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Synthesis and structural characterization of the adducts of silver(I) perchlorate and nitrate with triphenylphosphine and bis(pyrazolyl)methane ligands of 1:1:1 stoichiometry

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Abstract

Six new adducts of the form AgX:PPh_3:$H_2C(pz^x)_2$ (1:1:1) ($H_2C(pz^x)_2 = H_2C(pz)_2$ = bis(pyrazolyl)methane or $H_2C(pz^{Me2})_2$ = bis(3,5-dimethylpyrazolyl)methane; X = ClO_4, NO_3, SO_3CF_3) have been synthesized and characterized by analytical, spectroscopic (IR, far-IR, ^1H and ^{31}P NMR) and two of them also by single crystal X-ray diffraction studies for comparison with counterpart adducts with 2,2′-bipyridyl ('bpy') derivatives reported in a previous paper, the bpy-derived ligands forming five-membered chelate rings, while the present $H_2C(pz^x)_2$ should, potentially, form six-membered rings. Such is the case, the two adducts exhibiting quasi-planar N_2AgP coordination environments, perturbed by the approach of the oxyanion, unidentate in the case of the perchlorate but, in the case of the nitrate, an interesting disordered aggregate of differing unidentate modes.

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Keywords: Silver(I) complexes; Phosphines; N-donor ligands; Pyrazolylmethanes; X-ray; NMR

1. Introduction

In previous papers [1,2], we have described the synthesis and structural and spectroscopic characterization of a diverse array of adducts of 1:1:1 stoichiometry formed between AgX (X = perchlorate or nitrate (also carboxylate [3], not relevant here)), tertiary phosphine, and *N*,*N*′-bidentate bases derivative of 2,2′-bipyridyl ('bpy'), the latter capable of forming five-membered chelate rings; a number of adducts of 'dpa' (= bis(2-pyridyl)amine), potentially and actually capable of forming six-membered rings were also described. A number of group 11 metal complexes containing bis(pyrazol-1-yl)methanes (bidentate N-donor ligands firstly reported by Trofimenko [4]) has been recently described: closed-shell $[AgL_2]^+$ [5–8] and $[CuL_2]^+$ [9,10] (L = RR′C$(pz)_2$, R,R′ = H, Me, Ph, CH_2Ph, py, Fc) species, $[Cu_2(\mu\text{-}X)_2L_2]$ [11,12] (X = halogen or pseudo-halogen), $[CuL(NCMe)_2]^+$ and $[CuL(NCMe)]^+$ [13], L being bidentate chelate. A dinuclear $[Ag_2(\mu\text{-}L)_2](OTf)_2$ (OTf = trifluoromethanesulfonate) in which the ligand bridges both silver centres, has been also described [14]. Our group has reported the formation of adducts between copper salts and bidentate ligands $[H_2C(pz^x)_2]$ also in the presence of ancillary ligands such as mono- or bidentate P-donors [15,16], and, in the above context, we were interested to explore the nature of any counterpart silver adducts to the above, using for the purpose $H_2C(pz)_2$ = bis(pyrazolyl)methane and $H_2C(pz^{Me2})_2$ = bis(3,5-dimethyl)pyrazolylmethane, potentially capable of forming

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six-membered chelate rings as demonstrated elsewhere [8]. We record the results of this work hereunder.

2. Experimental

All syntheses and handling were carried out in the air. All chemicals were purchased from Aldrich and Lancaster and used without further purification. Elemental analyses (C, H, N) were performed in-house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin–Elmer System 2000 FT-IR instrument. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Mercury Plus Varian 400 NMR spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, and 162.1 MHz for ^{31}P) or on a Varian VXR-300 (300 MHz for ^{1}H, 75 MHz for ^{13}C, and 121.4 MHz for ^{31}P). H and C chemical shifts are reported in ppm versus $SiMe_4$, P chemical shifts in ppm versus H_3PO_4 85%.

2.1. Syntheses

Safety note. Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of materials should be prepared, and these should be handled with great caution.

2.1.1. $AgClO_4$:PPh_3:$H_2C(pz)_2$ (1:1:1) (**1**)

To a MeCN solution containing 0.207 g (1.0 mmol) of $AgClO_4$ and 0.262 g (1.0 mmol) of triphenylphosphine, 0.148 g (1.0 mmol) of $H_2C(pz)_2$ was added. The reaction was stirred under reflux for 14 h in a round-bottomed flask protected from the light. The solution was then evaporated and the residue washed with diethyl ether. A precipitate formed that has been identified as compound **1** (80% yield); m.p. 148–150 °C. *Anal.* Calc. for $C_{25}H_{23}N_4AgClO_4P$: C, 48.61; H, 3.75; N, 9.07. Found: C, 49.01; H, 3.64; N, 9.01%. IR (nujol, cm^{-1}): 3113w (CH) 1962w br, 1888w br, 1822w br, 1770w br (ClO_4), 1584w, 1514s (C$\cdots$C, C$\cdots$N), 1082 sbr 620 br, (ClO_4), 522s, 492s, 439m, 401m. ^{1}H NMR ($CDCl_3$): δ, 6.30 (br, 2H, $H4_{pz}$), 6.57 (br, 2H, CH_2), 7.27–7.43 (m, 17H, $CH_{Ph} + H5_{pz}$), 8.20 (br, 2H, $H3_{pz}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 15.5 (d, br, ^1J ($^{31}P, Ag) = 710$ Hz).

2.1.2. $AgNO_3$:PPh_3:$H_2C(pz)_2$ (1:1:1) (**2**)

Compound **2** was prepared following a procedure similar to that reported for **1** by using $AgNO_3$ (0.169 g, 1.0 mmol), PPh_3 (0.262 g, 1.0 mmol) and $H_2C(pz)_2$ (0.148 g, 0.1 mmol); m.p. 138–140 °C. *Anal.* Calc. for $C_{25}H_{23}N_5AgO_3P$: C, 51.74; H, 3.99; N, 12.07. Found: C, 51.92; H, 4.03; N, 11.65%. IR (nujol, cm^{-1}): 3102w (CH), 1891w, 1826w, 1766, 1741br (NO_3), 1584w, 1572w, 1517s (C$\cdots$C, C$\cdots$N), 1360brm 1309s br, 1284m (NO_3) 612w, 520m, 493m, 442w, 409w. ^{1}H NMR ($CDCl_3$): δ, 6.25 (t, 2H, $H4_{pz}$), 6.49 (s, 2H, CH_2), 7.44 (m, 15H, CH_{Ph}), 7.48 (s, 2H, $H5_{pz}$), 7.98 (d, 2H, $H3_{pz}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 15.0 (s, br); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 223 K): 15.4 (d, br, $^1J(^{31}P, Ag) = 680$ Hz).

2.1.3. $AgSO_3CF_3$:PPh_3:$H_2C(pz)_2$ (1:1:1) (**3**)

Compound **3** was prepared following a procedure similar to that reported for **1** by using $AgSO_3CF_3$ (0.256 g, 1.0 mmol), PPh_3 (0.262 g, 0.1 mmol) and $H_2C(pz)_2$ (0.148 g, 0.1 mmol); m.p. 168–171 °C. *Anal.* Calc. for $C_{26}H_{23}AgF_3N_4O_3PS$: C, 46.79; H 3.47; N, 8.39. Found: C, 47.21; H, 3.67; N, 8.12%. IR (nujol, cm^{-1}): 3137 (CH), 1573w, 1557w, 1537w, 1515m, 1504w ν(C$\cdots$C, C$\cdots$N), 1281s, 1245m, 1224m, 1211m, 1165m, 1140m 1093m (O_3SCF_3), 640s, 571m, 520s, 496s, 437m, 401m, 365m . ^{1}H NMR ($CDCl_3$): δ, 6.31 (t, 2H, $H4_{pz}$), 6.70 (s, 2H, CH_2), 7.38 (d, 2H, $H5_{pz}$), 7.45 (m, 15H, CH_{Ph}), 8.35 (d, 2H, $H3_{pz}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 16.1 (d, br, $^1J(^{31}P, Ag) = 727$ Hz).

2.1.4. $AgClO_4$:PPh_3:$H_2C(pz^{Me2})_2$ (1:1:1). MeCN (**4**)

To an MeCN solution containing 0.207 g (1.0 mmol) of $AgClO_4$ and 0.262 g (1.0 mmol) of triphenylphosphine, 0.408 g (2.0 mmol) of $H_2C(pz^{Me2})_2$ was added. The reaction was stirred under reflux for 24 h in a round-bottomed flask protected from the light. A colorless precipitate formed which was filtered off, washed with MeCN and identified as compound **4**. Upon slow evaporation at room temperature of the mother liquor, small crystals were formed that were identified as compound **4**; m.p. 158–160 °C. *Anal.* Calc. for $C_{31}H_{34}AgClN_5O_4P$: C, 52.08; H, 4.79; N, 9.80. Found: C, 52.40; H, 4.72; N, 9.71%. IR (nujol, cm^{-1}): 3132w (CH), 2250w (C–N), 1990w br, 1901w br, 1820w br, 1780w br (ClO_4), 1556s ν(C$\cdots$C, C$\cdots$N), 1074 sbr, 1031br ν(ClO_4), 625s br, 500s, 470w, 429w. ^{1}H NMR ($CDCl_3$): δ, 1.98 (s, 6H, 5-CH_{3pz}), 2.00 (s, 3H, CH_3CN), 2.48 (s, 6H, 3-CH_3pz), 5.89 (s, 2H, $H4_{pz}$), 6.31 (s, 2H, CH_2), 7.47 (m, 15H, CH_{Ph}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 294 K): 15.9 s br. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 223 K): 15.8 (d br, $^1J(^{31}P, Ag) = 680$ Hz).

2.1.5. $AgNO_3$:PPh_3:$H_2C(pz^{Me2})_2$ (1:1:1) (**5**)

Compound **5** was prepared following a procedure similar to that reported for **4** by using $AgNO_3$ (0.169 g, 1.0 mmol), PPh_3 (0.262 g, 1.0 mmol) and $H_2C(pz^{Me2})_2$ (0.408 g, 2.0 mmol); m.p. 197–198 °C. *Anal.* Calc. for $C_{29}H_{31}AgN_5O_3P$: C, 54.73; H, 4.91; N, 11.00. Found: C, 54.92; H, 4.78; N, 11.2%. IR (nujol, cm^{-1}): 3156w (CH) 1887w, 1830w, 1745w, 1678w, 1587w (NO_3) 1557s, 1521s, (C$\cdots$C, C$\cdots$N), 1340br, 1300br, 1260br (NO_3), 521s, 503m, 489s, 470w, 441w, 426w, 345w, 324w, 279w, 253w. ^{1}H NMR ($CDCl_3$): δ, 1.95 (s, 6H, 5-CH_{3pz}), 2.43 (s, 6H, 3-CH_{3pz}), 5.83 (s, 2H, $H4_{pz}$), 6.33 (s, 2H, CH_2), 7.47 (m, 15H, CH_{Ph}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): 15.6 (d, br, $^1J(^{31}P, Ag) = 574$ Hz).

2.1.6. AgO_3SCF_3:PPh_3:$H_2C(pz^{Me2})_2$ (1:1:1) (**6**)

Compound **6** was prepared following a procedure similar to that reported for **4** by using AgO_3SCF_3 (0.385 g, 1.5 mmol), PPh_3 (0.394 g, 1.5 mmol) and $H_2C(pz^{Me2})_2$ (0.594 g, 0.2 mmol); m.p. 176–178 °C. *Anal.* Calc. for $C_{30}H_{31}AgF_3N_4O_3PS$: C, 49.80; H, 4.32; N, 7.74. Found: C, 50.02; H, 4.60; N, 7.91%. IR (nujol, cm^{-1}): 3132w, 1968br, 1895br, 1817br, 1770br (O_3SCF_3), 1553s ν(C$\cdots$C, C$\cdots$N) 1290s, 1274s, 1245s, 1225s, 1164s, 1149s, 1094s (O_3SCF_3), 636s, 572m, 519s, 504s, 434w, 341w. ^1H NMR ($CDCl_3$): δ, 1.97 (s, 6H, 5-CH_{3pz}), 2.47 (s, 6H, 3-CH_{3pz}), 5.88 (s, 2H, $H4_{pz}$), 6.38 (s, 2H, CH_2), 7.49 (m, 15H, CH_{Ph}). $^{31}P\{^1H\}$ *NMR ($CDCl_3$, 293 K): 17.2 (d, br,* $^1J(^{31}P, Ag) = 600$ Hz).

2.2. Structural determinations

Full spheres of CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω-scans; monochromatic Mo Kα 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 in the full matrix least square refinements on $|F|$, refining anisotropic displacement parameter forms for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being included constrained at estimates. Conventional residuals R, R_w on $|F|$ are cited at convergence (reflection weights: $(\sigma^2(F) + 0.000 n_w F^2)^{-1}$). Neutral atom complex scattering factors were employed within the XTAL 3.7 program system [17]. Pertinent results are given in the table and figures, the latter showing non-hydrogen atoms with 50% probability amplitude ellipsoids, hydrogen atoms having arbitrary radii of 0.1 Å.

2.2.1. Crystal/refinement data

*2.2.1.1. $AgClO_4$:PPh_3: $H_2C(pz^{Me2})_2$ (1:1:1). MeCN (**4**).* $C_{31}H_{34}AgClN_5O_4P$, $M = 714.9$. Triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 8.364(1)$, $b = 10.341(2)$, $c = 19.042(3)$ Å, $\alpha = 89.824(4)$, $\beta = 83.061(4)$, $\gamma = 79.857(4)°$, $V = 1609$ Å^3. D_c $(Z = 2) = 1.47_5$ g cm^{-3}. $\mu_{Mo} = 0.80$ mm^{-1}; specimen: $0.32 \times 0.27 \times 0.04$ mm; 'T'$_{min/max} = 0.85$. $2\theta_{max} = 65°$; $N_t = 32547$; $N = 11238$ ($R_{int} = 0.038$), $N_o = 9408$; $R = 0.039$, $R_w = 0.051$ ($n_w = 4$).

*2.2.1.2. $AgNO_3$:PPh_3: $H_2C(pz^{Me2})_2$ (1:1:1) (**5**).* $C_{29}H_{31}AgN_5O_3P$, $M = 636.4$. Monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 7.926(1)$, $b = 33.117(5)$, $c = 10.928(2)$ Å, $\beta = 102.883(2)°$, $V = 2796$ Å^3. D_c $(Z = 4) = 1.51_2$ g cm^{-3}. $\mu_{Mo} = 0.82$ mm^{-1}; specimen: $0.24 \times 0.08 \times 0.07$ mm; 'T'$_{min/max} = 0.90$. $2\theta_{max} = 58°$; $N_t = 25604$; $N = 6958$ ($R_{int} = 0.026$), $N_o = 6149$; $R = 0.038$, $R_w = 0.047$.

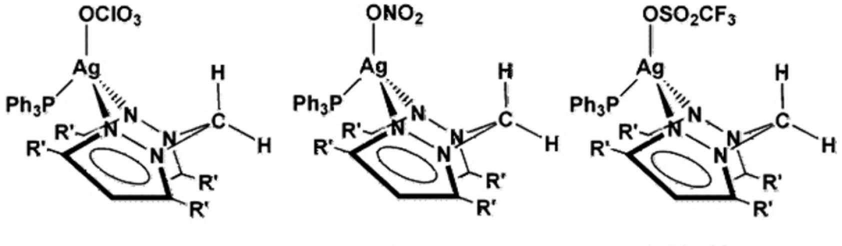
Variata. The oxygen atoms of the nitrate group were modelled as disordered over two sets of sites, occupancies refining to 0.866(7) and complement.

3. Results and discussion

The adducts AgX:PPh_3:$H_2C(pz)_2$ (1:1:1) ($H_2C(pz)_2$ = bis(pyrazolyl)methane, X = ClO_4, NO_3, SO_3CF_3) **1–3** (Chart 1) have been synthesized by reacting the N-donor ligand with a MeCN solution containing equimolar quantities of the PPh_3 and of the corresponding silver salts. When less than one equivalent of the $H_2C(pz)_2$ was used, some unreacted starting material was often recovered from the reaction. It is noteworthy that the ligands $H_2C(pz)_2$ and $H_2C(pz^{Me2})_2$ reacted in a different manner. In fact compounds AgX:PPh_3:$H_2C(pz^{Me2})_2$ (1:1:1) **4–6** (Chart 1) could be obtained only when a N-donor ligand:metal molar ratio of 2:1 was employed. Displacement of the phosphine donor from the silver centre in **1–6** was not observed either, when **1–6** was reacted with more than two equivalents of bis(pyrazolyl)alkanes. From the reaction between $(PR_3)_4AgNO_3$ or $(PPh_3)_4AgClO_4$ and bis(pyrazolyl)alkanes no adducts were isolated.

The IR spectra (some selected data are reported in Section 2) show all the bands required by the presence of the organic N-donor and phosphine ligand. Weak CH stretching vibrations due to the pseudo-aromatic rings are observed in the range 3150–3050 cm^{-1}, similar to those previously found in several bis(pyrazol-1-yl)alkane and pyrazole derivatives of zinc, cadmium, mercury and gold compounds [18–21]. Several weak to medium absorptions found between 1500 and 1600 cm^{-1} may be due to a ring breathing mode. Finally, in the region 900–600 cm^{-1} some absorptions assignable with certainty to C–H bending and ring deformation were always detected [22].

The IR spectra of the perchlorato derivatives **1** and **4** show two absorptions characteristic of a perchlorate group: a strong broad band in the range 1100–1050 cm^{-1} (ν_3) and a sharp medium or strong band at ~625 cm^{-1} (ν_4) [23].



1: R' = H
4: R' = Me

2: R' = H
5: R' = Me

3: R' = H
6: R' = Me

Chart 1.

These absorptions differ slightly from those reported for $[(PPh_3)_4Cu]ClO_4$ [24] and are indicative of a weakly interacting perchlorate group [25] in accordance with the single crystal X-ray study. The silver(I) nitrato derivatives **2** and **5** exhibit absorptions in the region 1400–1100 cm^{-1} which differ considerably from those found in $[(PPh_3)_4Ag]NO_3$ [26]. In both derivatives v_1 and v_4 differ in frequency by 70–90 cm^{-1}, suggesting for this compound in the solid state, the presence of a monodentate nitrato group [27].

In the IR spectra of derivatives **3** and **6**, containing the triflate group, absorptions in the 1000–1300 cm^{-1} region confirm the presence of unidentate weakly coordinated trifluoromethanesulfonate groups [28].

The ^1H and ^{31}P NMR spectra carried out in $CDCl_3$ for all compounds support the formulae proposed and show that the N- and P-donors have not undergone any structural changes upon coordination. From comparisons of chemical shift related to the same type of proton in the free base and in the silver(I) phosphino derivatives, we hypothesize that the complexes persist also in solution, larger coordination shifts being observed with respect to the analogous copper complexes [15,16]. We have found a pattern of chemical shifts in keeping with what has been previously described [29,30]. With exception of the 5-methyl protons in $H_2C(pz^{Me2})$ derivatives, which exhibit smaller coordination shifts to higher fields, all other proton signals shift to lower field upon coordination; the shift is generally appreciable for the bridging CH_2, 3-CH_3 and 3-CH groups.

The metal–$(N–N)_2C$ rings are expected in our compounds to be in the boat conformation, as confirmed by the X-ray studies. Consequently the two N–CH_2–N hydrogens ought to be different, cf. for example the AB_2 pattern being reported for $[H_2C(pz)_2PtCl_2]$ [31], in agreement with the well-established inertness of platinum(II). However in all compounds described here the N–CH_2–N hydrogens were found to be magnetically equivalent, at least at room temperature, so that, even when dissociation is not a cause, a rapid boat inversion must be assumed, probably through M–N bond breaking.

The ^{31}P NMR data (chemical shifts, Ag–^{31}P coupling constants) in CD_3CN solutions of all complexes confirm their stability in this solvent. The room temperature ^{31}P NMR spectra of complexes **2** and **4** consist of broad singlets, presumably in consequence of exchange equilibria that are reasonably fast in relation to the NMR time scale. Exchange is quenched at low temperature, and single unresolved doublets, arising from coupling between the phosphorus and silver atoms, are observed in the accessible temperature range. For all the other derivatives broad doublets were also observed at room temperature, suggesting that rapid exchange equilibria are not operative in these compounds.

It has been proposed [26,32] that the spin–spin coupling constant (*J*) between phosphorus and silver is dependant on the number of coordinated phosphorus atoms in the silver complex, and that it is possible to determine the number of the latter from measurement of the *J* values in the ^{31}P NMR spectra. On the basis of the detected values, $AgPN_2$ or $AgPN_2$ coordination environments perturbed by the presence of weakly bonded counter-ions or solvent molecules are found. The magnitude of the Ag–P coupling constants can be correlated to the counter-ion nature, the lower values being found in the complexes containing the more strongly coordinating NO_3 anion.

The results of the 'low'-temperature single crystal X-ray studies are consistent, in terms of stoichiometry and connectivity, with the formulations of **4** and **5** above. In each case, a single molecule, devoid of crystallographic symmetry, and, in the case of **4**, accompanied by a well-defined acetonitrile molecule of solvation, comprises the asymmetric unit of the structure. In each case, the molecule

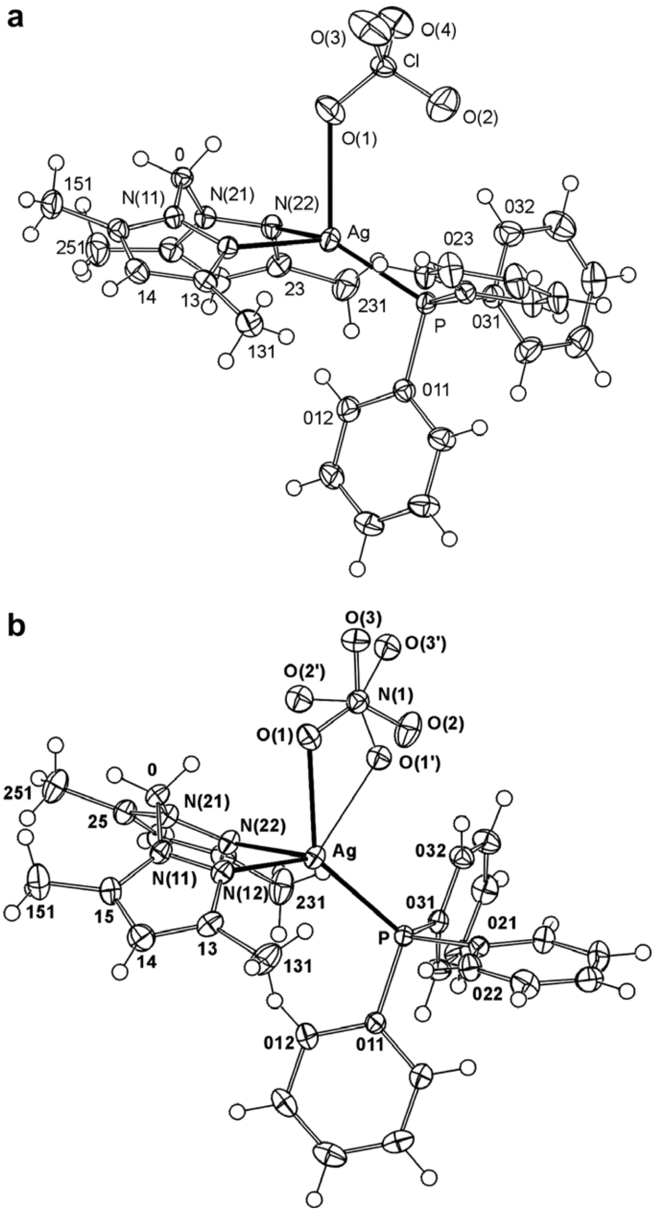


Fig. 1. Projections of single molecules of $AgX{:}PPh_3{:}L$, $X = ClO_4$, NO_3.

Table 1
Selected molecular descriptors

X/ligand	$O\mathrm{ClO_3}$/dpa[a,b]	$\mathrm{ONO_2}$/dpa[b]	$O\mathrm{ClO_3}/\mathrm{H_2C(pz^{Me2})_2}$ (**4**)	$O\mathrm{NO_2}/\mathrm{H_2C(pz^{Me2})_2}$ (**5**)[c]
Distances (Å)				
Ag–P	2.358(2)	2.3465(6)	2.3694(7)	2.3951(7)
Ag–N	2.274(6)	2.280(2)	2.304(2)	2.370(3)
	2.330(6)	2.364(2)	2.320(2)	2.366(2)
Ag–O	2.666(6)	2.452(2)	2.620(2)	2.437(3), 2.38(2)
Angles (°)				
P–Ag–N	141.8(2)	135.90(5)	129.50(5)	126.35(6)
	129.9(2)	125.24(5)	128.08(5)	120.47(6)
N–Ag–N	80.3(2)	79.20(8)	85.16(7)	83.12(8)
O–Ag–P	112.0(1)	119.92(5)	122.79(6)	134.72(7), 97.1(4)
O–Ag–N	85.0(2)	83.61(7)	94.03(7)	88.75(9), 126.9(4)
	92.7(2)	100.87(6)	83.70(7)	87.75(8), 101.2(4)
Ag–O–X	115.8(2)	111.3(2)	128.5(1)	117.5(2), 122(1)
Out-of-plane deviations of the silver atom (Å)				
$\mathrm{C_{4,5}N(1)}$	0.12(1)	0.166(4)	0.080(4)	1.133(5)
$\mathrm{C_{4,5}N(2)}$	0.82(1)	1.345(4)	1.298(4)	0.011(5)
Triphenylphosphine ligand torsion angles (°); carbon atoms are denoted by number only				
Ag–P–11–12	20.3(7)	12.0(2)	25.3(2)	7.4(2)
Ag–P–21–22	38.6(7)	42.1(3)	28.2(2)	62.8(2)
Ag–P–31–32	55.1(7)	44.9(2)	42.2(2)	56.8(2)

[a] Ag–O(2) is 3.020(2) Å.
[b] Refs. [1,2].
[c] Ag–O(2,2′) are 3.177(4) and 3.22(2) Å.

comprises a silver atom coordinated by a unidentate triphenylphosphine and a chelating *N*,*N*′-bidentate ligand, comprising a quasi-trigonal planar array about the silver atom, the planarity perturbed by the approach of a unidentate oxyanion normal to the plane. The molecules are depicted in Fig. 1, core geometries being given, together with those of the counterpart dpa arrays [1,2], in Table 1. (It is of interest that anion rather than solvent approach is the form of the out-of-plane weak interaction; Ag–NCMe interactions are well known and well defined, but in the present situation, at least, and in the context of other undefined lattice forces, are not competitive with that of the *O*-perchlorate.) The nitrate structure is of interest, the nitrate ion being disordered over a pair of sites, one predominant; in the alternative orientation, also unidentate, this coordinating oxygen atom lies toward the phosphorus donor, unusually so in the context of the other related compounds of Refs. [1,2]. An interesting feature of the silver atom environments in both the present and their dpa analogues (Table 1) is that, although here and in the other derivatives of Refs. [1,2], there is little or no evidence for any tendency in the silver atom environment toward two-coordination, the pair of Ag–N distances being essentially equal in all cases, there is a pronounced asymmetry in the deviation of the silver atom from the pair of aromatic ligand planes coordinating it, presumably concomitant on the interaction of these planes (with substituents in the present cases) with the triphenylphosphine ligand, an effect not evident in the compounds of Refs. [1,2] where the constraints on coplanarity of the two aromatic components of the *N*,*N*′-ligand are more demanding, an effect seemingly not correlating with the disposition of the donor plane with respect to the asymmetry of the phosphine ligand. A further feature of interest is that the present *N*,*N*′-ligand seemingly coordinates less strongly than does the dpa ligand (Table 1), despite the apparently alacrity with which L and related systems form silver(I) complexes, cf. the readiness of dpa to behave as a unidentate ligand [3].

Appendix A. Supplementary material

CCDC 609840 and 609841 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.2006.11.004.

References

[1] Effendy, F. Marchetti, C. Pettinari, B.W. Skelton, A.H. White, Inorg. Chim. Acta 360 (2007) 1424.
[2] C. Di Nicola, Effendy, F. Marchetti, C. Pettinari, B.W. Skelton, A.H. White, Inorg. Chim. Acta 360 (2007) 1433.
[3] Effendy, F. Marchetti, C. Pettinari, R. Pettinari, B.W. Skelton, A.H. White, Inorg. Chim. Acta 360 (2007) 1451.
[4] S. Trofimenko, J. Am. Chem. Soc. 70 (1970) 5118.
[5] D.L. Reger, J.R. Gardinier, M.D. Smith, Inorg. Chem. 43 (2004) 3825.

[6] D.L. Reger, J.R. Gardinier, Polyhedron 23 (2004) 291.

[7] D.L. Reger, K.J. Brown, J.R. Gardinier, M.D. Smith, Organometallics 22 (2003) 4973.

[8] A. Lorenzotti, F. Bonati, A. Cingolani, G.G. Lobbia, D. Leonesi, B. Bovio, Inorg. Chim. Acta 170 (1990) 199.

[9] J.L. Shaw, T.B. Cardon, G.A. Lorigan, C.J. Ziegler, Eur. J. Inorg. Chem. (2004) 1073.

[10] C.C. Chou, C.C. Su, H.L. Tsai, K.H. Lii, Inorg. Chem. 44 (2005) 628.

[11] Y. Xu, H.X. Li, W.H. Zhang, Y. Zhang, J.P. Lang, Acta Crystallogr., Sect. C 61 (2005) m4.

[12] L. Zhang, W.M. Bu, S.P. Yan, Z.H. Jiang, D.Z. Liao, G.L. Wang, Polyhedron 19 (2000) 1105.

[13] C.C. Chou, C.C. Su, A. Yeh, Inorg. Chem. 44 (2005) 6122.

[14] M.J. Calhorda, P.J. Costa, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, M. Naranjo, S. Quintal, Y.-J. Shi, M.D. Villacampa, Dalton Trans. (2006) 4104.

[15] C. Pettinari, F. Marchetti, R. Polimante, A. Cingolani, G. Portalone, M. Colapietro, Inorg. Chim. Acta 249 (1996) 215.

[16] C. Pettinari, G. Gioia Lobbia, G. Sclavi, D. Leonesi, M. Colapietro, G. Portalone, Polyhedron 14 (1995) 1709.

[17] S.R. Hall, D.J. du Bolay, R. Olthof-Hazekamp (Eds.), The XTAL 3.7 System, University of Western Australia, 2001.

[18] D. Leonesi, A. Lorenzotti, A. Cingolani, F. Bonati, Gazz. Chim. Ital. 111 (1981) 483.

[19] A. Lorenzotti, A. Cingolani, D. Leonesi, F. Bonati, Inorg. Chim. Acta 89 (1984) 113.

[20] J.G.A. Luijten, G.J.M. Van der Kerk, Recl. Trav. Chem. Pays-Bas 82 (1963) 1181.

[21] R. Gassend, J.C. Maire, J.C. Pommier, J. Organomet. 132 (1977) 69.

[22] H. Okkersen, W.L. Groeneveld, J. Reedijk, Recl. Trav. Chem. Pays-Bas 92 (1973) 945.

[23] M.R. Rosenthal, J. Chem. Educ. 50 (1973) 331.

[24] F.A. Cotton, D.M.L. Goodgame, J. Chem. Soc. (1960) 5267.

[25] R.J. Restivo, A. Costin, G. Ferguson, A.J. Carty, Can J. Chem. 53 (1975) 1949.

[26] E.L. Muetterties, C.W. Alegranti, J. Am. Chem. Soc. 94 (1972) 6386.

[27] K. Nakamoto, Complexes of sulphate, carbonate and related ligands, in: Infrared and Raman Spectra of Inorganic and Coordination Compounds, fifth ed., Wiley-Interscience Publications, John Wiley & Sons, Inc., New York, 1997, pp. 87–89, Part B.

[28] G.A. Lawrance, Chem. Rev. 86 (1986) 17.

[29] J.L. Burmeister, R.L. Hassel, R.J. Phelan, Inorg. Chem. 10 (1971) 2032.

[30] S.C. Jain, R. Rivest, Inorg. Chim. Acta 4 (1970) 291.

[31] G. Minghetti, M.A. Cinellu, A.L. Bandini, F. Demartin, M. Manassero, J. Organomet. Chem. 315 (1986) 387.

[32] R.G. Goel, P. Pilon, Inorg. Chem. 17 (1978) 2876.