Inorganica Chimica Acta 363 (2010) 2425–2429

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

The synthesis, structure, and luminescence of two silver(I)-dppm complexes based on sulfate anion and nitrogen heterocyclic ligands

Li-Li Song [a], Qiong-Hua Jin [a,*], Li-Na Cui [a], Cun-Lin Zhang [b]

[a] Department of Chemistry, Capital Normal University, Beijing 100048, China
[b] 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

A R T I C L E I N F O

Article history:
Received 27 January 2010
Received in revised form 28 March 2010
Accepted 30 March 2010
Available online 9 April 2010

Keywords:
Silver(I)
Sulfate
Bis(diphenylphosphino)methane
2-Aminopyrazine
Fluorescence

A B S T R A C T

At ambient temperature, two silver(I) complexes $[Ag_4(SO_4)_2(dppm)_4]\cdot 5CH_3CH_2OH\cdot 1/2H_2O$ (**1**) and $[Ag_2(SO_4)(dppm)_2(2\text{-}ampz)]\cdot CH_3OH\cdot H_2O$ (**2**) (dppm = bis(diphenylphosphino)methane, 2-ampz = 2-aminopyrazine) were obtained by the reaction of Ag_2SO_4 with dppm in the presence of pyrazine or 2-aminopyrazine. They are characterized by IR, X-ray crystallography, luminescence and ^1H, ^{31}P NMR spectroscopy. Complex **1** is a tetranuclear cluster. In complex **2**, the units $[Ag_2(SO_4)(dppm)_2]$ are connected by 2-aminopyrazine to form a 1D linear polymer. Due to the subtle interactions of different nitrogen heterocyclic ligands with silver ions, two SO_4^{2-} anions in **1** adopt μ_3-O, O′, O′ and unique μ_4-O, O, O′, O′ bonding modes respectively, while SO_4^{2-} anion in **2** adopts μ-O, O′ bonding mode.

1. Introduction

The metal coordination polymers have attracted great interests not only for their potential applications as functional materials, but also for their fascinating architectures [1–3]. The design and synthesis of metal coordination polymers can be influenced by many factors, especially influenced by the nature of metal ions, ligands, and anions [4–6]. The coordinated anions have been found to be efficient in influencing the structure of the d^{10} metal-dppm complexes, such as tetranuclear complexes $[Ag_4(\mu_3\text{-}Cl)(\mu\text{-}S_2O_3)(\mu\text{-}dppm)_3]$, $[Ag_4(\mu_3\text{-}S_2O_3)(\mu\text{-}S_2O_3)(\mu\text{-}dppm)_4]$ [7], $[Ag_2(\mu\text{-}OAc)_2(\mu\text{-}dppm)]_2$ [8] and $[Ag(\mu\text{-}SCN)_2(\mu\text{-}dppm)Ag]_2$ [9].

To our knowledge, Ag(I) complexes containing SO_4^{2-} anions are rare, and in these reported complexes the bonding mode of SO_4^{2-} anion can also influence the structure of the complex. The reported bonding modes of SO_4^{2-} are (I) O– (II) μ-O, O′ (III) μ_4-O, O′, O″, O″ (IV) μ_3-O, O′, O′ [10–13] (Scheme 1). However, due to the presence of many subtle interactions, the rational design and construction of specific architecture are still a challenge to chemists. In our previous work, we find that introducing nitrogen heterocyclic ligand into the reaction system is important for generating some intriguing architectures [14,15], for example Ag(I)-dppm complexes $[Ag_2(\mu\text{-}dppm)_2(\mu\text{-}SO_4)(2\text{-}amp)_2]\cdot CH_3OH$ (**3**) and $[Ag_4(\mu\text{-}dppm)_2(\mu\text{-}SO_4)_2(\mu\text{-}4,4'\text{-}bpy)_2]\cdot 2CH_3OH$ (**4**) are obtained by using nitrogen heterocyclic ligands 2-aminopyrimidine (2-amp) and 4,4′-bipyridine (4,4′-bpy), respectively [16]. In this paper, selecting pyrazine and 2-aminopyrazine as nitrogen heterocyclic ligands, two new silver(I) complexes $[Ag_4(\mu_3\text{-}SO_4)(\mu_4\text{-}SO_4)(\mu\text{-}dppm)_4]\cdot 5CH_3CH_2OH\cdot 1/2H_2O$ (1) and $[Ag_2(\mu\text{-}SO_4)(\mu\text{-}dppm)_2(2\text{-}ampz)]\cdot CH_3OH\cdot H_2O$ (2) were obtained. Complex **1** is a tetranuclear cluster, where the SO_4^{2-} anions adopt the μ_3-O, O′, O′ bonding mode (IV) and μ_4-O, O, O′, O′ bonding mode (V), the latter mode had not been reported (Scheme 1). In complex **2**, the units $[Ag_2(SO_4)(dppm)_2]$ are connected by 2-aminopyrazine to form a 1D linear polymer. They are characterized by X-ray crystallography, IR, luminescence, ^1H, ^{31}P NMR spectroscopy.

2. Experimental

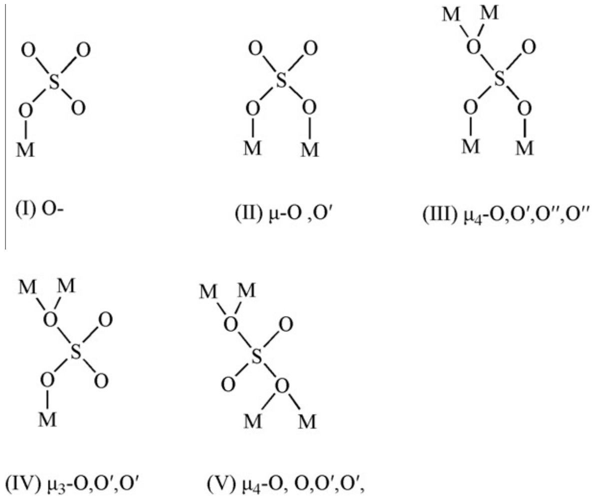
2.1. Materials and physical measurements

All reagents were supplied by J&K Chemical Ltd. and were used as received without further purification. All experiments were performed at ambient temperature. Elemental analyses (C, H, N) were performed on a Flash EA 1112 analyzer. IR spectra were recorded from KBr pellets on a Bruker EQUINOX 55 FT-spectrometer. NMR experiments were carried out on a JNM ECA-600 (JEOL) spectrometer. Emission spectrum was recorded on a Hitachi F-4500 Luminescence Spectrophotometer.

---

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

0020-1693/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2010.03.075



(I) O-

(II) μ-O ,O′

(III) μ_4-O,O′,O″,O″

(IV) μ_3-O,O′,O′

(V) μ_4-O, O,O′,O′,

Scheme 1. Five bonding modes of the SO_4^{2-} anion in the Ag(I) complexes.

2.2. Synthesis of the complex **1**

Complex **1** was obtained by reaction of Ag_2SO_4 (0.2 mmol, 0.0623 g), bis(diphenylphosphino)methane(dppm) (0.4 mmol, 0.1532 g), pyrazine (pz) (0.4 mmol, 0.0361 g) in a mixture of 5 ml dichloromethane, 5 ml methanol and 5 ml ethanol. They were stirred for 3 h and filtered. Colorless crystal was obtained from the filtrate after standing in the room temperature for several days. *Anal.* Calc. for $C_{110}H_{119}P_8S_2O_{13.5}Ag_4$: C, 55.03; H, 4.96. Found: C, 55.23; H.5.14%. IR data (cm^{-1}, KBr pellets): 3423m, 3050w, 1637w, 1482w, 1435s, 1400w, 1385w, 1308w, 1123s, 1099s,1025w, 1000w, 780w, 739s, 717w, 692s, 618m, 514w, 480w, 439w.

2.3. Synthesis of the complex **2**

Complex **2** was obtained by reaction of Ag_2SO_4 (0.2 mmol, 0.0623 g), bis(diphenylphosphino)methane(dppm) (0.4 mmol, 0.1536 g), 2-aminopyrazine (2-ampz) (0.4 mmol, 0.0381 g) in a mixture of 5 ml dichloromethane and 5 ml methanol. They were stirred for 3 h and filtered. Colorless crystal was obtained from the filtrate after standing in the room temperature for several days. *Anal.* Calc. for $C_{54}H_{55}N_3P_4SO_6Ag_2$: C, 53.27; H, 4.52; N, 3.45. Found: C, 53.46; H, 4.69; N, 3.62%. IR data (cm^{-1}, KBr pellets): 3442m, 1632w, 1534m, 1482w, 1435s, 1385w, 1096s, 778w, 741s, 718w, 692s, 618m, 515w, 479w, 423w.

2.4. X-ray crystallography

Single-crystal X-ray diffraction studies of complexes **1–2** were performed on a Bruker SMART diffractometer equipped with CCD area detector with a graphite monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo Kα radiation (λ = 0.71073 Å) by x scan mode. All data were corrected by semi-empirical method using SADABS program. The program SAINT was used for integration of the diffraction profiles.

All structures were solved by direct methods using SHELXS-97 program of the SHELXL-97 [17] package and refined with SHELXL-97 package [18]. Metal atom centers were located from the E-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinements were performed by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. All the hydrogen atoms were first found in difference electron density maps, and then placed in the calculated sites and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded. Further crystallographic data and experimental details for structural analyses of both complexes are summarized in Table 1, and selected bond lengths and angles for complexes **1–2** in Table 2.

Table 1
Crystallographic data and structure refinement summary complexes **1–2**.

	1	2
Formula	$C_{110}H_{119}P_8S_2O_{13.5}Ag_4$	$C_{54}H_{55}N_3P_4SO_6Ag_2$
Molecular weight	2400.41	1217.44
T (K)	298(2)	93(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	15.2615(14)	21.6443(3)
b (Å)	15.2652(14)	21.1753(3)
c (Å)	25.633(2)	13.4627(16)
α (°)	91.0540(10)	90.00
β (°)	94.0980(10)	90.00
γ (°)	111.8312(10)	90.00
V (Å^3)	5522.8(9)	6170.2(13)
Z	2	4
D_{calc} (mg m^{-3})	1.443	1.327
Crystal size (mm)	0.49 × 0.48 × 0.45	0.53 × 0.47 × 0.40
Goodness-of-fit F^2	1.037	1.003
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Final R_1 and wR_2 indices	R_1 = 0.0840 wR_2 = 0.2081	R_1 = 0.0562 wR_2 = 0.1636
R_1 and wR_2 indices (all data)	R_1 = 0.1862, wR_2 = 0.2817	R_1 = 0.0633, wR_2 = 0.1707
Maximum and minimum peaks (e Å^{-3})	1.428 and −1.323	1.487 and −0.676

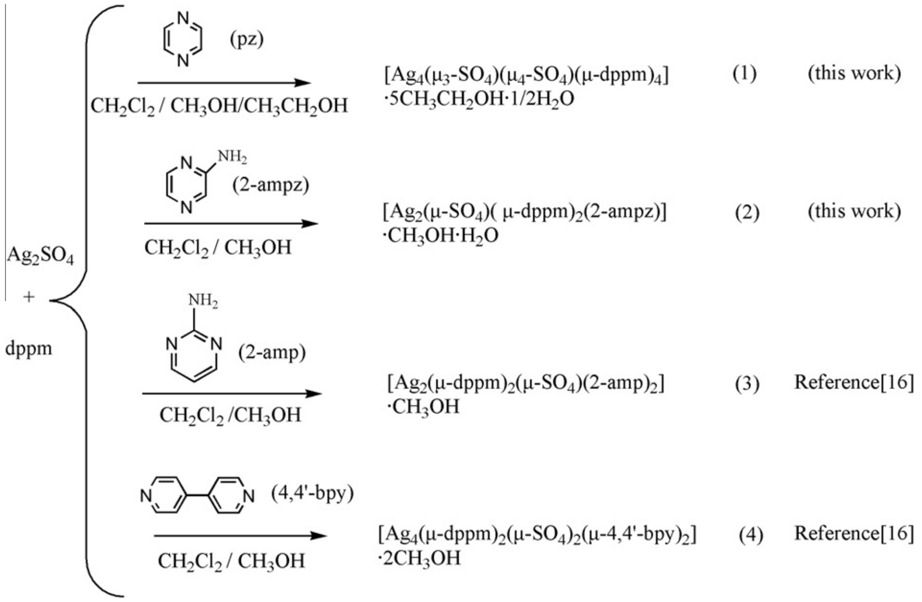
Table 2
Selected bond lengths (Å) and angles (°) for complexes **1–2**.

Complex ***1***			
Ag(1)–P(1)	2.441(3)	Ag(1)–P(8)	2.448(3)
Ag(1)–O(1)	2.331(9)	Ag(1)–O(5)	2.414(9)
Ag(2)–P(2)	2.447(3)	Ag(2)–P(3)	2.446(4)
Ag(2)–O(1)	2.329(9)	Ag(2)–O(6)	2.437(10)
Ag(3)–P(4)	2.465(4)	Ag(3)–P(5)	2.490(4)
Ag(3)–O(2)	2.714(10)	Ag(3)–O(6)	2.348(8)
Ag(4)–P(6)	2.482(4)	Ag(4)–P(7)	2.485(4)
Ag(4)–O(2)	2.526(10)	Ag(1)–O(7)	2.361(8)
P(1)–Ag(1)–P(8)	121.66(12)	P(3)–Ag(2)–P(2)	118.22(12)
P(4)–Ag(3)–P(5)	119.61(13)	P(6)–Ag(4)–P(7)	116.13(12)
Complex ***2***			
Ag(1)–P(1)	2.4244	Ag(1)–P(3)	2.4413
Ag(1)–O(1)	2.4287	Ag(1)–N(1)	2.507(6)
Ag(2)–P(2)	2.4556	Ag(2)–P(4)	2.4502
Ag(2)–O(2)	2.386(6)	Ag(2)–N(2)	2.491(5)
Ag(1)–Ag(2)	3.1301		
P(1)–Ag(1)–P(3)	145.82(6)	P(4)–Ag(2)–P(2)	141.42(7)
P(1)–Ag(1)–O(1)	116.21(13)	O(1)–Ag(1)–P(3)	97.66(13)
O(2)–Ag(2)–P(4)	107.73(16)	O(2)–Ag(2)–P(2)	109.16(18)

3. Results and discussion

3.1. Synthesis of the complexes

Recently, we have synthesized four complexes by the reactions of Ag_2SO_4 and dppm with nitrogen heterocyclic ligands. The synthetic routes are summarized in Scheme 2. The molar ratio of Ag_2SO_4:dppm:nitrogen heterocyclic ligand (1:2:2) and the choice of the solvent have great influence on the experimental products. The nitrogen heterocyclic ligands (2-aminopyrimidine, 4,4′-bipyridine and 2-aminopyrazine), which have strong coordination ability



Scheme 2. Four reactions of AgSO$_4$ with dppm and different nitrogen heterocyclic ligands.

with Ag atoms, act as bridging ligands. Furthermore, coordination modes of SO$_4^{2-}$ and dppm are the same in complexes **2**–**4**, where SO$_4^{2-}$ and dppm behave as bridging ligands. Different nitrogen heterocyclic ligands result in various crystal structures. In complex **2**, 2-aminopyrazine coordinate to Ag atoms by its heterocyclic nitrogen atoms and form hydrogen bonds with the sulfate anions by its amino groups. In complex **1** the pyrazine does not act as a ligand, but it facilitates the generation of the unique coordination mode of SO$_4^{2-}$ anion, which may be due to the subtle interaction of pyrazine with metal silver ions in the system.

*3.2. Description of the crystal structures of complexes **1–2***

*3.2.1. Crystal structure of complex **1***

The crystal structural analysis shows that in complex **1** four Ag atoms form a square, whose edges are bridged by four dppm ligands. Two types of coordination geometries are observed for the four independent Ag atoms. Ag(3) is coordinated by two phosphorus atoms from two dppm ligands and one oxygen atom from one SO$_4^{2-}$ to form a distorted trigonal pyramid. While Ag(1), Ag(2), and Ag(4) are coordinated by two phosphorus atoms from two dppm ligands and two oxygen atoms from two SO$_4^{2-}$ to form a distorted tetrahedron (Fig. 1a). Furthermore, two SO$_4^{2-}$ anions adopt different bonding modes. One SO$_4^{2-}$ anion adopts μ$_3$-O, O′, O′ bonding mode (IV) to bridge three Ag atoms, which is only observed in [Ag$_4$(L)$_2$(SO$_4$)$_2$(H$_2$O)$_4$] (L = 2-amino-4,6-dimethylpyrimidine) [13]. The other SO$_4^{2-}$ anion adopts a unique μ$_4$-O, O, O′, O′ bonding mode (V) to bridge four Ag atoms (Fig. 1b). Since two SO$_4^{2-}$ anions are coordinated to Ag atoms in different modes, the edges of the distorted square are not equivalent. Compared with similar compound Ag$_4$(μ$_3$-S$_2$O$_3$)(μ-S$_2$O$_3$)(μ-dppm)$_4$ [7], the average bond length of Ag–P (2.463) is 0.01 Å shorter, and P–Ag–P angle (118.9°) is 3.4° larger.

*3.2.2. Crystal structure of complex **2***

The crystal structural analysis shows that in complex **2** two four-coordinated Ag atoms are triply bridged by the two dppm ligands and one SO$_4^{2-}$ anion, forming an eight-member ring Ag$_2$P$_4$C$_2$ (Fig. 2a), where the SO$_4^{2-}$ anion adopts the μ-O, O′ bonding mode(II). The units [Ag$_2$(μ-SO$_4$)(μ-dppm)$_2$] are connected by 2-aminopyrazine to form a 1D linear polymer (Fig. 2b). The distance of the two silver atoms (3.1301 Å) is 0.21 Å shorter than the sum of the covalent radii (3.44 Å), which indicates that there exists Ag–Ag bond in complex **2.** Due to the presence of the bridging SO$_4^{2-}$ anion, the two Ag atoms in Ag$_2$(μ-P, P′-dppm)$_2$ core have different coordination environments, hence all bond lengths and angles in Ag$_2$(μ-P, P′-dppm)$_2$ unit are different. The crystal packing along *c* -axis shows the interactions among one-dimensional chains (Fig. 2c).

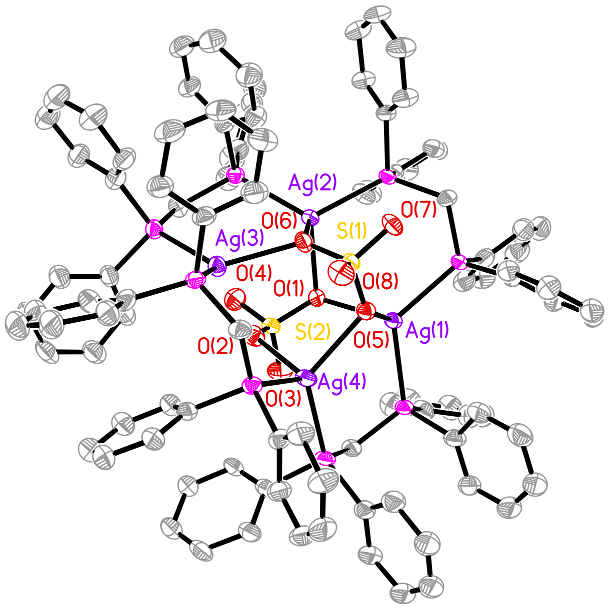


Fig. 1a. Perspective view of complex **1**. Hydrogen atoms are omitted for clarity.

3.3. Emission spectra of complexes

The solid-state fluorescence emission spectra of complex **1** and **2** were measured at room temperature, and the fluorescence emission spectra are displayed in Figs. 3a and 3b. When excited at 350 nm, complex **1** displays a fluorescence emission peak at

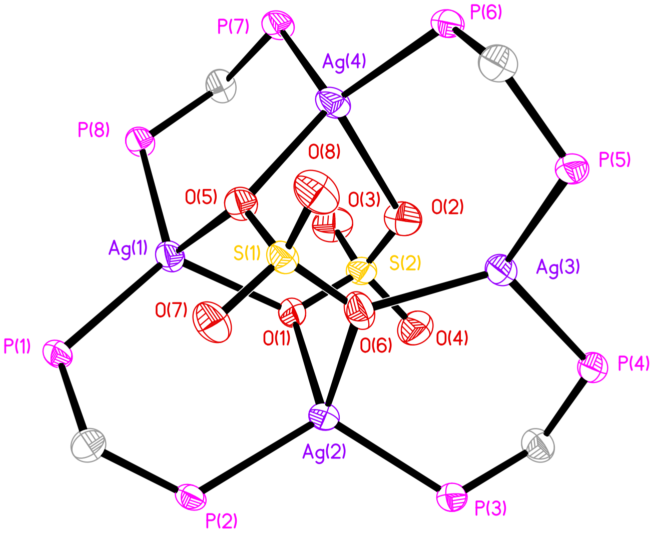


Fig. 1b. Perspective view of coordination geometries of two SO_4^{2-} anions.

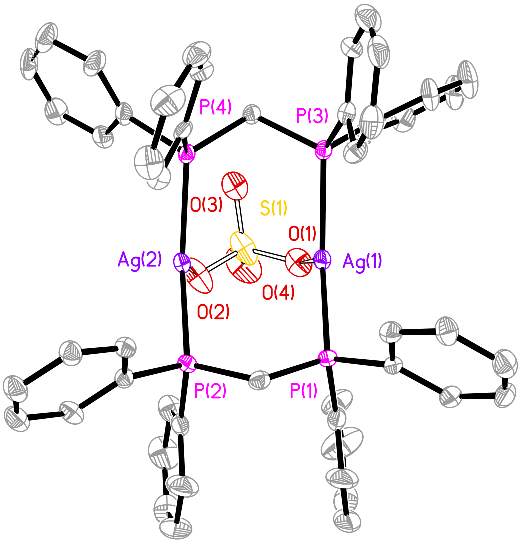


Fig. 2a. Perspective view of $[Ag_2(\mu\text{-}SO_4)(\mu\text{-dppm})_2]$ unit. Hydrogen atoms are omitted for clarity.

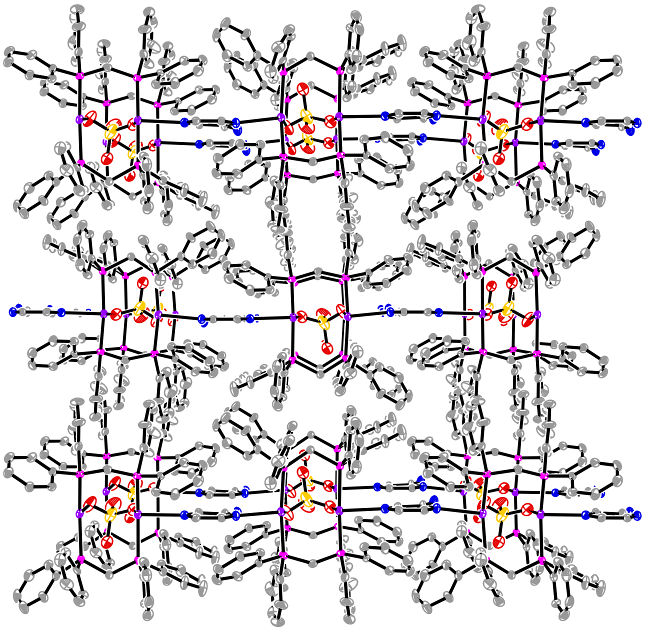


Fig. 2c. Crystal packing of complex **2** along *c*-axis.

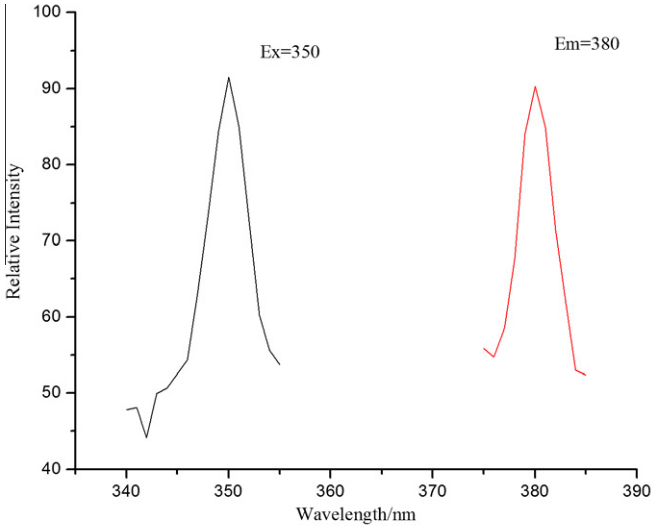


Fig. 3a. Emission spectra measured in the solid state at room temperature for complex **1**.

380 nm. The emission of complex **1** can be assigned to the metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT) between the silver(I) atom and the ligand dppm, because the free ligand dppm possesses similar emission (λ_{ex} = 322 nm, λ_{em} = 430 nm), although a sizable blue-shift (50 nm) is observed in **1**. Complex **2** displays a strong fluorescence emission peak at 504 nm (λ_{ex} = 350 nm). The introduction of nitrogen heterocyclic ligand leads to strong fluorescence character in complex **2**. It may be the MLCT or LMCT among the silver(I) atom and the ligands dppm and 2-ampz.

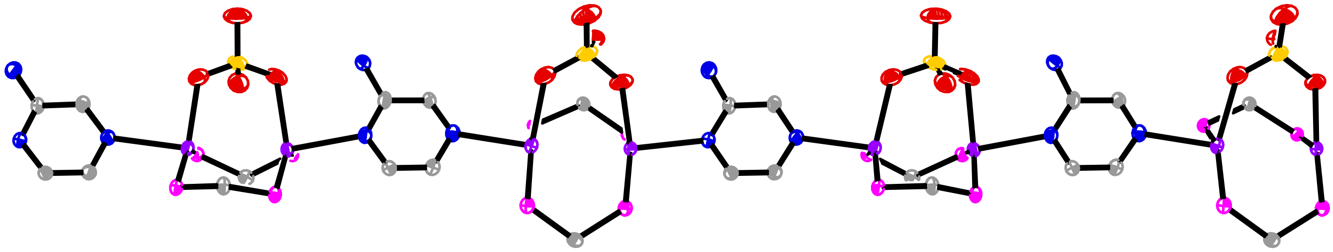


Fig. 2b. Perspective view of a 1D linear polymer of complex **2**.

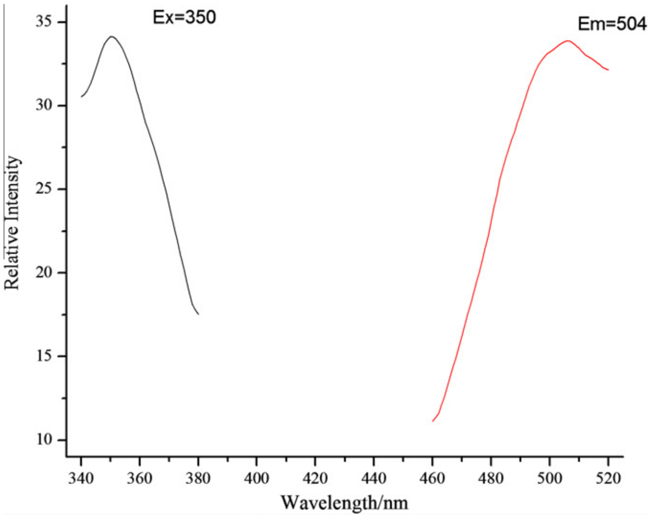


Fig. 3b. Emission spectra measured in the solid state at room temperature for complex **2**.

The luminescence of some mixed-ligand Cu(I) and Ag(I) has been reported [20,21]. Recently, we attend to use various auxiliary ligands to synthesize Cu(I)/Ag(I)-dppm complexes and investigate their luminescent properties [16,19,22]. It is well known that these emission spectra are very similar. Such similarities may be attributed to the existence of conjugate unsaturated ligands. This result may give important information for designing new luminescent metal complexes.

3.4. NMR spectra of complexes

The ^{1}H NMR and ^{31}P NMR spectra of complexes **1** and **2** have been measured at room temperature in DMSO. The ^{1}H NMR spectra of complex **1** and **2** show the broad multiplet in the range 7.06–7.69 ppm and 7.07–7.63 ppm, respectively, which is assigned as the signals of aromatic protons. There are the singlet at 6.41 ppm and the doublet at 7.82 and 7.85 ppm in complex **2**, which is attributed to the signals of 2-ampz protons. Compared with the free 2-ampz ligand (7.72, 7.90, 7.94 ppm), the signals of 2-ampz in **2** are shifted to the lower field.

^{31}P NMR spectra of compound **1** and **2** are well resolved, including the ^{107,109}Ag and ^{31}P coupling patterns. The $^1J(^{107,109}\text{Ag},^{31}\text{P})$ coupling constants of compound **1** and **2** are 1137 and 1199 Hz, respectively. Compared with the free dppm ligand (−22.7 ppm), the corresponding phosphorus resonances in the complex **1** and **2** shift to lower field, which is attributed to the fact that the donation of the electron pair on the phosphorus to the metal reduces the shielding at the phosphorus nucleus.

4. Conclusions

In summary, two new silver(I)-dppm complexes were synthesized and characterized. The results of this research not only illustrate that SO_4^{2-} anion has an important role in the formation of structure, but also give important information for designing new luminescent metal complexes.

Acknowledgements

This work has been supported by the National Science Foundation of China (Grant no. 20871085), the Committee of Education of Beijing Foundation of China (Grant no. KM200610028006), the Project-sponsored by SRF for ROCS and SEM, the subsidy of Beijing Personnel Bureau, National Keystone Basic Research Program (973 Program) under grant no. 2007CB310408, 2006CB302901, State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences.

Appendix A. Supplementary material

CCDC 759139 and 759140 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.03.075.

References

[1] W.-L. Zhang, Y.-Y. Liu, J.-F. Ma, Cryst. Growth Des. 8 (2008) 1250.
[2] J.-Q. Liu, W.-P. Wu, Y.-Y. Wang, W.-H. Huang, W.-H. Zhang, Q.-Z. Shi, J.S. Miller, Inorg. Chim. Acta 362 (2009) 1295.
[3] V. Vo, Y. Kim, N.V. Minh, C.S. Hong, S.J. Kim, Polyhedron 28 (2009) 1150.
[4] Y.-R. Zhong, M.-L. Cao, H.-J. Mo, B.-H. Ye, Cryst. Growth Des. 8 (2008) 2282.
[5] R.-L. Sang, L. Xu, Eur. J. Inorg. Chem. (2006) 1260.
[6] Q.-H. Jin, L.-L. Zhou, L.-J. Xu, Y.-Y. Zhang, C.-L. Zhang, X.-M. Lu, Polyhedron 29 (2010) 317.
[7] K. Matsumoto, R. Tanaka, Inorg. Chim. Acta 322 (2001) 125.
[8] S. Neo, Z.Y. Zhou, Inorg. Chem. 34 (1995) 520.
[9] Q.-H. Jin, K.-Y. Hu, L.-M. Chen, J.-J. Sun, L. Yang, P.-Z. Li, Z. Kristallogr. NCS 223 (2008) 79.
[10] M.-L. Tong, S.-L. Zheng, X.-M. Chen, Chem. Commun. (1999) 561.
[11] G.A. Bowmaker, J.V. Hanna, C.E.F. Rickard, A.S. Lipton, J. Chem. Soc., Dalton Trans. (2001) 20.
[12] N.R. Brooks, A.J. Blake, N.R. Champness, P. Hubbetstey, S.J. Teat, C. Wilson, M. Schroder, J. Chem. Soc., Dalton Trans. (2001) 2530.
[13] Y.H. Wang, K.L. Chu, H.C. Chen, C.W. Yeh, Z.K. Chan, M.C. Suen, J.D. Chen, J.C. Wang, Cryst. Eng. Commun. 91 (2006) 84.
[14] M.S. Balakrishna, R. Venkateswaran, S.M. Mobin, Inorg. Chim. Acta 362 (2009) 271.
[15] P. Rishikesh, K. Keisaku, Inorg. Chim. Acta 362 (2009) 3219.
[16] Q.-H. Jin, L.-L. Song, K.-H. Hu, L.-L. Zhou, Y.-Y. Zhang, R. Wang, Inorg. Chem. Commun. 13 (2010) 62.
[17] G.M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Solution, University of Gottingen, Gottingen, 1997.
[18] G.M. Sheldrick, SHELXS-97, Program for the Refinement of Crystal Structure, University of Gottingen, Germany, 1997.
[19] Q.-H. Jin, L.-M. Chen, L. Yang, P.-Z. Li, Inorg. Chim. Acta 362 (2009) 1743.
[20] V.W.W. Yam, W.K.M. Fung, K.K. Cheung, Organometallics 16 (1997) 2032.
[21] T. Tsukuda, A. Nakamura, T. Arai, Bull. Chem. Soc. Jpn. (2006) 288.
[22] Q.-H. Jin, L.-M. Chen, P.-Z. Li, S.-F. Deng, R. Wang, Inorg. Chim. Acta 362 (2009) 5224.