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Polynuclear silver(I) complexes of diphosphine ligands and isoquinoline: Synthesis, structural characterization and spectroscopic properties

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ABSTRACT

The reactions of diphosphine ligands and isoquinoline (i-C_9H_7N) with Ag salts in the mixed solvent of methanol (MeOH) and dichloromethane (CH_2Cl_2) generate the complexes $[Ag_2(dppm)_2(NO_2)_2]\cdot(i\text{-}C_9H_7N)_2$ (**1**), $[Ag_2(dppm)_2(i\text{-}C_9H_7N)_2(BF_4)](BF_4)$ (**2**), $\{[Ag(dppe)(i\text{-}C_9H_7N)_2](CF_3SO_3)\cdot(i\text{-}C_9H_7N)\}_n$ (**3**), $\{[Ag(dppb)(i\text{-}C_9H_7N)_2](BF_4)_2\cdot(i\text{-}C_9H_7N)_{0.5}\}_n$ (**4**) and $\{[Ag(dppb)(i\text{-}C_9H_7N)(CF_3SO_3)]\cdot(i\text{-}C_9H_7N)\}_n$ (**5**). These complexes were all characterized by IR, elemental analysis, X-ray diffraction, luminescence, ^{31}P and ^{1}H NMR spectroscopy. Complexes **1** and **2** have dinuclear structures, while complexes **3**, **4** and **5** have 1D infinite zigzag chain structures. Complexes **1** and **2** are metal clusters in which there exist Ag···Ag metal bonds, whilst in compounds **3**, **4** and **5**, two silver atoms are bridged by the diphosphine ligands to form the 1D infinite zigzag chains. Complexes **3** and **5** are 2D topologically promising architectures and complex **4** is a 3D topologically promising architecture. In addition, complexes **1**–**5** exhibit interesting fluorescence in the solid state at room temperature. At the same time, we also studied the terahertz spectra of the complexes, which show more accurate characteristics of each group of complex.

1. Introduction

In recent years, metal coordination polymers have attracted great interest, not only for their potential applications as functional materials, but also for their fascinating architectures [1–3]. Silver(I) complexes also have been widely studied because the silver(I) ion has a variety of coordinated models. Mono-, di- and tetranuclear complexes ($[Ag(PPh_3)(AMP)_2](BF_4)$, $[Ag_2(PPh_3)_4(AMP)_2(SO_4)]$, $[Ag_4(PPh_3)_4(AMP)_2(NO_3)_4]_n$, $[Ag_4(PPh_3)_4(AMP)_2(Ac)_4]_n$ (Ac = CH_3COO) and $[Ag(PPh_3)_2(HCOO)]\cdot CH_2Cl_2$) [4] have been reported in the literature. The silver(I) ion has an outer electronic configuration with a closed-shell structure (d^{10}). According to the HSAB concept [5], the silver(I) ion can be classified as a soft cation, hence can coordinate to N donor ligands since the N atom tends to construct strong binding with the soft Ag(I) center due to its soft base character. In 2013, a complex containing Ag(I) and bidentate nitrogen donors $[Ag_2C_2\cdot 4AgCF_3CO_2\cdot(bipyH)(CF_3CO_2)\cdot H_2O]$ [6] was synthesized. This complex is a metal cluster in which there exist Ag···Ag metal bonds. Furthermore, many topologically promising architectures containing Ag(I) ions and bidentate nitrogen donors have been constructed [7]. We have obtained a 2-D network constructed from the complex $\{[Ag_2(dppb)_3](CF_3SO_3)_2\cdot(4,4'\text{-bipy})\cdot(CH_3CN)_2\}_n$ (dppb = bis(diphenylphosphino)butane, 4,4′-bipy = 4,4′-bipyridine) [8].

Given the interesting electronic, medicinal and structural properties of silver(I) phosphine complexes, polymeric silver(I) complexes which are bridged by diphosphine ligands have been extensively studied. Coordinated to the Ag(I) ion, the diphosphine ligand can act as a monodentate ligand or as a bidentate ligand in the polymeric structures. In our previous work, we synthesized the complex $[Ag_2(NO_2)_2(dppm)_2]\cdot 2CH_3CN$ [9].

Complexes containing mixed ligands have been synthesized using the rigid ligand isoquinoline (i-C_9H_7N) in conjunction with the more flexible diphosphine ligands $Ph_2P(CH_2)_nPPh_2$. We have synthesized the dinuclear molecule $[Ag_2(dppm)_2(C_9H_7N)_2]$-$(CF_3SO_3)_2\cdot(C_9H_7N)$ [10] containing isoquinoline and the diphosphine ligand dppm. In this paper, we report the synthesis and characterization of complexes **1**–**5** which are di- and poly-nuclear silver(I) complexes containing isoquinoline, where the versatility

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of the coordination of the Ag(I) ion allows for a variety of coordination modes of the isoquinoline ligand. This article shows that linear and network polymers as well as metal clusters can be formed. Complexes **3**, **4** and **5** have topologically promising architectures. Although there are many reports on luminescent d^{10}-metal complexes, emissive Ag(I) complexes have been less studied because of their potential photosensitivity and limited luminescence. The luminescence of complexes **1**–**5** has been researched in this article and complexes **1** and **5** show three emission spectral peaks.

In addition, in this work, complexes **1**–**5** were characterized by Terahertz time-domain spectroscopy (THz-TDS). THz-TDS is a vibrational spectroscopic technique that is used to probe the infrared active vibrational modes in the far-infrared and sub-millimeter region of the electromagnetic spectrum by measuring ultrashort pulses of coherent terahertz radiation (0.1–4 THz) (3–133 cm^{-1}) [11]. Compared with conventional spectroscopic techniques, THz-TDS has a high signal-to-noise ratio. Although THz-TDS has been utilized in a wide range of research fields [12], this technique is seldom used for organic/inorganic compounds and inorganic–organic hybrids.

2. Experimental

2.1. Materials and measurements

All the chemical reagents, silver nitrite ($AgNO_2$), silver tetrafluoroborate ($AgBF_4$), silver trifluoromethanesulfonate ($AgCF_3SO_3$), bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,4-bis(diphenylphosphino)butane (dppb) and isoquinoline (i-C_7H_9N), were commercially available and used without further purification. Elemental analyses (C, H, N) were determined on an Elementar Vario MICRO CUBE (Germany) elemental analyzer. Infrared spectra were recorded on a Brucker EQUINOX 55 FT-IR spectrometer using KBr pellets in the range 400–4000 cm^{-1}. Excitation and emission spectra of the solid samples were recorded on an F-4500 fluorescence spectrophotometer at room temperature. ^1H and ^{31}P NMR spectra were recorded at room temperature with Varian VNMRS 600 MHz and 243 MHz spectrometers, respectively. The THz absorption spectra were recorded on a THz time domain device of Capital Normal University of China, based on photoconductive switches for the generation and electro-optical crystal detection of the far-infrared light, with the effective frequency in the range 0.2–4.0 THz [13,14].

2.2. Preparation of the complexes

2.2.1. Synthesis of $[Ag_2(dppm)_2(NO_2)_2]\cdot(i\text{-}C_9H_7N)_2$ (**1**)

Dppm (0.2 mmol, 0.0769 g) and i-C_9H_7N (0.2 mmol, 0.0264 g) were added into a stirring solution of $AgNO_2$ (0.2 mmol, 0.0308 g) in a mixture of CH_2Cl_2 (5 ml) and CH_3OH (5 ml) at ambient temperature. The mixture was then stirred for a further 5 h. The insoluble residues were removed by filtration and the brown filtrate was evaporated slowly at room temperature over about one week to yield white crystals. Yield: 70%. Anal. Calc. for $C_{68}H_{54}Ag_2N_4O_4P_4$: C, 61.19; H, 4.38; N, 4.20%; Found: C, 61.04; H, 4.14; N, 4.30%. IR (cm^{-1}, KBr pellets): 3422w, 3050 m, 2025w, 1957w, 1626 m, 1586 m, 1497w, 1481 m, 1433vs, 1381 m, 1307w, 1275 m, 1231vs, 1182s, 1142 m, 1097s, 1024w, 999 m, 943w, 869w, 840 m, 799s, 787s, 755s, 734vs, 721s, 691vs, 638 m, 514s, 483 m, 472 m, 450 m, 413w. ^1H NMR (600 MHz, $CDCl_3$, 298 K) δ, ppm: 3.6 (s, 4H, dppm-CH_2), 7.2–7.4 (m, with solvent signal peak overlap, dppm-ph), 7.6–8.0 (m, 10H, i-C_9H_7N), 8.5 (d, $J = 5.7$ Hz, 2H, -CH-i-C_9H_7N), 9.3 (s, 2H, –CH-i-C_9H_7N). ^{31}P NMR (243 MHz, $CDCl_3$) δ, ppm: 3.8 (br, $J_{Ag-P} = 459$ Hz).

2.2.2. Synthesis of $[Ag_2(dppm)_2(i\text{-}C_9H_7N)_2(BF_4)](BF_4)$ (**2**)

Follow a similar procedure as for **1**, dppm (0.2 mmol, 0.0769 g) and i-C_9H_7N (0.2 mmol, 0.0264 g) were added into a stirring solution of $AgBF_4$ (0.2 mmol, 0.0389 g) in a mixture of CH_2Cl_2 (5 ml) and CH_3OH (5 ml) at ambient temperature. The mixture was then stirred for a further 5 h. The insoluble residues were removed by filtration and the brown filtrate was evaporated slowly at room temperature over about a week to yield white crystals. Yield: 76%. Anal. Calc. for $C_{68}H_{58}Ag_2B_2F_8N_2P_4$: C, 57.66; H, 4.13; N, 1.98%; Found: C, 57.63; H, 4.15; N, 1.83%. IR (cm^{-1}, KBr pellets): 3415s, 3161s, 2426w, 1627s, 1588 m, 1483 m, 1435s, 1384vs, 1336w, 1312w, 1276w, 1096vs, 998s, 947 m, 872w, 831 m, 779s, 741s, 720 m, 691s, 637 m, 540 m, 517s, 479 m, 443w, 420w. ^1H NMR (600 MHz, $CDCl_3$, 298 K) δ, ppm: 3.9 (s, 4H, dppm-CH_2), 7.2–7.8 (m, with solvent signal peak overlap, dppm-ph, i-C_9H_7N), 8.3 (d, $J = 5.8$ Hz, 2H, -CH-i-C_9H_7N), 9.0 (s, 2H, –CH-i-C_9H_7N). ^{31}P NMR (243 MHz, $CDCl_3$) δ, ppm: 11.5 (d, $J_{Ag-P} = 522$ Hz).

2.2.3. Synthesis of $\{[Ag(dppe)(i\text{-}C_9H_7N)_2](CF_3SO_3)\cdot(i\text{-}C_9H_7N)\}_n$ (**3**)

Follow a similar procedure as for **1**, dppe (0.2 mmol, 0.0797 g) and i-C_9H_7N (0.2 mmol, 0.0264 g) were added into a stirring solution of AgOTf (0.2 mmol, 0.0514 g) in a mixture of CH_2Cl_2 (5 ml) and CH_3OH (5 ml) at ambient temperature. The mixture was then stirred for a further 5 h. The insoluble residues were removed by filtration and the brown filtrate was evaporated slowly at room temperature over about one week to yield white crystals. Yields: 66%. Anal. Calc. for $C_{54}H_{45}AgF_3N_3O_3P_2S$: C, 62.20; H, 4.35; N, 4.03%; Found: C, 62.33; H, 4.28; N, 3.83%. IR (cm^{-1}, KBr pellets): 3421w, 3054s, 2290w, 1627s, 1898w, 1628s, 1590s, 1577 m, 1498 m, 1482 m, 1434s, 1385s, 1268vs, 1222s, 1149vs, 1099s, 1052 m, 1031vs, 998 m, 946 m, 860 m, 830s, 809 m, 755s, 733vs, 717s, 694s, 661w, 637vs, 571 m, 514s, 480s, 456 m, 417w. ^1H NMR (600 MHz, $CDCl_3$, 298 K) δ, ppm: 2.2–2.6 (m, 4H, dppe-CH_2CH_2), 7.2–7.5 (m, with solvent signal peak overlap, dppe-ph), 7.6–8.0 (m, 10H, i-C_9H_7N), 8.5 (d, $J = 5.7$ Hz, 2H, -CH-i-C_9H_7N), 9.3 (s, 2H, -CH-i-C_9H_7N). ^{31}P NMR (243 MHz, $CDCl_3$) δ, ppm: 9.4 (d, $J^{19}{}_{F\text{-}P} = 547$ Hz), 4.7 (dd, $J^{109}_{Ag-P} = 287$ Hz, $J^{107}_{Ag-P} = 248$ Hz).

2.2.4. Synthesis of $\{[Ag(dppb)(i\text{-}C_9H_7N)_2](BF_4)_2\cdot(i\text{-}C_9H_7N)_{0.5}\}_n$ (**4**)

Follow a similar procedure as for **1**, dppb (0.2 mmol, 0.0853 g) and i-C_9H_7N (0.2 mmol, 0.0264 g) were added into a stirring solution of $AgBF_4$ (0.2 mmol, 0.0389 g) in a mixture of CH_2Cl_2 (5 ml) and CH_3OH (5 ml) at ambient temperature. The mixture was then stirred for a further 5 h. The insoluble residues were removed by filtration and the brown filtrate was evaporated slowly at room temperature over about one week to yield white crystals. Yields: 77%. Anal. Calc. for $C_4H_{45.5}AgBF_4N_{2.5}P_2$: C, 64.25; H, 4.86; N, 3.71%; Found: C, 64.01; H, 5.00; N, 3.57%. IR (KBr pellets, cm^{-1}): 3421w, 3052 m, 2933w, 2025w, 1968w, 1627s, 1587 m, 1497w, 1481w, 1455w, 1434s, 1382s, 1305w, 1276 m, 1257w, 1210w, 1179 m, 1092s, 1054vs, 997s, 945 m, 868w, 833s, 809 m, 741vs, 695vs, 637s, 543w, 517s, 482s, 410w. ^1H NMR (600 MHz, $CDCl_3$, 298 K) δ, ppm: 2.1–2.7 (m, 12H, dppp-$CH_2CH_2CH_2$), 7.3–7.5 (m, 48H, dppp-ph), 7.6–8.0 (m, 10H, i-C_9H_7N), 8.5 (d, $J = 5.7$ Hz, 2H, -CH-i-C_9H_7N), 9.3 (s, 2H, -CH-i-C_9H_7N). ^{31}P NMR (243 MHz, $CDCl_3$) δ, ppm: 9.6 (d, $J_{Ag-P} = 532$ Hz).

2.2.5. Synthesis of $\{[Ag(dppb)(i\text{-}C_9H_7N)(CF_3SO_3)]\cdot(i\text{-}C_9H_7N)\}_n$ (**5**)

Follow a similar procedure as for **1**, dppb (0.2 mmol, 0.0853 g) and i-C_9H_7N (0.2 mmol, 0.0264 g) were added into a stirring solution of AgOTf (0.2 mmol, 0.0514 g) in a mixture of CH_2Cl_2 (5 ml) and CH_3OH (5 ml) at ambient temperature. The mixture was then stirred for a further 5 h. The insoluble residues were removed by filtration and the brown filtrate was evaporated slowly at room temperature over about one week to yield white crystals. Yields: 79%. Anal. Calc. for $C_{47}H_{42}AgF_3N_2O_3P_2S$: C, 59.94; H, 4.50; N,