Synthesis, characterization and property of a mixed-valent Ag^I/Ag^{II} coordination polymer†

Di Sun,[a] Cheng-Feng Yang,[a] Hao-Ran Xu,[a] Hai-Xia Zhao,[a] Zhan-Hua Wei,[a] Na Zhang,[a] La-Jia Yu,[a] Rong-Bin Huang*[a] and Lan-Sun Zheng[ab]

A novel mixed-valent Ag^I/Ag^{II} coordination polymer $\{[Ag^I{}_2Ag^{II}{}_{0.5}(SO_4)(HSO_4)(pyz)_{2.5}]\cdot H_2O\}_n$ (1, pyz = pyrazine) was synthesized and characterized. The results show it presents semiconducting and photoluminescent properties.

Contrary to the ubiquitous silver ion with +1 oxidation state, its +2 oxidation state is relatively scarce and hard to access, owing to its instability in solution as well as in the solid-state, unless the Ag^{II} is protected against reduction to Ag^I by suitable ligands.[1] Recently, not only the structures of Ag^{II} complexes but also its promising properties have increasingly intrigued the scientific community.[2] The documented Ag^{II} complexes are captured by N-donor ligands of macrocycles,[3] porphyrins,[4] bipyridines[5] and pyridine-2-carboxylate derivatives[6] as well as occasional S-donor ligands[7] in which the Ag^{II} center is usually ligated with a square-planar geometry. Due to the paucity of Ag^{II} complexes as well as extension of our previous work,[8] we explored the synthesis of the novel Ag^{II} complex and surprisingly obtained a novel mixed-valent Ag^I/Ag^{II} coordination polymer (CP) $\{[Ag^I{}_2Ag^{II}{}_{0.5}(SO_4)(HSO_4)(pyz)_{2.5}]\cdot H_2O\}_n$ (1, pyz = pyrazine).

Pale-yellow crystals of complex 1 were readily synthesized via one-pot reaction of $AgNO_3$, $Na_2S_2O_8$ and pyz (molar ratio = 1:1:1) in acetonitrile–H_2O mixed solvent under ultrasonic conditions.‡ Phase purity of 1 is established by its powder X-ray diffraction pattern, which was consistent with that simulated on the basis of the single-crystal X-ray diffraction data (Fig. S1†). The characteristic IR bands at 1193 and 1120 cm^{-1} correspond to the asymmetric and symmetric S–O stretching vibrations respectively[9] (Fig. S2, ESI†). The presence of Ag^{II} is confirmed by the ESR spectrum of 1 (Fig. S3, ESI†), which elicits a distinct signal (g = 2.05) due to the d^9 electronic configuration of Ag(II).[10] Thermogravimetry indicates (Fig. S4, ESI†) complex 1 releases lattice water molecules up to 117 °C, then the guest-free framework begins to decompose above 117 °C along with the release of HSO_4^- and SO_4^{2-} anions, and the decomposition of pyz ligands. These results are well in agreement with the crystal structure of 1.

X-Ray diffraction study§ reveals that 1 crystallizes in the orthorhombic space group Pbcm, and as shown in Fig. 1, the

[a] Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China. E-mail: rbhuang@xmu.edu.cn
[b] State key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, China

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asymmetric unit contains two crystallographically independent Ag^I and half Ag^{II} ions, two and half pyz ligands, one SO_4^{2-}, one HSO_4^- as well as one lattice water molecule. The origin of SO_4^{2-} and HSO_4^- is associated with the reduction of $S_2O_8^{2-}$ by Ag(I).[1] It is of note that the S2–O8 distance (1.549(5) Å) is much longer than the other S–O distances (av. 1.433(6) Å) which enables us to unambiguously discriminate SO_4^{2-} and HSO_4^-. A similar result also has been observed in other publications.[11] Analysis of the local symmetry of the metal atoms and ligands show that Ag1 and one of pyz ligands reside on the crystallographic mirror plane (site occupancy factor (SOF) = 1/2). By consideration of the charge balance, the oxidation state of Ag1 should be assigned to +2, while both Ag2 and Ag3 are +1. Ag1 has distorted tetrahedral geometry and is coordinated by two pyz ligands and two SO_4^{2-} (Ag1–N1 2.186(7), Ag1–N2^i 2.198(6), Ag1–O2^{ii} 2.607(6) Å). The distortion of the tetrahedron can be indicated by the calculated value of the τ_4 parameter introduced by Houser[12] to describe the geometry of a four-coordinate metal system, which is 0.61 for Ag1 (for perfect tetrahedral geometry, τ_4 = 1; for a perfect square-planar geometry, τ_4 = 0). Both Ag2 and Ag3, coordinated by two N atoms and one O atom, show T-shaped geometry. The maximum N–Ag–N angles around Ag2 and Ag3 are 172.79(18) and 176.57(19)°, respectively. The Ag^{II}–N bond distances observed in 1 agree with those found in related systems, e.g., $Ag(pyz)_2(S_2O_8)$,[13] $Ag(2,2'-bipy)_2(NO_3)_2$,[14] and the Ag^I–N and Ag^I–O bond distances also fall in the normal ranges.[15]

Most reported Ag^{II} centers favor a square-planar geometry involving the formation of four hybrid dsp^2 bonds[16] as in the case of Cu^{II}.[17] However, this is clearly not the case for 1 in which the divalent Ag1 adopts an unexpected distorted tetrahedral geometry which may be exerted by a pair of adjacent
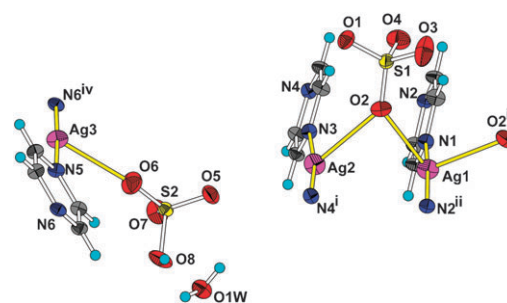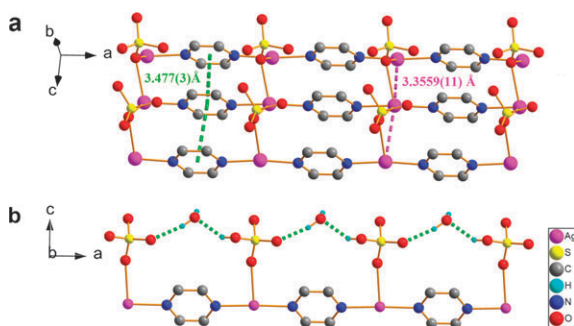

Fig. 1 (a) The coordination environments of Ag centers in 1 with thermal ellipsoids at 30% probability level. Symmetry codes: (i) x − 1, y, z; (ii) −x + 1, y + 1/2, −z + 1/2; (iii) −x + 1, y + 1/2, z; (iv) x + 1, y, z.

Fig. 2 Two kinds of 1D chain motifs in **1**: (a) part A (upper) incorporating $\pi \cdots \pi$ interactions and $Ag^I \cdots Ag^{II}$ interaction, and (b) part B with hydrogen bonds.

symmetry-related Ag^I ions involving rare $Ag^I \cdots Ag^{II}$ interaction (3.3559(11) Å). Despite that the mixed-valent Ag-containing complexes such as $Ag_2F(0,I)$, $AgO(I,III)$ and $Ag(I,III)$-cryptate[18] are well known, mixed $Ag(I,II)$ complexes,[19] especially Ag^I/Ag^{II}–CPs, are rarely reported so far, and to the best of our knowledge, complex **1** is the first mixed-valent Ag^I/Ag^{II} CP.

In the solid state, **1** features two kinds of independent 1D chains: (i) $[Ag^I_2Ag^{II}(SO_4)_2(pyz)_3]_n$ and (ii) $[Ag^I(pyz)(HSO_4)]_n$ (parts A and B, respectively) (Fig. 2). The μ_2-O,O-SO_4^{2-} anions bridge three approximately parallel Ag^{II}-pyz chains to form part A, in which the strong $\pi \cdots \pi$ stacking (3.477(3) Å) between adjacent pairs of pyz ligands and the above–mentioned $Ag^I \cdots Ag^{II}$ interaction consolidate the 1D $[Ag^I_2Ag^{II}(SO_4)_2(pyz)_3]_n$ chain. In part B, the 1D motif is a single chain containing monodentate HSO_4^- which interacts with lattice water molecule through O_{water}–H$\cdots$$O_{hydrosulfate}$ and $O_{hydrosulfate}$–H$\cdots$$O_{water}$ hydrogen bonds (Table S3, ESI†) to form the 1D supramolecular chain incorporating $C_2^2(6)$ linear motifs in graph-set notation.[20] There exists relatively weak $\pi \cdots \pi$ stacking (3.663(3) Å) between adjacent $[Ag^I(pyz)(HSO_4)]_n$ chains. The pyz rings in parts A and B have different orientations generating a mean dihedral angle of 49.8° (Fig. S5, ESI†). Moreover, parts A and B are linked through interchain O_{water}–H$\cdots$$O_{sulfate}$ hydrogen bonds (O1W–H1WA$\cdots$O1 2.770(7) Å) to form a 2D supramolecular sheet where parts A and B arrange alternately along the ac plane (Fig. S6, ESI†).

For comparison, another new 2D Ag–pyz–SO_4^{2-} ternary complex $\{[Ag^I(SO_4)_{0.5}(pyz)]\cdot H_2O\}_n$ (**2**) (see ESI†) containing only Ag(I) ions was also successfully synthesized and characterized. The asymmetric unit of **2** contains one Ag^I, one pyz and half SO_4^{2-} lying on the C_2 axis. The Ag^I is in a T-shaped geometry which is similar to that of univalent Ag2 and Ag3 ions in **1** (Fig. 3a). Differently, in **2**, the approximately orthogonal Ag–pyz linear chains are linked by μ_2-O,O'-SO_4^{2-} to form a 2D double-sheet (Fig. 3b). Interestingly, the SO_4^{2-} and water molecules are hydrogen bonded into a 2D anionic sheet without consideration of the Ag^I–pyz cationic chains (Fig. 3c). Considering the S atoms as four-connected nodes, this anionic sheet can be simplified to a 4^4-**sql** supramolecular net (Fig. 3d). The structural contrasts between **1** and **2** are undoubtedly associated with the valence-dependent inclusion.
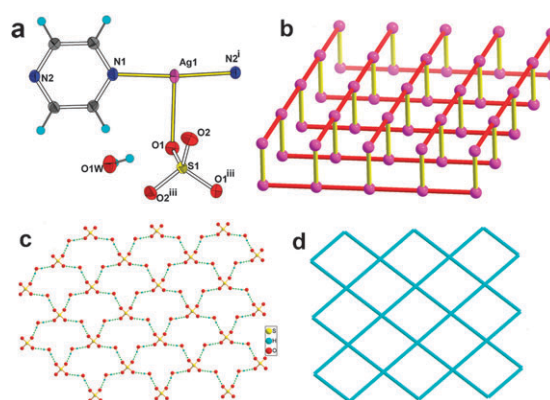

Fig. 3 (a) The coordination environment of Ag^I ion in **2** with thermal ellipsoids at 30% probability level. Symmetry codes: (i) $x - 1/2$, $y - 1/2$, z; (iii) $-x + 1$, y, $-z + 3/2$. (b) The 2D double-sheet, purple ball: Ag; red pillar: pyz; yellow pillar: SO_4^{2-}. (c) SO_4^{2-}–H_2O anionic sheet constructed via O_{water}–H$\cdots$$O_{sulfate}$. (d) Simplified anionic 4^4-**sql** supramolecular net in which S is a four-connected node.

Conductivity measurement (Fig. 4a) on a single crystal $(0.160 \times 0.035 \times 0.031$ cm) of **1** at room temperature shows that it exhibits semiconducting behavior with $\sigma = 2.73 \times 10^{-4}$ S cm^{-1}.[21] Although higher conductivity has been observed in discrete Ag-containing molecules, such as $[Ag_2(ophen)_2]$ (Hophen = $1H$-[1,10]phenanthrolin-2-one),[22] and Ag^I-aromatic compounds,[23] Ag-containing CPs with σ values higher than 10^{-4} S cm^{-1} are still rare (Table S4, ESI†). By examining its structure, the semiconducting property of **1** can be attributed to the somewhat delocalized character between Ag^I and Ag^{II} ions. The electron transfer takes place between adjacent Ag–pyz chains via two possible pathways: $\pi \cdots \pi$ and $Ag^I \cdots Ag^{II}$ interactions. Due to the lack of Ag$\cdots \pi$ interactions which play an essential role to provide the $\pi \rightarrow \pi^*$ and $\pi \rightarrow$ metal/metal $\rightarrow \pi^*$ electron-transfer pathways, **1** exhibits not too high conductivity compared to the well-known Ag^I-aromatic compounds.[23]

Both the absorption and photoluminescence spectra of **1** were measured in the solid state at room temperature. As shown in Fig. 4b, the absorption bands centered at 256 and 354 nm correspond to $\pi \rightarrow \pi^*$ transition of the pyz ligand and the ligand-to-metal charge transfer (LMCT) absorption band,
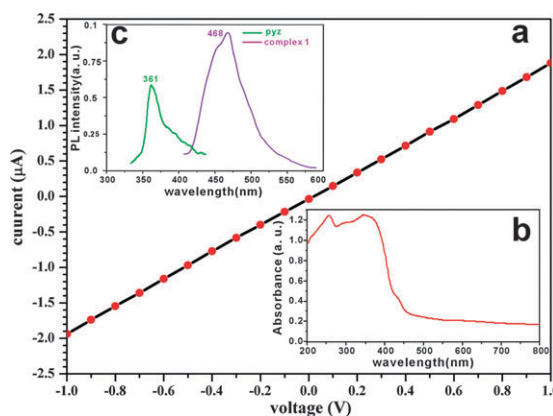

Fig. 4 (a) I–V plot at room temperature of **1**; (b) UV-Vis spectrum of **1** in the solid state; (c) photoluminescence of pyz and complex **1** in the solid state.

respectively. The pale-yellow color of powder of **1** is consistent with the weak absorption at 442 nm. Many heterometallic systems with d^9/d^{10} mixed electronic configurations exhibit rich luminescence behaviors in the solid state at ambient temperature.[24] In contrast, the luminescent properties of homometallic d^9/d^{10} systems have received less attention.[25] Excitation of solid sample **1** at 330 nm produces an emission with a maximum at *ca.* 468 nm (Fig. 4c). When compared to the photoluminescence spectrum of the free pyz ligand ($\lambda_{em} = 361$ nm), the emission band of **1** is red-shifted by more than 100 nm, which could be assigned to an admixture of LMCT and metal-centered (d–s/d–p) transitions[26] modified by $Ag^I \cdots Ag^{II}$ interactions.

In summary, we present an unprecedented 1D mixed-valent Ag^I/Ag^{II} CP which is synthesized by *in situ* redox reaction, and structurally characterized. Moreover, complex **1** exhibits semiconducting and photoluminescent properties.

Notes and references

‡ Synthesis of $\{[Ag^I_2Ag^{II}_{0.5}(SO_4)(HSO_4)(pyz)_{2.5}] \cdot H_2O\}_n$ (**1**): $AgNO_3$ (167 mg, 1 mmol), $Na_2S_2O_8$ (238 mg, 1 mmol) and pyz (80 mg, 1 mmol) in acetonitrile–H_2O media (10 ml, v/v = 1 : 1) were allowed to react in air under ultrasonic treatment (160 W, 40 kHz, 20 min) at 50 °C. The resultant colorless solution was allowed to evaporate slowly at room temperature for one week to give pale-yellow block crystals of **1**. The crystals were isolated by filtration and washed by deionized water and dried in air. Yield: *ca.* 87% based on Ag. Elemental analysis: Anal. Calc. for $Ag_5C_{20}H_{26}N_{10}O_{18}S_4$: C 17.64, H 1.92, N 10.28%. Found: C 17.61, H 1.85, N 10.19%. Selected IR peaks (cm^{-1}): 3453(s), 1631(m), 1389(s), 1193(s), 1120(s), 612(w).
§ *Crystal data* for **1**: $Ag_5C_{20}H_{26}N_{10}O_{18}S_4$, $M_r = 1362.14$ g mol^{-1}, orthorhombic, space group *Pbcm*, $Z = 4$, $T = 298(2)$ K, $a = 7.1428(19)$, $b = 14.203(4)$, $c = 35.245(10)$ Å, $V = 3575.6(17)$ Å^3, $D_c = 2.527$ g cm^{-3}, $R_1 = 0.0493$, w$R_2 = 0.1124$, $\mu = 3.015$ mm^{-1}, $S = 1.073$. X-Ray crystallographic data were collected with a Mo-Kα radiation source ($\lambda = 0.71073$ Å) by using a Rigaku IP diffractometer equipped with graphite monochromator. The structures were solved by direct methods and refined by full-matrix least-squares calculations (F^2) by using the SHELXTL-97 software. All non-H atoms were refined in the anisotropic approximation against F^2 for all reflections. The positions of the water H atoms were assigned to calculated positions with isotropic thermal parameters and refined with the O–H bond length restrained to 0.85 Å.

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