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Communication

Adducts of silver(I) nitrite with triphenylphosphine and *N*,*N*′-bidentate aromatic bases, L, of the form $AgNO_2$:PPh_3:L (1:1:1)

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Abstract

Adducts of the form $AgNO_2$:PPh_3: L (1:1:1) (L = 2,2′-bipyridyl (bpy), 1,10-phenanthroline (phen), 2,9-dimethylphenanthroline (dmp)) have been synthesized and characterized by analytical, spectroscopic (IR, far-IR, ^1H and ^{31}P NMR) studies, together with a single crystal X-ray study for the L = dmp adduct, for comparison with the recently reported counterpart adducts of silver(I) nitrate. While the silver(I) coordination environment is still dominated by the quasi-planar N_2AgP motif (Ag–P 2.378(1), Ag–N 2.364(3), 2.392(4) Å), the interaction of the nitrite is symmetrical (Ag–O 2.512(4), 2.543(5) Å) and invasive, the $PAgN_2$ angle sum diminished to 324.7°.

Keywords: Silver nitrite; Triphenylphosphine; Bidentate ligands; Single crystal X-ray study; NMR

In a recent report [1], in the context of a more wide-ranging study, we described a synthetic, structural and spectroscopic examination of the nature of complexes formed between silver(I) nitrate, tertiary phosphine ligand (R_3P) and oligodentate bases, L, derivative of 2,2′-bipyridyl ('bpy'), finding an array of $AgNO_3$:PR_3:L (1:1:1) complexes to be readily accessible. In those complexes, the coordination environment is dominated by a quasi-trigonal planar N_2AgL array, perturbed by the approach of the counterion diversely in unidentate, semi- and quasi-O,O′-bidentate mode, the nitrate counterion being the intermediate member in a range of studies encompassing oxyanions of increasing basicity: ClO_4 [2], NO_3 [1], carboxylate [3]. Although our interest in the complexes of silver(I) salts with group 15 donors has focussed primarily on the latter as oxyanion systems worthy of systematic study, other systems also featuring aspects of interest have attracted our attention from time to time, one such being nitrite [4,5], which differs appreciably from nitrate in its behaviour. The present work describes a minor foray into the systems of the above type using silver(I) nitrite rather than nitrate as the basis for complex formation; we describe here a less extensive systematic and spectroscopic study of its 1:1:1 complexes, with triphenylphosphine (as the representative of PR_3) and the variously flexible/rigid and more or less hindered *N*,*N*′-aromatic bidentate bases 2,2′-bipyridyl ('bpy') 1,10-phenanthroline ('phen') and 2,9-dimethylphenanthroline ('dmp'), together with a single crystal X-ray study of the latter adduct (Fig. 1).

The adducts [PPh_3AgNO_2]: L (1:1), **1**–**3** (Chart 1) [6] have been synthesized by the reaction of one or two equivalents of *N*,*N*′-bidentate aromatic ligand, L, derivative of 2,2′-bipyridyl, with one equivalent of the 1:1 silver(I) nitrite: triphenylphosphine adduct.

$$[(PPh_3)AgNO_2]_n + nL \overset{\text{solvent}}{\rightarrow} n\{[(PPh_3)\ AgNO_2] : L(1:1)\} \tag{1}$$

(**1**: L = phen, **2**: L = bpy, **3**: L = dmp)

The same products formed when $[(PPh_3)_xAgNO_2]$ ($x = 2$ or 3) were employed as the starting reagents. On the other hand, monodentate ligands such as imidazole (Him), or 1-methyl-1H-imidazole-2(3H)-thione (mimt) exhibit a different reactivity, their interaction with $[(PPh_3)_2AgNO_2]_n$

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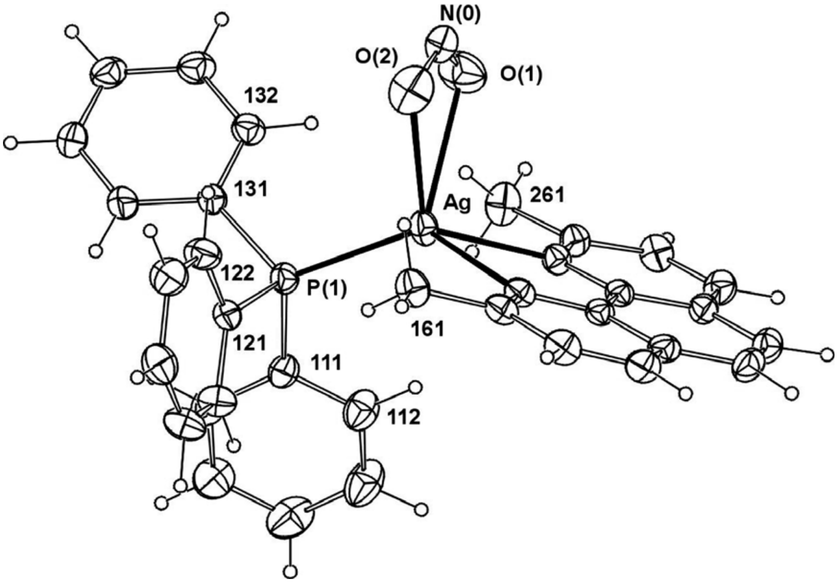
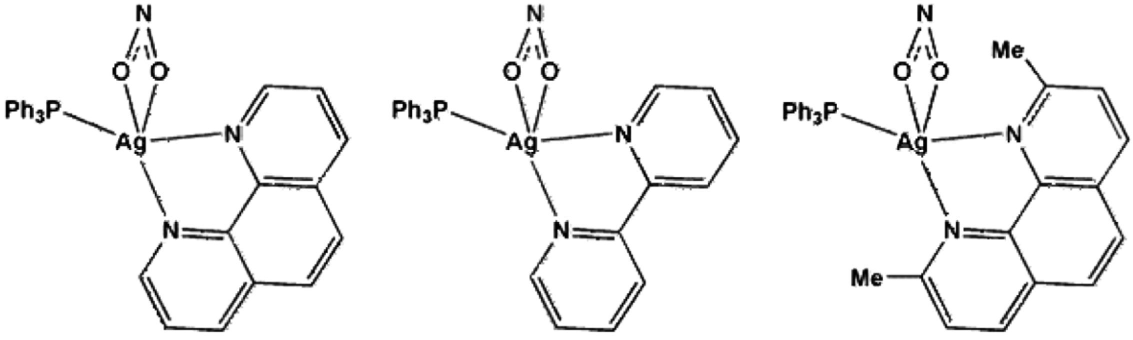


Fig. 1. A single molecule of $AgNO_2$: PPh_3:dmp (1:1:1) 3 projected normal to the Ag… nitrite axis (20% probability amplitude displacement ellipsoids (non-hydrogen atoms), hydrogen atoms having arbitrary radii of 0.1 Å). Ag–P,O(1,2), N(11,21) 2.378(1), 2.512(4), 2.543(5), 2.392(4), 2.364(3) Å; P–Ag–O(1,2),N(11,21) 119.2(1), 110.4(1), 126.72(8), 127.19(8), O(1)–Ag–O(2),N(11,21) 46.1(2), 111.2(1), 85.3(1), O(2)–Ag–N(11,21) 92.1(1), 118.9(1), N(11)–Ag–N(21) 70.8(1), Ag–O(1,2)–N(0) 98.6(3), 96.7(3)°. Torsion angles Ag–P–C(n11)–C(n12) ($n = 1$–3) are: 6.8(4), 68.0(4), 26.5(4)°. Ag lies 0.088(3) Å out of the dmp skeletal plane ($\chi^2 = 373$) and 0.07(2) Å out of the NO_2 plane.



1 **2** **3**

Chart 1.

yielding $[(PPh_3)_2AgNO_2]$: Him (1:1), **4**, [7] and $[(PPh_3)_2AgNO_2]$: mimt (1:2) [8], respectively, whereas the interaction of Him with $[(PPh_3)AgNO_2]$ gives the 1:1 adduct $[(PPh_3)AgNO_2]$: Him (1:1), **5**, [7].

All the compounds – air-stable, colourless materials – are insoluble in diethyl ether and ethanol, and soluble in chlorinated solvents, acetone, acetonitrile and DMSO. The conductivity measurements for **1** and **2** are in accordance with the neutral formulation found in the solid state for derivative **3**. Derivative **3** partly dissociates in dichloromethane according to the following equation:

$$[Ag(dmp)(PPh_3)NO_2] \rightarrow [(PPh_3)Ag(dmp)]^+ + (NO_2^-) \qquad (2)$$

The infrared spectra of **1**–**3** [9] are consistent with the formulations proposed showing all of the bands required by the presence of the organic N-donors and unidentate phosphine ligands [10]. In the far-IR spectra of all phosphino derivatives we assigned, on the basis of previous reports, the broad absorptions near 500 cm^{-1} and those at 480–400 cm^{-1} to Whiffen's y and t vibrations [11].

In the ^{1}H NMR solution spectra ($CDCl_3$, conc. = 4 mg/mL) of **1**–**3**, the signals due to the phosphine and N-donor ligands show a different pattern with respect to those found for the free donors, which can be taken as evidence for the existence of complexes also in the chlorinated solvent solution.

The room temperature ^{31}P NMR spectra of complexes **1**–**3** 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 (223 K), and one unresolved doublet or resolved pairs of doublets, arising from coupling between the phosphorus and silver atoms, are observed in the accessible temperature range. For example, two sets of doublets were found in the spectra of **1** at 223 K. The coupling constant determined for the doublet at *ca.* 18 ppm is typical of a $AgPN_2O_2$ environment, whereas the coupling constant values for the signal at *ca.* 11 ppm is 443 Hz, representative of an AgP_2O_2 coordination environment and suggesting a dissociation-equilibrium as that in Eq. (3).

$$2[\mathrm{Ag(phen)(PPh_3)(NO_2)}] \rightleftharpoons [\mathrm{Ag(PPh_3)_2(NO_2)}] + [\mathrm{Ag(phen)_2(NO_2)}] \qquad (3)$$

The results of the single crystal X-ray study for **3** [12] are consistent with the description of the array as of 1:1:1 $AgNO_2$: PR_3: dmp stoichiometry and connectivity, all components being closely associated as a single aggregate, one of which, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. As with the nitrate analogue, the core of the molecule comprises the tightly bound *P*Ph_3 and *N*,*N′*-dmp components, the $PAgN_2$ array comprising a quasi-trigonal planar array. In the counterpart nitrate structure [2] (which contains two independent molecules in the asymmetric unit), the planarity of each array is perturbed by the approach of semi-bidentate nitrate groups Ag–O(,O′) being 2.678(3) (3.008(3)) (mol. 1), 2.721(5) (3.012(6) Å) (mol. 2); the $PAgN_2$ angle sums are 354.6, 353.5°. Here, the nitrite approaches as a symmetrical bidentate ligand, bound much more strongly, the $PAgN_2$ angle sum being reduced to 324.7° and Ag–O,O′ much shorter (2.512(4), 2.543(5) Å). In compensation, in the nitrate, Ag–N (2.313(4) – 2.355(3), 〈〉 2.34(2) Å) are shorter than in the present (2.392(4), 2.364(3) Å); Ag–P (2.382(1) Å (×2)) are essentially identical. The disposition of the PPh_3 ligand appears to be influenced by the steric effect of the methyl groups, phenyl rings 1,3 straddling CH_3(261), while ring 2, confronting the approach of C(161) lies quasi-normal to that approach, seemingly without other substantial interaction since the pair of P–Ag–N angles are essentially identical (126.72(8), 127.19(9)°), although the two Ag–N distances differ by ca. 0.03 Å in the manner expected.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.11.010.

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[6] *Synthesis of* PPh_3AgNO_2*: phen (1:1).* H_2O (**1 · H_2O**). To an ethanol solution containing PPh_3AgNO_2 [5] (0.417 g, 1.0 mmol), phen (0.180 g, 1.0 mmol) was added. The solution was stirred with warming for 12 h and then cooled at 4 °C. A pale-yellow crystalline precipitate slowly formed, which was filtered off, washed with ethanol (5 mL), dried under reduced pressure and shown to be compound **1** (0.307 g , yield 50%). M.p. 179–182 °C. Anal. Calc. for $C_{30}H_{25}AgN_3O_3P$: C, 58.65; H, 4.10; N, 6.84%. Found: C, 58.53; H, 4.26; N, 6.64%. Λ_m (CH_2Cl_2, 10^{-3} M): 5.0 Ω^{-1} cm^2 mol^{-1}. *Synthesis of* PPh_3AgNO_2*: bpy (1:1)* (**2**). Compound **2** (0.115 g, yield 20%) has been prepared following a procedure similar to that reported for **1**. M.p. 185–187 °C. Anal. Calc. for $C_{28}H_{23}AgN_3O_2P$: C, 58.76; H 4.05; N, 7.34. Found: C, 58.45; H, 4.12; N, 7.23%. Λ_m (CH_2Cl_2, 10^{-3} M): 1.0 Ω^{-1} cm^2 mol^{-1}. *Synthesis of* PPh_3AgNO_2*: dmp (1:1)* (**3**). To a benzene solution containing PPh_3AgNO_2 [5] (0.417 g, 1.0 mmol), dmp (0.417 g, 2.0 mmol) was added. The solution was stirred under reflux for 12 h and then cooled at 4 °C.A colourless crystalline precipitate slowly formed, which was filtered off, washed with benzene (5 mL), dried under reduced pressure and shown to be compound **3** (0.312 g , yield 50%). Recrystallised from hot-benzene. M.p. > 200 °C dec. Anal. Calc. for $C_{32}H_{27}AgN_3O_2P$: C, 61.55; H, 4.36; N, 6.73%. Found: C, 61.23; H, 4.41; N, 6.54%. Λ_m (CH_2Cl_2, 10^{-3} M): 28.4 Ω^{-1} cm^2 mol^{-1}.

[7] *$(PPh_3)_2AgNO_2$: Him (1:1)* (**4**). Compound **4** (0.373 g, yield 50%) has been prepared following a procedure similar to that reported for **1**, by using $[(PPh_3)_2AgNO_2]$ and Him. M.p. 178 °C dec. Anal. Calc. for $C_{39}H_{34}AgN_3O_2P_2$: C, 62.75; H, 4.59; N, 5.63; O. Found: C, 62.62; H, 4.71; N, 5.48%. IR (nujol, cm^{-1}): 3100w (NH) 1583w, 1538w, 1437sh, 1331m, 1305m, 1199w, 823m, 516, 494s, 433s, 280m, 247w. ^1H NMR ($CDCl_3$, 293 K): δ, 6.99 (s, 1H, CH_{Him}), 7.2–7.8m (32H, $PC_{18}H_{15}$ + CH_{Him}). Λ_m (CH_2Cl_2, 10^{-3} M): 0.5 Ω^{-1} cm^2 mol^{-1}. *$(PPh_3)AgNO_2$: Him (1:1)* (**5**). Compound **5** (0.373 g, yield 50%) has been prepared following a procedure similar to that reported for **1**, by using $[(PPh_3)AgNO_2]$ and Him. M.p. 138–141°C dec. Anal. Calc. for $C_{21}H_{19}AgN_3O_2P$: C, 52.09; H, 3.95; N, 8.68. Found: C, 52.12; H, 3.91; N, 8.47%. IR (nujol, cm^{-1}): 3100w (NH) 1583w, 1535w, 1435sh, 1326m, 1237m, 849w, 825m, 511m, 503m, 493s, 433, 420w, 249w, 201w. ^1H NMR ($CDCl_3$, 293 K): δ, 7.0(s, 1H, CH_{Him}), 7.2–7.5; 7.6–7.8m (17H, $PC_{18}H_{15}$ + CH_{Him}). Λ_m (CH_2Cl_2, 10^{-3} M): 0.2 Ω^{-1} cm^2 mol^{-1}.

[8] C. Pettinari, manuscript in preparation.

[9] **1** · *H_2O*: IR (nujol, cm^{-1}): 3450br (OH) 3150w (CH), 1304w, 1221br (NO_2) 1153w, 1093w, 1026w, 995w, 969br; 840m (ONO) 742m, 725s, 694m, 512m, 500m, 438br. ^1H NMR ($CDCl_3$, 293 K): δ, 1.58 (s, 2H; H_2O), 7.2–7.4m (15H, $PC_{18}H_{15}$), 7.45–7.68m, 7.86s, 8.30–8.35m, 9.11–9.13m (8H, CH_{phen}). ^{31}P NMR ($CDCl_3$, 298 K): δ, 10.9 br. **2**: IR (nujol, cm^{-1}): 3160w (CH), 1305w, (NO_2) 1159br, 1093w, 995vw, 965br; 850w (ONO), 820w, 763sh, 722m, 694m, 667w, 649w, 638w, 619w; 518m, 506m, 491m (PPh_3) 437w, 419w, 412w, 395w. ^1H NMR ($CDCl_3$, 293 K): δ, 7.3–7.5m (15H, $PC_{18}H_{15}$), 7.63–7.70m, 7.82–7.91m, 8.43–8.47m, 8.71–8.73m (8H, CH_{bpy}). ^{31}P NMR ($CDCl_3$, 298 K): δ, 13.8 br.^{31}P NMR ($CDCl_3$, 223 K): δ, 11.7 dd ($^1J(^{31}P\text{-}^{109}Ag)$: 450 Hz; $^1J(^{31}P\text{-}^{107}Ag)$: 390 Hz), 18.9 dd ($^1J(^{31}P\text{-}^{109}Ag)$: 741 Hz; $^1J(^{31}P\text{-}^{107}Ag)$: 641 Hz). **3**: IR (nujol, cm^{-1}): 1616m, 1592m, 1551m, 1496s, 1430m, 1350m, 1204s (NO_2) 886w, 860s, 840w, 824w, 816w (ONO) 552s, 512m, 500m, 478s, 439m, 430s, 419m, 396w, 311w, 280w, 246w, 228w, 213w. ^1H NMR ($CDCl_3$, 293 K): δ, 2.87s (s, 6H CH_{3dmp}), 7.29–7.52m (15H, $PC_{18}H_{15}$), 7.70br, 8.14br, 8.18br (6H, CH_{dmp}). ^{31}P NMR ($CDCl_3$, 298 K): δ, 9.1 br.

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[12] *$AgNO_2$: PPh_3: dmp (1:1:1), 3.* $C_{32}H_{27}AgN_3O_2P$, $M = 624.4$. Monoclinic, space group $C2/c$ (C^6_{2h}, No.15), $a = 23.887(7)$, $b = 9.775(3)$, $c = 25.126(17)$ Å, $\beta = 98.45(5)°$, $V = 5803$ Å^3. D_c ($Z = 8$) = 1.42_9 g cm^{-3}. $\mu_{Mo} = 0.78$ mm^{-1}; specimen: 0.28 × 0.26 × 0.65 mm; $A^*_{min/max}$ (gaussian correction) = 1.16, 1.26. $2\theta_{max} = 50°$; monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; single counter instrument, $2\theta/\theta$ scan mode; *T ca.* 295 K. 10084 total reflections (hemisphere) merging to 5109 unique ($R_{int} = 0.042$), 3795 ($I > 3\sigma$ (I)) ‘observed’; $R = 0.043$, $R_w = 0.052$ (weights: $\sigma^2(F) + 0.0004(F^2)^{-1}$). CCDC 609969.