



Polynuclear silver(I) complexes of triphenylphosphine and 2-aminopyrimidine: Synthesis, structural characterization and spectroscopic properties

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ABSTRACT

The reactions of triphenylphosphine (PPh₃) and 2-aminopyrimidine (AMP) ligand with Ag salts in the mixed solvent of methanol (MeOH) and dichloromethane (CH₂Cl₂) lead to the mono-, di-, and tetranuclear complexes, [Ag(PPh₃)(AMP)₂](BF₄) (**1**), [Ag₂(PPh₃)₄(AMP)₂(SO₄)] (**2**), [Ag₄(PPh₃)₄(AMP)₂(NO₃)₄]_∞ (**3**) and [Ag₄(PPh₃)₄(AMP)₂(Ac)₄]_∞ (Ac = CH₃COO) (**4**) and [Ag(PPh₃)₂(HCOO)]·CH₂Cl₂ (**5**). Complexes **1** and **2** are of 1D infinite chain structure controlled by intermolecular hydrogen bonds of type R₂²(8). In complexes **3** and **4**, the 1D infinite chains are formed through the bridging-chelating anions (nitrate for **3** and acetate for **4**) and the N,N'-bridging ligand AMP. Five-coordinated modes of Ag(I) are observed in **3** and **4**. In the synthesis reaction of complex **5**, AMP only acts as catalyst rather than ligand. All the complexes are characterized by X-ray diffraction. Compounds **1–4** are also characterized by fluorescence and ¹H, ³¹P NMR spectroscopy.

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1. Introduction

In recent years, an increasing interest has developed towards the supramolecular compounds for their various attractive structures [1] and potential applications in homogeneous catalytic processes [2]. Because of its coordination diversity and flexibility, the d¹⁰ metal Ag(I) ion has been extensively used as the connecting node in the construction of supramolecular structures. Furthermore, many topologically promising architectures containing Ag(I) and bidentate nitrogen donors have been constructed [3].

2-Aminopyrimidine (AMP), with one hydrogen bond donor atom and two hydrogen bond acceptor atoms, is particularly attractive as a very simple self-complementary prototype for chain formation. Coordinated to the Ag(I), the ligand AMP can act as a monodentate ligand or as a bidentate ligand in polymer structures. In [Ru(AMP)(NH₃)₅](PF₆)₂ [4] and Cu(AMP)(2,6-dapy)·3H₂O (2,6-dapy = pyridine-2,6-dicarboxylato) [5], AMP ligand acts as a monodentate ligand, it is bounded to the metal *via* either the nitrogen atom of the amino group or the pyrimidyl nitrogen atoms. In the *trans*-Ni(SCN)₂(AMP)₂ [6], AMP ligand acts as a bidentate chelating ligand, it is bounded to the metal through one amine nitrogen atom and one pyrimidyl nitrogen atom. In the dinuclear complex, Zn₂(DPD)(AMP) (DPD = diporphyrindibenzofuran) [7], [Ag₂Cl₂(PPh₃)₂(2-AMP)]_∞ [8a] and [Ag₂Br₂(PPh₃)₂(2-AMP)]_∞ [8b], the

AMP ligand is bridged to the metal centers through the two pyrimidyl nitrogen atoms, while in the dinuclear complex [Pt₂(NO₃)₄(AMP)₂] [9], the AMP ligand is bridged to the metal center through one amino nitrogen atom and one pyrimidyl nitrogen atom. There is a tridentate coordination mode of AMP found in the complex [Ag₂(AMP)₂(SO₄)]_∞ [3].

In addition to the nature of the metal atoms and the ligands, counter anions also play important roles in determining the final structure of the product. Some Ag(I)X (X = Cl, Br) complexes with triphenylphosphine (PPh₃) and AMP have been reported [8–10], but there are few reports about Ag(I)X (X = BF₄, oxy-anions) complexes with PPh₃ and AMP.

In this paper, we studied the influence of several counter anions on the structures. Five new complexes [Ag(PPh₃)(AMP)₂](BF₄) (**1**), [Ag₂(PPh₃)₄(AMP)₂(SO₄)] (**2**), [Ag₄(NO₃)₄(PPh₃)₄(AMP)₂]_∞ (**3**) [Ag₄(Ac)₄(PPh₃)₄(AMP)₂]_∞ (Ac = CH₃COO) (**4**) and [Ag(PPh₃)₂(HCOO)]·CH₂Cl₂ (**5**) have been isolated and characterized by single crystal X-ray diffraction. Complexes **1** and **2** are of 1D infinite chain structure controlled by intermolecular hydrogen bonds of type R₂²(8) [11]. In complexes **3** and **4**, the 1D infinite chains are formed owing to the bridging-chelating anions (nitrate for **3** and acetate for **4**) and the N,N'-bridging ligand AMP. We attempted to obtain the Ag–AMP–PPh₃ complex containing formate (HCOO[−]), but unexpectedly complex **5** was generated, which maybe is due to the influence of the counter anion HCOO[−]. Herein, the reactions of AgX (X = BF₄[−], SO₄^{2−}, NO₃[−], Ac[−], HCOO[−], NO₂[−] and ClO₄[−]) with PPh₃ and AMP are studied.

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2. Experimental

2.1. Materials and measurements

All chemical reagents are commercially available and used without furthermore treatment. FT-IR spectra (KBr pellets) were measured on a Perkin–Elmer infrared spectrometer. C, H and N elemental analysis were carried out on a Elementar Vario MICRO CUBE (Germany) elemental analyzer. Room-temperature fluorescence spectra were measured on F-4500 FL Spectrophotometer. ^1H NMR and ^{31}P NMR were recorded at room temperature with a Bruker DPX 600 spectrometer.

2.2. Preparation of the complexes

2.2.1. Synthesis of $[\text{Ag}(\text{PPh}_3)(\text{AMP})_2](\text{BF}_4)$ (**1**)

AgBF_4 (0.1170 g, 0.6 mmol) was dissolved in the mixture of CH_2Cl_2 and MeOH (10 ml, $v/v = 1/1$), adding PPh_3 (0.1572 g, 0.6 mmol) and AMP (0.114 g, 1.2 mmol) into the reaction flask later. After stirring for 2 h and then filtrating, the filtrate was slow evaporated at ambient temperature. Four days later, a colorless block complex was obtained. Yield: 30%. *Anal.* Calc. for $\text{C}_{26}\text{H}_{25}\text{AgBF}_4\text{N}_6\text{P}$: C, 48.25; H, 3.89; N, 12.98. Found: C, 48.33; H, 3.73; N, 12.82%. IR (cm^{-1} , KBr pellets): 3317s, 3123m, 3122m, 1525m, 1485m, 1435s, 1415m, 1230w, 1104vs, 998s, 985s, 748s, 698s, 524m, 516m.

2.2.2. Synthesis of $[\text{Ag}_2(\text{PPh}_3)_4(\text{AMP})_2(\text{SO}_4)]$ (**2**)

Complex **2** has been prepared following a procedure similar to that for **1** by adding PPh_3 (0.1572 g, 0.6 mmol) and AMP (0.0285 g, 0.3 mmol) into the mixture of CH_2Cl_2 and MeOH (10 ml, $v/v = 1/1$) of Ag_2SO_4 (0.0612 g, 0.3 mmol). Yield: 65%. *Anal.* Calc. for $\text{C}_{82}\text{H}_{78}\text{Ag}_2\text{N}_6\text{O}_6\text{P}_4\text{S}$: C, 60.98; H, 4.87; N, 5.20. Found: C, 61.25; H, 5.01; N, 5.27%. IR (cm^{-1} , KBr pellets): 3426s, 3053, 1632w, 1479s, 1434s, 1309w, 1181w, 1091s, 1027m, 998m, 746s, 696s, 618w, 513s, 501s.

2.2.3. Synthesis of $[\text{Ag}_4(\text{NO}_3)_4(\text{PPh}_3)_4(\text{AMP})_2]_\infty$ (**3**)

The PPh_3 (0.1048 g, 0.4 mmol) and AMP (0.0190 g, 0.2 mmol) was added at room temperature to a mixture of CH_2Cl_2 and MeOH

(10 ml, $v/v = 1/1$) containing AgNO_3 (0.0680 g, 0.4 mmol), stirring for 2 h and then filtrating. The filtrate was allowed to stand at room temperature, the crystal was obtained by slow evaporation of the colorless solvent, which was filtered off and washed with Et_2O to give complex **3** as a colorless crystal. Yield: 80%. *Anal.* Calc. for $\text{C}_{80}\text{H}_{70}\text{Ag}_4\text{N}_{10}\text{O}_{12}\text{P}_4$: C, 50.08; H, 3.68; N, 7.29. Found: C, 50.35; H, 3.82; N, 7.33%. IR (cm^{-1} , KBr pellets): 3405m, 1631m, 1570m, 1480m, 1421m, 1384s, 1291s, 1189w, 1097w, 1028w, 998w, 746s, 693s, 518m, 503m.

2.2.4. Synthesis of $[\text{Ag}_4(\text{Ac})_4(\text{PPh}_3)_4(\text{AMP})_2]_\infty$ (**4**)

Complex **4** has been prepared following a procedure similar to that reported for **1** by adding PPh_3 (0.1048 g, 0.4 mmol) and AMP (0.0190 g, 0.2 mmol) into a mixture of CH_2Cl_2 and MeOH (10 ml, $v/v = 1/1$) containing AgAc (0.0668 g, 0.4 mmol). Yield: 76%. *Anal.* Calc. for $\text{C}_{44}\text{H}_{41}\text{Ag}_2\text{N}_3\text{O}_4\text{P}_2$: C, 55.43; H, 4.33; N, 4.41. Found: C, 55.29; H, 4.15; N, 4.44%. IR (cm^{-1} , KBr pellets): 3431s, 3054m, 1564s, 1480m, 1435s, 1386m, 1096s, 1208w, 998w, 797m, 746s, 695s, 653w, 518m, 503m.

2.2.5. Synthesis of $[\text{Ag}(\text{PPh}_3)_2(\text{HCOO})]\cdot\text{CH}_2\text{Cl}_2$ (**5**)

Complex **5** has been prepared following a procedure similar to that reported for **1** by adding PPh_3 (0.0524 g, 0.2 mmol) and AMP (0.0380 g, 0.4 mmol) into a mixture of CH_2Cl_2 and MeOH (10 ml, $v/v = 1/1$) containing $\text{Ag}(\text{HCOO})$ (0.0306 g, 0.2 mmol). Yield: 63%. *Anal.* Calc. for $\text{C}_{38}\text{H}_{33}\text{AgCl}_2\text{O}_2\text{P}_2$: C, 59.82; H, 4.33. Found: C, 59.76; H, 4.29%. IR (cm^{-1} , KBr pellets): 3051w, 1962w, 1889w, 1851w, 1584w, 1572w, 1479s, 1434s, 1329w, 1308m, 1265m, 1229s, 1155m, 1096s, 1070w, 1026m, 997m, 973w, 834w, 744s, 725m, 694s, 618w, 513s, 503s, 437w.

2.3. X-ray crystallographic study of complexes

Single crystals of the title complexes were mounted on a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation at 293(2) K. Semi-empirical absorption corrections were applied using SABABS program. All the structures were solved by direct methods using SHELXS program of the SHELXTL-97 [12] package and refined with SHELXL-97 [12]. Metal atom centers were located from the E-maps

Table 1
Crystal data for complexes **1–5**.

Compound	1	2	3	4	5
Formula	$\text{C}_{26}\text{H}_{25}\text{AgBF}_4\text{N}_6\text{P}$	$\text{C}_{82}\text{H}_{78}\text{Ag}_2\text{N}_6\text{O}_6\text{P}_4\text{S}$	$\text{C}_{80}\text{H}_{70}\text{Ag}_4\text{N}_{10}\text{O}_{12}\text{P}_4$	$\text{C}_{44}\text{H}_{41}\text{Ag}_2\text{N}_3\text{O}_4\text{P}_2$	$\text{C}_{38}\text{H}_{33}\text{AgCl}_2\text{O}_2\text{P}_2$
Formula weight	647.17	1615.18	1918.82	953.48	762.35
Crystal system	orthorhombic	monoclinic	triclinic	triclinic	triclinic
Space group	<i>Pbca</i>	<i>C2/c</i>	<i>P1</i>	<i>P1</i>	<i>P1</i>
<i>a</i> (Å)	18.600(2)	17.124(2)	11.397(8)	9.681(2)	10.866(1)
<i>b</i> (Å)	15.759(2)	21.649(2)	12.186(9)	15.033(2)	13.106(1)
<i>c</i> (Å)	19.368(2)	21.770(2)	15.077(1)	16.120(2)	14.172(2)
α (°)	90.00	90.00	93.845(4)	66.383(1)	105.169(3)
β (°)	90.00	108.366(2)	101.617(4)	75.824(1)	105.500(2)
γ (°)	90.00	90.00	99.259(4)	82.612(2)	103.150(1)
Volume (Å ³)	5677.3(10)	7659.5(13)	2013.5(2)	2082.8(5)	1778.5(3)
<i>Z</i>	8	4	1	2	2
D_{calc} (g/cm ³)	1.514	1.401	1.621	1.52	1.424
μ (mm ⁻¹)	0.819	0.679	1.104	1.062	0.839
$F(0\ 0\ 0)$	2608	3320	978	964	776
Crystal size (mm ³)	0.50 × 0.48 × 0.45	0.21 × 0.19 × 0.12	0.28 × 0.25 × 0.21	0.40 × 0.19 × 0.10	0.35 × 0.30 × 0.23
θ Range (°)	1.99–25.01	1.57–25.01	2.06–27.96	1.61–25.01	2.64–25.02
Reflections collected	27739	19280	21752	10494	9259
Reflections unique	4955	6755	9280	7108	6173
R_{int}	0.0454	0.0726	0.0231	0.0450	0.0184
Parameters	381	457	496	496	406
Goodness-of-fit on F^2	1.188	1.050	0.981	0.943	1.052
R_1 and wR_2	0.05, 0.1692	0.0576, 0.1330	0.0364, 0.0793	0.0828, 0.2098	0.0369, 0.0805
Maximum, minimum peaks (e Å ⁻³)	0.750, -0.457	0.748, -0.814	0.434, -0.301	3.897, -1.374	0.538, -0.584

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