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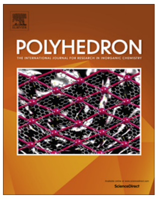

Synthesis, structural characterization, stability, antibacterial activity and spectroscopic properties (THz) of five new polynuclear silver(I) complexes with 1,10-phenanthroline derivative and 1,3-bis(diphenylphosphino)propane (dppp)

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ABSTRACT

The reactions of 1,3-bis(diphenylphosphino)propane (dppp) and 1,10-phenanthroline derivative with Ag salts in the mixed solvent of methanol and dichloromethane generate the corresponding complexes, $\{[Ag_2(dppp)_2(phen)_2](BF_4)_2(H_2O)_2\}_n$ (**1**) (dppp = 1,3-bis(diphenylphosphino)propane), $\{[Ag_2(dppp)_2(dmp)_2](CF_3SO_3)_2\}_n$ (**2**), $\{[Ag_2(dppp)_2(dmp)_2](BF_4)\}_n$ (**3**) (dmp = neocuproine), $\{[Ag_2(dppp)_2(Bphen)_2](CF_3SO_3)_2\}_n$ (**4**) and $\{[Ag_2(dppp)_2(Bphen)_2](ClO_4)\}$ (**5**) (Bphen = 4,7-diphenyl-1,10-diazaphenanthrene). All the complexes are characterized by X-ray diffraction, luminescence, ^{31}P, ^{1}H NMR spectroscopy and terahertz (THz) spectra. These five complexes are of dinuclear structures. The topological analysis of simplified underlying nets reveals that complexes **1**–**4** have topologically promising architectures formed through hydrogen bonds (F···H–C) between the C–H groups of aromatic ring and anions. Thermogravimetric analysis (TGA) shows the complexes **1**–**5** possess good thermal stability up to 300 °C.

1. Introduction

The silver(I) coordination polymers have attracted great interest not only for their extensive applications as functional materials, but also for their intriguing architectures [1–3]. Because of their potential applications in the fields of biological activity, catalysis and light emitting devices [4], the mixed IB metal complexes combining bisphosphines (PP) and aromatic diamine ligands have been intensively investigated during past years [4–8]. Only a few examples of silver(I) complexes with similar structures are reported in the literatures so far [9–13]. For examples, the dppp ligand was used to synthesize the $[Ag(dppp)(phen)](BF_4)$ complex [8]. and the ligand dppFc and bis(diphenylphosphanyl)ocarborane were used to synthesize $[Ag(PP)(phen)]^+$ derivatives [10,11]. It is noteworthy that Pettinari et al. have reported the dinuclear silver complexes of general formula $[(AgX)_2(PP)(NN)_2]$ ($X = ClO_4$ or NO_3), which have interesting structural features [8,13,13e]. Furthermore, various functional coordination topologies have been constructed by reaction of silver(I) ions with certain designed spacer ligands [14–18]. This is coupled with the flexibility of silver(I) center in the adoption of different coordination numbers and geometries with noncovalent interactions such as hydrogen bonding and π–π interaction among others [19]. For example, 1D $[Ag_2(\mu\text{-PTA})_2(\mu\text{-suc})]_n\cdot 2nH_2O$, 2D $[Ag_2(\mu\text{-PTA})_2(\mu_4\text{-adip})]_n\cdot 2nH_2O$, and 3D $[Ag_2(\mu_4\text{-PTA})(\mu_4\text{-mal})]_n$ [20] have been reported.

In addition, a pronounced attention has been aroused to the investigation of the new bioactive metal–organic framework materials (bioMOFs) combined with construction materials as potential antibacterial materials (e.g., antibacterial coating and antibacterial glass). Meanwhile, scientists are devoted to the synthesis of new silver complexes with the biological activity as possible alternatives to the traditional antibiotics. It is widely known that silver and its simple salts are valid antimicrobial agents. Among all the bioactive metals, silver exhibits the highest toxicity to bacteria, and simultaneously shows a relatively low toxicity to mammal

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cells. A large number of bioactive silver complexes have been reported [20]. It was observed that complexes having weak Ag–N bonds usually exhibit higher bioactivity than complexes possessing strong Ag–P bonds [20]. Antimicrobial activities of complexes with Ag–X (X = P, N) can be tuned by varying the space configuration of silver complexes and the number of silver atom [21]. Following this systematic studies on $[Ag(PP)(NN)]^+$ complexes, we are naturally interested in extending our investigation to analogous heteroleptic silver(I) complexes and expected to obtain the silver(I) complexes possessing bioMOFs. Here, five new polynuclear silver(I) complexes (containing Ag–N and Ag–P bonds) with 1,10-phenanthroline derivative and 1,3-bis(diphenylphosphino) propane (dppp) are synthesized and the antimicrobial properties of these complexes are detected.

Compared with the traditional spectrum technology, terahertz spectrum has a high noise ratio and special properties such as coherence, transient. The application of terahertz time-domain spectroscopy (THz-TDS) gradually developed from the narrow field (information technology, physics, materials) to a wider range of areas (such as chemistry, biology, and medicine areas) [22–25]. Due to its sensitivity, THz spectrum can be used to detect the intermolecular weak interaction such as hydrogen bond, van der Waals force, dipole rotation and vibration transition, the lattice of low-frequency vibration and so on. THz spectroscopy has been utilized to study the structures, configurations and environmental state of compounds by our group [26,27].

In this paper, we report the synthesis and characterization of di- and poly-nuclear silver(I) complexes containing dppp, where the versatility of coordination of silver(I) allows for a variety of coordination modes with the dppp ligand. Complexes **1**–**4** are of topologically promising architectures. The fluorescence spectra and THz-TDS of complexes **1**–**5** have been researched in this article. In addition, complexes **1**–**4** show significant antibacterial activity against the selected strains of Gram-negative (*Escherichia coli*) and Gram-positive (*Bacillus subtilis*, *Staphylococcus aureus*) bacteria.

2. Experimental section

2.1. Materials and measurements

All chemical reagents silver perchlorate ($AgClO_4$), silver tetrafluoroborate ($AgBF_4$), silver trifluoromethanesulfonate ($AgCF_3SO_3$), 1,10-phenanthroline (phen), 4,7-diphenyl-1,10-diazaphenanthrene (Bphen), Neocuproine (dmp), 1,3-bis(diphenylphosphino) propane (dppp) are commercially available and used without further purification. Elemental analyses (C, H, N) were determined on a Elementar Vario MICRO CUBE (Germany) elemental analyzer. Infrared spectra were recorded on a Bruker EQUINOX 55 FT-IR spectrometer using the KBr pellet in the range of 400–4000 cm^{-1}. Excitation and emission spectra of the solid samples were recorded on an F-4500 fluorescence spectrophotometer at room temperature. ^{1}H and ^{31}P NMR was recorded at room temperature with a Varian VNMRS 600 MHz and 243 MHz spectrometer, respectively. The THz absorption spectra were recorded on the THz time domain device of Capital Normal University of China, based on photoconductive switches for generation and electro-optical crystal detection of the far-infrared light, effective frequency in the range of 0.2–4.0 THz [28,29].

2.2. Preparation of the complexes

2.2.1. Synthesis of $\{[Ag_2(dppp)_2(phen)_2](BF_4)_2(H_2O)_2\}_n$ (**1**)

Dppp (0.2 mmol, 0.0825 g) was added into the stirring solution of $AgBF_4$ (0.2 mmol, 0.0384 g) in a mixture of CH_2Cl_2 (5 ml) and CH_3OH (5 ml) for 5 h at ambient temperature. The insoluble residues were removed by filtration, and the brown filtrate was evaporated slowly at room temperature for about one week to yield white crystals. After phen (0.2 mmol, 0.0361 g) was added into the stirring solution of crystals in mixing of CH_2Cl_2 (5 ml) and CH_3OH (5 ml) for 5 h. The insoluble residues were removed by filtration, and the brown filtrate was evaporated slowly at room temperature for about one week to yield white crystals. Yields: 66%. *Anal.* Calc. for $C_{78}H_{72}Ag_2B_2F_8N_4O_2P_4$: elemental analysis: C, 58.17; H, 4.47; N, 3.48%. Measured value: C, 58.85; H, 4.52; N, 3.47%. IR (cm^{-1}, KBr pellets): 3550w, 3051w, 2908w, 1621m, 1587m, 1570m, 1510s, 1483s, 1434s, 1422s, 1375m, 1309m, 1275s, 1221s, 1142s, 1057vs, 955s, 844s, 820m, 757s, 745s, 730s, 697s, 645m, 547s, 511s, 480s, 444s. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): $\delta = 1.2$–1.5 (m, 12H, dppp-$CH_2CH_2CH_2$), 7.2–7.4 (m, with solvent signal peak overlap, dppp-ph), 7.2–7.4 (m, $H^{3,8}$-phen), 7.7 (d, 4H, $H^{5,6}$-phen), 8.2–8.8 (m, 4H, $H^{2,9}$-phen) ppm. ^{31}P NMR (243 MHz, $CDCl_3$): $\delta = 4.8$ (d, $J_{Ag-P} = 420$ Hz), -5.9 (d, $J_{Ag-P} = 233$ Hz).

2.2.2. Synthesis of $\{[Ag_2(dppp)_2(dmp)_2](CF_3SO_3)_2\}_n$ (**2**)

Dppp (0.2 mmol, 0.0825 g) and dmp (0.2 mmol, 0.0417 g) were added into the stirring solution of $AgCF_3SO_3$ (0.2 mmol, 0.0514 g) in a mixture of CH_2Cl_2 (5 ml) and CH_3OH (5 ml) for 5 h at ambient temperature. The insoluble residues were removed by filtration, and the brown filtrate was evaporated slowly at room temperature for about a week to yield white crystals. Yields: 70%. *Anal.* Calc. for $C_{84}H_{76}Ag_2F_6N_4O_6P_4S_2$: elemental analysis: C, 57.48; H, 4.33; N, 3.19%. Measured value: C, 57.58; H, 4.42; N, 3.20%. IR(cm^{-1}, KBr pellets): 3434s, 3052s, 2919w, 1967w, 1620s, 1593s, 1556s, 1501vs, 1484vs, 1435vs, 1375s, 1359w, 1271vs, 1222vs, 1145vs, 1099vs, 1030vs, 998s, 956m, 854s, 804m, 783m, 743s, 729s, 698s, 636s, 571m, 548m, 513s, 478m, 445m. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): $\delta = 1.3$–1.5 (m, 4H, dppp-$CH_2\mathit{CH_2}CH_2$), 2.3–2.4 (br, 8H, dppp-$\mathit{CH_2}CH_2\mathit{CH_2}$, 12H, dmp-$CH_3$), 7.2–7.4 (m, with solvent signal peak overlap, dppp-ph, $H^{3,8}$-dmp), 7.6 (br, 4H, $H^{5,6}$-dmp), 7.9–8.1 (m, 4H, $H^{4,7}$-dmp) ppm. ^{31}P NMR (243 MHz, $CDCl_3$): $\delta = 1.7$ (d, $J_{Ag-P} = 366$ Hz), -5.9 (d, $J_{Ag-P} = 235$ Hz).

2.2.3. Synthesis of $\{[Ag_2(dppp)_2(dmp)_2](BF_4)\}_n$ (**3**)

Follow a similar procedure as **2**, dppp (0.2 mmol, 0.0825 g) and dmp (0.2 mmol, 0.0417 g) were added into the stirring solution of $AgBF_4$ (0.2 mmol, 0.0384 g) in a mixture of CH_2Cl_2 (5 ml) and CH_3OH (5 ml) for 5 h at ambient temperature. The insoluble residues were removed by filtration, and the brown filtrate was evaporated slowly at room temperature for about one week to yield white crystals. Yields: 70%. *Anal.* Calc. for $C_{83}H_{80}Ag_2B_2F_8N_4OP_4$: elemental analysis: C, 59.94; H, 4.82; N, 3.37%. Measured value: C, 60.09; H, 4.87; N, 3.40%. IR (cm^{-1}, KBr pellets): 3434s, 3051s, 2918s, 1620s, 1591s, 1556s, 1501vs, 1484vs, 1435vs, 1375s, 1306m, 1281m, 1221m, 1156m, 1059vs, 955s, 854s, 807s, 743s, 728m, 697vs, 647s, 548m, 513s, 480s, 444s. ^{1}H NMR (600 MHz, DMSO, 298 K): $\delta = 2.3$–2.5 (m, 8H, dppp-$\mathit{CH_2}CH_2\mathit{CH_2}$, 12H, dmp-$CH_3$), 3.3 (br, 4H, dppp-$CH_2\mathit{CH_2}CH_2$), 7.2–7.4 (m, with solvent signal peak overlap, dppp-ph, $H^{3,8}$-dmp), 7.7 (br, 4H, $H^{5,6}$-dmp), 8.0 (br, 4H, $H^{4,7}$-dmp) ppm. ^{31}P NMR (243 MHz, DMSO): $\delta = -4.017$ (d, $J_{Ag-P} = 287$ Hz), -4.52 (d, $J_{Ag-P} = 248$ Hz).

2.2.4. Synthesis of $\{[Ag_2(dppp)_2(Bphen)_2](CF_3SO_3)_2\}_n$ (**4**)

Follow a similar procedure as **2**, dppp (0.2 mmol, 0.0825 g) and Bphen (0.2 mmol, 0.0665 g) were added into the stirring solution of AgOTf (0.2 mmol, 0.0514 g) in a mixture of CH_2Cl_2 (5 ml) and CH_3OH (5 ml) for 5 h at ambient temperature. The insoluble residues were removed by filtration, and the brown filtrate was evaporated slowly at room temperature for about one week to yield white crystals. Yields: 66%. *Anal.* Calc. for $C_{104}H_{84}Ag_2F_6N_4O_6P_4S_2$: elemental analysis: C, 62.34; H, 4.20; N, 2.80%. Measured value: