as a 2 : 1 eletrolyte. Furthermore, the presence of the positive ion $[Ag_2(PP_3)_2]^{2+}$ at *m*/*z* 779 as the most intense peak (100% abundance) in the electron spray mass spectrum (ESMS) of complex **5** besides the existence of fragments $Ag_2(PP_3)(PP_2)$ (30% abundance) in its FAB mass spectrum, support a typical behaviour of a dinuclear and ionic species as described in Scheme 2. No fragments of higher mass than $Ag(PP_3)$ were

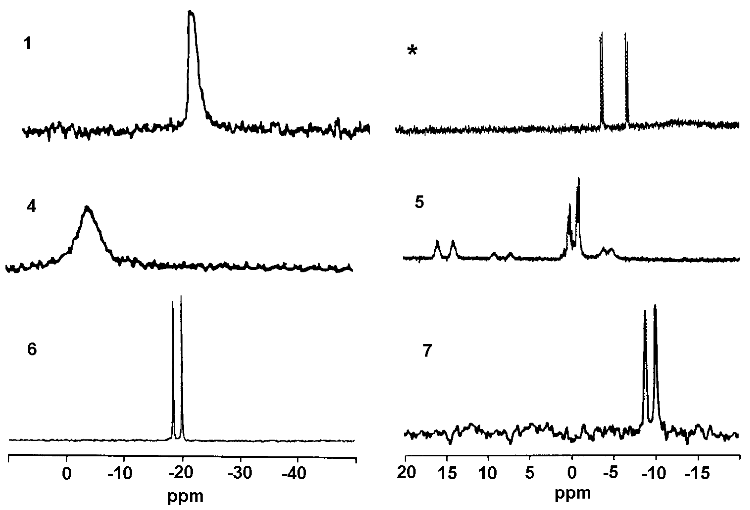


Fig. 1 ^{31}P-{^{1}H} NMR spectra at room temperature for complexes Ag(CP$_3$)Cl (**1**), Ag(PP$_3$)Cl (**4**), Ag(NP$_3$)Cl (**6**), Ag(NP$_3$)(NO$_3$) (**7**), Ag(CP$_3$)(NO$_3$)[28] (*) (CDCl$_3$) and [Ag$_2$(PP$_3$)$_2$](NO$_3$)$_2$ (**5**) (CD$_2$Cl$_2$).

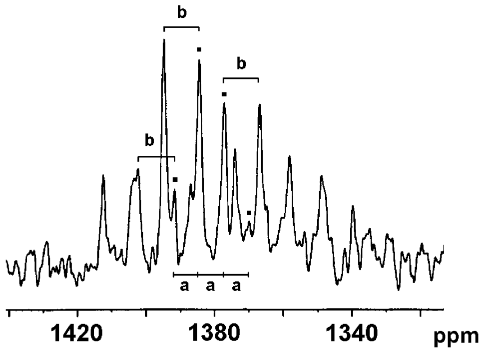


Fig. 2 ^{109}Ag NMR spectrum for [Ag$_2$(PP$_3$)$_2$](NO$_3$)$_2$ (**5**) in CD$_2$Cl$_2$: a) ^1J(AgP) = 170 Hz; b) ^1J(AgP) = 270 Hz.

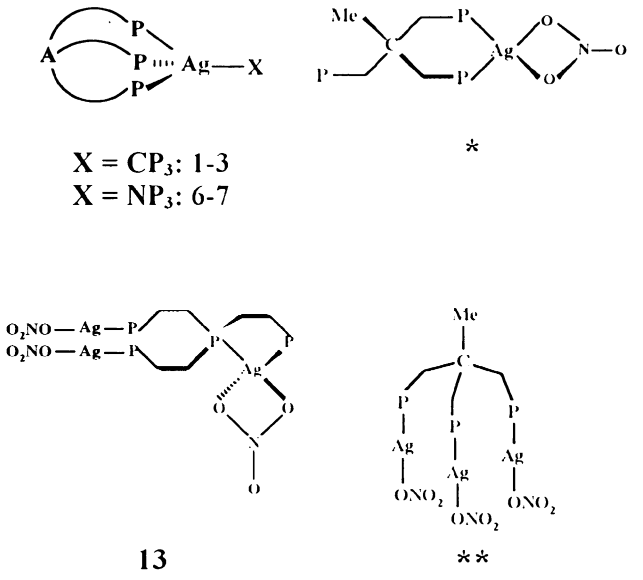


Fig. 3 Proposed structures in solution for Ag(CP$_3$)X [X = Cl (**1**), Br (**2**), I (**3**)], Ag(NP$_3$)X [X = Cl (**6**), NO$_3$ (**7**)], Ag(CP$_3$)(NO$_3$) (*), Ag$_3$(PP$_3$)(NO$_3$)$_3$ (**13**) and Ag$_3$(CP$_3$)(NO$_3$)$_3$ (**).

found in the FAB mass spectrum of **4** and the conductor behaviour of the potential mononuclear compound in DMF solution, is presumably due to some exchange processes of the chloro atom coexisting as ligand and counter ion in this solvent and/or to a total replacement of chloride by solvent molecules. However, on the basis of the ^{31}P-{^{1}H} NMR data at 233 K in CD$_2$Cl$_2$ (Table 1) the existence in solution of **4** as [Ag$_2$(PP$_3$)$_2$-Cl]Cl, should not be excluded. The dynamic behaviour of the potential monocationic complex could be parallel to that shown in Scheme 2, containing now AgP$_3$ and AgP$_3$Cl environments.

From the solution studies of 1 : 1 complexes we conclude that while for halide compounds [Ag(CP$_3$)X (**1**–**3**), Ag(NP$_3$)Cl (**6**)] a similar coordination mode of the phosphine in solution can be proposed (Fig. 3), for the nitrate derivatives Ag(CP$_3$)(NO$_3$),[28] [Ag$_2$(PP$_3$)$_2$](NO$_3$)$_2$ (**5**) and Ag(NP$_3$)(NO$_3$) (**7**), the structures are strongly dependent on the tripodal ligand used. Only the tripodal ligand PP$_3$ involves the apical atom in coordination to silver(I) (Scheme 2, Fig. 3).

2 : 1 and 3 : 1 Complexes. These complexes and particularly those derived from silver(I) halides showed low solubilities in the common organic solvents.

Except for Ag$_2$(PP$_3$)(NO$_3$)$_2$ (**11**) all 2 : 1 and 3 : 1 complexes (Scheme 1) show a single resonance in their ^{31}P-{^{1}H} NMR spectra at room temperature in agreement with a fluxional behaviour characteristic of the coordination chemistry of silver. For complex Ag$_3$(PP$_3$)(NO$_3$)$_3$ (**13**) the single broad signal at δ 7.4 in (DMF + CDCl$_3$) is an unresolved pair of doublets. At 253 K the signal splits (Table 1) into two overlapped broad doublets at δ 7.6 and 10.4, from which the ^1J(AgP) values of 512 and 752 Hz are indicative of Ag(I) bound to two and one ^{31}P atoms respectively. On the basis of these data a structure as shown in Fig. 3 can be proposed for complex **13**. This structure differs from that one found in solution for Ag$_3$(CP$_3$)(NO$_3$)$_3$[28] where the ^1J($^{107/109}$AgP) values of 694/801 Hz are consistent with each Ag being coordinated to only one P, and the nitrate acting as monodentate ligand. The non-coordinating C atom in apical position of CP$_3$ generates only linear Ag(I) environments.

Although ^1J(AgP) coupling constants values were not available from the ^{31}P-{^{1}H} NMR spectrum of the complex Ag$_2$(PP$_3$)(NO$_3$)$_2$ (**11**) in CDCl$_3$ (Table 1), on the basis of the presence of three resonances at δ 49.4, 12.6 and 10.0 with integration ratios 1 : 1 : 2, respectively, a structure containing linear and tetrahedral Ag(I) and participation of nitrate anions as ligands can be proposed. The position of the broad signal at δ 49.4 is characteristic of oxidized apical phosphorus of PP$_3$.

The complexes Ag$_2$(CP$_3$)I$_2$ (**10**) and Ag$_2$(PP$_3$)(NO$_3$)$_2$ (**11**) behave as non conductors in DMF solutions (12.1 and 9.7 ohm^{-1} cm^2 mol^{-1} respectively). However, the nitrate derivatives with NP$_3$, Ag$_2$(NP$_3$)(NO$_3$)$_2$ (**12**) and Ag$_3$(NP$_3$)(NO$_3$)$_3$ (**14**) behave as 2 : 1 (148.8 ohm^{-1} cm^2 mol^{-1}) and 3 : 1 (182.3 ohm^{-1}cm^{2}mol^{-1}) electrolytes, respectively, because of the replacement of nitrate by solvent molecules, in good agreement with the behaviour previously found for Ag$_3$(CP$_3$)(NO$_3$)$_3$ in the same solvent.[28] These similarities between nitrate derivatives of CP$_3$ and NP$_3$ lead to suppose the exclusion of the apical nitrogen atom in the coordination to silver(I). An intermediate behaviour between a 2 : 1 and 1 : 1 electrolyte was observed for complex $Ag_3(PP_3)(NO_3)_3$ (**13**), presumably due to the participation of the apical phosphorus atom in the coordination about silver(I) as proposed in Fig. 3. The presence of Ag_2LX fragments for all these 2 : 1 and 3 : 1 complexes and Ag_3LX_2 (**14**) in the FAB mass spectra confirm the existence of polynuclear systems.

Conversion of stoichiometries

The reactions of $Ag_2(NP_3)(NO_3)_2$ (**12**) and $Ag_3(NP_3)(NO_3)_3$ (**14**) with NP_3 and of $Ag_3(PP_3)(NO_3)_3$ (**13**) with PP_3 were followed by $^{31}P-\{^1H\}$ NMR and the results listed in Table 1 show that the conversion of stoichiometries and structures to those of complexes prepared in 1 : 1 metal : ligand ratio took place in solution (eqn. (1))

$$\mathrm{Ag}_m\mathrm{LX}_m + (m-1)\mathrm{L} \rightarrow \frac{m}{m}, (\mathrm{AgLX})_m, \tag{1}$$
$$m' = 1\text{: L} = \mathrm{NP}_3;\ m = 2,\ \mathrm{X} = \mathrm{NO}_3(\mathbf{12});\ m = 3,\ \mathrm{X} = \mathrm{NO}_3(\mathbf{14}) \rightarrow (\mathbf{7})$$
$$m' = 2\text{: L} = \mathrm{PP}_3;\ m = 3,\ \mathrm{X} = \mathrm{NO}_3(\mathbf{13}) \rightarrow (\mathbf{5})$$

The single resonance observed in the $^{31}P-\{^1H\}$ NMR spectra for complexes $Ag_2(NP_3)(NO_3)_2$ (**12**) (δ −2.9 in $CDCl_3$) and $Ag_3(NP_3)(NO_3)_3$ (**14**) (δ 0.6 in DMSO-d_6) shifts and converts into the doublets at δ −8.5 [^1J(AgP) = 343 Hz] and −4.1 [^1J(AgP) = 336 Hz] by addition of 1 and 2 molar equivalents of NP_3, respectively, with formation of complex $Ag(NP_3)(NO_3)$ (**7**). Subsequent additions of NP_3 produce a decrease in ^1J(AgP) (243 Hz when 4.0 molar equivalents of NP_3 were added to complex **12**, Table 1) indicating the formation of AgP_4 species. Likewise, the broad resonance at δ 7.4 in $CDCl_3$/DMF (r.t.) for complex $Ag_3(PP_3)(NO_3)_3$ (**13**) converts by addition of 2 molar equiv. of PP_3 into two doublets at δ −3.1 and 12.4 assigned to complex $[Ag_2(PP_3)_2](NO_3)_2$ (**5**) (Table 1). After addition of the third equivalent of PP_3 signals attributed to free ligand (δ −14.9 and −10.7) together with those belonging to the complex **5** [δ −2.6 and 12.4; ^1J(AgP) = 191 and 442 Hz respectively] were observed.

The structural changes found by addition of ligand to the polynuclear nitrate complexes (2 : 1 and 3 : 1) can be associated in all cases to ring-closure processes. Similar ring-closure reactions were previously detected when the linear triphosphine, $Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$ (P_3) was added to polynuclear ionic $[Pt(P_3)Cl][Pt_2(P_3)Cl_5]$ and neutral, $Pt_3(P_3)_2Cl_6$ complexes of platinum(II) with formation of $[Pt(P_3)Cl]Cl$.[42]

The titrations with CP_3 of complexes **8**–**10** to form the corresponding 1 : 1 complexes were also monitored by $^{31}P-\{^1H\}$ NMR. However, the appearance of broad resonances did not allow to obtain useful information.

Solid state studies

1 : 1 Complexes. The single silver-halogen vibrational frequency found in the far IR spectra of halide complexes **1**–**4** and **6** is consistent with the presence of terminal Ag–X bonds.[6] The splitting of ν_a(N–O) observed for complex $Ag(NP_3)(NO_3)$ (**7**) is in accordance with results obtained from X-ray crystallography studies[26] revealing the presence of coordinated nitrate. However the only frequency without splitting (1383 cm^{-1}) found for complex $Ag_2(PP_3)_2(NO_3)_2$ (**5**) assignable to ν_a(N–O) suggests the presence of ionic nitrate[39] in the solid state.

The best way to confirm the geometry of these complexes in solid state is by X-ray diffraction studies. The crystal structures of $Ag(CP_3)I$ (**3**) and $Ag(NP_3)(NO_3)$ (**7**) were previously reported by Camalli and Caruso[24] and Fackler, Jr. and coworkers[26] respectively, and they consist of mononuclear compounds with CP_3 and NP_3 acting as tridentate chelating ligands. In this work we report the crystal structure of $Ag(NP_3)Cl$ (**6**). This compound was crystallized as colourless rods from a mixture of CH_2Cl_2 and CH_3CN. A summary of crystal structure parameters, data collection and refinement is given in Table 2. The ORTEP diagram with numbering scheme is shown in Fig. 4 and selected bond lengths and angles are given in Table 3. This compound crystallises in space group *P*1 and consists of monomeric, neutral $Ag(NP_3)Cl$ units with the silver atom in a slightly distorted tetrahedral environment bound to all three P atoms of NP_3 and the Cl atom. The N atom does not appear to participate in the coordination and it is located at a distance of 3.126 Å from the metal. This distance is greater than that found for $Ag(NP_3)(NO_3)$ (**7**)[26] [2.55(1) Å]. The Ag–Cl and Ag–P bond distances are in agreement with the same distances found for other silver(I) complexes with tetrahedral AgP_3Cl environments such as $Ag(PPh_3)_3Cl$[43] or Ag(TP)Cl[44] (TP = bis[2-(diphenylphosphino)phenyl]phenylphosphine). The Ag(I) atom is found to be out of the P_3 plane on the side of the chloro ligand giving rise to P–Ag–P angles very close to those of the tetrahedral geometry. The distortion from this geometry is higher for complex $Ag(NP_3)(NO_3)$ (**7**) and particularly higher for complex $Ag(CP_3)I$ (**3**).[24] While the packing diagram for **3** and **7** involves four molecules in the unit cell, only one is involved for complex **6**.

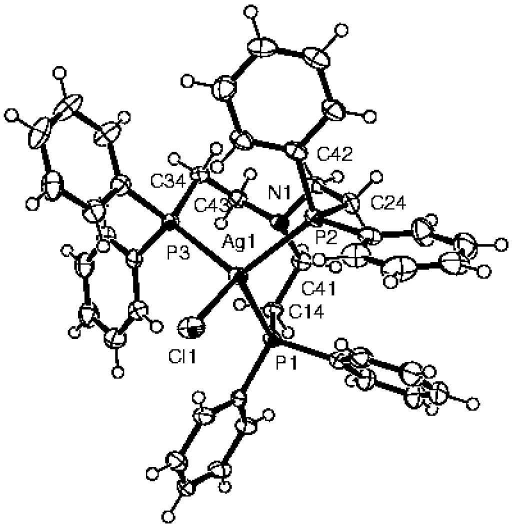


Fig. 4 ORTEP diagram for the crystal structure of $Ag(NP_3)Cl$ (**6**).

From these crystallographic studies and by comparison with solution studies we can conclude that complex **6** together with complexes **3** and **7** have the same structural behaviour in solution and solid state.

2 : 1 and 3 : 1 Complexes. The position and number of bands assigned in the far IR spectra to ν(Ag–X) for complexes $Ag_2(CP_3)X_2$ (**8**–**10**) indicate that X is coordinating to silver(I) in a bridging mode.[45] Because of the splitting of ν_a(N–O) in the IR spectra of the nitrate derivatives, $Ag_2(PP_3)(NO_3)_2$ (**11**), $Ag_2(NP_3)(NO_3)_2$ (**12**), $Ag_3(PP_3)(NO_3)_3$ (**13**) and $Ag_3(NP_3)(NO_3)_3$ (**14**), the structures seem to involve the participation of nitrate groups as coordinating ligands in accordance with structures proposed in solution.

The very short structural information obtained for halide complexes $Ag_2(CP_3)X_2$ (**8**–**10**) in solution found compensation in solid state with the formation of crystals suitable for X-ray crystallography studies.

From solutions of $Ag(CP_3)Cl$ (**1**) and $Ag(CP_3)Br$ (**2**) in DMF colourless plates and prisms of **8**·2DMF and **9**, respectively, were obtained. Compound **10** crystallized from DMSO solutions in colourless prisms as the solvate **10**·3DMSO. The crystal structures of **8**·2DMF, **9**, and **10**·3DMSO are monoclinic, all with space group $P2_1/c$, and their crystallographic data are given in Table 2. In all three complexes the structures consist of

Table 2 Crystallographic data for **6**, **8**·2DMF, **9** and **10**·3DMSO

Complex	**6**	**8**·2DMF	**9**	**10**·3DMSO
Empirical formula	$C_{42}H_{42}NP_3ClAg$	$C_{47}H_{53}Cl_2P_3Ag_2N_2O_2$	$C_{41}H_{39}Br_2P_3Ag_2$	$C_{47}H_{57}I_2P_3Ag_2S_3O_3$
Formula weight	797.00	1057.46	1000.19	1328.56
Temperature/K	293(2)	293(2)	293(2)	293(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Crystal size/mm	0.58 × 0.23 × 0.19	0.22 × 0.22 × 0.12	0.39 × 0.30 × 0.18	0.34 × 0.17 × 0.07
Colour/habit	Colourless/rod	Colourless/plate	Colourless/prism	Colourless/prism
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P1$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	8.895(4)	18.060(3)	19.486(3)	13.926(4)
b/Å	10.339(4)	14.866(3)	9.7523(13)	19.209(5)
c/Å	10.809(4)	18.468(4)	20.388(3)	19.642(5)
α/°	74.50(2)	90	90	90
β/°	80.92(2)	105.862(4)	95.638(4)	98.190(5)
γ/°	79.66(2)	90	90	90
V/Å^3	936.0(6)	4769.5(16)	3855.5(9)	5201(2)
Z	1	4	4	4
D_c/Mg m^{-3}	1.414	1.473	1.723	1.697
μ/mm^{-1}	0.769	1.072	3.242	2.190
F(000)	410	2152	1976	2624
θ range for data collection/°	2.88–25.01	1.17–27.08	1.05–30.54	1.48–23.35
Index ranges	$-10 \le h \le 10$	$-23 \le h \le 15$	$-27 \le h \le 25$	$-15 \le h \le 10$
	$-12 \le k \le 12$	$-18 \le k \le 18$	$-12 \le k \le 13$	$-21 \le k \le 21$
	$-12 \le l \le 12$	$-21 \le l \le 22$	$-28 \le l \le 29$	$-21 \le l \le 21$
Reflections collected	8884	28519	47731	23626
Independent reflections	6564 [$R_{int} = 0.0102$]	9827 [$R_{int} = 0.1558$]	11712 [$R_{int} = 0.0720$]	7508 [$R_{int} = 0.1791$]
Max., min. transmission		0.8821, 0.7983	0.5930, 0.3645	0.8618, 0.5230
Data/restraints/parameters	6564/3/433	9827/0/479	11712/0/434	7508/0/481
Goodness of fit on F^2	1.025	0.811	0.887	0.888
Final R indices	$R_1 = 0.0174$, $wR_2 = 0.0454$	$R_1 = 0.0524$, $wR_2 = 0.0882$	$R_1 = 0.0345$, $wR_2 = 0.0665$	$R_1 = 0.0889$, $wR_2 = 0.2137$
R indices (all data)	$R_1 = 0.0178$, $wR_2 = 0.0456$	$R_1 = 0.2436$, $wR_2 = 0.1311$	$R_1 = 0.1232$, $wR_2 = 0.0949$	$R_1 = 0.2818$, $wR_2 = 0.3008$
Largest diff. peak and hole (e Å^{-3})	0.368 and −0.606	0.587 and −0.686	0.626 and −0.639	2.256 and −1.891

Table 3 Selected bond lengths (Å) and angles (°) for **6**

Ag(1)–Cl(1)	2.593(1)	Ag(1)–P(1)	2.517(1)
Ag(1)–P(2)	2.516(1)	Ag(1)–P(3)	2.549(1)
P(2)–Ag(1)–P(1)	105.63(3)	P(3)–Ag(1)–Cl(1)	108.03(3)
P(1)–Ag(1)–P(3)	108.16(3)	P(1)–Ag(1)–Cl(1)	109.32(3)
P(2)–Ag(1)–P(3)	108.66(3)	P(2)–Ag(1)–Cl(1)	116.76(3)
Ag(1) ··· ·N(1)	3.126		

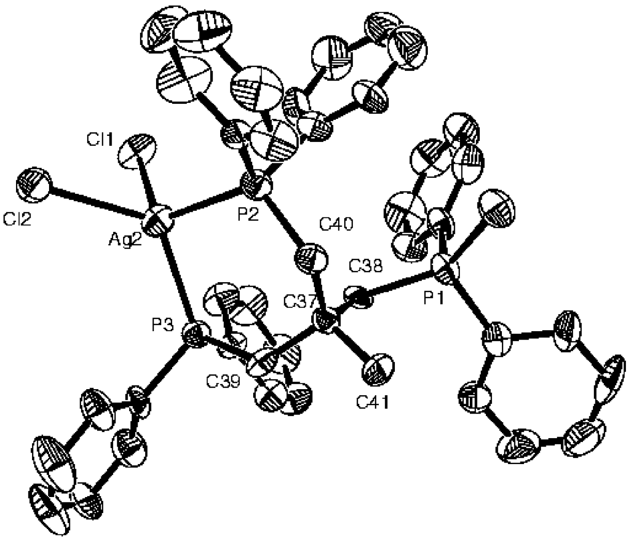


Fig. 5 ORTEP view of the asymmetric unit for complex **8**.

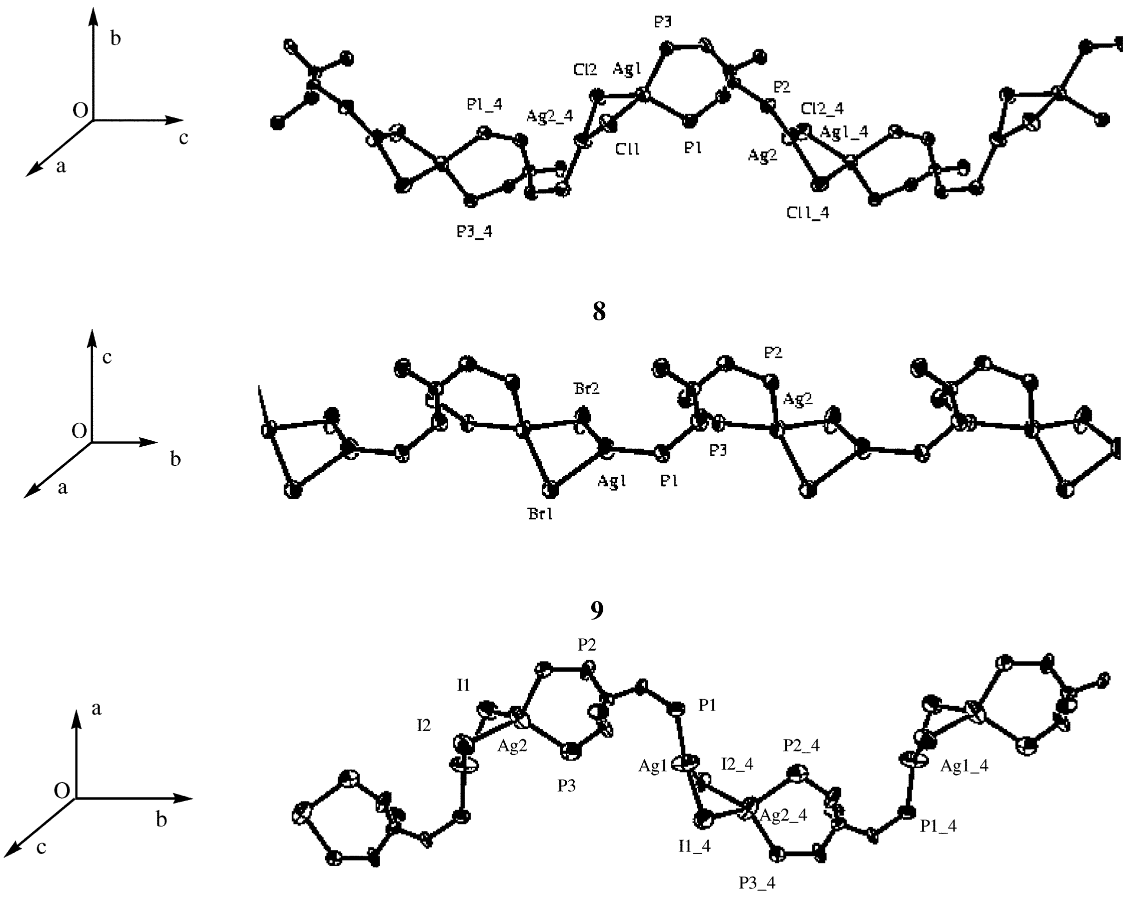
Table 4 Selected interatomic distances (Å) and bond angles (°) and important noncovalent contacts for **8**·2DMF, **9** and **10**·3DMSO

	8·2DMF	**9**	**10**·3DMSO
Ag(1)–P(1)	2.364(3)	2.392(11)	2.415(6)
Ag(2)–P(3)	2.463(2)	2.498(11)	2.504(7)
Ag(2)–P(2)	2.502(3)	2.484(11)	2.590(8)
Ag(1)–X(2)#2	2.469(3)	2.576(7)	2.774(3)
Ag(1)–X(1)#2	2.498(3)	2.666(6)	2.793(3)
Ag(2)–X(1)	2.620(3)	2.762(6)	2.888(3)
Ag(2)–X(2)	2.642(3)	2.727(6)	2.880(3)
P(3)–Ag(2)–P(2)	97.77(8)	97.82(4)	95.50(2)
P(1)–Ag(1)–X(1)#2	127.15(9)	123.41(3)	130.73(18)
P(1)–Ag(1)–X(2)#2	136.80(9)	139.42(3)	129.45(19)
P(3)–Ag(2)–X(1)	114.24(8)	126.91(3)	118.12(18)
P(2)–Ag(2)–X(2)	115.37(9)	114.76(3)	116.34(19)
P(2)–Ag(2)–X(1)	117.07(9)	111.78(3)	119.07(19)
P(3)–Ag(2)–X(2)	126.05(8)	115.99(3)	117.17(18)
X(2)#2–Ag(1)–X(1)#2	94.75(9)	96.36(2)	97.03(9)
X(1)–Ag(2)–X(2)	87.96(8)	90.78(19)	92.60(8)
Ag(2) ··· Ag(1)#1	3.385(12)	3.321(6)	3.391(3)

repeating asymmetric units, $AgPCP_2AgX_2$ (Fig. 5 for X = Cl) giving rise to infinite chains where three- [Ag(1)] and four-coordinate silver(I) [Ag(2)] coexist (Fig. 6). Table 4 shows selected interatomic distances (Å) and bond angles (°). The shortest Ag–P bond distances are found in the three-coordinate silver environment $PAgX_2$ which is almost planar with the phosphorus atom deviating from the plane by 0.047 (Cl), 0.039 (Br) and 0.079 (I) Å with the sum of the angles around the silver atom not differing much from 360° [358.7° (Cl), 359.2° (Br), 357.2° (I)].

In general, the decrease in the halogen electronegativity leads to an increase in the Ag–P bond lengths. The Ag–P bond lengths in complex $Ag(CP_3)I$ (**3**) [2.510(5), 2.527(6) and 2.555(5) Å] are greater than Ag(1)–P(1) [2.415(6) Å] and Ag(2)–P(3) [2.504(7) Å] and lower than Ag(2)–P(2) [2.590(8) Å] distances in complex $Ag_2(CP_3)I_2$ (**10**).

The Ag(1) also shows shorter Ag–X bond distances than Ag(2) and, as expected, both Ag(1)–I and Ag(2)–I distances corresponding to bridging bonds are longer than Ag–I bond lengths in complex $Ag(CP_3)I$ (**3**) containing only terminal Ag–I bonds.

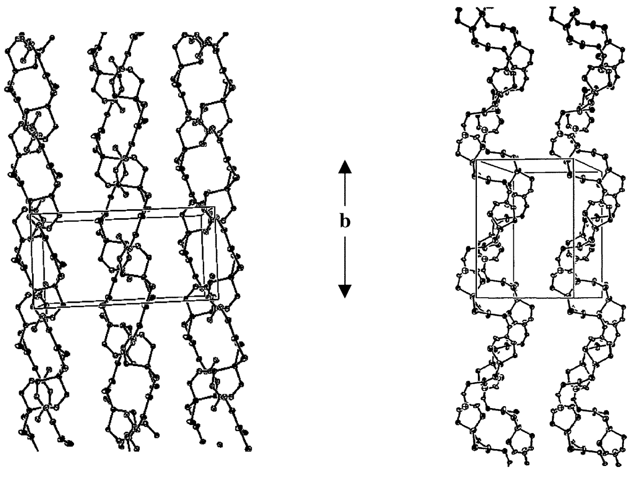


8

9

10

Fig. 6 Fragment of an infinite chain for **8**, **9** and **10**. Phenyl rings are omitted for clarity.



9 **10**

Fig. 7 Propagation of four linear chains for complex **9** and two zigzag chains for complex **10** running along the *b* axis of the unit cell. Phenyl rings are omitted for clarity.

The distorted tetrahedral environment in the P_2AgX_2 silver coordination sphere is evident from the P–Ag–P and X–Ag–X angles which are significantly lower than 109° or from the P–Ag–X angles which are higher than 109° in all three cases. Similar trends in deviations from the tetrahedral geometry were observed for P–Ag–P and P–Ag–X angles in complex $Ag(CP_3)I$ (**3**).

There is only a weak Ag(1) ··· Ag(2)# interaction [3.385(12), X = Cl (**8**); 3.321(6), X = Br (**9**); 3.391(3), X = I (**10**)] between three- and four-coordinate silver atoms of two different asymmetric units and bridged by two halogen atoms. The predictions by IR about the presence of halogens bridging two silver centres were now confirmed.

Crystals of $Ag_2(CP_3)Cl_2$ (**8**) and $Ag_2(CP_3)I_2$ (**10**) are made up of infinite zigzag chains which involve monomer units related within the chains by glide planes (**8**) or screw axes along the chains (**10**) and with the solvent molecules occupying the voids formed between them. There are two chains running through the unit cell along the *c* and *b* axis for **8** and **10**, respectively (Figs. 6, 7). The number of asymmetric units per chain along the propagation axis for **8** and **10** is two. However crystals of complex $Ag_2(CP_3)Br_2$ (**9**) are made up of infinite linear chains with the monomer units related solely by translation. There are now four chains running through the unit cell (Fig. 7) with only one asymmetric unit per chain along the *b* axis. The high calculated density for **9** ($D_c = 1.723$ Mg m^{-3}) is indicative that the cavities of the tunnels generated along the propagation axis are not large enough to accommodate solvent molecules.

The shortest Ag ··· Ag distances between chains involving three- and four-coordinate silver(I) centres are 11.697 Å for complex **9** and 16.586 and 17.229 Å for complexes **8** and **10**, respectively.

The neutral polymeric chains found in complexes **8**–**10** are not connected by H-bonding. They are independent infinite chains held together by chain–chain (**9**) and chain–solvent–chain van der Waals interactions (**8**, **10**).[46] This contrasts with the double and higher order helices in coordination polymers where the strands of the helix are independent infinite chains, connected by noncovalent forces, quite analogous to the situation in DNA.[21] Efficient π-stacking interactions involving phenyl rings of CP_3 between neighbouring chains probably strongly support the cohesion of the crystals. The crystal structures of **8**, **9** and **10** constitute the first examples of infinite chains found for metal complexes of tripodal polyphosphines as CP_3, PP_3 or NP_3. The structural characteristics of these neutral polymeric chains in the solid state can explain the unsuccessful attempts to prepare the corresponding 3 : 1 adducts.

Conclusions

While the 1 : 1 complexes of silver(I) halides with pendant triphosphines as CP_3 and NP_3 show the same coordination mode of the ligand through the 3 P atoms, the structures in solution of the 1 : 1 nitrate derivatives are strongly dependent on the phosphine used, revealing AgP_2, $AgP_3 + AgP_4$ and AgP_3 environments for CP_3, PP_3 and NP_3 complexes, respectively, in consistence with the formation of a dinuclear cationic system in the case of PP_3. The 2 : 1 and 3 : 1 complexes of silver(I) nitrate with these triphosphines involve the participation of nitrate anion as coordinating ligand and convert into the corresponding 1 : 1 complex by addition of phosphine. The crystal structures of the 2 : 1 adducts of silver(I) halides with CP_3, $Ag_2(CP_3)X_2$ (X = Cl, Br, I), consist of two infinite zigzag (X = Cl, I) or four linear chains (X = Br) which run along the unit cell. Silver(I) is three- and four-coordinate and bridged by two halogen atoms. The zigzag arrangement (X = Cl, I) generates cavities with appropriate size to accommodate solvent molecules. Further additions of AgX to these 2 : 1 adducts did not lead to the formation of $Ag_3(CP_3)X_3$ complexes.

Acknowledgements

We thank Xunta de Galicia for financial support. Crystallographic data for complex **6** were measured at the University of Edinburgh, UK, and intensity measurements of crystals for complexes **8**, **9** and **10** were performed at the Unidade de Raios X, RIAIDT, University of Santiago de Compostela, Spain.

References

1 (*a*) C. A. Crawford, E. F. Day, W. E. Streib, J. C. Huffman and G. Christou, *Polyhedron*, 1994, **13**, 2933; (*b*) M.-L. Tong, X.-M. Chen, B.-H. Ye and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 5278.

2 P. Di Bernardo, G. Dolcetti, R. Portanova, M. Tolazzi, G. Tomat and P. Zanonato, *Inorg. Chem.*, 1990, **29**, 2859.

3 M. R. Churchill, J. Donahue and F. J. Rotella, *Inorg. Chem.*, 1976, **15**, 2752.

4 B. K. Teo and J. C. Calabrese, *Inorg. Chem.*, 1976, **15**, 2467.

5 M. Bardají, O. Crespo, A. Laguna and A. K. Fischer, *Inorg. Chim. Acta*, 2000, **304**, 7.

6 G. A. Bowmaker, Effendy, P. J. Harvey, P. C. Helay, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1996, 2459.

7 E. R. T. Tiekink, *Coord. Chem.*, 1988, **17**, 239.

8 A. Baiada, F. H. Jardine and R. D. Willet, *Inorg. Chem.*, 1990, **29**, 3042.

9 G. Wulfsberg, D. Jackson, W. IIsley, S. Dou, A. Weiss and J. Gagliardi Jr., *Z. Naturforsch., Teil A*, 1992, **47**, 75.

10 G. A. Bowmaker, Effendy, J. V. Hanna, P. C. Healy, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1993, 1387.

11 P. G. Jones, *Acta Crystallogr., Sect. C.*, 1993, **49**, 1148.

12 G. A. Bowmaker, Effendy, P. J. Harvey, P. C. Healy, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1996, 2449.

13 M. Camalli and F. Caruso, *Inorg. Chim. Acta*, 1988, **144**, 205.

14 A. Del Zotto, P. Di Bernardo, M. Tolazzi, G. Tomat and P. Zanonato, *J. Chem. Soc., Dalton Trans.*, 1993, 3009.

15 D. Arffandi, S. J. Berners-Price, Effendy, P. J. Harvey, P. C. Healy, B. E. Ruch and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1997, 1411.

16 S.-M. Kuang, L.-M. Zhang, Z.-Z. Zhang, B. M. Wu and T. C. W. Mak, *Inorg. Chim. Acta*, 1999, **284**, 278.

17 Z.-M. Che, H.-K. Yip, V. W.-W. Yam, P.-Y. Cheung, T.-F. Lai, S.-J. Shieh and S.-M. Peng, *J. Chem. Soc., Dalton Trans.*, 1992, 427.

18 A. L. Airey, G. F. Swiegens, A. C. Willis and S. B. Wild, *Inorg. Chem.*, 1997, **36**, 1588.

19 S. Sailaja and M. V. Rajasekharan, *Inorg. Chem.*, 2000, **39**, 4586.

20 C.-T. Chen and K. S. Suslick, *Coord. Chem. Rev.*, 1993, **128**, 293.

21 O. Kahn and C. J. Martínez, *Science*, 1998, **279**, 44.

22 M. Bertelli, L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Mater. Chem.*, 1997, **7**, 1271.

23 J. F. Corrigan, D. Fenske and W. P. Power, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1176.

24 M. Camalli and F. Caruso, *Inorg. Chim. Acta*, 1990, **169**, 189.

25 S. L. James, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1998, 2323.

26 M. N. I. Khan, R. J. Staples, C. King, J. P. Fackler Jr. and R. E. P. Winpenny, *Inorg. Chem.*, 1993, **32**, 5800.

27 M. Barrow, H. B. Bürgi, M. Camalli, F. Caruso, E. Fisher, L. M. Venanzi and L. Zambonelli, *Inorg. Chem.*, 1983, **22**, 2356.

28 P. Sevillano, M. E. García, A. Habtemaniam, S. Parsons and P. J. Sadler, *Metal-Based Drugs*, 1999, **6**, 211.

29 M. M. Taqui Khan and E. Rama Rao, *Polyhedron*, 1988, **7**, 29.

30 L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, 1968, **90**, 5443.

31 Bruker, SMART and SAINT, Area Detector Control and Integration Software, Bruker Analytical X-ray Instruments Inc., Madison, WI, USA, 1997.

32 G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1997.

33 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

34 G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

35 *International Tables for X-ray Crystallography*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1995, vol. C.

36 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.

37 A. L. Balch and E. Y. Fung, *Inorg. Chem.*, 1990, **29**, 4764.

38 J. Zank, A. Schier and H. Schmidbaur, *Z. Naturforsch., Teil B*, 1997, **52**, 1471.

39 P. F. Barron, J. C. Dyason, P. C. Healy, L. M. Engelhardt, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1986, 1965.

40 (*a*) K. Zangger and I. M. Armitage, *Metal-Based Drugs*, 1999, **6**, 239; (*b*) C.-M. Che, M. C. Tse, M. C. W. Chan, K.-K. Cheung, D. L. Phillips and K.-H. Leung, *J. Am. Chem. Soc.*, 2000, **122**, 2464.

41 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.

42 M. I. García-Seijo, A. Castiñeiras, B. Mahieu, L. Jánosi, Z. Berente, L. Kóllar and M. E. García-Fernández, *Polyhedron*, 2001, **20**, 855.

43 A. Cassel, *Acta Crystallogr., Sect. B*, 1981, **37**, 229.

44 J. Zank, A. Schier and H. Schmidbaur, *J. Chem. Soc., Dalton Trans.*, 1999, 415.

45 S. Attar, N. W. Alcock, G. A. Bowmaker, J. S. Frye, W. H. Bearden and J. H. Nelson, *Inorg. Chem.*, 1991, **30**, 4166.

46 O. Mamula, A. V. Zelewsky, T. Bark and G. Bernardinelli, *Angew. Chem., Int. Ed.*, 1999, **38**, 2945.