

Two New Silver(I) Ammine Complexes by Displacement Reaction Between $[\text{Ag}(\text{NH}_3)_2]^+$ Ions and Different Pyridine-4,5-Imidazoledicarboxylic Acids

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Keywords: Ammine ligands; Pyridine-4,5-imidazoledicarboxylic acid; Silver; Substitution reaction; X-ray diffraction

Abstract. $[\text{Ag}(\text{NH}_3)_2]^+$ ions are chosen as an initial reaction precursor because of its simple displacement reaction and intrinsic arrangement as well as specific coordination directionality. Two new silver(I) ammine complexes, $\text{Ag}_2(\text{NH}_3)_2\text{HL}^2$ (**2**) and $\text{Ag}_2(\text{NH}_3)_2\text{HL}^3$ (**3**), were obtained by a simple substitution reaction between $[\text{Ag}(\text{NH}_3)_2]^+$ ions and pyridine-4,5-imidazoledicarboxylic acid $[\text{H}_3\text{L}^2 = 2\text{-(3'-pyridyl) 4,5-im-}$

idazoledicarboxylic acid and $\text{H}_3\text{L}^3 = 2\text{-(4'-pyridyl) 4,5-imidazoledicarboxylic acid}$]. Silver dimers are connected into a 2D layer and 1D chain in complexes **2** and **3**, respectively. In complex **2** two kinds of displacement reactions (mono-substituting and bis-substituting) occurred between the ammine molecules in $[\text{Ag}(\text{NH}_3)_2]^+$ ions and H_3L^2 , however, only the mono-substituting reaction occurs in complex **3**.

Introduction

The research interest in coordination polymers is rapidly increasing because of their intriguing structures and wide potential applications as functional materials.^[1–9] Promising results were achieved and startling applications are being developed, however, the rational design and synthesis of coordination polymers with unique structure and function still remain a long-term challenge. The self-assembly process of coordination polymers is frequently influenced by various factors such as medium, pH value of solution, temperature, the nature of metal ions, coordination arrangement, stereochemistry, and number of coordination donors provided by organic ligands.^[10–16] Insight into the self-assembly process can be obtained by carrying out systematic studies under completely similar reaction conditions, while imposing subtle alterations such as changing the anions, the crystallization solvent, pH value of solution, or substituent groups of organic ligands, etc. These strategies undoubtedly help to shed light on the prediction, design, and synthesis of the target complexes.

Silver is a particularly versatile transition metal in its coordination number and arrangement,^[17–19] but the silver coordination geometry in $[\text{Ag}(\text{NH}_3)_2]^+$ ion always keeps linear.^[20] Compared with the Ag^+ ion, $[\text{Ag}(\text{NH}_3)_2]^+$ as the selected connector features two special characteristics: (1) The preparation

of silver coordination complexes under aqueous conditions often results in the formation of very insoluble “silver salts”, however, the use of ammoniacal conditions can enhance the solubility of the silver connectors and organic linkers. (2) $[\text{Ag}(\text{NH}_3)_2]^+$ with an intrinsic geometry as well as specific coordination directionality can guarantee subsequent substitution processes that occur between the connectors and the organic ligands.

Pyridine-4,5-imidazoledicarboxylic acids as selected organic ligands are introduced based on following considerations: (1) Similar to 4,5-imidazoledicarboxylic acid, the pyridine-4,5-imidazoledicarboxylic acids, which can be partly or fully deprotonated dependent on the pH level, are especially good linkers not only because of their various coordination modes to metal ions, but also because of their abilities to act as hydrogen-bond acceptors and donors to assemble various supramolecular structures.^[21, 22] (2) The different coordination activity between imidazole groups and carboxylate groups with metal ions results in selective substitution reactions. (3) The two nitrogen atoms in the imidazole ring can gear the coordination orientation, which is similar to Si–O–Si bond angles in zeolites or $M\text{--}IM\text{--}M$ bond angles in zeolitic imidazolate frameworks (ZIF).^[23, 24] (4) The study on coordination chemistry of pyridine-4,5-imidazoledicarboxylic acids is relatively rare.^[21, 22]

Recently, a new silver(I) ammine complex based on 4,5-imidazoledicarboxylic acid, namely, $[\text{Ag}_2(\text{C}_5\text{H}_2\text{N}_2\text{O}_4)(\text{NH}_3)_2]$ (**1**), has been reported by our group, in which only one NH_3 molecular in one $[\text{Ag}(\text{NH}_3)_2]^+$ ion was displaced.^[25] The relative studies were carried out through reactions of $[\text{Ag}(\text{NH}_3)_2]^+$ ion and derivatives of 4,5-imidazoledicarboxylic acid to investigate the influence of different organic linkers with 4,5-imidazoledicarboxylic acid on the construction of silver(I) ammine frameworks. Two new silver(I) ammine complexes based on

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/zaac.201000269> or from the author.

different pyridine-4,5-dicarboxylic acids, namely, $\text{Ag}_2(\text{NH}_3)\text{HL}^2$ (**2**) and $\text{Ag}_2(\text{NH}_3)_2\text{HL}^3$ (**3**) were synthesized at room temperature. By comparison, different pyridine-4,5-imidazoledicarboxylic acids, which adopt various coordination modes, and steric hindrance are crucial factors for the formation of the different silver(I) ammine frameworks.

Experimental Section

Materials and Methods: All chemicals purchased were of reagent grade and used without further purification. Elemental analysis (C, H, N) was performed with a Perkin–Elmer 240C elemental analyzer. The IR spectrum was measured with a Perkin–Elmer Spectrum One FT-IR spectrometer using KBr pellets. Thermogravimetric analysis (TGA) was performed with a Perkin–Elmer TGA-7000 thermogravimetric analyzer under flowing air at a temperature ramp rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. The luminescence properties were measured with a Perkin–Elmer LS55 spectrometer.

Syntheses of H_3L^2 and H_3L^3

The preparation of H_3L^2 was presented as an example, and H_3L^3 was obtained by essentially the same procedure as H_3L^2 .

Synthesis of 2-(3'-Pyridyl)-benzimidazole: A mixture of *o*-phenylenediamine (2.16 g, 20 mmol), nicotinic acid (2.46 g, 20 mmol), and polyphosphoric acid (PPA, 50 g) was stirred at $180\text{ }^\circ\text{C}$ for 4 h under nitrogen. Afterwards, the mixture was cooled to $100\text{ }^\circ\text{C}$ and poured into water (400 mL). After the PPA was dissolved, the resulting solution was cooled and the pH was adjusted to 7 by the addition of NaOH. The precipitated solid was filtered off. The crude product was recrystallized from alcohol and water, the yields obtained 50 %.

Synthesis of H_3L^2 : 2-(3'-pyridyl)-benzimidazole (1.8 g, 9.3 mmol) was added to a mixture of concentrated sulfuric acid (15 mL) and water (19 mL) at $90\text{ }^\circ\text{C}$. This was followed by the careful addition of powdered potassium dichromate (12 g). After 20 minutes the mixture was quenched with ice-cold water and cooled to $0\text{ }^\circ\text{C}$. Crystallization was induced by scratching the sides of the vessel. The precipitated acid was filtered and washed with water, alcohol, and finally with diethyl ether.

Syntheses of Complexes **2** and **3**

Synthesis of $\text{Ag}_2(\text{NH}_3)\text{HL}^2$ (2**):** A solution of H_3L^2 (10 mg, 0.05 mmol) in water (2 mL) containing triethylamine (14 μL , 1 mmol) was directly mixed with a solution of AgNO_3 in aqueous ammonia (2 mL, 25 %) and the resulted yellow solution was allowed to crystallize slowly at room temperature in the dark. After one week, brown single crystals suitable for X-ray diffraction in 35 % yield (based on H_3L^2) were collected by filtration, washed with small amounts of water and dried in air. $\text{C}_{10}\text{H}_8\text{Ag}_2\text{N}_4\text{O}_4$ (463.94): calcd.: C 25.86; H 1.72; N 10.35 %; found: C 25.91; H 1.66; N 10.37 %. IR (KBr): $\tilde{\nu} = 3415\text{ w}$, 3132 m , 1602 s , 1358 s , 1068 m , 739 s , 628 m cm^{-1} (w = weak, m = medium, s = strong).

Synthesis of $\text{Ag}_2(\text{NH}_3)_2\text{HL}^3$ (3**):** Complex **3** was prepared in the same way with complex **2** except that H_3L^3 (10 mg, 0.05 mmol) was used instead of H_3L^2 (10 mg, 0.05 mmol). After one week, brown single crystals suitable for X-ray diffraction in 51 % yield (based on H_3L^3) were collected by filtration, washed with small amounts of water and

dried in air. $\text{C}_{10}\text{H}_{11}\text{Ag}_2\text{N}_5\text{O}_4$ (480.98): calcd.: C 24.95; H 2.29; N 12.47 %; found: C 24.91; H 2.36; N 12.37 %. IR (KBr): $\tilde{\nu} = 3300\text{ w}$, 3142 m , 1668 m , 1607 s , 1347 s , 1065 m , 783 s , 668 m cm^{-1} .

Crystal Structure Determination: The crystal structures were determined by single-crystal X-ray diffraction. The reflection data were collected with a Bruker P4 CCD area-detector diffractometer (Mo- K_α radiation, graphite monochromator) at room temperature with ω -scan mode. Empirical adsorption correction was applied to all data using the SADABS program. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL 97 software.^[26] Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference maps and refined with isotropic temperature factors in complexes **2** and **3**. All calculations were carried out using SHELXTL 97 and PLATON 99.^[27] The crystallographic data and pertinent information are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. Hydrogen bonds are listed in Table 3.

CCDC-742091 and CCDC-742092 for complexes **2** and **3**, respectively, contain the supplementary crystallographic data. These data can be obtained free of charge from CCDC The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223336033; or E-Mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Supporting Information (see footnote on the first page of this article): Coordination environments of the silver atoms in complexes **2** and **3**. TGA curves of complexes **2** and **3**.

Results and Discussion

Synthesis

Crystals of silver carboxylate complexes in good quality could be obtained from the mixture of $\text{Ag}[(\text{NH}_3)_2]\text{NO}_3$, aqueous ammonia, and derivatives of 4,5-imidazoledicarboxylic acid, however, reactions of derivatives of 4,5-imidazoledicarboxylic acid with silver(I) ions in presence of a base like NaOH usually result in insoluble colorless solids, which obstruct further structural studies by X-ray single crystal diffraction. The derivatives of 4,5-imidazoledicarboxylic acid containing triethylamine are easier to solve in water than those containing ammonia or NaOH. Ammonia here may serve as: (a) a ligand competing with carboxylate oxygen that keeps the coordination arrangement of silver linear; (b) a ligand to form $[\text{Ag}(\text{NH}_3)_2]^+$, which may slower the reaction rate between Ag^+ and the organic linker and can facilitate the growth of single crystals.

Crystal Structure of Complex **2**

The crystal structure analysis reveals that complex **2** crystallizes in monoclinic system with space group $P2_1/n$. The asymmetric unit consists of two crystallographically independent Ag^+ ions, one partly deprotonated 2-(3'-pyridyl) 4,5-imidazoledicarboxylic acid (HL^2) ligand and one ammonia molecule. The Ag1 atom adopts a linear arrangement constructed by two nitrogen atoms from an ammonia molecule (N1) and from the

Table 1. Crystal data and structure refinement for **2** and **3**.

Complex	2	3
Empirical formula	C ₁₀ H ₈ Ag ₂ N ₄ O ₄	C ₁₀ H ₁₁ Ag ₂ N ₅ O ₄
Formula weight	463.94	480.98
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / Å	11.3560(7)	10.2073(4)
<i>b</i> / Å	7.0833(5)	9.9453(4)
<i>c</i> / Å	15.1125(10)	13.4594(6)
α / °	90	90
β / °	101.3750(10)	111.8280(10)
γ / °	90	90
Volume / Å ³	1191.74(14)	1268.37(9)
<i>Z</i>	4	4
ρ_{calc} / g·cm ^{−3}	2.586	2.519
Absorption coef. / mm ^{−1}	3.306	3.113
Crystal size / mm	0.21 × 0.24 × 0.29	0.24 × 0.15 × 0.08
θ range / °	2.06–26.10	2.62–26.09
Reflections collected	6387	6857
Unique reflections (<i>R</i> _{int})	2366 [<i>R</i> (int) = 0.0265]	2517 [<i>R</i> (int) = 0.0218]
Completeness to theta	99.7 %	99.7 %
Goodness-of-fit on <i>F</i> ²	1.051	1.084
<i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)] ^{a)}	<i>R</i> ₁ = 0.0241, <i>wR</i> ₂ = 0.0530	<i>R</i> ₁ = 0.0246, <i>wR</i> ₂ = 0.0609
<i>R</i> (all data) ^{a)}	<i>R</i> ₁ = 0.0312, <i>wR</i> ₂ = 0.0558	<i>R</i> ₁ = 0.0264, <i>wR</i> ₂ = 0.0617

a) $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; $wR = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Bond lengths / Å and angles / ° for complexes **2** and **3**.

2			
Ag(1)–N(1)	2.119(4)	Ag(2)–N(4)	2.178(3)
Ag(1)–N(2)	2.129(3)	N(1)–Ag(1)–N(2)	168.51(13)
Ag(1)–Ag(2)	3.106(5)	N(3)–Ag(2)–N(4)	177.31(11)
Ag(2)–N(3)	2.174(3)		
3			
N(1)–Ag(1)#1	2.151(3)	N(4)–Ag(1)–N(1)#2	174.41(13)
Ag(1)–N(4)	2.142(3)	Ag(2)–N(2)	2.153(3)
Ag(1)–Ag(2)	3.136(4)	N(5)–Ag(2)–N(2)	178.73(13)
Ag(2)–N(5)	2.136(3)		

Symmetry transformations used to generate equivalent atoms: #1: $-x+3/2, y+1/2, -z+3/2$; #2: $-x+3/2, y-1/2, -z+3/2$.

imidazole unit (N2) of HL² ligand, respectively. Ag2 adopts a coordination arrangement similar to the one of Ag1, but the two nitrogen atoms stem from the imidazole unit (N3) and the pyridyl group (N4) of two different HL² ligands, as shown in Figure S1a (Supporting information). The Ag–N distances range from 2.119(4) to 2.178(3) Å, and the N–Ag–N bond angles range from 168.51(13) to 177.31(11)°. The bond lengths and bond angles of silver in complex **2** are similar with the reported complex, Ag(im), (Him = imidazole),^[28] and the corresponding bond lengths and angles around the silver ions are given in Table 2. It is worth to note that the bond lengths of Ag–O [*d*(Ag1···O3) = 2.7631 Å, *d*(Ag2···O1) = 2.6975 Å] are much longer than those observed in the reported silver carboxylate complexes,^[29] which indicate weak interactions between the silver atoms and the carboxylate oxygen atoms. It is assumed that the silver atom adopts linear coordination arrange-

Table 3. Hydrogen bonds for complexes **2** and **3**.

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	<DHA
2				
N1–H1···O4#1	0.704	2.393	3.088	169.66
N1–H2···O2#2	0.845	2.152	2.982	167.48
N1–H3···O1#3	0.861	2.228	3.088	175.51
O2–H8···O4#4	1.082	1.348	2.427	174.00
3				
N4–H10···O3#5	0.900	2.218	3.095	164.72
N5–H7···O2#6	0.823	2.395	3.171	157.49
N4–H11···O2	0.882	2.566	3.395	156.92
N5–H6···O4#7	0.935	2.085	3.014	171.95
N5–H8···O4#8	0.815	2.535	3.156	133.93
N4–H9···O1#9	0.803	2.133	2.935	176.48

Symmetry codes: #1: $-x+3/2, y-1/2, -z+3/2$; #2: $-x+5/2, y-1/2, -z+3/2$; #3: $x, y-1, z$; #4: $-x+2, -y+1, -z+2$; #5: $-x+1, -y+2, -z+1$; #6: $-x+1/2, y-1/2, -z+3/2$; #7: $x, y-1, z$; #8: $-x+1, -y+2, -z+2$; #9: $-x+1/2, y-1/2, -z+3/2$.

ment. The weak interactions between silver atoms and the carboxylate oxygen atoms result in a Ag–IM–Ag angle (149.93°) that deviates from Si–O–Si (145°).

In complex **2**, Ag1 and Ag2 are joined into a Ag1...Ag2 dimer through short Ag...Ag interactions [$d(\text{Ag1}\cdots\text{Ag2}) = 3.1065(5) \text{ \AA}$]. Two Ag dimers were assembled into a $\text{Ag}_2(\text{HL}^2)_2\text{Ag}_2$ building block through two imidazole groups from two different HL^2 ligands (Figure 1). Strong $\pi\cdots\pi$ interactions between HL^2 ligands (face-to-face distance of $3.3655 \text{ \AA}$ and offset angle 7.07°) enforce the $\text{Ag}_2(\text{HL}^2)_2\text{Ag}_2$ building block. The $\text{Ag}_2(\text{HL}^2)_2\text{Ag}_2$ building blocks are linked into a 2D layer through the interaction between Ag2 and pyridyl group of 2-(3'-pyridyl) 4,5-imidazoledicarboxylic acid along the *bc* plane (Figure 1). Interestingly, Ag2 ions are linked by HL^2 ligand in a μ_3 mode (Figure S1b) into a left-hand and a right-hand 2_1 helix with helical pitch of $7.833 \text{ \AA}$ along *b* axis in the 2D layer, respectively (Figure 2). Left-hand and right-hand chains are joined together through short Ag1...Ag2 contacts. Hydrogen bonds within layers further enforce the 2D structure stability (N1–H1...O4, N1–H3...O1 and O2–H8...O4).

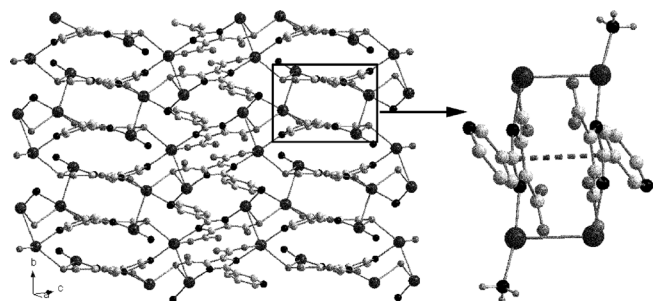


Figure 1. 2D layer constructed by $\text{Ag}_2(\text{HL}^2)_2\text{Ag}_2$ units in complex **2**.

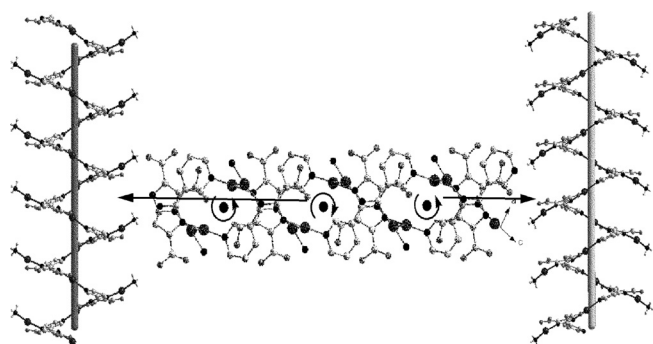


Figure 2. Alternative left-hand and right-hand helical chains in 2D layer of complex **2**.

Crystal Structure of Complex **3**

The crystal structure analysis reveals that complex **3** crystallize in monoclinic system with space group $P2_1/n$. The asymmetric unit consists of two crystallographically independent Ag^+ ions, one partly deprotonated 2-(4'-pyridyl) 4,5-imidazoledicarboxylic acid (HL^3) ligand and two ammonia molecules. The atoms Ag1 and Ag2 both adopt a linear arrangement con-

structed by two nitrogen atoms from an ammonia molecule and from the imidazole unit of HL^3 ligand, respectively (Figure S2a). The Ag–N distances range from $2.136(3)$ to $2.153(3) \text{ \AA}$, and the N–Ag–N bond angles range from $174.41(13)$ to $178.73(13)^\circ$. The corresponding N–Ag–N bond angles listed in Table 2 further illustrate that linear coordination environments with minor geometric variation exist for complex **3**. The bond lengths of Ag–O [$d(\text{Ag1}\cdots\text{O3}) = 2.5598 \text{ \AA}$, $d(\text{Ag2}\cdots\text{O2}) = 2.5751 \text{ \AA}$] are slightly shorter than those observed in complexes **1** and **2**, which indicate that the weak interactions between Ag^1 and the carboxylate oxygen atom in complex **3** are stronger than those in complexes **1** and **2**, however, this is not able to change the coordination orientation of the imidazole ring in HL^3 ligand.

In complex **3**, the atoms Ag1 and Ag2 are assembled into a Ag1...Ag2 dimer through short Ag...Ag interactions [$d(\text{Ag1}\cdots\text{Ag2}) = 3.1361(4) \text{ \AA}$]. Due to larger steric hindrance of 4,5-imidazoledicarboxylic acid, the HL^3 ligands in the silver dimer are perpendicular to one another, the corresponding torsion angle amounts 92.299° . Larger steric hindrance of the organic linkers prevents formation of silver tetramers as complex **1**. Each silver dimer is linked into a 1D chain by two HL^3 ligands (Figure S2b). Compared with complex **2**, the pyridyl group of HL^3 is not coordinated to the silver atom, so a 2D layer like that of complex **2** is not formed. Hydrogen bonds within the chain further enforce the 1D structure stability (N5–H6...O4, N4–H11...O2). The 1D chain is linked into a 3D supramolecular network through hydrogen bonds among chains (Figure 3), and the corresponding hydrogen bonds are listed in Table 3.

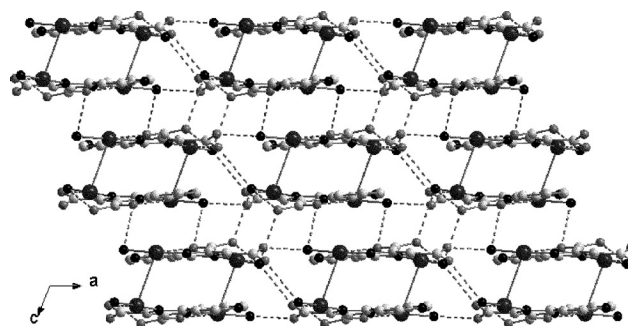


Figure 3. 3D supramolecular network in complex **3**.

TG Curves of Complexes **2** and **3**

The thermal behavior of complex **2** was studied from 25°C to 700°C under air. The thermogravimetric analysis (Figure S3) revealed that complex **2** decomposes through two major processes. The first loss amounts approximately 28.05 % in the range of $200\text{--}345^\circ\text{C}$, corresponding to the weight loss of NH_3 and part of the HL^2 ligand. The second weight loss occurs between 345 and 434°C and is characteristic of the combustion of the remaining part of the HL^2 ligand moiety. The total weight loss of complex **2** amounts to 54.06 % (calcd. 53.44 %).

The thermogravimetric analysis of complex **3** (Figure S4) revealed that complex **3** also decomposes through two major processes. The first loss amounts approximately 25.67 % in the range of 200–340 °C, corresponding to the weight loss of NH₃ and part of the HL³ ligand. The second weight loss (26.44 %) occurs between 340 and 400 °C and is assigned to the combustion of the remaining part of the HL³ ligand moiety. The total weight loss of complex **3** amounts to 52.11 % (calcd. 55.09 %).

Luminescence Properties

The photoluminescence spectra of complexes **2** and **3** as well as those of the ligands H₃L² and H₃L³ are shown in Figure 4. The ligands H₃L² and H₃L³ both exhibit blue photoluminescence with emission maxima at 440 and 468 nm upon excitation at 380 nm, respectively. Similarly, complexes **2** and **3** also exhibit blue photoluminescence with emission maxima at 441 and 422 nm upon excitation at 365 nm, respectively. Compared with the photoluminescence spectra of H₃L² and complex **2**, we find that the maximum emission wavelength of complex **2** is similar to that of H₃L² ligand. Although the maximum emission wavelengths of complex **3** undergo a very slight blueshift, the emission bands for complexes **3** are very similar to those found for the free H₃L³ ligand in terms of position and band shape. Therefore, the emission bands of complexes **2** and **3** are mainly due to an intraligand emission state similar with the reported d¹⁰ metal complexes with N-donor carboxylate ligands.^[30, 31] The intensity increase of the luminescence for these complexes than their corresponding ligands may be attributed to the chelation of the ligand to the metal atom, which increases the rigidity of HL² or HL³ and reduces the nonradiative relaxation process.

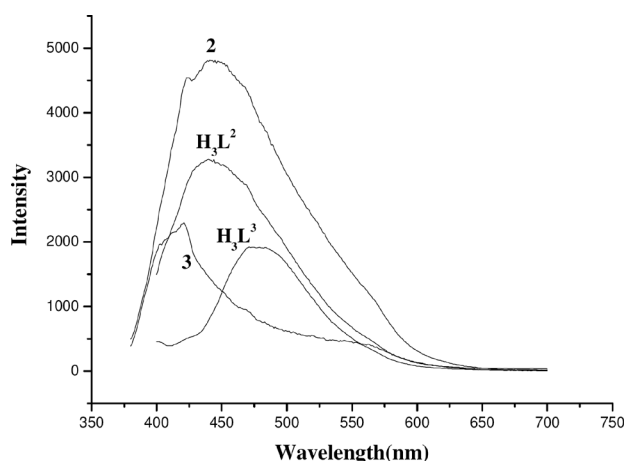


Figure 4. Solid-state emission spectra for complexes **2** and **3** as well as ligands H₃L² and H₃L³ at room temperature.

Discussion

Although the rational design and synthesis of target complexes is still a great challenge, exploiting a simple system

that allows modeling and the study of phenomena, which are superimposed upon a more complicated, multi-component system, is helpful to establish general principles. After careful consideration, [Ag(NH₃)₂]⁺ ions are chosen as an initial reaction precursor because of its simple displacement reaction and intrinsic arrangement as well as specific coordination directionality. We obtained three silver(I) ammine complexes when [Ag(NH₃)₂]⁺ ions react with the organic linkers containing 4,5-imidazoledicarboxylic acid. X-ray single crystal diffraction reveals that the coordinations of Ag^I in complexes **1–3** are basically linear within minor differences. The mono-substituting reaction of [Ag(NH₃)₂]⁺ ions occurred in complexes **1** and **3**, however, both mono- and bis-substituting reactions occurred in complex **2**. The possible reasons of the formation of this kind of silver(I) ammine complexes are as follows: (1) coordination selectivity and orientation of the ligands H₃L¹–H₃L³ play an important role in the formation of silver(I) ammine complexes, (2) the strong negative induction effect of carboxylate decreases the coordination ability of the imidazole group of the organic linkers containing 4,5-imidazoledicarboxylic acid, (3) compared with nitrogen donors, such as imidazole, 4,4'-bipyridine, and pyrazine etc., larger steric hindrance of the organic linkers containing 4,5-imidazoledicarboxylic acid prevents further displacement reactions of the [Ag(NH₃)₂]⁺ ions. In complexes **1–3**, 4,5-imidazoledicarboxylic acid results in the formation of silver tetramer in complex **1**, however, the larger steric hindrance of pyridine-4,5-imidazoledicarboxylic acid prevents the silver dimers to form silver tetramers in complexes **2** and **3** through short Ag...Ag contacts. The organic linkers containing 4,5-imidazoledicarboxylic acid play an important role in the formation of silver(I) ammine complexes: they (1) act as bridging bis-monodentate nitrogen donors, (2) prevent the further formation of displacement reaction of [Ag(NH₃)₂]⁺ ions due to steric hindrance, (3) act as a good acceptor of hydrogen bonds.

Conclusions

[Ag(NH₃)₂]⁺ ions are chosen as initial reaction precursor because of their simple displacement reaction and intrinsic arrangement as well as specific coordination directionality. Two new silver(I) ammine complexes were obtained by a simple substitution reaction between [Ag(NH₃)₂]⁺ ions and different pyridine-4,5-imidazoledicarboxylic acids. The results revealed that the organic linkers containing 4,5-imidazoledicarboxylic acid play an important role in the formation of silver(I) ammine complexes: they (1) act as bridging bis-monodentate nitrogen donors, (2) prevent the further formation of displacement reaction of [Ag(NH₃)₂]⁺ ions due to steric hindrance, (3) act as a good acceptor of hydrogen bonding. Although we are so far unable to control the formation of target silver ammine complexes, the unusual bonding configuration of silver(I) ammine complexes resulting from [Ag(NH₃)₂]⁺ ion and the derivatives of 4,5-imidazoledicarboxylic acid may be useful for designing new silver-based materials. Study on the porous metal-organic frameworks constructed by the organic linkers containing 4,5-imidazoledicarboxylic acid will be reported.

Acknowledgement

This work was supported by the *Natural Science Young Scholars Foundation of North University of China* and the *Scientific Research Start-up Foundation of North University of China*.

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Received: July 6, 2010

Published Online: September 29, 2010