

Syntheses, structures and luminescence of silver(I) sulfonate complexes with PPh₃ ligand

Fang-Fang Li^a, Jian-Fang Ma^{a,*}, Jin Yang^a, Heng-Qing Jia^b, Ning-Hai Hu^b

^a Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China

^b Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

Received 23 August 2005; received in revised form 29 October 2005; accepted 3 November 2005

Available online 19 December 2005

Abstract

In this paper, four new luminescent silver(I) sulfonate complexes with PPh₃, namely Ag(L1)(PPh₃)₂ (**1**), Ag(L2)(PPh₃)₃ (**2**), [Ag₂(L3)(PPh₃)₄(H₂O)]·1.5CH₃CN·0.5H₂O (**3**) and [Ag₄(L4)(PPh₃)₁₀]·8H₂O (**4**), where L1 = *p*-toluenesulfonate, L2 = 1-naphthalenesulfonate, L3 = 3-carboxylate-4-hydroxybenzenesulfonate, L4 = 1, 3, 6, 8-pyrenetetrasulfonate and PPh₃ = triphenylphosphine, have been synthesized and characterized. The crystal structures were determined by single-crystal X-ray diffraction method. Compounds **1**, **2**, **3** and **4** adopt discrete structures rather than polymeric structures. Compounds **1** and **2** show mononuclear structures while **3** and **4** are dinuclear and tetranuclear molecules, respectively. Moreover the numbers of PPh₃ molecules coordinating to one silver center are two or three. The photoluminescent properties of **1**, **2** and **3** are discussed.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Crystal structure; Photoluminescence; Silver; Sulfonate; Triphenylphosphine

1. Introduction

In recent years amount of reports concerned with the silver(I) sulfonate compounds with no auxiliary donor ligand have been published [1]. Most silver(I) sulfonates show two-dimensional lamellar polymeric structures [1a–c] or three-dimensional polymeric structures [1e–h]. Since silver ion favors coordination to soft bases such as ligands containing P atoms, a considerable amount of silver compounds containing PPh₃ as a soft bulky co-ligand have been synthesized and characterized [2]. The coordination chemistry of tertiary phosphines with silver atoms is a well-established field. However, silver(I) sulfonate complexes with PPh₃ ligand have been reported sparsely [3]. In this work, four new silver sulfonate compounds incorporating PPh₃ ligands have been reported. The sulfonate ligands depicted in Scheme 1 were selected because of the structural varieties among them. Four silver compounds **1–4** based on mixed sulfonate ligand and PPh₃ ligand, namely Ag(L1)(PPh₃)₂ (**1**), Ag(L2)(PPh₃)₃ (**2**), [Ag₂(L3)(PPh₃)₄(H₂O)]·1.5CH₃CN·0.5H₂O (**3**) and [Ag₄

(L4)(PPh₃)₁₀]·8H₂O (**4**) have been described with twofold aims: one is to obtain the coordination information between silver sulfonates and PPh₃ ligand; and the other is to investigate the effect produced by PPh₃ auxiliary donor ligand on the structures of silver sulfonates. All crystal structures have been determined by single-crystal X-ray diffraction. The characterization of **1–4** has also been carried out by elemental analysis, FT-IR and ³¹P NMR spectroscopy.

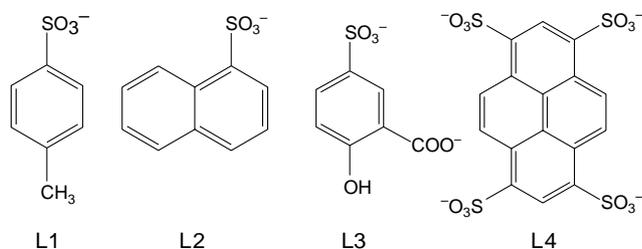
2. Experimental

2.1. Synthesis

2.1.1. Ag(L1)(PPh₃)₂ (**1**)

An aqueous solution (10 ml) of HL1 (0.190 g, 1 mmol) was added Ag₂CO₃ (0.166 g, 0.6 mmol) and stirred for several minutes until no CO₂ was given out, then filtered. The filtrate was added triphenylphosphine (0.525 g, 2 mmol) in methanol, and white precipitate formed immediately. The precipitate was dissolved by dropwise addition of acetonitrile. Colorless crystals were obtained from the filtrate after standing in the dark room for several days (0.450 g, yield: 56%); calcd for Ag(L1)(PPh₃)₂: C, 64.27; H, 4.64; found: C, 63.99; H, 4.67%. IR (KBr, cm⁻¹) 3446(ms), 3051(ms), 2360(s), 2342(s), 1480(ms), 1435(vs), 1190(s), 1127(s), 1095(s), 1039(ms),

* Corresponding author. Tel.: +86 431 509 8620; fax: +86 431 568 4009.
E-mail address: jianfangma@yahoo.com.cn (J.-F. Ma).



Scheme 1. The structures of the sulfonate ligands in this work.

1006(s), 815(ms), 743(s), 694(vs), 570(s), 512(s). NMR (CDCl₃, rt), ³¹P{¹H}: δ = 10.29 (s).

2.1.2. Ag(L2)(PPh₃)₃ (2)

A mixture of sodium 1-naphthalenesulfonate (0.115 g, 0.5 mmol) and AgNO₃ (0.085 g, 0.5 mmol) in water (5 ml) was stirred for 5 min, then filtered. Triphenylphosphine (0.262 g, 1 mmol) in methanol (10 ml) was added to the filtrate, and white precipitate was obtained. The precipitate was subsequently dissolved in a minimum volume of acetonitrile. Colorless crystals were obtained by slow evaporation in the dark room for several days (0.245 g, yield: 67%); calcd for Ag(L2)(PPh₃)₃: C, 69.76; H, 4.76; found: C, 69.42; H, 4.70%. IR (KBr, cm⁻¹) 3446(w), 3051(ms), 2360(s), 2339(ms), 1479(vs), 1434(vs), 1385(vs), 1307(ms), 1093(ms), 1070(w), 1028(ms), 998(ms), 850(w), 745(vs), 695(vs), 615(w), 512(vs), 427(w). NMR (CDCl₃, rt), ³¹P{¹H}: δ = 9.05 (s).

2.1.3. [Ag₂(L3)(PPh₃)₄(H₂O)] · 1.5CH₃CN · 0.5H₂O (3)

A mixture of 5-sulfosalicylic acid (0.109 g, 0.5 mmol) and NaOH (0.040 g, 1.0 mmol) in water (5 ml) was added AgNO₃ (0.170 g, 1.0 mmol) to give a clear solution. Then

ethanol (15 ml) was added to the solution, and white precipitate formed immediately. The precipitate was collected by filtration, and dissolved in water again. To the solution was added triphenylphosphine (0.524 g, 2 mmol) in methanol (10 ml), and the white solid that immediately precipitated was subsequently dissolved in a minimum volume of acetonitrile. Yellow crystals were obtained from the filtrate after slow evaporation in the dark room for several days (0.385 g, yield: 50%); calcd for [Ag₂L3(PPh₃)₄(H₂O)] · 1.5CH₃CN · 0.5H₂O: C, 62.75; H, 4.59; N, 1.34; found: C, 62.50; H, 4.53; N, 1.41%. IR (KBr, cm⁻¹) 3446(w), 3053(ms), 2360(vs), 2338(s), 1622(ms), 1478(s), 1434(vs), 1372(ms), 1149(ms), 1095(ms), 1021(s), 891(w), 831(vw), 746(s), 694(vs), 671(s), 592(ms), 512(s), 413(ms). NMR (CDCl₃, rt), ³¹P{¹H}: δ = 10.01 (s).

2.1.4. [Ag₄(L4)(PPh₃)₁₀] · 8H₂O (4)

Aqueous solution of NH₃ was added to a mixture of sodium 1,3,6,8-pyrenetetrasulfonate (Na₄L4) (0.061 g, 0.1 mmol) and AgNO₃ (0.068 g, 0.4 mmol) in methanol (10 ml) until a clear solution was obtained. Then triphenylphosphine (0.210 g, 0.8 mmol) in methanol (10 ml) was added. The mixture was heated and stirred for several minutes until the precipitate was dissolved completely. After filtration, the yellow product was obtained by evaporating the filtrate in the dark room for several days, and was recrystallized from methanol (0.211 g, yield: 71%); calcd for [Ag₄L4(PPh₃)₁₀] · 8H₂O: C, 63.34; H, 4.66; found: C, 63.30; H, 4.58%. IR (KBr, cm⁻¹) 3445(ms), 3052(s), 2360(s), 2338(s), 1966(w), 1650(ms), 1558(ms), 1479(s), 1434(vs), 1398(w), 1309(w), 1235(s), 1171(s), 1095(s), 1040(s), 1013(s), 994(ms), 921(w), 834(w), 743(vs), 694(vs), 656(vs), 587(s), 568(w), 512(vs), 439(w). NMR (CDCl₃, rt), ³¹P{¹H}: δ = 9.44 (s).

Table 1

Crystal data and structure refinements for compounds 1–4

	1	2	3	4
Formula	C ₄₃ H ₃₇ O ₃ P ₂ SAg	C ₆₄ H ₅₂ O ₃ P ₃ SAg	C ₈₂ H _{71.5} O _{7.5} N _{1.5} P ₄ SAg ₂	C ₁₉₆ H ₁₇₂ O ₂₀ P ₁₀ S ₄ Ag ₄
Formula weight	803.60	1101.90	1569.59	3716.76
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> –1	<i>P</i> –1
<i>A</i> (Å)	15.619(5)	13.020(2)	12.602(5)	13.3518(6)
<i>B</i> (Å)	12.921(5)	24.695(4)	13.376(5)	19.6573(8)
<i>c</i> (Å)	19.429(5)	16.425(3)	26.011(5)	20.0069(6)
<i>A</i> (°)	90	90	76.466(5)	60.943(1)
<i>B</i> (°)	108.572(5)	95.623(4)	76.910(5)	85.559(1)
<i>γ</i> (°)	90	90	61.914(5)	80.269(1)
<i>V</i> (Å ³)	3717(2)	5256(2)	3726(2)	4524.0(3)
<i>Z</i>	4	4	2	1
<i>R</i> _{int}	0.0359	0.0977	0.0421	0.0437
<i>R</i> 1(<i>I</i> > 2σ(<i>I</i>))	0.0372	0.0611	0.0606	0.0470
<i>wR</i> 2(<i>I</i> > 2σ(<i>I</i>))	0.0778	0.0812	0.1054	0.1295
<i>D</i> _c /g cm ⁻³	1.436	1.393	1.399	1.364
<i>F</i> (000)	1648	2272	1608	1910
μ/mm ⁻¹	0.724	0.562	0.695	0.625
Reflections collected	16114	33105	23596	28890
Unique reflections	7058	12377	16566	20256
Observed reflections (<i>I</i> > 2(<i>I</i>))	4887	6022	8714	13354

2.2. Crystal structure determination and physical measurements

Experimental details of the X-ray analyses are provided in Table 1. Diffraction intensities for the compounds 1–4 were collected on a Bruker Apex CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda=0.71069$ Å). The structures were solved with the direct method of SHELXS-97 [4] and refined with full-matrix least-squares techniques using the SHELXL-97 program [5] within WINGX [6]. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms on carbon atoms were generated geometrically. Analytical expression of neutral-atom scattering factors were employed, and anomalous dispersion corrections incorporated [7]. Drawings were produced with SHELXTL-PLUS [8].

CCDC-271368 (compound 1), CCDC-271370 (compound 2), CCDC-271372 (compound 3) and CCDC-271374 (compound 4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

The FT-IR spectra were recorded from KBr pellets in range 4000–400 cm $^{-1}$ on a Mattson Alpha-Centauri spectrometer. Elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer. The emission/excitation spectra were recorded on a Varian Cary Eclipse spectrometer. The NMR spectra were recorded on a Bruker AV300 Spectrometer in CDCl $_3$. Chemical shifts (ppm) are cited relative to 85% H $_3$ PO $_4$ (external 31 P).

3. Results and discussion

3.1. Photoluminescence

The luminescent properties of compounds 1–3 were investigated in the solid state. The photoluminescent spectra of 1–3 and free ligands are depicted in Fig. 1. HL1 displays emission maximum at 289 nm. Compound 1 and PPh $_3$ show emission with maxima at 487 and 447 nm, respectively. Compared with the emission of HL1 and PPh $_3$, red shifts of 198 and 40 nm occur, respectively, upon the formation of compound 1. The resemblance of the emission spectra of the compound 1 with that of the free PPh $_3$ indicates that the luminescence of the compound 1 is PPh $_3$ -based emission. Compound 2 exhibits emission maximum at 386 nm upon excitation at 330 nm. HL2 and PPh $_3$ show emission with maxima at 394 and 447 nm, respectively. Compared with the emission of the free ligands HL2 and PPh $_3$, blue shifts of 8 and 61 nm, respectively, have been observed upon the formation of compound 2. The resemblance of the emission spectra of the compound 2 with that of the free HL2 indicates that the luminescence of the compound 2 is HL2-based emission. Compound 3 shows an emission with maximum at 405 nm. Free ligands H $_2$ L3 and PPh $_3$ show emission with maxima at 392 and 447 nm, respectively. The resemblance of the emission spectra of 3 with that of the free HL3 indicates that the luminescence of the compound 3 is HL3-based emission. In comparison with compound 1, blue shifts of 101 and 82 nm have been observed in compounds 2 and 3, respectively, due to the replacement of L1 anion by L2 and L3 anions, respectively. The luminescence of compounds 1, 2 and 3 should originate from the transitions between the energy levels of sulfonate anion and/or neutral ligand. The shifts of the emission bands

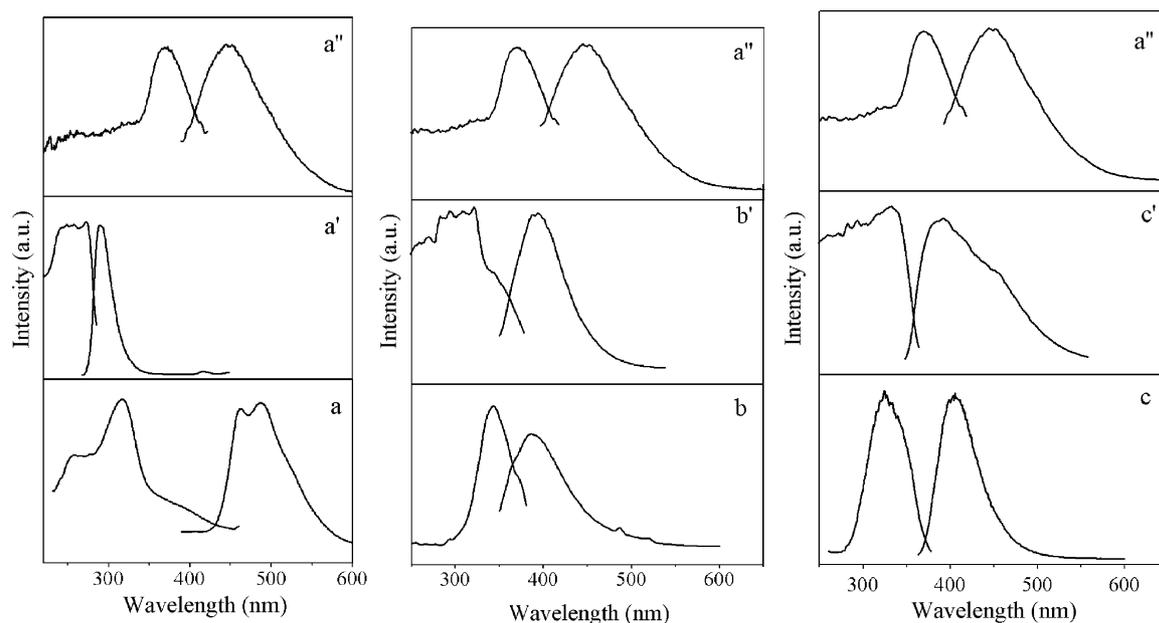


Fig. 1. Solid-state photoluminescent spectra of 1 (a), 2 (b) and 3 (c) and free ligands [HL1(a') HL2(b'), H $_2$ L3(c') and PPh $_3$ (a'')] at room temperature.

are attributed to both the deprotonation of the sulfonic acid and the coordination action of the sulfonate anion and PPh_3 to silver ions.

3.2. Crystal structures

Selected bond distances and angles are given in Table 2. $[\text{Ag}(\text{L1})(\text{PPh}_3)_2]$ (**1**) is a ternary silver compound with *p*-toluenesulfonate anion and triphenylphosphine. Compound **1** (Fig. 2) shows a highly different structural feature from AgL1 (compound **5**) [1c]. Compound **1** contains discrete molecules which are packed by Van der Waals interactions. Silver ion is four-coordinate with two sulfonate oxygen atoms from one sulfonate group with $\text{Ag}(1)\text{--O}(3)$ and $\text{Ag}(1)\text{--O}(2)$ distances being 2.375(2) and 2.696(2) Å, respectively, and two phosphorous atoms from two PPh_3 molecules with $\text{Ag}(1)\text{--P}(1)$ and $\text{Ag}(1)\text{--P}(2)$ distances being 2.4370(9) and 2.436(1) Å, respectively, the $\text{O}(3)\text{--Ag}(1)\text{--P}(2)$, $\text{O}(3)\text{--Ag}(1)\text{--P}(1)$ and $\text{P}(2)\text{--Ag}(1)\text{--P}(1)$ angles being 111.56(6), 120.27(6) and 124.61(3)°, respectively, whose sum is 356.44° deviating slightly from 360°. $\text{Ag}(1)$, $\text{O}(3)$, $\text{P}(1)$ and $\text{P}(2)$ atoms are almost coplanar, while $\text{Ag}(1)$ deviates from this plane slightly.

Compared with compound **5**, the sulfonate groups in compound **1** possess bidentate chelating mode rather than μ_5 -bridging mode of compound **5**. This consequence may result

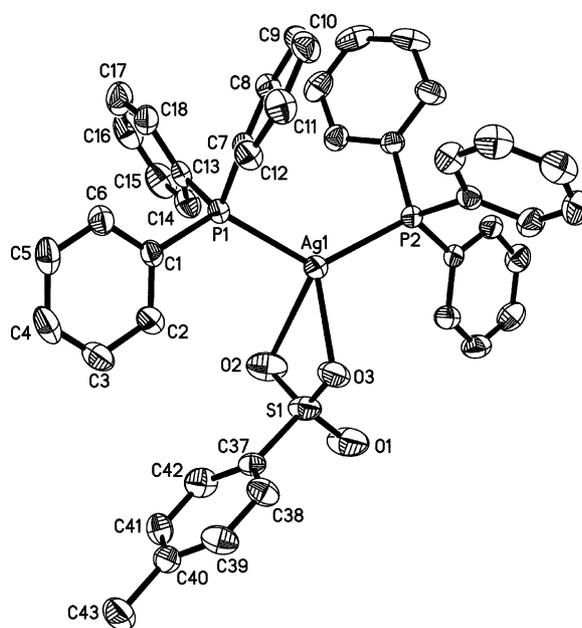


Fig. 2. Molecular structure of $[\text{Ag}(\text{L1})(\text{PPh}_3)_2]$ **1**. All the H atoms are omitted for clarity.

Table 2
Selected bond distances (in Å) and angles (in °) for compounds **1–4**

$\text{Ag}(\text{L1})(\text{PPh}_3)_2$ (1)			
$\text{Ag}(1)\text{--O}(3)$	2.375(2)	$\text{Ag}(1)\text{--O}(2)$	2.696(2)
$\text{Ag}(1)\text{--P}(2)$	2.436(1)	$\text{Ag}(1)\text{--P}(1)$	2.4370(9)
$\text{O}(3)\text{--Ag}(1)\text{--P}(2)$	111.56(6)	$\text{O}(3)\text{--Ag}(1)\text{--P}(1)$	120.27(6)
$\text{P}(2)\text{--Ag}(1)\text{--P}(1)$	124.61(3)	$\text{S}(1)\text{--O}(3)\text{--Ag}(1)$	103.0(1)
$\text{Ag}(\text{L2})(\text{PPh}_3)_3$ (2)			
$\text{Ag}(1)\text{--O}(1)$	2.416(3)	$\text{Ag}(1)\text{--P}(1)$	2.523(1)
$\text{Ag}(1)\text{--P}(2)$	2.529(1)	$\text{Ag}(1)\text{--P}(3)$	2.533(1)
$\text{O}(1)\text{--Ag}(1)\text{--P}(1)$	104.81(9)	$\text{O}(1)\text{--Ag}(1)\text{--P}(2)$	89.81(9)
$\text{P}(1)\text{--Ag}(1)\text{--P}(2)$	118.31(4)	$\text{O}(1)\text{--Ag}(1)\text{--P}(3)$	110.54(9)
$\text{P}(1)\text{--Ag}(1)\text{--P}(3)$	117.66(4)	$\text{P}(2)\text{--Ag}(1)\text{--P}(3)$	111.50(4)
$[\text{Ag}_2(\text{L3})(\text{PPh}_3)_4(\text{H}_2\text{O})] \cdot 1.5\text{CH}_3\text{CN} \cdot 0.5\text{H}_2\text{O}$ (3)			
$\text{Ag}(1)\text{--O}(5)$	2.387(3)	$\text{Ag}(1)\text{--P}(2)$	2.461(2)
$\text{Ag}(1)\text{--P}(1)$	2.465(2)	$\text{Ag}(1)\text{--N}(1)$	2.632(7)
$\text{Ag}(2)\text{--O}(1)$	2.389(3)	$\text{Ag}(2)\text{--P}(4)$	2.436(1)
$\text{Ag}(2)\text{--P}(3)$	2.447(2)	$\text{Ag}(2)\text{--OW1}$	2.512(6)
$\text{O}(5)\text{--Ag}(1)\text{--P}(2)$	103.8(1)	$\text{O}(5)\text{--Ag}(1)\text{--P}(1)$	123.80(9)
$\text{P}(2)\text{--Ag}(1)\text{--P}(1)$	128.35(5)	$\text{O}(5)\text{--Ag}(1)\text{--N}(1)$	91.4(2)
$\text{P}(2)\text{--Ag}(1)\text{--N}(1)$	105.1(2)	$\text{P}(1)\text{--Ag}(1)\text{--N}(1)$	93.4(2)
$\text{O}(1)\text{--Ag}(2)\text{--P}(4)$	112.5(1)	$\text{O}(1)\text{--Ag}(2)\text{--P}(3)$	110.7(1)
$\text{P}(4)\text{--Ag}(2)\text{--P}(3)$	129.44(5)	$\text{O}(1)\text{--Ag}(2)\text{--OW1}$	83.0(2)
$\text{P}(4)\text{--Ag}(2)\text{--OW1}$	110.4(2)	$\text{P}(3)\text{--Ag}(2)\text{--OW1}$	99.6(2)
$[\text{Ag}_4(\text{L4})(\text{PPh}_3)_{10}] \cdot 8\text{H}_2\text{O}$ (4)			
$\text{Ag}(1)\text{--O}(1)$	2.521(2)	$\text{Ag}(1)\text{--P}(1)$	2.5405(9)
$\text{Ag}(1)\text{--P}(2)$	2.5028(9)	$\text{Ag}(1)\text{--P}(3)$	2.5120(8)
$\text{Ag}(2)\text{--O}(4)$	2.306(2)	$\text{Ag}(2)\text{--P}(4)$	2.505(1)
$\text{Ag}(2)\text{--P}(5)$	2.4509(9)		
$\text{O}(1)\text{--Ag}(1)\text{--P}(1)$	99.12(6)	$\text{P}(2)\text{--Ag}(1)\text{--O}(1)$	90.94(6)
$\text{P}(3)\text{--Ag}(1)\text{--O}(1)$	111.67(6)	$\text{P}(2)\text{--Ag}(1)\text{--P}(1)$	114.64(3)
$\text{P}(2)\text{--Ag}(1)\text{--P}(3)$	116.65(3)	$\text{P}(3)\text{--Ag}(1)\text{--P}(1)$	118.37(3)
$\text{O}(4)\text{--Ag}(2)\text{--P}(4)$	98.94(7)	$\text{O}(4)\text{--Ag}(2)\text{--P}(5)$	134.35(7)
$\text{P}(5)\text{--Ag}(2)\text{--P}(4)$	126.50(3)		

from the PPh_3 ligands that occupy the coordination sites of Ag ions. Thus the sulfonate group can coordinate to less Ag ions than that in compound **5**. Therefore, the number of Ag ions bonded to one sulfonate group decreased from five in compound **5** to one in compound **1**. Since PPh_3 is a bulky and terminal ligand, and precludes the formation of polymeric structures, compound **1** has a discrete structure instead of polymeric structure.

X-ray crystallography has established that compound **2** containing L2 and PPh_3 also shows a discrete structure. Ag center is also four-coordinate as that observed in compound **1** (Fig. 3), having one oxygen atom from sulfonate group with $\text{Ag}(1)\text{--O}(1)$ distance being 2.416(3) Å and three phosphorous atoms from three PPh_3 ligands with $\text{Ag}(1)\text{--P}(1)$, $\text{Ag}(1)\text{--P}(2)$ and $\text{Ag}(1)\text{--P}(3)$ distances being 2.523(1), 2.529(1) and 2.533(1) Å, respectively, the $\text{O}(1)\text{--Ag}(1)\text{--P}(1)$, $\text{O}(1)\text{--Ag}(1)\text{--P}(2)$, $\text{O}(1)\text{--Ag}(1)\text{--P}(3)$, $\text{P}(1)\text{--Ag}(1)\text{--P}(2)$, $\text{P}(1)\text{--Ag}(1)\text{--P}(3)$ and $\text{P}(2)\text{--Ag}(1)\text{--P}(3)$ angles being 104.81(9), 89.81(9), 110.54(9), 118.31(4), 117.66(4) and 111.50(4)°, respectively. Therefore, the coordination geometry of silver center can be considered as a distorted tetrahedron with one oxygen atom and three phosphorous atoms at the vertex positions. Ag–P distances are longer than those of compound **1** since the steric repulsion among three PPh_3 molecules is stronger than that between two PPh_3 molecules.

The polymeric structure of silver 1-naphthalenesulfonate $[\text{AgL2}]$ (**6**) has been studied in a previous report [1b]. As could be expected, the presence of PPh_3 results in drastic changes between compound **2** and compound **6**. Compound **2** shows discrete structure rather than polymeric structure with the same reasons as that for compound **1**. Since the introduction of auxiliary ligands, the number of the coordination sites for the sulfonate groups decreases, and the drastic structure changes

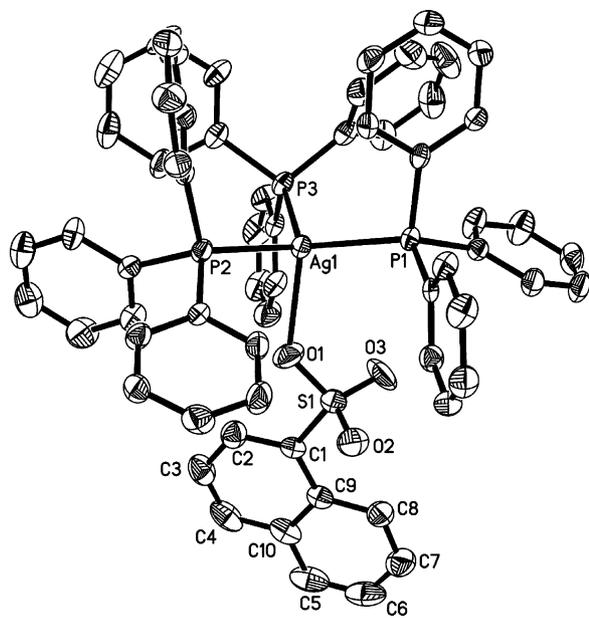


Fig. 3. Molecular structure of $[\text{Ag}(\text{L}2)(\text{PPh}_3)_3]$ **2**. All the H atoms are omitted for clarity.

occur. In compound **6** there were two distinct 6-coordinate silver centers and two unique L2 ligands in the structure. Ag1 coordinates only to sulfonate groups and Ag2 is 6-coordinate with four bonds to sulfonate oxygen donors and two π interaction with the naphthyl ring. As a result of the presence of PPh_3 , however, there is only one unique silver center and one unique L2 ligand and no π interaction formed in compound **2**. Moreover silver center only provides one coordination site for sulfonate oxygen atoms.

The study on the silver compounds with multifunctional sulfonate ligands is still seldom [1g], particularly the silver(I) sulfonate compounds containing auxiliary ligands. L3 is a sulfonate-carboxylate ligand containing hydroxyl group, in which $-\text{SO}_3^-$, $-\text{CO}_2^-$ and $-\text{OH}$ are three potential coordinating groups. In this work, compound **3** containing L3 and PPh_3 ligand has been synthesized. Compound **3** also shows a discrete structure as compounds **1** and **2**. There exist one kind of crystallographically unique L2 ligand and two kinds of crystallographically unique silver centers in compound **3** as shown in Fig. 4. Ag1 is coordinated by one carboxylate oxygen atom with $\text{Ag}(1)-\text{O}(5)$ distance being 2.387(3) Å and two phosphorous atoms from two PPh_3 ligands with $\text{Ag}(1)-\text{P}(1)$ and $\text{Ag}(1)-\text{P}(2)$ distances being 2.465(2) and 2.461(2) Å, respectively. $\text{Ag}(1)-\text{N}(1)_{\text{MeCN}}$ distance of 2.632(7) Å is much longer than normal value, and there is no bonding action between Ag1 and acetonitrile molecule. The $\text{O}(5)-\text{Ag}(1)-\text{P}(2)$, $\text{O}(5)-\text{Ag}(1)-\text{P}(1)$ and $\text{P}(2)-\text{Ag}(1)-\text{P}(1)$ angles are 103.84(10), 123.80(9) and 128.35(5)° respectively, whose sum is 355.99° deviating from 360° slightly. Therefore Ag(1), O(5), P(1) and P(2) are almost coplanar, while Ag1 deviates slightly from this plane, so the geometry of Ag1 can be described as a distorted trigon, which is different from that of silver center of compounds **1** and **2**. Ag2 center is four-coordinate, having a

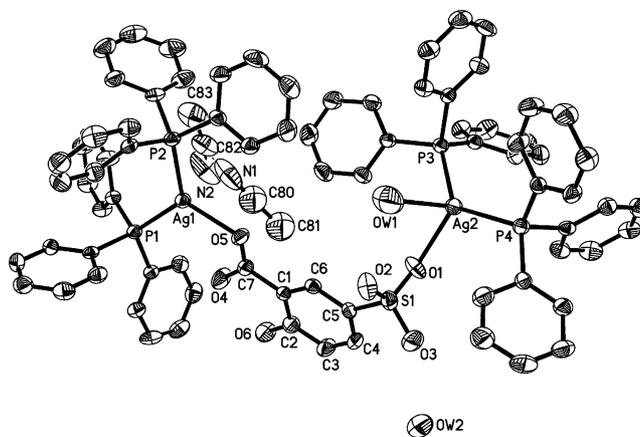


Fig. 4. Molecular structure of $[\text{Ag}_2\text{L}3(\text{PPh}_3)_4(\text{H}_2\text{O})] \cdot 1.5\text{CH}_3\text{CN} \cdot 0.5\text{H}_2\text{O}$ **3**. All the H atoms are omitted for clarity.

distorted tetrahedral geometry composed of bonds from one sulfonate oxygen atom with $\text{Ag}(2)-\text{O}(1)$ distance being 2.389(3) Å, one water molecule with $\text{Ag}(2)-\text{OW}1$ distance being 2.512(6) Å and two phosphorous atoms from two PPh_3 molecules with $\text{Ag}(2)-\text{P}(3)$ and $\text{Ag}(2)-\text{P}(4)$ distances being 2.447(2) and 2.436(1) Å respectively. Both $-\text{COO}^-$ and $-\text{SO}_3^-$ coordinate to silver ions in the monodentate mode.

In contrast to compound $[\text{Ag}_2\text{L}3(\text{H}_2\text{O})]$ (**7**) [1g], compound **3** has undergone great changes in structures. Compound **7** shows a three-dimensional polymeric structure, while compound **3** has a discrete structure. The structural changes may also be explained by the coordination effect of PPh_3 . The number of silver ions bonded to one L3 ligand in compound **3** (two silver ions) is fewer than that in compound **7** (eight silver ions in all). The consequence may be attributed to PPh_3 which replace the coordination sites of L3 anion. In compound **3** the $-\text{OH}$ group is uncoordinated group while it is coordinated in compound **7**. In addition, the coordination numbers of silver ions in compound **7** are 5 and 6, whereas in compound **3**, there exist only three- and four-coordinate silver centers.

L1, L2 and L3 are monosulfonate ligand, and compounds **1–3** all display discrete structures. In order to explore whether silver compound containing multisulfonate anion and PPh_3 molecule also forms discrete structure, L4 was selected as a tetrasulfonate ligand. Crystal structure of compound **4** determined by X-ray diffraction is illustrated in Fig. 5. Compound **4** shows a discrete centrosymmetric structure. There exist two crystallographically unique silver centers with different coordination environments. Ag1 is coordinated by one sulfonate oxygen atom [$\text{Ag}(1)-\text{O}(1)=2.521(2)$ Å] and three phosphorous atoms [$\text{Ag}(1)-\text{P}(1)=2.5405(9)$ Å, $\text{Ag}(1)-\text{P}(2)=2.5028(9)$ Å, $\text{Ag}(1)-\text{P}(3)=2.5120(8)$ Å], showing a distorted tetrahedral geometry. Ag2 center is coordinated by one sulfonate oxygen atom [$\text{Ag}(2)-\text{O}(4)=2.306(2)$ Å] and two phosphorous atoms [$\text{Ag}(2)-\text{P}(4)=2.505(1)$ Å, $\text{Ag}(2)-\text{P}(5)=2.4509(9)$ Å]. The $\text{O}(4)-\text{Ag}(2)-\text{P}(5)$, $\text{O}(4)-\text{Ag}(2)-\text{P}(4)$ and $\text{P}(5)-\text{Ag}(2)-\text{P}(4)$ angles are 134.35(7), 98.94(7) and 126.50(3)°, respectively, whose sum is 359.79°. Therefore, Ag(2), O(4), P(4) and P(5) are almost coplanar, and Ag(2) has

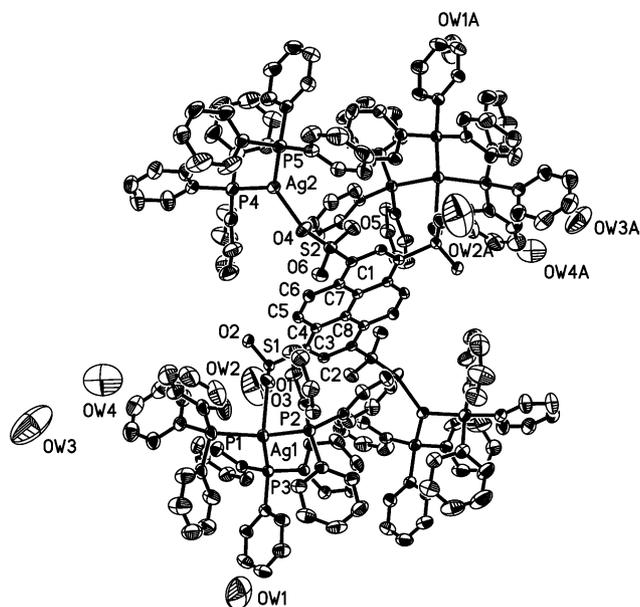


Fig. 5. Molecular structure of $[Ag_4L_4(PPh_3)_{10}] \cdot 8H_2O$ **4**. All the H atoms are omitted for clarity.

a distorted trigonal coordination geometry. Each sulfonate group coordinates to only one silver ion, which is similar to that observed in compounds **1**, **2** and **3**. Although each of Ag(1) and Ag(2) is bonded to one sulfonate oxygen atom, the numbers of PPh₃ molecules bonded to Ag(1) and Ag(2) are two and three, respectively. This difference may be on account of the steric repulsion among the PPh₃ molecules. Moreover it is noteworthy that compound **4** represents the first silver tetrasulfonate with discrete structure. In addition there are eight lattice water molecules in the unit cell, which do not show any covalent interactions in the structure. We failed to obtain the structure of silver 1,3,6,8-pyrenetetrasulfonate. Since L4 contains four sulfonate groups, this compound is supposed to have a 3D polymeric structure.

L1, L2 and L3 anions can be considered as derivatives of phenylsulfonate anion with different substituted groups, while L4 is a tetrasulfonate anion. Although L1, L2, L3 and L4 have highly different structural features, each of compounds **1–4** containing PPh₃ molecules displays a discrete structure. PPh₃ is a terminal ligand with bulky volume, and is a strong ligand for silver ion. Thus the coordination sites of sulfonate groups in compounds **5–7** are occupied by PPh₃ molecules, and the number of silver ions bonded to each sulfonate group decreases, and the dimensionality of the compound decreases to zero, and a discrete structure is formed. Above consequences indicate that PPh₃ ligand plays a dominant role in the formation of structural feature of compounds **1–4** even though L1, L2, L3 and L4 are different from each other.

The ³¹P NMR spectra measured at room temperature in CDCl₃ of four compounds **1–4** have shown only one resonance at δ 10.29, 9.05, 10.01 and 9.44, respectively, presumably in consequence of exchange equilibrium that are reasonably fast in relation to the NMR time scale. The chemical shifts are similar to the observed values for PPh₃ ligands coordinated to

silver(I) and can be compared with those of related compounds: $[Ag_2(pz)_2(PPh_3)_2]$ at δ 9.87 and $[Ag_2(pz)_2(PPh_3)_3]$ at δ 6.13 [9]. There should be various degrees of association in addition to dissociation of PPh₃ and perhaps also of sulfonate anions, i.e. an equilibrium based on dynamic exchange, which takes place very rapidly on the NMR time-scale, just as observed in $[Ag(im)(PPh_3)_3]$ [10], and $[Ag_2(pz)_2(PPh_3)_3]$ [9].

3.3. Conclusion

Four new silver(I) sulfonate compounds incorporating PPh₃ acting as an auxiliary donor ligand have been synthesized and characterized. The structures of these compounds have been determined by single-crystal X-ray analysis. All compounds have discrete structures rather than polymeric structures as a result of the presence of the bulky terminal ligand PPh₃. In addition the compounds **1–3** display room-temperature photoluminescence.

Acknowledgements

We thank the National Natural Science Foundation of China (No. 20471014), the Fok Ying Tung Education Foundation and the Natural Science Foundation of Jilin province (China) for Support.

References

- [1] G.K.H. Shimizu, G.D. Enright, C.I. Ratcliffe, K.F. Preston, J.L. Reid, J.A. Ripmeester, Chem. Commun. (1999) 1485; A.P. Côté, G.K.H. Shimizu, Inorg. Chem. 43 (2004) 6663; G.K.H. Shimizu, G.D. Enright, C.I. Ratcliffe, G.S. Rego, J.L. Reid, J.A. Ripmeester, Chem. Mater. 10 (1998) 3282; G. Bernardinelli, E.A.C. Lucken, M. Costines, Z. Kristallogr. 195 (1991) 145; S.K. Mäkinen, N.J. Melcer, M. Parvez, G.K.H. Shimizu, Chem. Eur. J. 7 (2001) 5176; D.F. Sun, R. Cao, Y.C. Liang, M.C. Hong, Chem. Lett. (2002) 198; J.F. Ma, J. Yang, S.L. Li, S.Y. Song, H.-J. Zhang, H.S. Wang, K.Y. Yang, Cryst. Growth Des. 5 (2005) 807; Y.J. Pan, F.J. Meng, X.J. Wang, H.L. Zhu, D.Q. Wang, Z. Kristallogr. NCS 218 (2003) 253; P.F. Charbonnier, Acta Cryst. B33 (1977) 2824; P.F. Charbonnier, R.F.H. Loiseleur, Acta Cryst. B34 (1978) 3598; P.F. Charbonnier, R.F.H. Loiseleur, Acta Cryst. B35 (1979) 1773; P.F. Charbonnier, R.F.H. Loiseleur, Acta Cryst. B37 (1981) 822; A.D. Kulynych, G.K.H. Shimizu, CrystEngComm 18 (2002) 102; G.K.H. Shimizu, G.D. Enright, G.S. Rego, J.A. Ripmeester, Can. J. Chem. 77 (1999) 313.
- [2] D. Bratislav, S. Oliver, S. Hubert, Inorg. Chem. 44 (2005) 673; K. Nomiya, N.C. Kasuga, I. Takamori, K. Tsuda, Polyhedron 6 (1998) 3519; T. Wu, D. Li, X.L. Feng, J.W. Cai, Inorg. Chem. Commun. 6 (2003) 886; G.A. Bowmaker, J.V. Hanna, C.E.F. Rickard, A.S. Lipton, J. Chem. Soc. Dalton Trans. (2001) 20.
- [3] P. Römbke, P. Römbke, A. Schier, H. Schmidbauer, Z. Naturforsch. 58b (2003) 168; M. Bardaji, O. Crespo, A. Laguna, A.K. Fischer, Inorg. Chim. Acta 304 (2000) 7; R. Terroba, M.B. Hursthouse, M. Laguna, A. Mendia, Polyhedron 18 (1999) 807; H. Lang, M. Weinmann, M. Winter, M. Leise, W. Imhof, J. Organomet. Chem. 503 (1995) 69; M.J. Mays, J. Bailey, J. Chem. Soc. Dalton Trans. (1977) 578; M.M. Artigas, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, M.D. Villacampa, Inorg. Chem. 36 (1997) 6454; L. Lettko, J.S. Wood, M.D. Rausch, Inorg. Chim. Acta 308 (2000) 37; D.F. Sun, R. Cao, W.H. Bi, X.J. Li, Y.Q. Wang, M.C. Hong, Eur. J. Inorg. Chem. (2004) 2144.
- [4] G.M. Sheldrick, SHELXS-97, A Program for Automatic Solution of Crystal Structure, University of Goettingen, Germany, 1997

- [5] G.M. Sheldrick, *SHELXL-97*, A Programs for Crystal Structure Refinement, University of Goettingen, Germany, 1997
- [6] L.J. Farrugia, *WINGX*, A Windows Program for Crystal Structure Analysis, University of Glasgow, Glasgow, UK, 1988.
- [7] *International Tables for X-ray Crystallography*, vol. C, Kluwer Academic Publisher, Dordrecht, 1992
- [8] G.M. Sheldrick, *SHELXTL PLUS*, Structure Determination Program, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1990
- [9] G.A. Ardizzioia, G. La Monica, A. Maspero, M. Moret, N. Masciocchi, *Inorg. Chem.* 36 (1997) 2321.
- [10] K. Nomiya, K. Tsuda, Y. Tanabe, H. Nagano, *J. Inorg. Biochem.* 69 (1998) 9.