



Synthesis, structure and terahertz spectra of six Ag(I) complexes of bis(diphenylphosphino)methane with 4,4'-bipyridine and its derivations

Qi-Ming Qiu^a, Xu Huang^a, Yin-Hua Zhao^a, Min Liu^b, Qiong-Hua Jin^{a,*}, Zhong-Feng Li^a, Zhen-Wei Zhang^c, Cun-Lin Zhang^c, Qing-Xuan Meng^d

^a Department of Chemistry, Capital Normal University, Beijing 100048, China

^b The College of Materials Science and Engineering, Beijing University of Technology, Beijing 100022, China

^c Beijing Key Laboratory for Terahertz Spectroscopy and Imaging, Key Laboratory of Terahertz Optoelectronics, Ministry of Education, Department of Physics, Capital Normal University, Beijing 100048, China

^d Daxing High School Attached to CNU, Beijing 102600, China

ARTICLE INFO

Article history:

Received 26 November 2013

Accepted 22 March 2014

Available online 1 April 2014

Keywords:

Silver(I) complexes

Bis(diphenylphosphino)methane

4,4'-Bipyridine and its derivations

Terahertz time-domain spectroscopy

Crystal structure

ABSTRACT

The reactions of silver salts AgX [X = OTf (OTf = CF₃SO₃), ClO₄ and BF₄] and bis(diphenylphosphino)methane (dppm) with 4,4'-bipyridine (bipy) and its derivations [1,2-di(4-pyridyl)ethane (dpa), 1,2-di(4-pyridyl)ethylene (dpe), 1,3-bis(4-pyridyl)propane (bpp)] lead to six silver(I) complexes: {[Ag₂(dppm)₂(OTf)₂(μ-bipy)](OTf)₂·2CH₃OH (**1**)}, {[Ag₂(dppm)₂(μ-bpp)(OTf)](OTf)·CH₃OH)_n (**2**)}, {[Ag₂(dppm)₂(CH₃CN)₂(μ-dpa)](ClO₄)₄·2CH₃CN (**3**)}, [Ag₂(dppm)₃(ClO₄)₂ (**4**)}, {[Ag₂(dppm)₂(μ-bipy)(CH₃CN)](BF₄)₂)_n (**5**)} and {[Ag₂(dppm)₂(μ-dpe)(CH₃CN)](BF₄)₂)_n (**6**)}. Complexes **1** and **3** are tetranuclear complexes with two eight-membered Ag₂P₄C₂ rings bridged by bipy and dpa respectively. **2**, **5** and **6** are of infinite chain structures formed by [Ag₂(dppm)₂] units linked by bpp, bipy and dpe respectively. **4** is a binuclear compound with two silver atoms bridged by three dppm ligands. All complexes are characterized by X-ray diffraction, fluorescence, ¹H and ³¹P NMR spectroscopy and terahertz time-domain spectroscopy (THz-TDS).

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Coordination polymers are metal–ligand compounds that extend “infinitely” in one, two or three dimensions via more or less covalent metal–ligand bonding [1]. The interaction between bidentate diphosphines R₂P(R')_nPR₂ and silver salts has recently attracted a great deal of interest because the resulted complexes have found applications in homogeneous catalysis [2] and anti-tumor compounds [3]. Dppm complexes containing structure unit [M₂(dppm)₂] have been intensively investigated [4,5]. Meanwhile among various types of spacing ligands, the flexible N-donor ligands are widely used in the construction of novel supramolecular frameworks including diverse noncovalent interactions [6], and they exhibit special adaptability for coordination requirements [7]. So far, a large range of infinite frameworks, including honeycomb, diamond, square grids, ladder, brick, octahedral and T-shaped have been generated [8,9]. The metal–organic hybrid supramolecular compounds have been widely used in many fields, such as catalysis

* Corresponding author. Tel.: +86 010 68903033; fax: +86 010 68902320.

E-mail address: jinqh@cnu.edu.cn (Q.-H. Jin).

[10], magnetism [11], gas separation materials [12] and nanomaterial precursors [13]. In our former work, we have obtained [Ag₄(μ-dppm)₂(μ-SO₄)₂(μ-bipy)₂]·2CH₃OH [14] and {[Cu₂(dppm)₂(bipy)(CF₃SO₃)](CF₃SO₃)(CH₃OH)_n [15]. In this paper, versatile coordinated N-donor ligands are specially chosen to obtain the frameworks of d¹⁰ metal-dppm complexes. In addition, low-valent metal complexes are difficult to be obtained in pure water solution. So the people consider the solvent CH₃CN which contains –C≡N organic group and the solvent CH₃OH which is the simplest amphiphile which contains hydrophobic (–CH₃) group and hydrophilic (–OH) group [16]. These two solvents not only adjust the weak solubility of the reactant Ag(I) salts effectively but also coordinate with the metal ion. Six novel complexes **1–6** have been isolated and characterized by single crystal X-ray diffraction, fluorescence, ¹H and ³¹P NMR spectroscopy and terahertz time-domain spectroscopy (THz-TDS).

THz-TDS is a vibrational spectroscopic technique that probes the infrared active vibrational modes in the far-infrared and sub-millimeter region of the electromagnetic spectrum using ultrashort pulses of coherent terahertz radiation (0.1–4.0 THz). Furthermore, the THz spectrum in the measurement range can offer new

information about the skeletal vibration. The THz spectrum can only be measured for polar molecule. It enables the characterization of solid-state materials through the excitation of soft intramolecular vibrational modes as well as intermolecular modes and hydrogen-bonding networks inherent to the molecular assembly in the solid state [17].

Very recently, a series of new Cu(I)–PPh₃ complexes of mercaptan ligands were characterized by THz-TDS. The results show that the difference of anion can affect the THz spectra of compounds, and THz-TDS may be a sensitive strategy to determine some of the inorganic–organic hybrid complexes, especially those isostructural complexes which are difficult to identify by other spectroscopy [18]. To continue our study, in this work, the THz spectra of complexes **1–6**, AgOTf, AgClO₄, AgBF₄ and relative ligands are first measured. The obtained data can possibly provide new information which can be used in many fields, such as biological and clinical applications [19], pharmaceutical [20], electronic [21], photonic [22] materials.

2. Experimental

2.1. Materials and measurements

All chemical reagents are commercially available and used without further treatment. All the chemicals were purchased from 'Jinan Camolai Trading Company'. FT-IR spectra (KBr pellets, 4000–400 cm⁻¹) were measured on a Perkin-Elmer Infrared spectrometer. Elemental analyses (C, H, N) were determined on Elementar Vario MICRO CUBE (Germany) elemental analyzer. Room-temperature fluorescence spectra were measured on F-4500 FL Spectrophotometer. ¹H NMR was recorded at room temperature with a Varian VNMRS 600 MHz spectrometer and ³¹P NMR was recorded at room temperature with a Bruker DPX 162 MHz spectrometer. 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. The preparation of the samples is by pressing the pure crystals into powder and detected at N₂ atmosphere to avoid the influence of water vapor. The thickness of the samples complexes **1–6** and ligands are about 1 mm.

2.2. Preparation of the complexes

2.2.1. Synthesis of {[Ag₂(dppm)₂(OTf)]₂(μ-bipy)}(OTf)₂·2CH₃OH (**1**)

AgCF₃SO₃ (0.4 mmol, 0.1028 g) was dissolved in the mixture of CH₂Cl₂ (5 mL) and MeOH (5 mL), adding dppm (0.4 mmol, 0.1538 g) and bipy·2H₂O (0.1 mmol, 0.0192 g) into the reaction flask later. The solution was stirred for 6 h at room temperature in the dark. The filtrate was then washed with water and CH₂Cl₂. Subsequent slow evaporation of the filtrate resulted in the formation of colorless and transparent crystals of the title complex. The crystals were washed by ether. Yield: 0.13 g, 47%. *Anal. Calc.* for C₁₁₆H₁₀₄Ag₄F₁₂N₂O₁₄P₈S₄: C, 49.97; H, 3.76; N, 1.01. Found: C, 49.83; H, 3.79; N, 1.04%. IR (cm⁻¹, KBr pellets): 2948w, 2025w, 1595m, 1437s, 1275s, 1224s, 1156s, 1027s, 999m, 742s, 692s, 637s, 573m, 471w. ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 3.9 (br, 8H, dppm-CH₂), 7.0–7.5 (m, overlapping with the solvent signal, dppm-Ph + bipy-H), 8.6 (d, 4H, bipy-H) ppm. ³¹P NMR (162 MHz, CDCl₃, 298 K): δ = 8.7–11.9 (d, ¹J(¹⁰⁹Ag–³¹P) = 518 Hz), –1.0 to 1.9 (d, ¹J(¹⁰⁷Ag–³¹P) = 470 Hz) ppm, γ(¹⁰⁹Ag)/γ(¹⁰⁷Ag) = 1.10.

2.2.2. Synthesis of {[Ag₂(dppm)₂(μ-bpp)(OTf)](OTf)·CH₃OH}_n (**2**)

Complex **2** has been prepared following a procedure similar to that for **1** by adding dppm (0.2 mmol, 0.0769 g) and bpp (0.1 mmol, 0.0198 g) into the mixture of CH₂Cl₂ (5 mL) and MeOH (5 mL) of AgCF₃SO₃ (0.2 mmol, 0.0514 g). After slow evaporation of the filtrate at ambient temperature for 6 days, colorless and transparent crystals of the title complex were obtained. The crystals were washed by ether. Yield: 0.074 g, 49%. *Anal. Calc.* for C₆₆H₆₂Ag₂F₆N₂O₇P₄S₂: C, 52.39; H, 4.13; N, 1.85. Found: C, 52.38; H, 4.14; N,

Table 1
Crystallographic data for complexes **1–6**.

Complex	1	2	3	4	5	6
Formula	C ₁₁₆ H ₁₀₄ Ag ₄ F ₁₂ N ₂ O ₁₄ P ₈ S ₄	C ₆₆ H ₆₂ Ag ₂ F ₆ N ₂ O ₇ P ₄ S ₂	C ₁₂₀ H ₁₁₂ Ag ₄ Cl ₄ N ₆ O ₁₆ P ₈	C ₇₅ H ₆₆ Ag ₂ Cl ₂ O ₈ P ₆	C ₆₂ H ₅₅ Ag ₂ B ₂ F ₈ N ₃ P ₄	C ₆₄ H ₅₇ Ag ₂ B ₂ F ₈ N ₃ P ₄
Formula weight	2785.50	1512.92	2715.20	1567.74	1355.83	1381.37
T (K)	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)
Crystal system	monoclinic	monoclinic	triclinic	tetragonal	triclinic	triclinic
Space group	P2/c	P	P	P4 ₁ ,2	P	P
Crystal size (mm)	0.50 × 0.40 × 0.28	0.48 × 0.40 × 0.37	0.40 × 0.37 × 0.25	0.45 × 0.39 × 0.30	0.49 × 0.45 × 0.26	0.37 × 0.20 × 0.16
a (Å)	22.096(2)	19.375(2)	11.153(1)	20.926 (2)	11.103(1)	11.211(1)
b (Å)	15.508(1)	18.358(2)	13.793(2)	20.926 (2)	15.490(1)	14.902 (1)
c (Å)	18.308(2)	10.730(1)	21.427(2)	33.857(3)	18.705(2)	18.698(1)
α (°)	90	90	93.9(1)	90	92.5 (1)	86.8(10)
β (°)	105.6(1)	117.9(1)	99.8(1)	90	95.5(1)	87.1(1)
γ (°)	90	90	110.9(1)	90	110.8(1)	85.6 (1)
V (Å ³)	6041.8(10)	3373.6(5)	3003.6(6)	14826(2)	2983.6(6)	3106.4(5)
Z	2	2	1	8	2	2
D _{calc} (Mg/m ³)	1.531	1.489	1.501	1.405	1.509	1.477
θ Range (°)	25.02	25.01	25.02	25.02	25.02	25.02
F(000)	2812	1536	1378	6384	1372	1396
Data/restraint/parameters	10654/0/760	4621/0/438	10464/0/779	13101/0/839	10383/0/797	10813/0/749
Reflections collected	30009	8483	15210	74755	15080	15677
Goodness-of-fit (GOF) on F ²	1.097	1.071	1.044	1.110	1.047	1.012
R _{int}	0.0532	0.0340	0.0294	0.0925	0.0343	0.0345
R ₁ [I > 2σ(I)] ^a	0.0545	0.0367	0.0416	0.0868	0.0448	0.0524
wR ₂ [I > 2σ(I)] ^b	0.1372	0.0936	0.0904	0.2270	0.0956	0.1200
R ₁ (all data) ^a	0.1113	0.0472	0.0776	0.1216	0.0835	0.0951
wR ₂ (all data) ^b	0.1884	0.1050	0.1155	0.2622	0.1218	0.1488

^a $R = \sum(|F_o| - |F_c|) / \sum|F_o|$.

^b $wR = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(F_o^2)]^{1/2}$.

Download English Version:

<https://daneshyari.com/en/article/1336393>

Download Persian Version:

<https://daneshyari.com/article/1336393>

[Daneshyari.com](https://daneshyari.com)