

# Synthesis, Crystal Structure and Characterization of Two Polymeric Silver(I) Complexes Containing Imidazolate Anions

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Two new imidazolate-containing complexes,  $[\text{Ag}_5(\text{Im})_5]_n$  (1) and  $[\text{Ag}(2\text{-MeIm})]_n$  (2), were prepared and characterized by X-ray single crystal structure determination. (1) consists of 1-D chains running along three different directions, namely  $[2 \bar{1} \bar{1}]$ ,  $[2 \bar{1} \bar{1}]$  and  $[2 \bar{1} \bar{1}]$ . This type of packing of chains is unusual. The chains are linked to form a three-dimensional structure through weak Ag...Ag interactions. The silver(I) atom in each chain is linearly coordinated by two nitrogen atoms from different imidazolates and the 1-D chain is somewhat helical due to the geometrical constraints imposed by the 1,3-arrangement of the nitrogen atoms in the imidazolate bridges. (2) is a linear chain in which each silver(I) atom is two-coordinated with the different bridged methylimidazolate nitrogen atoms. The two structures were refined to  $R_1 = 0.0315$  for (1) and  $R_1 = 0.0495$  for (2). Complexes (1) and (2) are sparingly soluble and very stable in  $\text{CH}_3\text{CN}$  containing  $0.1 \text{ mol} \cdot \text{L}^{-1}$  of  $n\text{-Bu}_4\text{NBF}_4$  in the range 2.0 to  $-2.0 \text{ V}$  at room temperature and do not undergo any redox process. When being boiled in a solution of 30% sodium hydroxide for two hours, the large colorless prismatic crystals of (1) and (2) remain unchanged. TG/DTG analyses shows that the two complexes begin to decompose at  $382^\circ\text{C}$  for (1) and  $357^\circ\text{C}$  for (2).

**Keywords** Silver(I) complexes, pyridine complexes, X-ray crystal structure

## INTRODUCTION

Because of the importance of the involvement of histidine in enzymic catalysis, much of the interest in imidazolate bridging has been in a bio-inorganic context, and particularly in the

chemistry of metalloprotein superoxide dismutases. The imidazolate anion, obtained by deprotonation of imidazole, is capable of acting as a bridging ligand. However, the 1,3-arrangement of the nitrogen atoms imposes geometrical constraints such that only one imidazolate bridge is possible between two metal centres. Accordingly, imidazolate-bridged transition metal complexes show high linearity (Steel, 1990). Indeed, many oligomeric and polymeric transition metal complexes have been known for some time to contain imidazolate bridges (Ashby et al., 1978; Carlucci et al., 1994; Inoue and Kubo, 1976; Sundberg and Martin, 1974; Trofimenko, 1972, 1986). But none of those containing silver(I) are believed to be polymeric and are difficult to crystallize (Masciocchi et al., 1994, 1995; Nomiya et al., 1998), and can only be obtained as microcrystalline materials; therefore, all structural information must be extracted from powdered samples only (Masciocchi et al., 1995). Recently, Masciocchi reported the structure of polymeric silver(I) imidazolate  $[\text{Ag}(\text{im})]_n$  (Masciocchi et al., 1994, 1995; Nomiya et al., 1998) by using powder X-ray diffraction data (Masciocchi et al., 1995), and it was found by Nomiya that this compound has excellent antibacterial and antifungal activities (Nomiya et al., 1997). We have reported a study on the cytotoxicity of some silver(I) complexes recently (Chen et al., 2001a and b; Zhu et al., 2001, 2003a, 2003b). In order to investigate the cytotoxicity of silver(I) complexes with imidazolate-containing ligands, we prepared silver(I) complexes containing imidazolate-bridges and determined their molecular structures.

## EXPERIMENTAL

### Materials

Reagents were used as obtained from the Second Chemicals Factory of Shanghai, P.R. China without further purification. Solvents were purified by standard methods before use. The two complexes reported in this article were prepared by a procedure similar to that described by Masciocchi and coworkers (Masciocchi et al., 1994); however, we obtained

Received 8 August 2003; accepted 7 July 2004..

The authors thank the Education Office of Hubei Province, P.R. China for research grant No. 2002B29002 and the Natural Science Foundation of Hubei Province, P.R. China for research grant No. 2003ABB010.

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well-crystallized single crystal samples. C, H, and N elemental analyses were performed with a Perkin-Elmer elemental analyser.

### Electrochemical Analysis

The cyclic voltammograms were measured on an electrochemical analyzer over 2.0 to  $-2.0$  V at room temperature with a sample concentration of  $1.0 \times 10^{-4}$  mol  $\cdot$  L $^{-1}$  in MeCN solution containing *n*-Bu $_4$ NBF $_4$  (0.1 mol  $\cdot$  L $^{-1}$ ) and the scan rate of 100 mV  $\cdot$  s $^{-1}$ . A platinum wire working electrode, a platinum plate auxiliary electrode and a saturated calomel electrode (SCE) reference electrode were employed. All potentials were measured with respect to SCE and the experiments were carried out at ca. 20 °C.

### TG/DTG Analysis

The TG/DTG measurements were carried out by a thermogravimetric analysis system (Model: DSC-822e, Mettler Toledo Company, Switzerland) under high-purity N $_2$ . The amounts of the samples used for TG/DTG analyses were 5.070 mg for (1) and 6.123 mg for (2), and the heating rate was 10 °C min $^{-1}$ .

### X-ray Crystallography

Crystal structure determination was carried out with a Siemens R3m diffractometer equipped with graphite-monochromated MoK $\alpha$  ( $\lambda = 0.71073$ ) with Lorentz polarization and absorption corrections. Accurate cell parameters were derived from least-squares fitting of 25 independent reflections in the 7–15° range. Observable reflections with  $I \geq 2\sigma(I)$  were used in the structure solution and refinements. The structures were solved by direct methods and refined on F $^2$  by full-matrix least-squares methods using SHELX-97. All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were placed in the calculated positions and were assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they are attached and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure-factors calculations. The absolute structure for (1) has been determined with a Flack parameter of  $-0.07(7)$ .

### Synthesis of C $_6$ H $_5$ COOAg

To a suspension solution of C $_6$ H $_5$ CO $_2$ H (12.2 g, 0.1 mol in 100 mL water) was added an aqueous solution of NaOH (4.0 g, 0.1 mol in 10 mL water) with stirring. The resulting solution (pH = 9) was colorless. With slow stirring, to the above solution was added a solution of AgNO $_3$  (17 g, 0.1 mol in 100 mL acetonitrile). Upon slow evaporation in air for 48 h, colorless prismatic crystals were deposited and were collected by filtration, washed with water and dried in a

vacuum desiccator over silica gel; yield, 22 g (95%). Anal. calcd. for C $_7$ H $_5$ AgO $_2$  (FW 229.10): C, 36.72; H, 2.20; Ag, 47.11. Found: C, 36.70; H, 2.30; Ag, 47.02%.

### Synthesis of [Ag $_5$ (Im) $_5$ ] $_n$ (1)

To a 1:1 (v/v) water/acetonitrile solution of [Ag $_2$ (C $_6$ H $_5$ CO $_2$ ) $_2$ ] (229 mg, 1 mmol in 10 mL solution) was added a solution of imidazole (136 mg, 2 mmol in 5 mL acetonitrile). The pH value of the resulting solution is 7. Upon slow vaporating in air for two days, large colorless crystals of (1) suitable for X-ray single crystal determination were deposited and collected by filtration, washed with water, acetonitrile and diethyl ether and dried in a vacuum desiccator over silica gel; yield, 284 mg (81%). Anal. calcd. for C $_3$ H $_3$ N $_2$ Ag (FW 175.07): C, 20.60; H, 1.73; N, 16.01. Found: C, 20.58; H, 1.75; N, 16.92%.

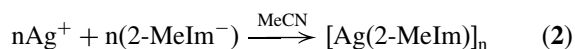
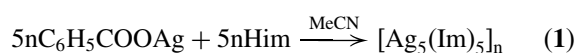
### Synthesis of [Ag(2-Melm)] $_n$ (2)

Replacing imidazole with 2-methylimidazole in the same procedure as for (1), large colorless prismatic crystals of (2) were obtained; yield, 322 mg (85%). Anal. calcd. for C $_4$ H $_5$ N $_2$ Ag (FW 189.10): C, 25.42; H, 2.67; N, 14.82. Found: C, 25.44; H, 2.69; N, 14.65%.

## RESULTS AND DISCUSSION

### Preparation of (1) and (2)

The formation of the two complexes can be expressed as the following equations:



Acetonitrile is the most suitable solvent for the syntheses of the two complexes. When the pH = 6.5–8, large crystals are deposited. According to the insolubility of (1) and (2) in common solvents, it is estimated that the values of 'n' in the formulas of (1) and (2) are close to  $\infty$ . Equimolar amounts of SCN $^-$  or SO $_4^{2-}$  anions, which form very stable compounds with Ag $^+$  ions, do not affect the yields for the formation of (1) and (2). When the pH value is more than 9, a lot of powdered solid will precipitate from the clear reaction solution in a few minutes. We failed to obtain large crystals by recrystallization from the powder solid. When the pH value is less than 5, there is no solid formed in a week.

### Physical Properties

Complexes (1) and (2) are stable in CH $_3$ CN containing 0.1 mol  $\cdot$  L $^{-1}$  of *n*-Bu $_4$ NBF $_4$  in the range 2.0 to  $-2.0$  V at

room temperature and do not undergo any redox processes, which agrees with the very high stability of the two complexes to strong acids and strong bases. When being boiled in a solution of 30% sodium hydroxide (or 37% hydrochloric acid, 10% ammonium thiocyanide, or 10% ethylenetetraacetate) for two hours, the large colorless prismatic crystals of (1) and (2) remain unchanged. However, when heated to boil the microcrystals of (1) and (2) can be easily destroyed in the above solutions. So we expect that the large single crystals of the two complexes (1) and (2) may be developed into some special materials, such as high-temperature tolerable materials.

### Structure Description of $[\text{Ag}_5(\text{Im})_5]_n$ (1)

Complex (1) crystallizes in the orthorhombic system with the space group  $P2_12_12_1$ , as summarized in Table 1.

The structure determination of (1) revealed three different one-dimensional chains running along three different

TABLE 1  
Crystal data<sup>a</sup> for (1) and (2)

Compound	(1)	(2)
Formula	$\text{C}_{30}\text{H}_{30}\text{Ag}_{10}\text{N}_{20}$	$\text{C}_4\text{H}_5\text{AgN}_2$
Fw	1749.44	188.97
Crystal size	$0.10 \times 0.15 \times 0.50$	$0.30 \times 0.35 \times 0.45$
Space group	$P2_12_12_1$	$Cc$
$a$ (Å)	10.798(4)	10.848(3)
$b$ (Å)	13.449(4)	5.9560(10)
$c$ (Å)	14.978(6)	7.875(2)
$\alpha$ (°)	90	90
$\beta$ (°)	90	92.51
$\gamma$ (°)	90	90
$U$ (Å <sup>3</sup> )	2175.1(4)	508.3(2)
$Z$	2	4
$\mu$ (mm <sup>-1</sup> ) (Mo-K $\alpha$ )	0.71073	0.71073
$T$ (K)	293	293
$D_x$ (g cm <sup>-3</sup> )	2.671	2.469
$\mu$ (MoK $\alpha$ ) (cm <sup>-1</sup> )	4.446	3.815
No. of unique reflections	2587	812
No. of observed [ $I \geq 3\sigma(I)$ ]	2144	607
$F(000)$	1640	360
$R_1$ ( $I > 2\sigma(I)$ ) <sup>a</sup>	0.032	0.049
$wR_2$ (all data) <sup>a</sup>	0.061	0.068

$$^a R_1 = \frac{\sum \|F_o\| - |F_c|}{\sum \|F_o\|}, wR_2 = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}, w = [\sigma^2(F_o)^2 + (0.1(\max(0, F_o^2) + 2F_c^2)/3)^2]^{-1}.$$

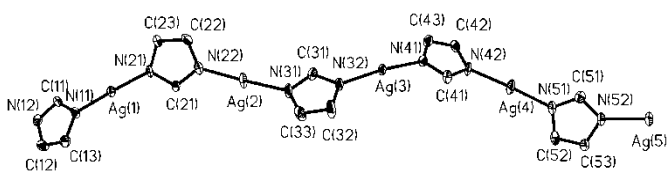


FIG. 1. A perspective view showing the coordination environment in complex (1).

directions, namely  $[2 \bar{1} \bar{1}]$ ,  $[\bar{2} \bar{1} \bar{1}]$ , and  $[2 \bar{1} \bar{1}]$  (the Ag–Ag distance between the adjacent chains is 3.936 Å), as shown in Figures 1 and 2, based upon five crystallographically nonequivalent Ag sites, forming pentanuclear silver entities. Every silver(I) atom in the  $\text{Ag}_5$  unit is linearly coordinated by two nitrogen atoms from different imidazoles, as displayed in Table 2 (the N–Ag–N angles range from 170.1 to 176.5°). The average Ag–N bond length (2.076 Å) is comparable with those in the similar complex  $[\{\text{Ag}(\text{im})\}_n]$  (Masciocchi et al., 1995), but is significantly shorter than the complexes containing silver-imine bonds (Zhu et al., 1999, 2000), indicating the much stronger Ag–N interaction in (1) or in the complex  $[\text{Ag}(\text{Im})_n]$  (Nomiya et al., 1998).

There are five different dihedral angles between the adjacent imidazolato rings, 5.2° around Ag(1), 52.9° (around Ag(2)), 58.2° (around Ag(3)), 42.9° (around Ag(4)) and 34.5° around Ag(5), which are greatly different from those found in the complex  $[\{\text{Ag}(\text{im})\}_n]$ .

A great deal of weak interactions (Ag...Ag distances between 3.120 and 3.266 Å) among the silver atoms in neighboring chains link the chains into a three-dimensional, single-screw structure.

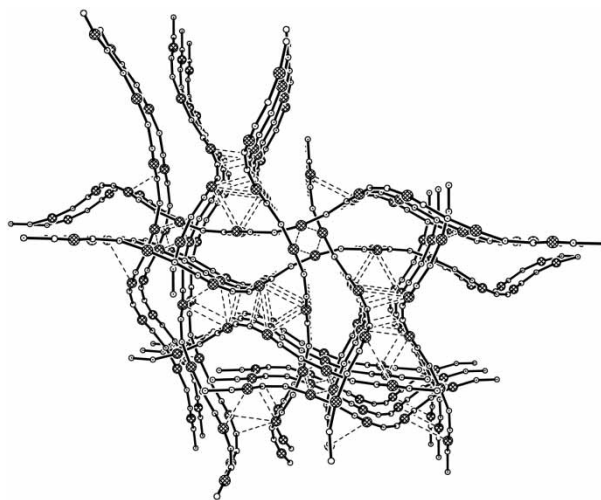


FIG. 2. A perspective view of complex (1) showing the one-dimensional chains running along three different directions  $[2 \bar{1} \bar{1}]$ ,  $[\bar{2} \bar{1} \bar{1}]$ , and  $[2 \bar{1} \bar{1}]$ .

TABLE 2  
Selected bond lengths (Å) and angles (°) for the complexes (1) and (2)

(1)			
Ag(1)–N(11)	2.069(8)	Ag(1)–N(42)	2.063(8)
Ag(1)–Ag(2a)	3.1203(14)	Ag(1)–Ag(2b)	3.2261(13)
Ag(2)–N(21)	2.065(7)	Ag(2)–N(52)	2.078(8)
Ag(1)–Ag(2c)	3.1203(14)	Ag(1)–Ag(2d)	3.2261(13)
Ag(3)–N(31)	2.072(7)	Ag(3)–N(22)	2.088(7)
Ag(4)–N(12e)	2.071(7)	Ag(4)–N(32)	2.079(7)
Ag(4)–Ag(5f)	3.2656(16)	Ag(5)–N(51)	2.075(7)
Ag(5)–N(41)	2.082(7)	Ag(5)–Ag(4g)	3.2656(15)
N(42)–Ag(1)–N(11)	176.2(3)	N(42)–Ag(1)–Ag(2a)	92.2(2)
N(11)–Ag(1)–Ag(2a)	90.4(2)	N(42)–Ag(1)–Ag(2b)	92.7(2)
N(11)–Ag(1)–Ag(2b)	87.3(2)	Ag(2)–Ag(1a)–Ag(2b)	136.72(3)
N(21)–Ag(2)–N(52)	171.1(4)	N(21)–Ag(2)–Ag(1c)	88.7(2)
N(52)–Ag(2)–Ag(1c)	95.9(2)	N(21)–Ag(2)–Ag(1d)	90.6(2)
N(52)–Ag(2)–Ag(1d)	91.3(2)	Ag(1)–Ag(2c)–Ag(1d)	136.03(3)
N(31)–Ag(3)–N(22)	174.9(3)	N(12)–Ag(4e)–N(32)	170.1(3)
N(12)–Ag(4e)–Ag(5f)	80.7(2)	N(32)–Ag(4)–Ag(5f)	108.4(2)
N(51)–Ag(5)–N(41)	176.5(4)	N(51)–Ag(5)–Ag(4g)	80.2(3)
N(41)–Ag(5)–Ag(4g)	101.8(2)		
(2)			
Ag(1)–N(1)	2.012(8)	Ag(1)–N(2a)	2.110(11)
N(1)–Ag(1)–N(2a)	148.5(5)		

### Structure Description of [Ag(2-Melm)]<sub>n</sub> (2)

The structure of (2) displays a linear arrangement in which each silver(I) atom is two-coordinated with different bridging methylimidazolate nitrogen atoms. The structure is highly symmetrical and the coordination environments of the silvers are similar. The coordination environment of compounds (2) and the repeated unit are shown in Figure 3. The average Ag–N bond length (2.06(1) Å) is close to that in complex (1). The N–Ag–N angle in the chain is 148.5(5)°, which is significantly smaller than that (> 170°) in (1), being likely due to the effect of the repelling interaction between the methyl groups in (2). We can see from Figure 4

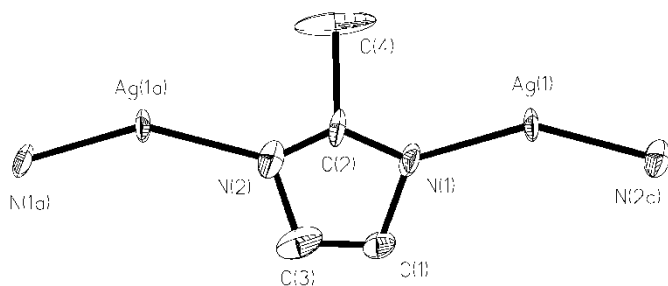


FIG. 3. A perspective view showing the coordination environment in complex (2).

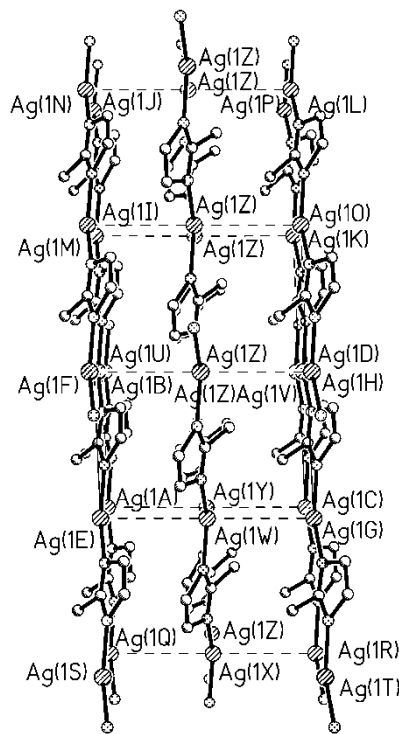


FIG. 4. A perspective view of a part of [Ag(2-Melm)]<sub>n</sub> (2). Hydrogen atoms are omitted for clarity.

that all the methyl groups of the methylimidazolates in one chain point in one direction. There exist weak silver-silver interactions (Ag...Ag distances 3.933 and 3.942 Å) between the chains, which join the complex to form a three-dimensional structure.

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