

Synthesis of Silver(I) Complexes Containing N and P Donor Ligands

Sarath D. Perera*#

Department of Chemistry, The Open University of Sri Lanka, Sri Lanka


Abstract

Treatment of one equivalent of 3,4,5,6-tetraphenyl-2,2'-bipyridine (tpbpy) with AgClO_4 afforded $[\text{Ag}(\text{tpbpy})]\text{ClO}_4$ (**1a**). Similarly, $[\text{Ag}(\text{tpbpy})]\text{BF}_4$ (**1b**) was prepared using AgBF_4 . Reaction of two equivalents of tpbpy with AgClO_4 yielded the homoleptic Ag(I) complex $[\text{Ag}(\text{tpbpy})_2]\text{ClO}_4$ (**2**). The four-coordinate heteroleptic Ag(I) complex $[\text{Ag}(\text{tpbpy})(\text{xantphos})]\text{ClO}_4$ (**3**) containing both N and P donor ligands was prepared by treating AgClO_4 with a (1:1) mixture of tpbpy and 4,5-bis(diphenylphosphino)-9,9'-dimethylxanthene (xantphos). $[\text{Ag}(\text{dmbpy})(\text{xantphos})]\text{ClO}_4$ (**4**) (dmbpy = 6,6'-dimethyl-2,2'-bipyridine) was prepared in a similar manner. Reaction of one equivalent of xantphos with AgClO_4 in acetonitrile produced the labile three-coordinate Ag(I) complex $[\text{Ag}(\text{xantphos})(\text{MeCN})]\text{ClO}_4$ (**5**). Treatment of (**5**) with one equivalent of tpbpy or dmbpy afforded the heteroleptic complexes (**3**) and (**4**), respectively. Reaction of (**5**) with one equivalent of 4'-(4-methylphenyl)-2,2':6',2''-terpyridine

*Correspondence should be addressed to **Prof. K. S. D. Perera**, Department of Chemistry, Faculty of Natural Sciences, The Open University of Sri Lanka.

#Dedicated to the memory of Professor Bernard Leslie Shaw FRS of University of Leeds who died on 8th November 2020 at the age of 90 years

Email: ksper@ou.ac.lk

 <https://orcid.org/0000-0001-5917-7327>

(Received 07th January 2021; Revised 1st April 2021; Accepted 4th June 2021 © OUSL)



This article is published under the Creative Commons Attribution-Share Alike 4.0 International License (CC-BY-SA). This license permits use, distribution and reproduction in any medium; provided it is licensed under the same terms and the original work is properly cited.

(ttpy) afforded the five-coordinate Ag(I) complex [Ag(xantphos)(ttpy)]ClO₄ (**6**). Treatment of AgClO₄ with one equivalent of bis(diphenylphosphino)methane (dppm) in a (1:1) solvent mixture of chloroform and methanol resulted in the formation of [Ag₂(μ-dppm)₂][ClO₄]₂ (**7**). Reaction of (**7**) with one equivalent of 3,6-di(2-pyridyl)-4,5-diphenyl-pyridazine (dppz) gave the binuclear complex [Ag₂(μ-dppm)₂{μ-dppz}][ClO₄]₂ (**8**). Above complexes were characterized by a combination of elemental analysis, IR, Mass and NMR spectroscopy.

Keywords: homoleptic, heteroleptic Ag(I) complexes, xantphos, dppm, pyridyl ligands

Introduction

Pharmaceutical application of silver was first recognized with the use of silver nitrate (AgNO₃) in the early 1800s for the treatment of ulcers. Silver complexes containing ligands such as N-heterocyclic carbenes (NHC), N-heterocycles and phosphines possess several properties: - ranging from antimicrobial, antibacterial, anti-inflammatory and antiseptic to anti-neoplastic activity (Medici et al., 2016; Kızrak et al., 2019; Jimenez et al., 2017). Water-soluble homoleptic Ag(I) complexes of the type [Ag(N[^]N)₂](CF₃SO₃) based on adamantylamines showed antibacterial properties (Jimenez et al., 2017). Many applications of silver nanoparticles are known in addition to their antimicrobial property (Handoko & Gulo, 2019; Abbas et al., 2018). Silver(I) salts are good catalysts for alkyne-based organic reactions such as alkynylation, hydrofunctionalization, cycloaddition, cycloisomerization and cascade reactions (Fang & Bi, 2015). Coordination complexes of Ag(I) centre usually exhibit linear, tetrahedral or trigonal planar geometry with ligands containing donor atoms such as C[^]N (NHC) (**I**, **II**) (Medici et al., 2016; Kokunov et al., 2016; Hasson et al., 2019; Athi & Gülle, 2019), N[^]N (**III-VII**) (Durini et al., 2017; Carbonell-Vilar et al., 2019; Xing et al., 2020; Fresta et al., 2019), N[^]N[^]N (**VIII**) (Jimenez et al., 2017; Artem'ev et al., 2019), P[^]P (**IX-XI**) (Kaltzoglou et al., 2007; Bruce et al., 2016; Hutton et al., 1983; Gimeno et al., 1995), P[^]N (**XII, XIII**) (Hung-Low & Klausmeyer,

2008; Škoch et al., 2017; Artem'ev, 2020), P^NP (**XIV**) (Nayeri et al., 2020) (Figure 1).

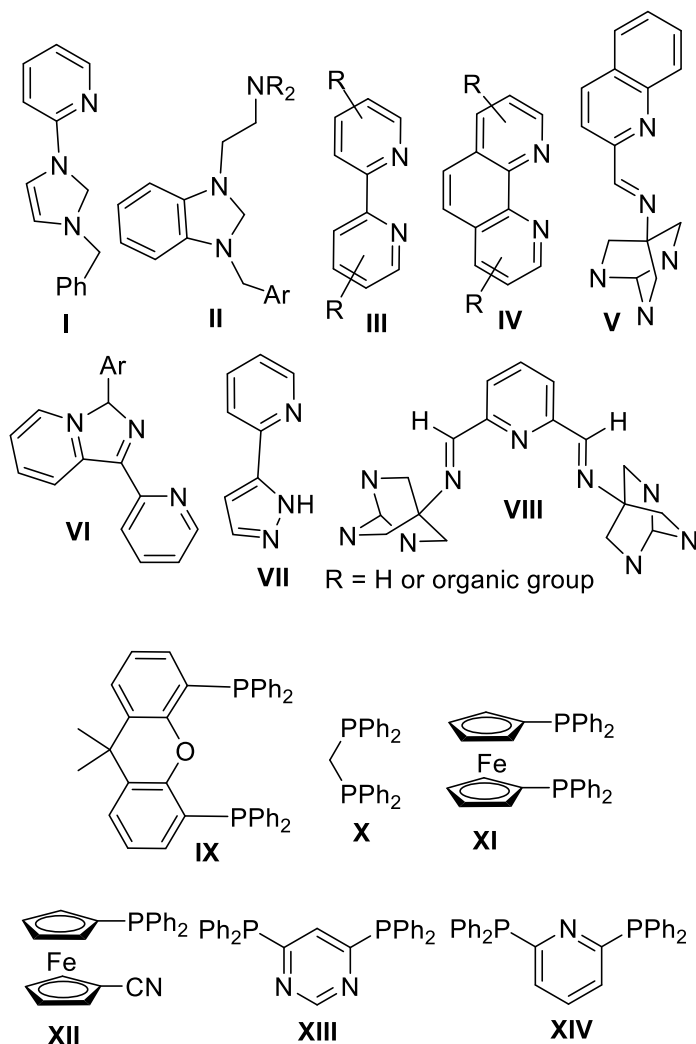


Figure 1. Molecular structures of ligands **I - XIV**.

Ag(I) centres form mononuclear (Medici et al., 2016), binuclear (Medici et al., 2016; Hung-Low & Klausmeyer, 2008; Artem'ev, *et al.*, 2020), trinuclear (Artem'ev et al., 2019; Nayeri et al., 2020), tetranuclear (Medici et al., 2016; Nayeri et al., 2020) and polynuclear (Medici et al., 2016; Škoch et al., 2017; Artem'ev et al., 2020) complexes with pyridines, bipyridines, diphosphines and

pyridyl phosphines; some of these complexes show weak Ag-Ag interaction. A few basic mononuclear, binuclear and trinuclear Ag(I) complexes with linear, trigonal planar and tetrahedral geometries are shown in Figure 2.

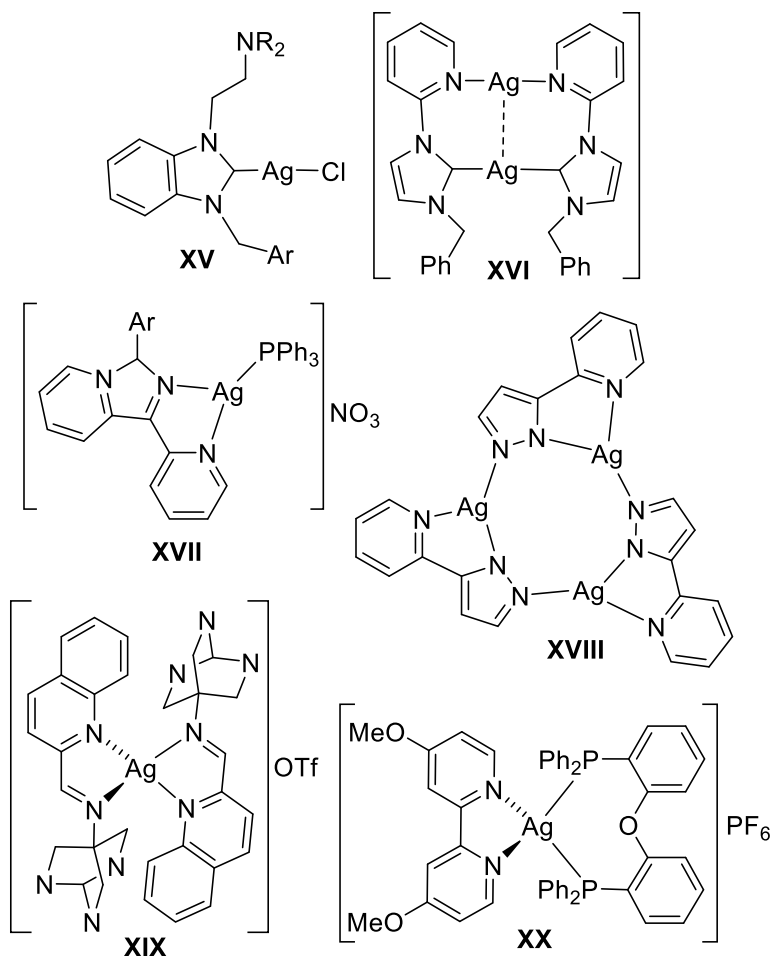


Figure 2. Molecular structures of complexes **XV- XX**.

First examples of emissive square-planar Ag(I) complexes $[\text{Ag}(\text{N},\text{N}'\text{-Py}_3\text{PO})_2]\text{X}$ ($\text{X} = \text{OTf}, \text{ClO}_4$) were reported recently by reacting tris(2-pyridyl)phosphine oxide (Py_3PO) with Ag(I) salts (Artem'ev et al., 2019). Five- and six-coordinated Ag(I) complexes are less common (Medici et al., 2016; Jimenez et al., 2017; Nayeri et al., 2020, Artem'ev et al., 2019). Two examples of octahedral Ag(I) complexes

include $[\text{Ag}(\text{N},\text{N}',\text{N}''\text{-Py}_3\text{PO})_2]\text{BF}_4$ (Artem'ev et al., 2019) and $[\text{Ag}(\text{N},\text{N}',\text{N}''\text{-VIII})_2]\text{OTf}$ (Jimenez et al., 2017).

Silver is a less expensive metal with promising catalytic, structural and photophysical properties which can be tuned with other co-ligands (Artem'ev et al., 2020), thus, it is of interest to explore the chemistry of Ag(I) centres with different chelating ($\text{N}^{\wedge}\text{N}$), ($\text{N}^{\wedge}\text{N}^{\wedge}\text{N}$) and ($\text{P}^{\wedge}\text{P}$) donor ligands. Here we report studies carried out to synthesise Ag(I) complexes using 3,4,5,6-tetraphenyl-2,2'-bipyridine (tpbpy), 6,6'-dimethyl-2,2'-bipyridine (dmbpy), 4'-(4-methylphenyl)-2,2':6',2''-terpyridine (ttpy), 3,6-di(2-pyridyl)-4,5-diphenyl-pyridazine (dppz), 4,5-bis(diphenylphosphino)-9,9'-dimethylxanthene (xantphos), and bis(diphenylphosphino)methane (dppm). The bidentate dmbpy ligand and terdentate ttpy ligand are planar symmetrical molecules whilst tpbpy is a bulky unsymmetrical bidentate ligand. The symmetrical dppz ligand has four nitrogen donors which can bridge two metal centres or produce polynuclear complexes.

Methodology

All the experiments were carried out in an inert atmosphere of dinitrogen or argon. IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer fitted with a diffuse reflectance accessory. Electrospray mass spectra were obtained on a Micromass LCT electrospray mass spectrometer. MALDI-TOF mass spectra were recorded on a Waters MALDI-QTOF Premier spectrometer using α -cyano-4-hydroxy cinnamic acid matrix. Accurate mass spectra were referenced against Leucine Enkephalin. Elemental analyses were carried out on a Carlo Erba 1006 automatic analyser. NMR spectra were recorded on a DPX 400 spectrometer operating at 400.13 MHz for ^1H and 100.62 MHz for ^{13}C ; the ^1H and ^{13}C chemical shifts (δ) are in ppm with respect to TMS while coupling constants (J) are in Hz. ^{31}P NMR spectra were recorded at 161.02 MHz and are standardized with respect to phosphoric acid. AgBF_4 , AgClO_4 , 6,6'-dimethyl-2,2'-bipyridine (dmbpy), 4,5-bis(diphenylphosphino)-9,9'-dimethylxanthene (xantphos) and bis(diphenylphosphino)methane (dppm) were purchased from Aldrich. 3,4,5,6-tetraphenyl-2,2'-bipyridine

(tpbpy), 4'-(4-methylphenyl)-2,2':6',2''-terpyridine or tolylterpyridine (ttpy) and 3,6-di(2-pyridyl)-4,5-diphenyl-pyridazine (dppz) were prepared according to literature procedures (Ollangnier, *et al.*, 2008; Schubert, *et al.*, 2006; Gil, *et al.*, 2011).

[Ag(tpbpy)]ClO₄ (1a)

A solution of AgClO₄ (9 mg, 0.0434 mmol) in methanol (1 mL) was added to a solution of 3,4,5,6-tetraphenyl-2,2'-bipyridine (tpbpy) (20 mg, 0.0434 mmol) in dichloromethane (1 mL) to yield a colourless solution and the reaction mixture was heated to 50 °C for 1 h. The solution was concentrated to a low volume under reduced pressure to yield (**1a**) as a white solid, (20 mg, 71%). Found: 61.63; H, 4.02; N 4.03, calcd. (%) for C₃₄H₂₄ClN₂O₄Ag: C, 61.14; H, 3.62; N 4.19. IR (neat, cm⁻¹): 1579, 1477, 1404, 1269, 1094, 833, 792, 750 and 703. Maldi (DCM, m/z): found: 567.0973; calcd. 567.0990 for C₃₄H₂₄N₂Ag, [M-ClO₄]⁺. ¹H NMR (400 MHz, CDCl₃): 8.57 (d, br, 1H, ³J(HH) = 4.0 Hz, H^{Py}), 7.50-7.39 (m, 2H, H^{Py}) 7.32-7.24 (m, 2H, H^{Ph} overlaps with chloroform signal), 7.22-7.12 (m, 3H, H^{Ph}), 7.10-6.94 (m, 9H, H^{Ph}), 6.88 (d, 2H, ³J(HH) = 7.0 Hz, H^{Ph}), 6.85-6.77 (m, 3H, H^{Py} & H^{Ph}) and 6.73 (d, 2H, ³J(HH) = 6.5 Hz, H^{Ph}).

[Ag(tpbpy)]BF₄ (1b)

A solution of AgBF₄ (8.4 mg, 0.0431 mmol) in methanol (1 mL) was added to a solution of 3,4,5,6-tetraphenyl-2,2'-bipyridine (20 mg, 0.0434 mmol) in dichloromethane (1 mL) to give a colourless solution. After 3 h, the solvent was removed under reduced pressure and the residue triturated with methanol to yield (**1b**) as a white solid, (18 mg, 64%). Found: 61.95; H, 4.00; N 4.05, calcd. (%) for C₃₄H₂₄BN₂F₄Ag: C, 62.32; H, 3.69; N 4.28. IR (neat, cm⁻¹): 3057, 1592, 1536, 1470, 1443, 1397, 1058, 1029, 832, 763 and 699. Maldi (DCM, m/z): Found: 567.0963, calcd. 567.0990, for C₃₄H₂₄N₂Ag, [M-BF₄]⁺. ¹H NMR (400 MHz, CDCl₃): 8.57 (d, br, 1H, ³J(HH) = 4.5 Hz, H^{Py}), 7.52-7.39 (m, 2H, H^{Py}) 7.26 (d, 2H, ³J(HH) = 7.5 Hz, H^{Ph}), 7.21-7.11 (m, 3H, H^{Ph}), 7.10-6.95 (m, 9H, H^{Ph}), 6.88 (d, 2H, ³J(HH) = 7.0 Hz, H^{Ph}), 6.84-6.76 (m, 3H, ³J(HH) = 7.5 Hz, H^{Py} & H^{Ph}) and 6.73 (d, 2H, ³J(HH) = 7.0 Hz, H^{Ph}).

[Ag(tpbpy)₂]ClO₄ (2)

3,4,5,6-Tetraphenyl-2,2'-bipyridine (22 mg, 0.048 mmol) and AgClO₄ (4.8 mg, 0.023 mmol) in acetonitrile (1.5 mL) were heated under reflux for 3 h. The resulting colourless solution was concentrated to obtain a low volume and diethyl ether was added to yield **(2)** as a white solid (23 mg, 88%). Found: C, 70.63; H, 4.17; N 4.72, calcd. (%) for C₆₈H₄₈ClN₄O₄Ag·0.5CH₂Cl₂: C, 70.26; H, 4.22; N 4.79. IR (neat) cm⁻¹: 3057, 1592, 1535, 1473, 1443, 1395, 1088, 998, 765 and 658. Mass (acetone, m/z): found: 1027.2948, calcd. 1027.2930 for C₆₈H₄₈N₄Ag, [M-ClO₄]⁺. ¹H NMR (400 MHz, CDCl₃): 8.57 (d, 2H, ³J(HH) = 4.5 Hz, H^{Py}), 7.51-7.24 (m, 2H, H^{Py}), 7.33-7.24 (m, 4H, overlaps with the solvent peak), 7.22-7.11 (m, 6H, H^{Ph}), 7.10-6.94 (m, 18H, H^{Ph}), 6.88 (d, 4H, ³J(HH) = 7.5 Hz, H^{Ph}), 6.85-6.77 (m, 6H, H^{Py} & H^{Ph}) and 6.73 (d, 2H, ³J(HH) = 7.5 Hz, H^{Ph}).

[Ag(xantphos)(tpbpy)]ClO₄ (3)

A suspension containing 4,5-bis(diphenylphosphino)-9,9-dimethyl xanthene (xantphos) (41 mg, 0.071 mmol), 3,4,5,6-tetraphenyl-2,2'-bipyridine (tpbpy) (33 mg, 0.071 mmol) and AgClO₄ (14 mg, 0.067 mmol) in acetonitrile (3 mL) was heated under reflux for 2 h. The resulting colourless solution was concentrated to a low volume and diethyl ether was added to yield **(3)** as a white solid (77 mg, 91%). Found: C, 69.85; H, 4.47; N 2.22, calcd. (%) for C₇₃H₅₆ClN₂O₅P₂Ag: C, 70.34; H, 4.53; N 2.25. Mass (acetone, m/z): found: 1145.2926, calcd. 1145.2919 for C₇₃H₅₆N₂OP₂Ag, [M-ClO₄]⁺. IR (neat, cm⁻¹): 3054, 1596, 1548, 1436, 1399, 1220, 1083, 746 and 695. ¹H NMR (400 MHz, CDCl₃): 7.67 (d, 2H, H^{Py}), 7.49-7.32 (m, 5H, H^{Ph/Ar/Py}), 7.27-7.00 (m, 19H, H^{Ph/Ar/Py}), 6.99-6.76 (m, 18H, H^{Ph/Ar/Py}), 6.72-6.60 (m, 4H, H^{Ph/Ar/Py}), 6.55-6.26 (br, 2H, H^{Ph/Ar/Py}) and 1.69 (br, 6H, Me). ³¹P NMR (161 MHz, CDCl₃): -5.4 (dd), ¹J(¹⁰⁷AgP) = 384 Hz and ¹J(¹⁰⁹AgP) = 444 Hz.

[Ag(xantphos)(tpbpy)]ClO₄ (3) from [Ag(xantphos)(MeCN)]ClO₄

[Ag(xantphos)(MeCN)]ClO₄ **(5)** (15 mg, 0.018 mmol) and 3,4,5,6-tetraphenyl-2,2'-bipyridine (9 mg, 0.0195 mmol) were dissolved in dichloromethane (1.5 mL) to yield a colourless solution. After 2 h, it was concentrated, and hexane was added to deposit **(3)** as a white solid (19 mg, 84%). Characterizing data are as same as given above for **(3)**.

[Ag(xantphos)(dmbpy)]ClO₄ (4)

A suspension containing 4,5-bis(diphenylphosphino)-9,9'-dimethylxanthene (xantphos) (82 mg, 0.14 mmol), 6,6'-dimethyl-2,2'-bipyridine (dmbpy) (25 mg, 0.135 mmol) and AgClO₄ (29 mg, 0.14 mmol) in acetonitrile (5 mL) was heated under reflux for 1 h. The resulting colourless solution was concentrated to yield **(4)** as a white solid (111 mg, 82%). Found: C, 63.55; H, 4.40; N 2.60, calcd. (%) for C₅₁H₄₄ClN₂O₅P₂Ag: C, 63.14; H, 4.57; N 2.89. Maldi (MeCN, m/z): Found: 685.1021, calcd. 685.0979 for C₃₉H₃₂OP₂Ag, [Ag(xantphos)]⁺. IR (neat, cm⁻¹): 3049, 2961, 1594, 1574, 1435, 1402, 1222, 1085, 785, 736 and 692. ¹H NMR (400 MHz, CDCl₃): 8.23 (d, 2H, ³J(HH) 8.0 Hz, H^{Py}), 8.00 (t, 2H, ³J(HH) 7.5 Hz, H^{Py}), 7.66 (d, 2H, ³J(HH) 7.5 Hz, H^{Ar}), 7.33 (t, 4H, ³J(HH) 7.5 Hz, H^{Ph/Ar}), 7.30-7.23 (m, 2H, H^{Ph/Ar} overlap with the solvent peak), 7.22-7.12 (m, 8H, H^{Ph/Ar/Py}), 7.09-6.98 (m, 8H, H^{Ph/Ar}), 6.66-6.58 (m, 2H, H^{Ph/Ar}), 2.17 (s, 6H, Me), and 1.74 (s, 6H, Me). ³¹P NMR (161 MHz, CDCl₃): -6.2 (dd) ¹J(¹⁰⁷AgP) = 357 Hz and ¹J(¹⁰⁹AgP) = 412 Hz.

[Ag(xantphos)(dmbpy)]ClO₄ (4) from [Ag(xantphos)(MeCN)]ClO₄

[Ag(xantphos)(MeCN)]ClO₄ **(5)** (20 mg, 0.024 mmol) and 6,6'-dimethyl-2,2'-bipyridine (6 mg, 0.035 mmol) were dissolved in dichloromethane (1.5 mL) to yield **(4)** as a colourless solution. After 3 h, it was concentrated, and hexane was added to yield a white solid (22 mg, 95%). Characterizing data are same as given above for **(4)**.

[Ag(xantphos)(MeCN)]ClO₄ (5)

4,5-Bis(diphenylphosphino)-9,9'-dimethylxanthene (xantphos) (164 mg, 0.28 mmol) and AgClO₄ (58 mg, 0.28 mmol) were heated under reflux in acetonitrile (10 mL) for 2 h. The resulting colourless solution was concentrated to yield **(5)** as a white solid (191 mg, 83%). Found: C, 59.27; H, 4.06, N, 1.75 calcd. (%) for C₄₁H₃₅ClNO₅P₂Ag: C, 59.55; H, 4.27, N, 1.69. Maldi (MeCN, m/z): found: 685.0958, calcd. 685.0979 for C₃₉H₃₂OP₂Ag, [M-ClO₄]⁺. IR (neat, cm⁻¹): 2978, 2937, 2270, 1586, 1480, 1445, 1403, 1236, 1109, 1059, 789, 746 and 694. ¹H NMR (400 MHz, CDCl₃): 7.62 (d, 2H, ³J(HH) 7.5 Hz, H^{Ar}), 7.41-7.27 (m, 20H, H^{Ph}), 7.16 (t, 2H, ³J(HH) 7.5 Hz, H^{Ar}), 6.71 (m, 2H, H^{Ar}), 2.04 (s, 3H, MeCN), and 1.69 (s, 6H,

Me). ^{31}P NMR (161 MHz, CDCl_3): -5.3 (dd), $^1\text{J}(^{107}\text{AgP}) = 461$ Hz and $^1\text{J}(^{109}\text{AgP}) = 532$ Hz.

[Ag(xantphos)(ttpy)] ClO₄ (6)

[Ag(xantphos)(MeCN)]ClO₄ (**5**) (15 mg, 0.018 mmol) and tolylterpyridine (ttpy) (7 mg, 0.021 mmol) were dissolved in dichloromethane (1.5 mL) to yield a colourless solution. After 3 h, it was concentrated, and hexane added to yield (**6**) as a white solid (18 mg, 90%). Found: C, 65.26; H, 4.31; N 3.72. calcd.(%) for C₆₁H₄₉N₃AgClO₅P₂·0.25CH₂Cl₂, C, 65.07; H, 4.41; N 3.72. Mass (acetone, m/z): found: 1008.2442, calcd. 1008.2402 for C₆₁H₄₈O₅N₃P₂Ag, [Ag(ttp)(xantphos)]⁺. IR (neat, cm⁻¹): 3054, 2960, 1600, 1584, 1567, 1477, 1434, 1402, 1220, 1089, 789, 746 and 694. ^1H NMR (400 MHz, CDCl_3): 8.44 (s, 2H, H^{3'}), 8.27 (d, 2H, $^3\text{J}(\text{HH})$ 7.7 Hz, H³), 8.21 (s, 2H, H⁶), 7.85 (d, 2H, $^3\text{J}(\text{HH})$ 8.0 Hz, H^{Ar}), 7.65 (d, 2H, $^3\text{J}(\text{HH})$ 7.5 Hz, H^{xan}), 7.58 (vt, 2H, $^3\text{J}(\text{HH})$ 7.5 Hz, H⁴), 7.42 (d, 2H, $^3\text{J}(\text{HH})$ 8.0 Hz, H^{Ar}), 7.34-7.24 (m, 8H, H^{Ph}), 7.22-6.96 (m, 16H, H^{Ph} H^{xan} & H⁵), 6.63 (m, 2H, H^{xan}), 2.49 (s, 3H, Me) and 1.72 (s, 6H, Me-xan). ^{31}P NMR (161 MHz, CDCl_3): -6.2 (br, d), $^1\text{J}(^{107/109}\text{AgP})_{\text{av}} = 402$ Hz. ^{13}C NMR (101 MHz, CDCl_3 , δ in ppm): 155.99, 154.90, 153.63, 151.50, 149.46 (C⁶), 137.93 (C⁴), 133.14 (C^{Ph}), 132.56, 131.34 (C^{xan}), 130.23 (C^{Ar}), 129.02 (C^{Ph}), 128.88 (C^{Ph}), 127.31 (C^{Ar}), 127.25 (C^{xan}), 124.56, 122.63 (C³), 120.67 (C³), 29.20 (Me^{xan}) and 21.39 (Me^{tol}).

[Ag₂(μ -dppm)₂](ClO₄)₂ (7)

A solution containing bis(diphenylphosphino)methane (dppm) (54 mg, 0.14 mmol) and AgClO₄ (29 mg, 0.14 mmol) in a degassed mixture of chloroform and methanol (1:1) (4 mL) was heated under reflux for 1.5 h. The solution was concentrated to a low volume to yield white crystals, which were filtered off and washed with cold methanol (71 mg, 85%). Found: C, 50.45; H, 3.40, calcd. (%) for C₅₀H₄₄Cl₂O₈P₄Ag₂: C, 50.75; H, 3.75. IR (neat) cm⁻¹: 3057, 1590, 1480, 1438, 1085, 990, 700 and 680. Maldi (MeCN, m/z): found: 1080.9888, calcd. 1080.9980 for C₅₀H₄₄ClO₄P₄Ag₂, [M-ClO₄]⁺. Found: 491.0232, calcd. 491.0248 for C₂₅H₂₂P₂Ag, [Ag(dppm)]⁺. Found: 875.1442, calcd. 875.1444 for C₅₀H₄₄P₄Ag, [Ag(dppm)₂]⁺. ^1H NMR (400 MHz, CDCl_3): 7.64-7.55 (br, m, 16H, H^{Ph}), 7.41-7.31 (m, 24H, H^{Ph}) and 3.95 (m, 4H, J(PH) ca. 5 Hz, CH₂). ^1H NMR (400

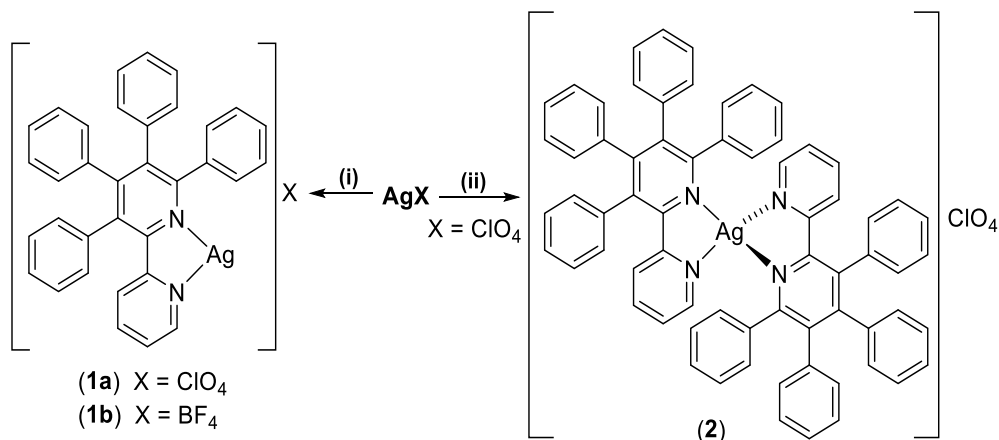
MHz, CD₃CN, δ): 7.54-7.50 (br, m, 16H, H^{Ph}), 7.44 (t, 8H, J 7.5 Hz, H^{Ph}), 7.33 (t, 16H, J 7.7 Hz, H^{Ph}) and 3.74 (m, 4H, J(PH) 4.8 Hz, CH₂). ³¹P NMR (161 MHz, CDCl₃): 10.4 (m, 2nd order), Tentative ¹J(¹⁰⁷AgP) = 499 & ¹J(¹⁰⁹AgP) = 576 Hz. ³¹P NMR (161 MHz, CD₃CN): 7.0 (br, dt, 2nd order), N = 36.2 Hz, ¹J(AgP)_{av} = 507 Hz. ¹³C NMR (101 MHz, CD₃CN, δ): 134.02 (t, J(PC) 3.4 Hz), 132.30 (s), 131.13 (m, J(PC) ca. 10 Hz), 130.02 (s), and 25.53 (m, J(PC) ca. 7 Hz).

[Ag₂(μ-dppm)₂(μ-dppz)](ClO₄)₂ (8**)**

3,6-Di(2-pyridyl)-4,5-diphenyl-pyridazine (dppz) (6 mg, 0.0155 mmol) was added to a solution of [Ag₂(μ-dppm)₂](ClO₄)₂ (**7**) (18 mg, 0.0152 mmol) in dichloromethane (1.5 mL) to give a colourless solution. This solution was allowed to concentrate at room temperature for 5 h. Addition of diethyl ether precipitated (**8**) as a light off-white solid (21 mg, 88%). Found: C, 56.24; H, 3.92; N 3.29, calcd. (%) for C₇₆H₆₂Cl₂N₄O₈P₄Ag₂·1.0CH₂Cl₂: C, 55.89; H, 3.90; N 3.39. IR (neat) cm⁻¹: 3656, 3057, 1590, 1483, 1435, 1377, 1083, 998, 739 and 689. Maldi (MeCN, m/z): Found: 1080.9933, calcd. 1080.9980 for C₅₀H₄₄ClO₄P₄Ag₂, [Ag₂(dppm)₂ClO₄]⁺. ¹H NMR (400 MHz, CDCl₃): 8.00 (br, d, 2H, J(HH) 4.0 Hz, H_{Py}), 7.53 (br, m, 4H), 7.40 (br, t, 2H, J(HH) 8.0 Hz), 7.36-7.25 (br, m, 28H), 7.24-7.16 (br, m, 8H), 7.15-7.03 (br, m, 16H), 6.86 (br, m, 2H, J(HH) 8.0 Hz) and 3.76 (br, m, 4H, CH₂). ³¹P NMR (161 MHz, CDCl₃): -5.7 (br, dt), ¹J(^{107/109}AgP)_{av} = 449 Hz.

Results and Discussion

First, the coordination chemistry of the Ag(I) centre with the bulky bidentate nitrogen-donor ligand 3,4,5,6-tetraphenyl-2,2'-bipyridine (tpbpy) was studied. The two-coordinate Ag(I) complex of the type [Ag(tpbpy)]⁺ (**1**) was prepared by treating AgClO₄ or AgBF₄ with one equivalent of the ligand (Scheme 1).

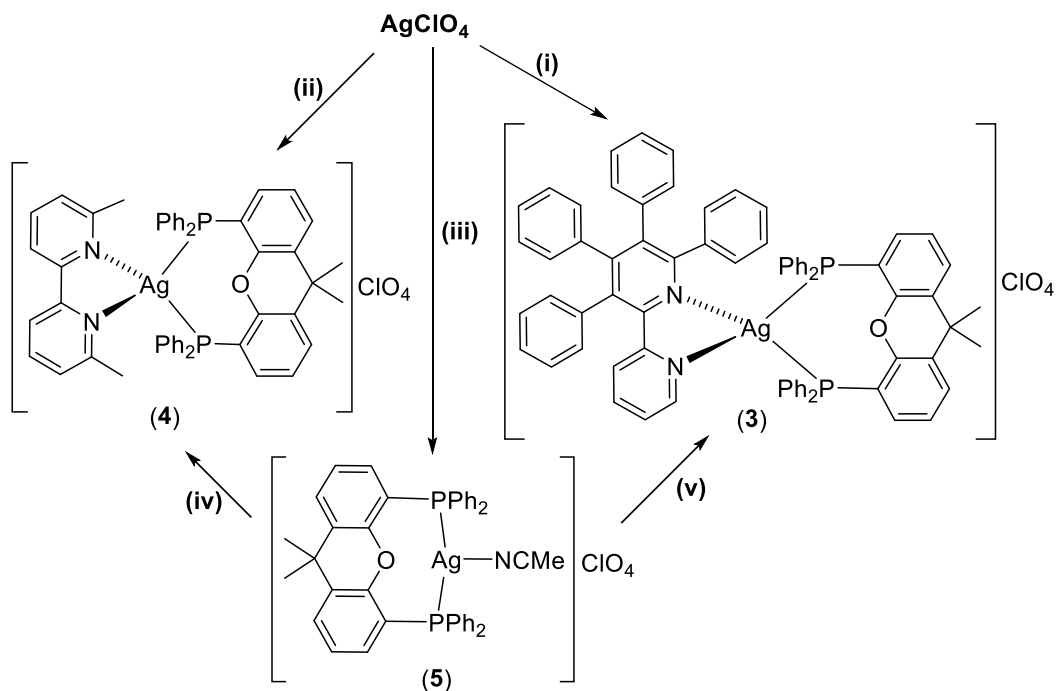


Scheme 1. Synthetic routes to **(1)**-**(2)**. (i) 1 equiv. tpbpy; (ii) 2 equiv. tpbpy

This complex and other Ag(I) complexes were characterized by a combination of elemental analysis, IR, Mass and NMR spectroscopy. Mass spectrum of **(1a)** indicated an accurate mass value of (m/z 567.0973) for the $[M-\text{ClO}_4]^+$ ion and elemental analyses confirmed the proposed structure with the composition C₃₄H₂₄ClN₂O₄Ag. The four-coordinate Ag(I) complex $[\text{Ag}(\text{tpbpy})_2]\text{ClO}_4$ **(2)** was isolated in 88% yield as a white solid by reacting AgClO₄ with two equivalents of tpbpy in acetonitrile. The elemental analysis and mass spectral analyses (m/z 1027.2948 for $[M-\text{ClO}_4]^+$) confirmed the proposed structure with the composition C₆₈H₄₈ClN₄O₄Ag.

Four-coordinate heteroleptic Ag(I) complexes containing both P and N donor ligands can be achieved by reacting silver(I) salt with a (1:1) mixture of bidentate (P[^]P) and (N[^]N) ligands. The four-coordinate Ag(I) complex $[\text{Ag}(\text{xantphos})(\text{tpbpy})]\text{ClO}_4$ **(3)** was obtained as a white solid in 91% yield by treating AgClO₄ with a (1:1) molar ratio of tpbpy and xantphos in acetonitrile. The ³¹P-¹H spectrum of **(3)** showed a doublet of doublets (or two doublets coupled to two isotopes of silver) at -5.4 ppm with ¹J(¹⁰⁷AgP) = 384 Hz and ¹J(¹⁰⁹AgP) = 444 Hz. ¹J(AgP) values agree with the published data (M. C. Gimeno, *et al.*, 1995). Similarly, the complex $[\text{Ag}(\text{xantphos})(\text{dmbpy})]\text{ClO}_4$ **(4)** (dmbpy = 6,6'-dimethyl-2,2'-bipyridine) was isolated as a white solid with 82% yield. The ³¹P-

$\{^1\text{H}\}$ spectrum of **(4)** showed a doublet of doublets at -6.2 ppm with $^1J(^{107}\text{AgP}) = 357$ Hz and $^1J(^{109}\text{AgP}) = 412$ Hz.

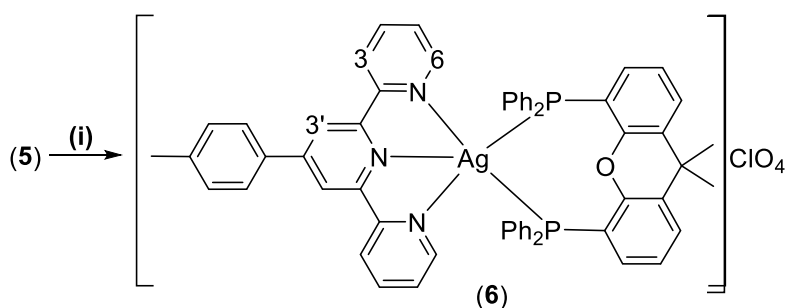


Scheme 2. Synthetic routes to **(3)**-**(5)**. (i) tpbpy and xantphos (1:1); (ii) dmbpy and xantphos (1:1); (iii) 1 equiv. xantphos.; (iv) 1 equiv. tmbpy ; (v) 1 equiv. tpbpy

The possibility of stepwise preparation of heteroleptic complexes of the type $[\text{Ag}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^+$ *via* the complex $[\text{Ag}(\text{P}^{\wedge}\text{P})(\text{labile ligand})]^+$ was explored by replacing the labile ligand with a bidentate ligand $\text{N}^{\wedge}\text{N}$ as shown in scheme 2. Treatment of AgClO_4 with one equivalent xantphos in acetonitrile gave a white solid with 83% yield. Characterizing of data including elemental analysis suggests it to be a three-coordinate Ag(I) complex $[\text{Ag}(\text{NCMe})(\text{xantphos})]\text{ClO}_4$ **(5)**. It showed a phosphorus-31 resonance at -5.3 ppm (dd) with $^1J(^{107}\text{AgP}) = 461$ Hz and $^1J(^{109}\text{AgP}) = 532$ Hz. The proton resonance of the coordinated MeCN appeared as a singlet at 2.04 ppm. Treatment of this Ag(I) complex **(5)**, containing a labile acetonitrile ligand, with one equivalent of tpbpy gave the heteroleptic complex

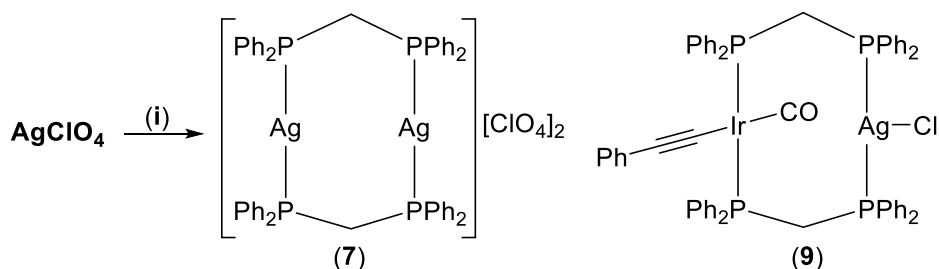
$[\text{Ag}(\text{tpbpy})(\text{xantphos})]\text{ClO}_4$ (**3**) in 84% yield. Similarly, $[\text{Ag}(\text{dmbpy})(\text{xantphos})]\text{ClO}_4$ (**4**) was prepared in 95% yield.

The five-coordinate heteroleptic complex $[\text{Ag}(\text{xantphos})(\text{ttpy})]\text{ClO}_4$ (**6**) was prepared in 90% yield by treating (**5**) with one equivalent of ttpy in dichloromethane (Scheme 3). Elemental analysis and mass spectral data of (**6**) agreed well with the composition $\text{C}_{61}\text{H}_{49}\text{N}_3\text{ClO}_5\text{P}_2\text{Ag}$. The proton NMR and phosphorus-31 NMR data suggest (**6**) to be a symmetrical molecule; only one set of signals was observed for H3, H3' and H6 protons. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum showed a broad doublet centred at -6.2 ppm with average $^1J(^{107/109}\text{AgP})$ of 402 Hz.



Scheme 3. Synthetic routes to (**6**) (i) 1 equiv. ttpy.

The chemistry of AgClO_4 with the diphosphine, bis(diphenylphosphino)methane (dppm) was then studied. The diphosphine dppm is known to bridge two metal centres than forming 4-membered chelate rings. “A-frame” Ag(I) complexes $[\text{Ag}_2(\text{dppm})_2(\text{FBF}_4)_2]$, $[\text{Ag}_2(\text{dppm})_2(\text{PO}_2\text{F}_2)]\text{PF}_6$ and $[\text{Ag}_2(\text{dppm})_2(\text{MeCN})_2(\text{PO}_2\text{F}_2)]\text{PF}_6$ have been structurally characterised (Bruce, *et. al.*, 2016). In order to prepare a binuclear complex of the type $[\text{Ag}_2(\mu\text{-dppm})_2]^{2+}$, the reaction was carried out in chloroform and methanol in the absence of MeCN. Treatment of AgClO_4 with one equivalent of dppm in a (1:1) mixture of chloroform and methanol resulted in the formation of $[\text{Ag}_2(\mu\text{-dppm})_2][\text{ClO}_4]_2$ (**7**) as a white solid in 85% yield (Scheme 4).



Scheme 4. Synthetic routes to **(7)** (i) 1 equiv. dpmm and the molecular structure of **(9)**

Elemental analysis confirmed the proposed structure with the composition $C_{50}H_{44}Cl_2P_4O_8Ag_2$. The proton resonance at 3.95 ppm (4H, broad multiplet) was assigned to the CH_2 groups. The $^{31}P\{-^1H\}$ NMR spectrum was recorded in $CDCl_3$ (Figure 3); it showed a complex second order spin system centred at 10.4 ppm with probable $^1J(^{107}AgP) = 499$ and $^1J(^{109}AgP) = 576$ Hz; very similar spectrum was reported for the P_2AgCl moiety of the binuclear complex $[(PhC_2(OC)Ir(\mu-dppm)_2AgCl)]$ **(9)** (Hutton et al., 1983).

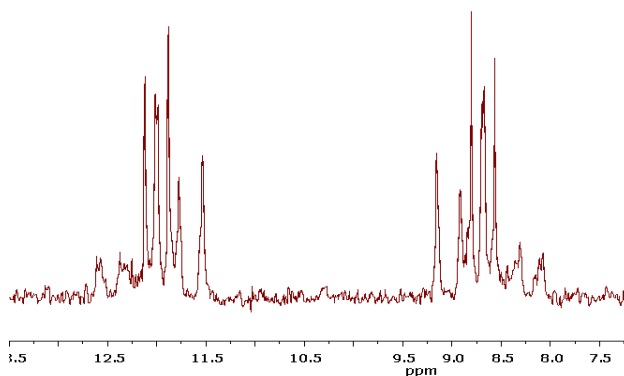


Figure 3. The $^{31}P\{-^1H\}$ NMR spectrum of **(7)** in $CDCl_3$.

In CD_3CN for **(7)**, simplified $^{31}P\{-^1H\}$ NMR spectrum was observed: 7.0 (br, dt, 2nd order), $N = 36.2$ Hz, $^1J(AgP)_{av} = 507$ Hz (Figure 4), probably due to coordination and exchange of CD_3CN molecules to $Ag(I)$ centres.

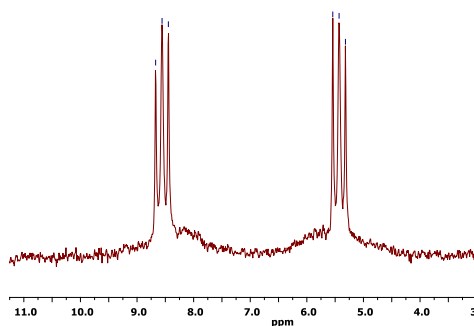
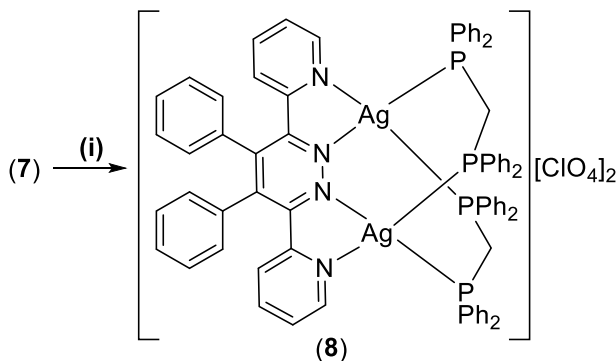


Figure 4. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of **(7)** in CD_3CN

Treatment of complex **(7)** with one equivalent of dppz in dichloromethane afforded an off-white solid of $[\text{Ag}_2(\mu\text{-dppm})_2\{\mu\text{-dppz}\}][\text{ClO}_4]_2$ (**8**) in 88% yield (Scheme 5). The elemental and mass spectral analyses (m/z 1080.9933 for $[\text{M}\text{-ClO}_4]^+$) confirmed the proposed structure with the composition $\text{C}_{76}\text{H}_{62}\text{Cl}_2\text{N}_4\text{O}_8\text{P}_4\text{Ag}_2$. In the ^1H NMR spectrum, the proton attached to carbon adjacent to nitrogen of the pyridyl group appeared at 8.00 ppm as a broad doublet ($^3J(\text{HH}) = 4.0$ Hz) whilst CH_2 protons appeared as a multiplet at 3.76 ppm.



Scheme 5. Synthetic routes to **(8)** (i) 1 equiv. dppz.

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum showed a second order spin system centred at -5.7 ppm (br, dt) with average $^1J(^{107/109}\text{AgP}) = 449$ Hz. $[\text{Cu}_2(\mu\text{-dppm})_2\{\mu\text{-3,6-di(2-pyridyl) tetrazine}\}][\text{PF}_6]_2$ was prepared in a similar manner (Perera, 2020) and the crystal structure of the

analogous heteroleptic Cu(I) complex $[\text{Cu}_2(\mu\text{-dppm})_2\{\mu\text{-dppz}\}][\text{NO}_3]_2$ has been reported (Gil et al., 2011).

Conclusions

We have developed synthetic routes to homoleptic Ag(I) complexes of the type $[\text{Ag}(\text{N}^{\wedge}\text{N})]^+$ and $[\text{Ag}(\text{N}^{\wedge}\text{N})_2]^+$. Four-coordinate heteroleptic complexes of the type $[\text{Ag}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^+$ can be prepared by mixing both P[∧]P and N[∧]N to a solution of AgClO₄ in acetonitrile or by adding one equivalent of a bidentate N[∧]N ligand to a solution of $[\text{Ag}(\text{NCMe})(\text{P}^{\wedge}\text{P})]^+$. Five-coordinate heteroleptic complex $[\text{Ag}(\text{xantphos})(\text{tppy})]\text{ClO}_4$ was synthesised. A route to binuclear heteroleptic Ag(I) complex containing bridging ligands 3,6-di(2-pyridyl)-4,5-diphenyl-pyridazine and dppm was developed.

Acknowledgements

Author wishes to thank the Trinity College Dublin for a Research Fellowship (2011) and Professor S. M. Draper for laboratory facilities and other support. Author is also grateful Dr. John O'Brien and Dr. M. Ruether for recording NMR spectra; Dr. Martin Feeney for providing mass spectral data. An abstract of this study was presented at the Annual Sessions of the Institute of Chemistry, Ceylon in 2018.

References

- Abbas, M., Naeem, N., Iftikhar, H. & Latif, U. (2018). *Synthesis, characterization and antimicrobial properties of silver nanocomposites*. IntechOpen.
- Artem'ev, A. V., Ryzhikov, M. R., Berezin, A. S., Kolesnikov, I. E., Samsonenko, D. G. & Bagryanskaya, I. Y. (2019). Photoluminescence of Ag (I) complexes with a square-planar coordination geometry: the first observation. *Inorganic Chemistry Frontiers*, 6(10), 2855-2864. DOI: 10.1039/C9QI00657E.

- Artem'ev, A. V., Davydova, M. P., Berezin, A. S. & Samsonenko, D. G. (2020). Synthesis and thermochromic luminescence of Ag(I) complexes based on 4, 6-bis (diphenylphosphino)-pyrimidine. *Inorganics*, 8(9), 46. DOI: 10.3390/inorganics8090046.
- Atlı, D. D. & Gülle, S. (2019). Dinuclear N-heterocyclic carbene silver complexes: Synthesis, luminescence and catalytic studies. *Journal of Molecular Structure*, 1179, 576-580. DOI:10.1016/j.molstruc.2018.11.053.
- Bruce, M. I., Nicholson, B. K., Skelton, B. W., White, A. H. & Zaitseva, N. N. (2016). Structural characterization of some adducts of the form $[M_2(\mu\text{-dppm})_2(\text{MeCN})_x]X_2$ [M = Cu, Ag; X = ClO₄, BF₄, PF₆; dppm = (Ph₂P)₂CH₂; x = 0-4]. *Inorganica Chimica Acta*, 453, 647-653. DOI: org/10.1016/j.ica.2016.09.018.
- Carbonell-Vilar, J. M., Fresta, E., Armentano, D., Costa, R. D., Viciano-Chumillas, M. & Cano, J. (2019). Photoluminescent Cu(I) vs. Ag(I) complexes: slowing down emission in Cu(I) complexes by pentacoordinate low-lying excited states. *Dalton Transactions*, 48(26), 9765-9775. doi.org/10.1039/C9DT00772E.
- Durini, S., Ardizzoia, G. A., Therrien, B. & Brenna, S. (2017). Tuning the fluorescence emission in mononuclear heteroleptic trigonal silver(I) complexes. *New Journal of Chemistry*, 41(8), 3006-3014. doi.org/10.1039/C6NJ04058F.
- Fang, G. & Bi, X. (2015). Silver-catalysed reactions of alkynes: recent advances. *Chemical Society Reviews*, 44(22), 8124-8173. doi.org/10.1039/C5CS00027K.
- Fresta, E., Carbonell-Vilar, J. M., Yu, J., Armentano, D., Cano, J., Viciano-Chumillas, M. & Costa, R. D. (2019). Deciphering the electroluminescence behavior of Silver(I)-complexes in light-emitting electrochemical cells: limitations and solutions toward highly stable Devices. *Advanced Functional Materials*, 29(31), 1901797. doi.org/10.1002/adfm.201901797.
- Gil, B., Cooke, G., Nolan, D., ÓMáille, G. M., Varughese, S., Wang, L., & Draper, S.M. (2011) A dinuclear extension to

- constrained heteroleptic Cu(I) systems. *Dalton Trans*, 40, 8320. doi.org/10.1039/C1DT10275C.
- Gimeno, M. C., Jones, P. G., Laguna, A. & Sarroca, C. (1995). Synthesis of silver(I) complexes with 1,1'-bis (diphenylphosphino)ferrocene (dppf). Crystal structures of [Ag(dppf)(PPh₃)]ClO₄·2CH₂Cl₂, [Ag(dppf)₂]ClO₄·2CHCl₃ and [Ag(dppf)(phen)]ClO₄ (phen = 1,10-phenanthroline). *Journal of the Chemical Society, Dalton Transactions*(9), 1473-1481. doi.org/10.1039/DT9950001473.
- Handoko, C. T., Huda, A., & Gulo, F. (2019). Synthesis pathway and powerful antimicrobial properties of silver nanoparticle: A critical review. *Asian J. Sci. Res*, 12, 1-17. DOI: 10.3923/ajsr.2019.1.17.
- Hasson, M. M., Al-Zaidi, B. H. & Ismail, A. H. (2019). Synthesis and characterization of Ag(I) complexes derived from new N-heterocyclic carbenes. *Asian Journal of Chemistry*, 31(5), 1149-1152. doi:10.14233/ajchem.2019.2187.7
- Hung-Low, F. & Klausmeyer, K. K. (2008). Silver coordination complexes of 2-(diphenylphosphinomethyl)pyridine and their bipyridine derivatives. *Inorganica Chimica Acta*, 361(5), 1298-1310. doi.org/10.1016/j.ica.2007.08.015.
- Hutton, A. T., Pringle, P. G. & Shaw, B. L. (1983). Heterobimetallic iridium or rhodium. m-bis(diphenylphosphino)methane complexes with copper(I), silver(I), or gold(I). A silver hydride complex and the crystal structure of [(PhCC)(OC)Ir(μ-Ph₂PCH₂PPh₂)₂CuCl]. *Organometallics*, 2(12), 1889-1891. doi.org/10.1021/om50006a037.
- Jimenez, J., Chakraborty, I., Del Cid, A. M. & Mascharak, P. K. (2017). Five- and six-coordinated silver(I) complexes derived from 2,6-(pyridyl)iminodiadamantanes: sustained release of bioactive silver toward bacterial eradication. *Inorganic chemistry*, 56(9), 4784-4787. doi.org/10.1021/acs.inorgchem.7b00621.
- Jimenez, J., Chakraborty, I., Rojas-Andrade, M. & Mascharak, P. K. (2017). Silver complexes of ligands derived from adamantylamines: Water-soluble silver-donating compounds

- with antibacterial properties. *Journal of inorganic biochemistry*, 168, 13-17. doi. org/10.1016/j.jinorgbio.2016.12.009.
- Kaltzoglou, A., Cox, P. & Aslanidis, P. (2007). Silver (I) bromide complexes of the rigid diphosphanes 1,2-bis(diphenyl phosphano)benzene (dppbz) and 4, 5-bis (diphenylphosphano) -9,9-dimethyl-xanthene (xantphos): Crystal structures of [Ag(μ_2 -Br)(dppbz)]₂, [AgBr(xantphos)] and [AgBr(xantphos)(py₂SH)]. *Polyhedron*, 26(8), 1634-1642. doi. org/10.1016/j.poly.2006.12.006.
- Kızrak, Ü., Çiftçi, O., Özdemir, İ., Gürbüz, N., Düşünceli, S. D., Kaloğlu, M. & Özdemir, İ. (2019). Amine-functionalized silver and gold N-heterocyclic carbene complexes: Synthesis, characterization and antitumor properties. *Journal of Organometallic Chemistry*, 882, 26-32. doi. org/10.1016/j.jorganchem.2018.12.018.
- Kokunov, Y. V., Kovalev, V., Gorbunova, Y. E., Kozyukhin, S. & Sakharov, S. (2016). Synthesis, crystal structure, and luminescent properties of silver complexes with 2-methylquinoline. *Russian Journal of Inorganic Chemistry*, 61(12). 1538-1544. DOI: 10.1134/S003602361612007X.
- Medici, S., Peana, M., Crisponi, G., Nurchi, V. M., Lachowicz, J. I., Remelli, M. & Zoroddu, M. A. (2016). Silver coordination compounds: A new horizon in medicine. *Coordination Chemistry Reviews*, 327, 349-359. doi. org/10.1016/j.ccr.2016.05.015.
- Nayeri, S., Jamali, S., Jamjah, A., Shakirova, J. R., Tunik, S. P., Gurzhiy, V., Samouei, H. & Shahsavari. H. R. (2020). Five- and six-coordinated silver(I) complexes formed by a metallomacrocyclic ligand with a "Au₂N₂" donor group: Observation of pendulum and linear motions and dual phosphorescence. *Inorg. Chem.*, 59 (8) 5702-5712. <https://doi.org/10.1021/acs.inorgchem.0c00482>.
- Ollagnier, C. M., Perera, S. D Fitchett, C. M. & Draper, S. M. (2008). Rhodium and palladium complexes of a pyridyl-

centred polyphenylene derivative. *Dalton Transactions*(2), 283-290. doi. org/10.1039/ B709818A.

Perera, S. D. (2020). Synthesis of homo and heteroleptic Cu(I) complexes with chelating N and P donor ligands, *Rajarata University Journal*, **5** (1), 29-34. ISSN: 2362-0080

Schubert, U., Hofmeier, H. & Newkome, G. R. (2006). *Modern terpyridine chemistry*: John Wiley & Sons.

Škoch, K., Císařová, I. & Štěpnička, P. (2017). Silver (I) complexes with 1'-(diphenylphosphino)-1-cyanoferrocene and nitrite or nitrate supporting ligands. *Inorganic Chemistry Communications*, **84**, 234-236. doi. org/10.1016/j.inoche.2017.08.033

Xing, L.-R., Lu, Z., Li, M., Zheng, J. & Li, D. (2020). Revealing high-lying intersystem crossing in brightly luminescent cyclic trinuclear CuI/AgI complexes. *The Journal of Physical Chemistry Letters*, **11**(6), 2067-2073. doi. org/10.1021/acs.jpcllett.9b03382