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Silver(I) complexes with the mixed P/O donor ligand Ph₂P(CH₂)₂O(CH₂)₂O(CH₂)₂PPh₂ (L¹) and the crystal structures of [Ag(L¹)](CF₃SO₃), [Ag₂(L¹)₃](CF₃SO₃)₂ and [Ag(L¹)(NO₃)]

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Abstract

The Ag(I) salts AgY (Y = ClO₄, CF₃SO₃, NO₃, Cl or I) react with one molar equivalent of the diphosphinodiether ligand $Ph_2P(CH_2)_2O(CH_2)_2Ph_2$ (L¹) to give 1:1 species of stoichiometry Ag(L¹)Y. The structures of these species have been investigated in solution by ³¹P NMR spectroscopy and for [Ag(L¹)](ClO₄), [Ag(L¹)](CF₃SO₃) and [Ag(L¹)(NO₃)] in the solid state by single crystal X-ray diffraction. In particular, the ¹⁰⁷Ag–P and ¹⁰⁹Ag–P coupling constants provide a convenient method for identifying the solution speciation, especially for the occurrence of anion coordination in the nitrate and halide complexes. The conclusions from the NMR spectroscopic studies are also consistent with the solid state structures. Addition of a further equivalent of L¹ to [Ag(L¹)](CF₃SO₃) results in a very significant drop in the Ag–P coupling constants, indicative of higher P-coordination at Ag(I), now involving three P-donor atoms. This conclusion is also borne out by a crystallographic study on [Ag₂(L¹)₃](CF₃SO₃)₂ which shows a dinuclear cation with one chelating L¹ and one bridging L¹ ligand coordinated to each metal centre, giving a distorted trigonal planar geometry. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Silver(I) complexes; Mixed P/O donor ligands; Crystal structures; NMR spectroscopy

1. Introduction

We have been interested for some time in the coordinating properties of mixed phosphathia and phosphaoxa ligands. These are of interest since they allow the coordinating properties of both donor atom types to be investigated in a single ligand and may promote unusual metal complexes [1-5]. Furthermore, depending on the actual metal ion, one or other of the donor atom types may not interact significantly. For example, we have shown that the dinuclear $[Au_2{Ph_2P(CH_2)_2}-S(CH_2)_2S(CH_2)_2Ph_2}_2]Cl_2$ adopts an unusual helical structure through coordination via the P atoms only, with one Cl⁻ anion occupying the metallocyclic cavity [1]. Also, Gray and co-workers have shown that ligands of the form $Ph_2P\{(CH_2)_2O\}_n(CH_2)_2Ph_2$ (n = 3 or 5) function as *cis*-chelating bidentate ligands to Mo te-

tracarbonyl via the P atoms, affording metallocyclic complexes which then bind alkali metal ions through the ether oxygens [6]. They have also shown that $[Pt(H_2O){Ph_2P{(CH_2)_2O}_4(CH_2)_2PPh_2}]^{2+}$ involves coordination to Pt(II) through both P atoms and one ether oxygen, as well as the aquo ligand [7]. Very recently, Mirkin and co-workers have demonstrated that under appropriate conditions the phosphathia ligand $o-C_6H_4{S(CH_2)_2PPh_2}_2$ forms an unusual neutral metallocyclic complex with Rh(I), via a halide-induced ring opening reaction [8]. In the course of our recent work we have demonstrated that $Ph_2P(CH_2)_2O(CH_2)_2$ - $O(CH_2)_2PPh_2$ (L¹) reacts with AgBF₄ or with AuCl(tht) and $TlPF_6$ to give the linear, two-coordinate $[Ag(L^1)]$ - BF_4 or $[Au(L^1)]PF_6$, respectively, both of which were crystallographically characterised [4]. The occurrence of two-coordinate Ag(I) species involving only phosphine ligands is relatively rare, other examples include $[Ag{P(tol)_3}_2]^+$, $[Ag(P'Bu_3)_2]^+$ and $[Ag{P(NMe_2)_3}_2]^+$ [9-11]. This prompted us to investigate whether other factors would lead to L^1 altering its mode

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of coordination to Ag(I), and whether we would be able to detect this in solution through ³¹P NMR spectroscopic studies. In this paper we report our findings, including the preparations of a series of other Ag(I)complexes of L¹ incorporating a variety of different anions, and using different ratios of $Ag:L^1$. Crystal structures of specific examples are also included.

2. Results and discussion

The silver(I) complexes were prepared in good yield by treatment of the appropriate silver salt with one (or two for $[Ag_2(L^1)_3](CF_3SO_3)_2)$ molar equivalent(s) of L^1 in CH₂Cl₂ at 0 °C (or reflux for the Cl and I derivatives) in foil-wrapped flasks to protect the solutions from bright light, followed by precipitation with diethyl ether. Reaction of Ag(CF₃SO₃) with two molar equivalents of L^1 repeatedly yielded the 2:3 Ag: L^1 complex, and we saw no evidence for the formation of $[Ag(L^{1})_{2}](CF_{3}SO_{3})_{2}$ despite using excess L¹, whereas reaction of L¹ with two molar equivalents of AgI afforded the dinuclear species $(AgI)_2(L^1)$. The electrospray mass spectra of the 1:1 Ag:L¹ salts each show peaks with the correct isotopic distribution for $[Ag(L^{1})]^{+}$ (m/z = 593, 595), in addition Ag(L¹)I shows peaks with the correct isotopic distribution for $[Ag_2(L^1)_2I]^+$. The mass spectrum of $[Ag_2(L^1)_3]$ - $(CF_3SO_3)_2$ shows peaks consistent with $[Ag(L^1)_2]^+$ $(m/2)^+$ z = 1079, 1081) and $[Ag(L^1)]^+$ (m/z = 593, 595). These data, together with elemental microanalyses and ¹H NMR spectroscopy, confirm the stoichiometries of the products as $Ag(L^1)X$ (X = ClO₄, CF₃SO₃, NO₃, Cl or I), $[Ag_2(L^1)_3](CF_3SO_3)_2$ and $[(AgI)_2(L^1)]$.

We have shown previously that $J(^{107}Ag-P)$ and $J(^{109}Ag-P)$ for $[Ag(L^1)]BF_4$ are 523 and 601 Hz, respectively and a crystallographic analysis of this salt revealed two-coordinate Ag(I)—see above [4]. It is known that the magnitude of the Ag-P coupling constants in silver phosphine complexes varies with coordination number at silver, becoming smaller as the coordination number increases [12,13]. We have there-

Table 1 ${}^{31}P{}^{1}H$ NMR data ^a

Compound	δ^{31} P (ppm)	¹ J ^{107/109} Ag–P (Hz)		
$\overline{Ag(L^1)BF_4}$	-3.4	523, 601		
$Ag(L^1)CF_3SO_3$	-1.4	511, 582		
$Ag(L^1)ClO_4$	-0.7	522, 604		
$Ag(L^1)NO_3$	-1.9	497, 568		
$Ag(L^1)Cl$	-5.5	438, 505		
$Ag(L^1)I$	-5.4	410, 473		
$(AgI)_2(L^1)$	-22.9	458, 536		
$Ag_2(L^1)_3(CF_3SO_3)_2$	-5.4	332, 380		

^a Spectra recorded in CH₂Cl₂/CDCl₃.

fore probed the solution coordination environment at Ag(I) in the range of compounds incorporating different anions by ³¹P NMR spectroscopy. In all cases the ³¹P NMR spectra exhibit a single phosphorus environment with a resonance to high frequency of free L^1 (δ ${}^{31}P = -21.3$). In most cases the room temperature spectra reveal two doublets, consistent with coupling to $^{107/109}$ Ag (both I = 1/2, 49%, 51% abundant respectively), although for some, the solutions had to be cooled to observe these couplings, consistent with high lability. The chemical shift data and couplings are given in Table 1. In all cases the ratio of the ${}^{107}Ag - P/{}^{109}Ag -$ P coupling constants is close to 0.87, consistent with the relative magnetogyric ratios. The data show that for the NO_3^- , Cl^- and I^- complexes there is a significant reduction in the coupling constants (cf. the BF_4^{-} salt), strongly suggesting some interaction of these relatively strongly coordinating anions with the Ag(I) centre, increasing the formal coordination number at Ag(I). In contrast, the coupling constants for the ClO_4^- and the 1:1 Ag:L¹ CF₃SO₃⁻ salts show virtually no change, consistent with retention of the linear P2-donor set seen for the BF_4^- salt. The resonance for $(AgI)_2(L^1)$ is significantly to low frequency of those for the 1:1 Ag:L¹ species, but clearly shows coupling to ^{107/109}Ag at low temperature. Addition of a further molar equivalent of L^1 to $[Ag(L^1)](CF_3SO_3)$ leads to a dramatic reduction in $J^{107/109}$ Ag–P, strongly suggesting generation of a higher coordination number at Ag(I). In fact, the coupling constants for [Ag₂(L¹)₃](CF₃SO₃)₂ of 332 and 380 Hz are intermediate between those seen for P_2 coordination from L^1 on Ag(I) (523, 601 Hz—see above) and P_4 coordination at Ag(I), e.g. in tetrahedral [Ag(dppe)₂]⁺, ${}^{1}J({}^{107}\text{Ag}-\text{P}) = 231, {}^{1}J({}^{109}\text{Ag}-\text{P}) = 266$ Hz [14]. These data suggest that $[Ag_2(L^1)_3]^{2+}$ probably involves P_3 coordination at Ag(I). It is notable that ³¹P NMR spectroscopy shows that addition of a further molar equivalent of L^1 to $[Ag(L^1)(NO_3)]$ leads to dissociation of the ligating nitrate and formation of $[Ag_2(L^1)_3]^{2+}$, the nitrate now functioning as counterion. In order to investigate whether these solution effects were mirrored in the solid state, crystallographic analyses were undertaken on $[Ag(L^1)](ClO_4)$, $[Ag(L^1)](CF_3SO_3)$, $[Ag_2(L^1)_3]$ - $(CF_3SO_3)_2$ and $[Ag(L^1)(NO_3)]$.

[Ag(L¹)](ClO₄) (monoclinic, C2/c, Z = 4, a = 15.8420(2), b = 13.2335(3), c = 15.7553(3) Å, $\beta = 118.012(2)^{\circ}$) is isostructural with [Ag(L¹)]BF₄, [4] with crystallographic two-fold symmetry and linear Ag(I) coordinated to the two P-donor atoms of L¹, d(Ag-P) = 2.405(1) Å and $\angle P(1)-Ag(1)-P(1^*) = 165.16(7)^{\circ}$. The crystal structure of [Ag(L¹)](CF₃SO₃), although not isostructural, shows (Fig. 1, Table 2) a very similar geometry at Ag(I) which coordinates to both P atoms of L¹ giving an approximately linear arrangement with no interaction between the triflate anion and the silver ion, Ag-P(1) = 2.4070(9),



Fig. 1. View of the structure of the Ag-containing species in $[Ag(L^1)](CF_3SO_3)$. CH_2Cl_2 with numbering scheme adopted. Ellipsoids are drawn at 40% probability. H atoms are omitted for clarity.

Table 2

Selected bond lengths (Å) and bond angles (°) for $[Ag(L^1)]\text{-}(CF_3SO_3)\text{-}CH_2Cl_2$

2.4070(9)
2.4172(9)
167.55(3)

Ag–P(2) = 2.4172(9) Å, $\angle P(1)$ –Ag–P(2) = 167.55(3)°. In contrast, the crystal structure of [Ag(L¹)(NO₃)] shows (Fig. 2, Table 3) the silver centre coordinated to the two P atoms from L¹, with additional weak interac-

Table 3 Selected bond lengths (Å) and bond angles (°) for $[Ag(L^1)(NO_3)]$

Rond lengths	
Ag(1)-P(1)	2.412(2)
Ag(1) - P(2)	2.616(2)
Ag(1)–O(3)	2.675(7)
Ag(1)–O(4)	2.496(9)
Bond angles	
P(1)-Ag(1)-P(2)	139.2(1)
P(1)-Ag(1)-O(3)	106.9(2)
P(1)-Ag(1)-O(4)	115.9(2)
P(2)-Ag(1)-O(3)	110.2(1)
P(2)–Ag(1)–O(4)	101.2(1)
O(3)–Ag(1)–O(4)	49.2(2)

tions to two O atoms from an asymmetrically bound bidentate NO_3^{-} ligand, Ag-O = 2.496(9), 2.675(7) Å. The overall coordination geometry is distorted psuedotetrahedral, with $\angle P(1)-Ag(1)-P(2) = 139.2(1)^{\circ}$. The structure of $[Ag_2(L^1)_3](CF_3SO_3)_2$ shows that the cation is centrosymmetric (Fig. 3, Table 4) with each of the two Ag atoms coordinated to one chelating L^1 via the two P donors, and to one P donor atom from a bridging L^1 . Thus each Ag(I) ion is in a distorted trigonal planar environment of three P atoms, with no Ag–O interactions. The angles around Ag(I) lie in the range 114.10(4)-125.84(4)°. The Ag-P bond lengths (2.4494(12), 2.4551(12), 2.4729(12) Å) are slightly longer than those in the linear two-coordinate species $[Ag(L^1)]^+$, consistent with the increase in coordination number.

Thus, the solid state structures of these complexes are entirely consistent with the conclusions from the ${}^{31}P$



Fig. 2. View of the structure of $Ag(L^1)(NO_3)$ with numbering scheme adopted. Ellipsoids are drawn at 40% probability. H atoms are omitted for clarity.



Fig. 3. View of the structure of the Ag-containing species in $[Ag_2(L^1)_3](CF_3SO_3)_2$ with numbering scheme adopted. Ellipsoids are drawn at 40% probability. H atoms and phenyl rings are omitted for clarity. Atoms marked with a prime are related by a crystallographic inversion centre.

NMR spectra described above. It is somewhat surprising that there is no interaction between the ether oxygen atoms and the silver(I) ion in any of these species, but that NO_3 does interact significantly despite the low affinity of Ag(I) for O-donor ligands.

These results demonstrate that L^1 is a very versatile ligand to silver(I), readily altering its mode of coordination and conformation to accommodate changes at the metal centre. Furthermore, the structures identified for the complexes in the solid state are consistent with the conclusions from the solution NMR studies, with the ¹⁰⁷Ag-³¹P and ¹⁰⁹Ag-³¹P coupling constants changing in a predictable way with changes in the coordination number and environment at Ag(I).

3. Experimental

Infrared spectra were recorded as KBr or CsI discs using a Perkin–Elmer 1710 spectrometer over the range 4000–220 cm⁻¹. Mass spectra were run by positive ion electrospray (MeCN solution) using a VG Biotech platform. ¹H NMR spectra were recorded in CDCl₃ using a Bruker AM300 spectrometer. ³¹P{¹H} NMR spectra were recorded in CH₂Cl₂ containing approximately 10– 15% CDCl₃ using a Bruker AM360 or DPX400 spectrometer operating at 145.8 or 162.0 MHz, respectively and are referenced to 85% H₃PO₄ ($\delta = 0$). Microanalyses were undertaken by the University of Strathclyde microanalytical service. L¹ was prepared as described previously [4].

Table 4								
Selected	bond	lengths	(Å)	and	bond	angles	(°)	for
$[Ag_2(L^1)_2]$	ICF-SO	2)2						

Bond lengths	
Ag(1) - P(1)	2.4494(12)
Ag(1) - P(2)	2.4551(12)
Ag(1)–P(3)	2.4729(12)
Bond angles	
P(1)-Ag(1)-P(2)	125.84(4)
P(1)-Ag(1)-P(3)	114.10(4)
P(2)-Ag(1)-P(3)	119.93(4)

3.1. Preparations

 $Ag(L^{1})(CF_{3}SO_{3})$: To a degassed solution of L¹ (0.100 g, 0.206 mmol) in CH₂Cl₂ (20 cm³) at 0 °C was added Ag(CF₃SO₃) (0.053 g, 0.206 mmol). The resulting solution was stirred for approximately 3 h in a foil-wrapped flask. The solution was then concentrated in vacuo to approximately 5 cm³ and hexane (ca. 30 cm³) was added to afford a white solid, which was filtered and dried in vacuo. Yield 72%, 0.110 g. Anal. Found: C, 50.1; H, 4.3. Calc. for C₃₁H₃₂AgF₃O₅P₂S: C, 50.1; H, 4.3%. Electrospray mass spectrum (MeCN): found m/z = 595, 593. Calc. for $[^{109}Ag(L^1)]^+$ 595, $[^{107}Ag(L^1)]^+$ 593. ¹H NMR: δ 7.3–7.6 (m, Ph, 20H), 3.6–3.8 (m, CH₂O, 8H), 2.7 (m, CH₂P, 4H). IR (cm⁻¹): 3059 w, 2961 w, 2925 w, 2866 w, 1560 w, 1484 m, 1439 m, 1349 m, 1271 s, 1221 m, 1147 m, 1122 m, 1097 m, 1023 s, 904 w, 795 m, 750 m, 691 s, 667 m, 637 s, 513 s, 463 w, 433 w, 349 w.

Ag(*L*¹)(*NO*₃): Method as above giving a white solid. Yield 43%. *Anal.* Found: C, 54.9; H, 4.7. Calc. for C₃₀H₃₂AgNO₅P₂: C, 54.9; H, 4.9%. Electrospray mass spectrum (MeCN): found *m*/*z* = 595, 593. Calc. for [¹⁰⁹Ag(L¹)]⁺ 595, [¹⁰⁷Ag(L¹)]⁺ 593. ¹H NMR: δ 7.3−7.7 (m, Ph, 20H), 3.5−3.8 (m, CH₂O, 8H), 2.6 (m, CH₂P, 4H). IR (cm⁻¹): 3051 w, 2955 w, 2959 w, 1484 m, 1435 m, 1384 s, 1297 s, 1187 w, 1130 m, 1100 s, 1034 w, 998 m, 894 w, 821 w, 741 m, 694 m, 517 m, 473 w, 438 w.

Ag(*L*₁)(*ClO*₄): Method as above, giving a white solid. Yield 42%. *Anal.* Found: C, 50.6; H, 4.7. Calc. for C₃₀H₃₂AgClO₆P₂·1/2CH₂Cl₂: C, 49.8; H, 4.5%. Electrospray mass spectrum (MeCN): found *m*/*z* = 595, 593; Calc. for [¹⁰⁹Ag(L¹)]⁺ 595, [¹⁰⁷Ag(L¹)]⁺ 593. ¹H NMR: δ 7.4–8.0 (m, Ph, 20H), 3.7–4.0 (m, CH₂O, 4H), 3.5 (m, CH₂O, 2H), 2.8 (m, CH₂O, 2H), 2.6 (m, CH₂P, 4H). IR (cm⁻¹): 3046 w, 2956 w, 2907 w, 2862 w, 1560 w, 1473 m, 1463 w, 1438 s, 1406 w, 1367 m, 1346 m, 1306 w, 1285 m, 1237 w, 1221 m, 1185 w, 1164m, 1097 vs br, 995 s, 909 m, 884 m, 792 m, 759 s, 748 s, 710 m, 694 s, 623 s, 548 w, 523 m, 510 m, 463 m, 419 w, 362 w.

Ag(*L*¹)*Cl*: Method as above, except the CH₂Cl₂ solution was refluxed. Yield 54%. *Anal.* Found: C, 55.2; H, 5.5. Calc. for C₃₀H₃₂AgClO₂P₂·1/2CH₂Cl₂: C, 54.5; H, 4.9%. Electrospray mass spectrum (MeCN): found *m*/*z* = 595, 593. Calc. for [¹⁰⁷Ag(L¹)]⁺ *m*/*z* = 593, [¹⁰⁹Ag(L¹)]⁺ *m*/*z* = 595. ¹H NMR: δ 7.4–7.7 (m, Ph, 20H), 3.8 (m, CH₂O, 4H), 3.7 (s, CH₂O, 4H), 2.6 (m, CH₂P, 4H). IR (cm⁻¹): 3061 w, 2970 w, 2864 w, 1540 w, 1489 m, 1441 m, 1359 m, 1262 m, 1190 w, 1103 s, 1036 m, 809 m, 751 m, 698 m, 621 w, 545 w, 515 m, 486 w, 445 w, 410 w. *A*_m (CH₂Cl₂, 10⁻³ mol dm⁻³) = 1.7 ohm⁻¹ cm² mol⁻¹.

 $Ag(L^{1})I$: Method as above, with refluxing CH₂Cl₂. Yield 84%. *Anal.* Found: C, 50.0; H, 4.5. Calc. for C₃₀H₃₂AgIO₂P₂: C, 50.3; H, 4.6%. Electrospray mass spectrum (MeCN): found m/z = 1315, 593, 595. Calc. for [¹⁰⁹Ag₂(L¹)₂I]⁺ 1317, [¹⁰⁷Ag(L¹)]⁺ 593, [¹⁰⁹Ag(L¹)]⁺ 595. ¹H NMR: δ 7.3–7.7 (m, Ph, 20H), 3.8 (m, CH₂O, 4H), 3.6 (s, CH₂O, 4H), 2.6 (m, CH₂P, 4H). IR (cm⁻¹): 3069 w, 2960 w, 2935 w, 2870 w, 1590 w, 1484 m, 1431 m, 1359 m, 1312 w, 1187 w, 1100 s, 1036 w, 989 m, 890 m, 850 w, 744 m, 692 m, 619 w, 540 w, 507 m. $\Lambda_{\rm m}$ (CH₂Cl₂, 10⁻³ mol dm⁻³) = 1.9 ohm⁻¹ cm² mol⁻¹.

 $[(AgI)_2(L^1)]$: Method as above, with refluxing CH₂Cl₂ and using two molar equivalents of AgI. Yield 41%. Anal. Found: C, 38.0; Н, 3.5. Calc. for C₃₀H₃₂Ag₂I₂O₂P₂: C, 37.7; H, 3.4%. Electrospray mass spectrum (MeCN): found m/z = 593, 595. Calc. for $[^{107}Ag(L^1)]^+$ 593, $[^{109}Ag(L^1)]^+$ 595. ¹H NMR: δ 7.3–7.7 (m, Ph, 20H), 3.8 (m, CH₂O, 4H), 3.6 (s, CH₂O, 4H), 2.6 (m, CH₂P, 4H). IR (cm⁻¹): 3069 w, 2945 w, 2859 w, 1572 w, 1482 m, 1435 m, 1357 m, 1308 w, 1260 m, 1185 w, 1158 w, 1096 s, 1025 w, 996 m, 975 w, 788 m, 741 m, 694m, 618 w, 512 m, 482 w. $\Lambda_{\rm m}$ (CH₂Cl₂ 10⁻³ $mol dm^{-3}$) = 1.6 ohm⁻¹ cm² mol⁻¹.

[$Ag_2(L^1)_3$](CF_3SO_3)₂: Method as above but using two molar equivalents of L¹. Yield 23%. *Anal.* Found: C, 56.7; H, 5.1. Calc. for C₉₂H₉₆Ag₂F₆O₁₂P₆S₂: C, 56.0; H, 4.9%. Electrospray mass spectrum (MeCN): found m/z = 1079, 1081, 593, 595. Calc. for [$^{107}Ag(L^1)_2$]+ 1079, [$^{109}Ag(L^1)_2$]+ 1081, [$^{107}Ag(L^1)$]+ 593, [$^{109}Ag(L^1)_2$]+ 1079, 1H NMR: δ 7.3–7.6 (m, Ph, 20H), 3.5–3.7 (m, CH₂O, 8H), 2.6 (br, CH₂P, 4H). IR (cm⁻¹): 3062 w, 2950 w, 2930 w, 2874 w, 1484 m, 1437 m, 1403 m, 1364 m, 1266 s, 1224 m, 1148 m, 1100 s, 1033 m, 999 m, 911 w, 750 s, 697 s, 638 s, 518 s, 524 w, 486 w.

3.2. X-ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 5. The crystals were grown by vapour diffusion of diethyl ether into solutions of the complexes in CH₂Cl₂ at approximately -15 °C. Data collection used a Rigaku AFC7S fourcircle diffractometer or an Enraf-Nonius Kappa CCD diffractometer operating at T = 150 K and using graphite-monochromated Mo K α X-radiation ($\lambda =$ 0.71073 Å). Structure solution and refinement were routine, except for some disorder in some of the C atoms associated with the phenyl groups in $[Ag(L^1)(NO_3)]$ which was modelled satisfactorily using partial occupancies [15-17]. Selected bond lengths and angles are given in Tables 2-4.

4. Supplementary material

Cystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 164925–164928. Copies of this information may be obtained free of charge from

Crystallographic data and structure refinement parameters

Complex	$[Ag(L^1)](CF_3SO_3).CH_2Cl_2$	$[Ag_{2}(L^{1})_{3}](CF_{3}SO_{3})_{2}$	$[Ag(L^{1})(NO_{3})]$
Empirical formula	C ₃₂ H ₃₄ AgCl ₂ F ₃ O ₅ P ₂ S	$C_{92}H_{96}Ag_2F_6O_{12}P_6S_2$	$C_{30}H_{32}AgNO_5P_2$
Formula weight	828.39	1973.45	656.40
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\overline{1}$	$P\overline{1}$	C2/c
Unit cell dimensions			
a (Å)	10.0928(1)	11.0275(1)	25.87(7)
b (Å)	10.4575(1)	12.5004(2)	9.20(2)
<i>c</i> (Å)	16.5622(2)	16.9448(2)	24.74(4)
α (°)	90.5877(5)	80.7110(8)	90
β (°)	90.8655(5)	81.7090(8)	101.1(2)
γ (°)	100.5412(5)	76.0320(5)	90
$V(Å^3)$	1718.22(3)	2223.47(5)	5777.8(2)
Ζ	2	1	8
μ (Mo K α) (cm ⁻¹)	9.49	6.67	8.46
Unique observed reflections	7022	10186	5427
Reflections observed $[I_o > n\sigma(I_o)]$	5031, $n = 3$	7028, $n = 3$	3725, $n = 2$
Parameters	415	541	437
R	0.039	0.058	0.050
R _w	0.048	0.067	0.070

 $R = \Sigma \left(\left| F_{\rm obs} \right|_i - \left| F_{\rm calc} \right|_i \right) / \Sigma \left| F_{\rm obs} \right|_i; \ R_{\rm w} = \left[\Sigma \ w_i (\left| F_{\rm obs} \right|_i - \left| F_{\rm calc} \right|_i \right)^2 / \Sigma \ w_i \left| F_{\rm obs} \right|_i^2 \right].$

The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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