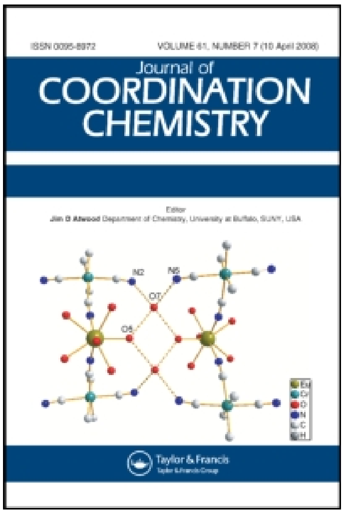

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A linear chain polymer {Ag$_2$[S$_2$P(OC$_2$H$_5$)$_2$]$_2$(bix)}<i>_n with multiple emission and red luminescence

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A linear chain polymer $\{Ag_2[S_2P(OC_2H_5)_2]_2(bix)\}_n$ with multiple emission and red luminescence

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The linear chain $\{Ag_2[S_2P(OC_2H_5)_2]_2(bix)\}_n$ **1** was obtained from reaction of $Ag[S_2P(OC_2H_5)_2]$ with bix (bix = 1,4-bis(imidazole-l-ylmethyl)benzene). Compound **1** consists of a dinuclear module with intramolecular Ag $\cdots$ Ag interactions (2.9842(5) Å). This interaction shows a profound influence on the observed multiple luminescence emissions for **1**. Crystal data for **1** at 293(2) K: Space group $P\bar{1}$, $a = 9.7158(1)$, $b = 9.8273(2)$, $c = 10.0758(2)$ Å, $\alpha = 70.989(1)$, $\beta = 89.308(1)$, $\gamma = 63.868(1)^\circ$, $V = 806.75(2)$ Å^3, $Z = 1$, $R_1 = 0.0294$.

Keywords: Dithiophosphonate; Silver(I); Luminescence; Ag $\cdots$ Ag interactions

1. Introduction

Polynuclear metal complexes, particularly those of d^{10} electronic configuration, have attracted much attention for their ability of rich luminescent properties [1–3]. Many polynuclear gold(I) complexes based on dithiophosphonate ligands have been reported and the importance of Au–Au interactions in the luminescent behavior has been established [4–7]. Surprisingly, for polynuclear Ag(I) complexes containing dithiophosphonate ligands, no studies on their luminescent properties have been reported. In fact, silver(I) compounds usually exhibit emission at low temperature, especially with chalcogenides and acetylides as bridging ligands [8–10]. There are only a few monomeric or polymeric silver(I) complexes that exhibit luminescent properties at room temperature [11, 12]. Here, we report the synthesis and crystal structure of a dinuclear Ag(I) polymer containing both dithiophosphonate and bix; this compound displayed unusual multiple emissions with blue and red luminescence at room temperature.

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Table 1. Crystallographic data for **1**.

Compound	**1**
Temperature (K)	293(2)
Empirical formula	$C_{22}H_{34}Ag_2N_4O_4P_2S_4$
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.7158(1)
b (Å)	9.8273(2)
c (Å)	10.0758(2)
α (°)	70.989(1)
β (°)	89.308(1)
γ (°)	63.868(1)
Volume (Å^3)	806.75(2)
Z	1
Formula weight	824.45
Density (Calcd) (Mg m^{-3})	1.697
Absorption coefficient (mm^{-1})	1.605
F(000)	414
Reflections measured	6200
Independent reflections	3627
Observed reflection	3260
Refinement method	Full-matrix least-squares on F^2
Parameter/restraints/data (obs.)	172/0/326
Final R indices ([$I > 2\sigma(I)$])	$R_1 = 0.0294$, $wR_2 = 0.0740$
R indices (all)	$R_1 = 0.0332$, $wR_2 = 0.0769$
Goodness-of-fit	1.037
Largest and mean δ/σ	0.001, 0.000

2. Experimental

All chemical reagents are commercially available and used without further purification. Bix was prepared as described in the literature [13]. Elemental analyses of C, H and N were carried out on an Elemental Vario EL III microanalyzer. The IR spectrum was recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using a KBr pellet in the range 4000–400 cm^{-1}. Fluorescent analyses were performed on an Edinburgh Instruments analyzer model FLS920.

2.1. *Syntheses*

$Ag[S_2P(OC_2H_5)_2]$ (0.146 g, 0.5 mmol) and bix dihydrate (0.138 g, 0.5 mmol) were dissolved in 10 mL of CH_2Cl_2 and 2 mL of CH_3OH. The mixture was stirred for 15 min and filtered. The filtrate was kept in air at room temperature. After a few days colorless block crystals of **1** were obtained in 85% yield. Anal. Calcd: C, 28.14; H, 3.21; N, 7.42%. Found: C, 28.32; H, 3.31; N, 7.29%. IR data (KBr pellet, cm^{-1}): 3445s, 3119w, 2974w, 1618m, 1515m, 1444w, 1388w, 1233m, 1088w, 1041s, 1016s, 955s, 776s, 667s, 538s, 502w.

2.2. *Crystal structure determination*

Colorless, block crystals of **1** (0.40 × 0.20 × 0.20 mm) were used for X-ray analyses. Data collections were performed on a Rigaku mercury CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied by using the SADABS program [14] for the Siemens area detector. The programs for structure solution and refinement are SHELXS-97 [15] and SHELXL-97 [16], respectively. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically. Crystallographic data are summarized in table 1 and selected bond distances and angles are given in table 2.

3. Results and discussion

3.1. *Crystal structure*

As shown in figure 1, **1** consists of alternating $Ag_2[S_2P(OC_2H_5)_2]_2$ groups and bix ligands with a crystallographic center of inversion on the mid-point of the

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

Ag(1)–N(1)	2.230(2)	C(6)–C(7)	1.352(4)
Ag(1)–S(2)#1	2.5061(6)	C(8)–C(9)	1.510(3)
Ag(1)–S(1)	2.6350(7)	C(9)–C(11)	1.389(3)
Ag(1)–S(2)	2.9306(7)	C(9)–C(10)	1.391(3)
Ag(1)–Ag(1)#1	2.9842(5)	C(10)–C(11)#2	1.383(3)
N(1)–C(5)	1.315(3)	C(11)–C(10)#2	1.383(3)
N(1)–C(6)	1.372(3)	O(1)–P(1)	1.5791(17)
N(2)–C(5)	1.340(3)	O(2)–P(1)	1.5952(17)
N(2)–C(7)	1.369(3)	P(1)–S(1)	1.9708(9)
N(2)–C(8)	1.463(3)	P(1)–S(2)	2.0045(9)
C(1)–O(1)	1.452(3)	C(8)–C(9)	1.510(3)
C(1)–C(2)	1.487(4)	C(9)–C(11)	1.389(3)
C(3)–O(2)	1.440(3)	C(9)–C(10)	1.391(3)
C(3)–C(4)	1.491(4)		
N(1)–Ag(1)–S(2)#1	124.02(6)	N(2)–C(7)–H(7A)	126.9
N(1)–Ag(1)–S(1)	113.85(6)	N(2)–C(8)–C(9)	111.60(19)
S(2)#1–Ag(1)–S(1)	114.77(2)	C(11)–C(9)–C(10)	118.4(2)
N(1)–Ag(1)–S(2)	104.08(6)	C(11)–C(9)–C(8)	120.3(2)
S(2)#1–Ag(1)–S(2)	113.953(17)	C(10)–C(9)–C(8)	121.3(2)
S(1)–Ag(1)–S(2)	74.72(2)	C(11)#2–C(10)–C(9)	120.7(2)
N(1)–Ag(1)–Ag(1)#1	135.14(6)	C(11)#2–C(10)–H(10A)	119.6
S(2)#1–Ag(1)–Ag(1)#1	63.827(17)	C(9)–C(10)–H(10A)	119.6
S(1)–Ag(1)–Ag(1)#1	95.332(19)	C(10)#2–C(11)–C(9)	120.9(2)
S(2)–Ag(1)–Ag(1)#1	50.126(15)	C(10)#2–C(11)–H(11A)	119.5
C(5)–N(1)–C(6)	105.4(2)	C(9)–C(11)–H(11A)	119.5
C(5)–N(1)–Ag(1)	128.57(17)	C(1)–O(1)–P(1)	120.68(17)
C(6)–N(1)–Ag(1)	125.94(16)	C(3)–O(2)–P(1)	120.94(16)
C(5)–N(2)–C(7)	106.9(2)	O(1)–P(1)–O(2)	100.04(9)
C(5)–N(2)–C(8)	127.0(2)	O(1)–P(1)–S(1)	107.63(7)
C(7)–N(2)–C(8)	126.0(2)	O(2)–P(1)–S(1)	111.39(8)
N(1)–C(5)–N(2)	111.7(2)	O(1)–P(1)–S(2)	112.18(7)
N(1)–C(5)–H(5A)	124.1	O(2)–P(1)–S(2)	107.58(7)
N(2)–C(5)–H(5A)	124.1	S(1)–P(1)–S(2)	116.77(4)
C(7)–C(6)–N(1)	109.7(2)	P(1)–S(1)–Ag(1)	88.54(3)
C(7)–C(6)–H(6A)	125.2	P(1)–S(2)–Ag(1)#1	104.36(3)
N(1)–C(6)–H(6A)	125.2	P(1)–S(2)–Ag(1)	79.98(3)
C(6)–C(7)–N(2)	106.3(2)	Ag(1)#1–S(2)–Ag(1)	66.047(17)
C(6)–C(7)–H(7A)	126.9		

Symmetry code: 1 $-x$ $-y$ $-z$; #2 $-x+1$ $-y+1$ $-z-1$.

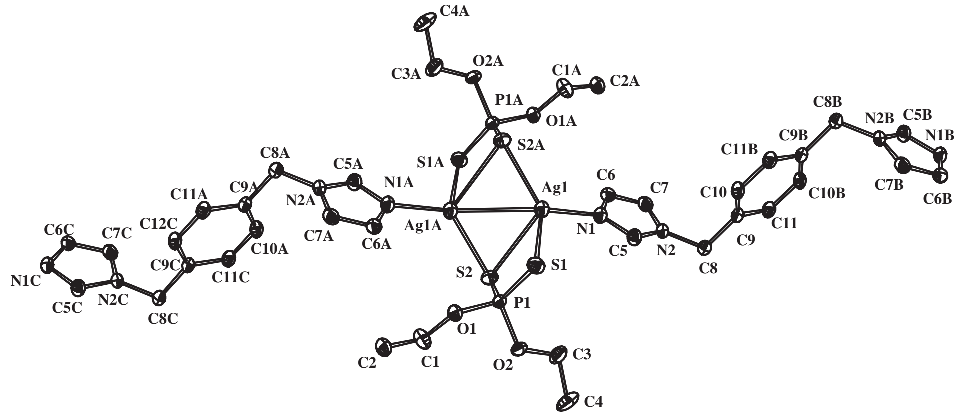

Figure 1. Atomic labeling of **1**. Displacement ellipsoids are plotted at the 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry labels: A: $-x$ $-y$ $-z$, B: $1-x$ $1-y$ -1 $-z$, C: $-1+x$ $-1+y$ $1+z$.

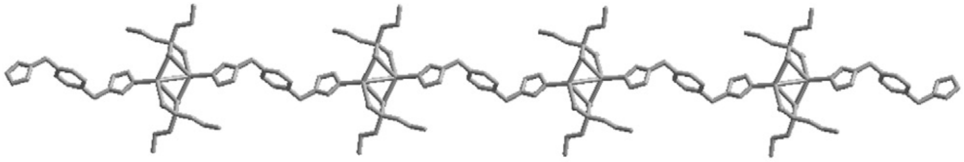

Figure 2. The linear chain of **1**.

Ag$\cdots$Ag distance. The silver atom is four-coordinate, being bonded to three sulfur atoms [Ag1–S1 2.6350(7), Ag1–S2 2.9306(7), Ag1–S2A 2.5061(6) Å] and a nitrogen atom of bix [Ag–N1 2.230(2) Å]. The angles around the silver range from 74.72(2) to 124.02(6)°. Therefore the coordination sphere of the silver is highly irregular with variation in bond lengths and angles. In **1**, the bix ligands all adopt *trans* conformation and link the $Ag_2[S_2P(OC_2H_5)_2]_2$ units to form a linear chain (figure 2). Three rings (two imidazole rings and one benzene ring) in each ligand are not in a plane with the mean deviation from the planes N1–C5–N2–C6–C7 (1), C9–C10–C11B–C9B–C10B–C11 (2) being 0.0016 and 0.0017 Å, respectively. Furthermore the dihedral angle between the planes (1) and (2) is 86.5°. The striking feature of **1** is that two $[S_2P(OC_2H_5)_2]^-$ ligands bridge two silver atoms. The bonding of the dithiophosphate sulfur atoms is very different; S2 is bonded to both silver atoms to form a planar four-member ring, while S1 is bonded to only one silver. Thus the $[S_2P(OC_2H_5)_2]^-$ ligand is tridentate, bridging and chelating. The structure contains an eight-membered ring with Ag–S crossing interaction and can be described as chair-shaped. This shape is similar to previously reported complexes [17, 18]. However, in **1** the Ag1$\cdots$Ag1A distance of 2.9842(5) Å is much shorter than the former complexes, and well below the sum of the van der Waals radii of two silver atoms 3.44 Å [19] and very close to the Ag–Ag separation in silver metal (2.89 Å), suggesting significant Ag$\cdots$Ag interactions. There are no significant intermolecular Ag$\cdots$Ag interactions in the solid state, and the closest Ag$\cdots$Ag distance is 7.795(2) Å.

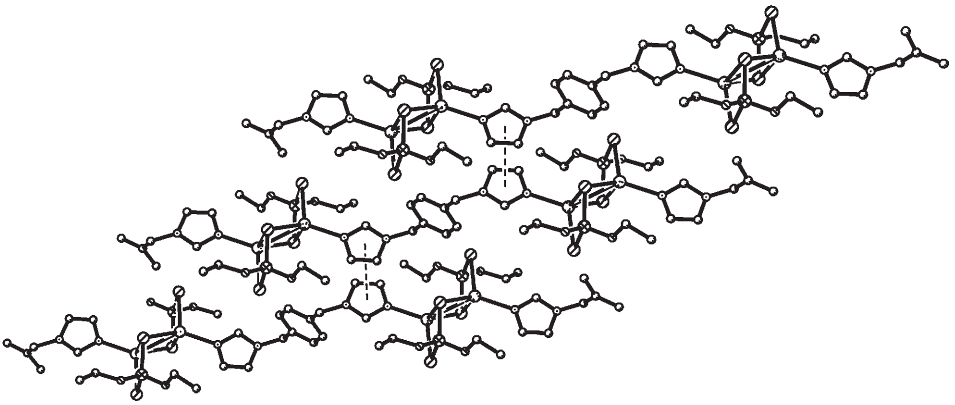

Figure 3. A two-dimensional supramolecular layer constructed by π–π interactions (dashed line).

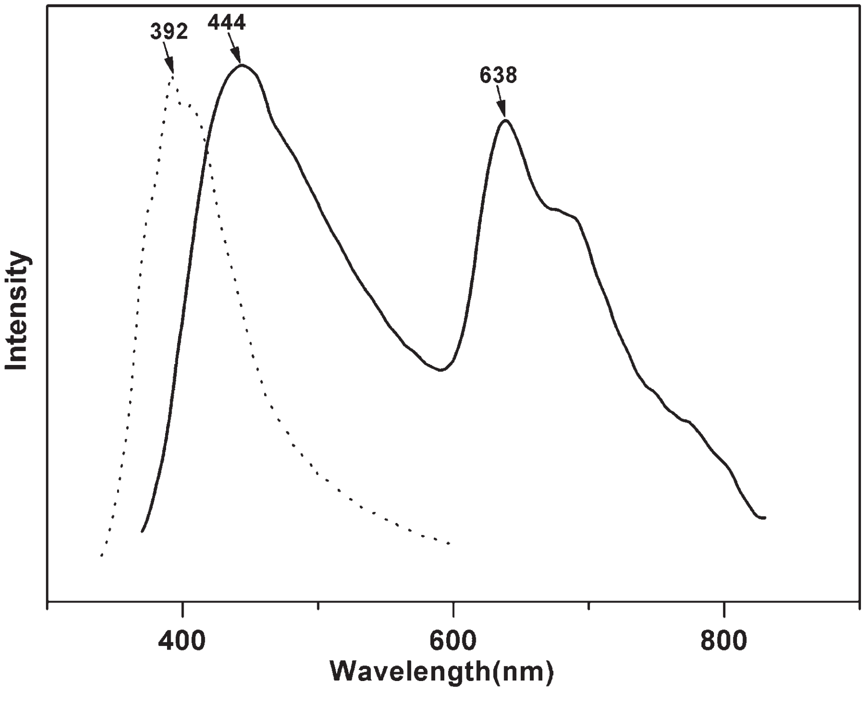

Figure 4. Emission spectra of ligand bix excited at 350 nm (dotted line) and **1** excited at 354 nm (solid line) in the solid state at room temperature.

Parallel aromatic imidazole rings of the bix ligands in adjacent chains interact with an offset face to face separation of ca. 3.3 Å and centroid-centroid distance of ca. 3.6 Å, indicating significant π–π interactions [20]. So the linear chains are organized into a 2-D molecular network by π–π stacking interactions (figure 3).

The IR spectrum of the polymer has medium absorption peaks at 1618, 1515 and 1444 cm^{-1}, attributable to the bix ligands. Strong absorptions at 1016 and 667 cm^{-1}

are characteristic bands for ν(P–O) and ν(P–S) of the $[S_2P(OC_2H_5)_2]^-$ ligand, respectively.

3.2. *Luminescence properties*

The emission spectrum of **1** shows unusual multiple emission bands at room temperature. When excited at 354 nm, it displays a strong blue emission band at $\lambda_{max} = 444$ nm and a strong red band at $\lambda_{max} = 638$ nm. The higher-energy band of 444 nm is attributed to neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature and can be tentatively attributed to intraligand emission states based on the emission feature of free bix ligand ($\lambda_{ex} = 350$ nm, $\lambda_{em} = 392$ nm) [21]. A clear red shift of the emission of this band may result from aromatic π–π stacking interactions in the solid state. Luminescence of dinuclear gold(I) dithiolate systems showed an emission arising from a S–Au charge-transfer transition, LMCT, with contributions from the metal–metal bond formed in the excited state, LMMCT [9, 10]. Similar to Au complexes, the low-energy emission band of **1** has been proposed to arise from a LMMCT [$RS^- \rightarrow Ag2$] excited state, but further exact assignments have not been carried out. TGA analyses show that the onset temperature for decomposition is 148°C. The stability of the complex makes it a potential candidate for multiple optical device.

In conclusion, the results presented here demonstrate interesting multiple emission properties for the dinuclear silver(I) complex connected by bix ligands. We expect the result to be extended to other similar silver-sulfur compounds with flexible N-donor ligands, wherein the $Ag \cdots Ag$ interactions may influence their luminescence properties.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 297431 for **1**. Copies of this information may be obtained from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44–1223–336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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