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两个含 1-(1-萘甲基)咪唑的化合物:晶体结构和弱相互作用

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摘要:1-(1-萘甲基)咪唑(L)和盐酸反应生成 1-(1-萘甲基)咪唑盐酸盐 L·HCl (1),在这个化合物中通过 π-π 堆积相互作用和氢键形成了二维超分子层。1-(1-萘甲基)咪唑(L)和 $AgPF_6$ 反应生成单核银配合物$[L]_2AgPF_6$ (**2**),在这个化合物中通过 2 个类型的 π-π 堆积相互作用形成了二维超分子层。测定了 L,**1** 和 **2** 的荧光发射光谱。

关键词:萘甲基咪唑;银配合物;π-π 堆积相互;氢键
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Two New Compounds with 1-(1-Naphthylmethyl)imidazole: Crystal Structure and Weak Interactions

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Abstract: 1-(1-Naphthylmethyl)imidazole (L) was reacted with hydrochloric acid to afford 1-(1-Naphthylmethyl) imidazolium chloride, L·HCl (**1**). In compound **1** 2D supramolecular layers were formed through π-π stacking interactions and hydrogen bonds. Reaction of L with $AgPF_6$ afforded a mononuclear complex, $[L]_2AgPF_6$ (2). In complex **2** 2D supramolecular layers are formed through both types of π-π stacking interactions. The fluorescence emission spectra of L, **1** and **2** are described. CCDC: 648611, **1**; 648610, **2**.

Key words: naphthylmethylimidazole; silver complex; π-π interactions; hydrogen bonds

0 Introduction

Metallosupramolecular species assembled from transition metals and organic ligands with novel structures and properties have been extensively studied due to their intriguing structural diversity and potential applications as functional materials[1,2]. In crystal engineering the most important diving forces are coordination[3,4], however, some weak interactions, such as hydrogen bonding[5,6] and π-π stacking interactions[7], often affect the structures of complexes, and they can further link discrete subunits or low-dimentional entities into high-dimentional supramolecular networks[8,9]. Ligands containing imidazolyl ring play important roles in coordination chemistry, and they can coordinate with a variety of transition metals to form one-, two- and three-

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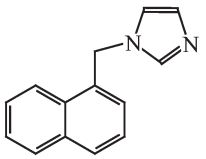
dimentional coordination polymers throuth the use of nitrogen atom of imidazolyl[10,11]. Herein, we report the preparations, crystal structures and weak interactions of 1-(1-naphthylmethyl)imidazolium chloride L·HCl (**1**) and silver complex $[L]_2AgPF_6$ (**2**) (L=1-(1-naphthylmethyl)imidazole).



L

1 Experimental

1.1 Physical measurements

Melting points were determined with a Boetius Block apparatus. ^{1}H NMR spectra was recorded on a Varian Mercury Vx 300 spectrometer at 300 MHz. Chemical shifts, δ, are reported in ppm relative to the internal standard TMS for ^{1}H NMR. Elemental analyses were measured using a Perkin-Elmer 2400C Elemental Analyzer. IR spectra (KBr) were taken on an Bruker Equinox 55 spectrometer. The luminescent spectra were conducted on Cary eclipse fluorescence spectrophotometer.

1.2 Synthesis of 1-(1-naphthylmethyl) imidazole (L)

A 1,4-dioxane solution (50 mL) of imidazole (2.119 g, 31 mmol) was added to a suspension of oil-free sodium hydride (1.364 g, 34 mmol) in 1,4-dioxane (100 mL) and stirred for 1 h at 90 ℃. Then a 1,4-dioxane (50 mL) solution of 1-chloromethylnaphthalene (5.000 g, 28 mmol) was added dropwise to above the solution. The mixture was stirred for 22 h at 90 ℃, and a brown solution was obtained. The solvent was removed with a rotary evaporator and H_2O (100 mL) was added to the residue. Then the solution was extracted with CH_2Cl_2 (3×50 mL), and the extracting solution was dried with anhydrous $MgSO_4$. After removing CH_2Cl_2, a brown viscous solid was obtained, which was recrystallized from EtOAc/petroleum ether to give a white solid of 1-(1-naphthylmethyl) imidazole. Yield: 5.011 g (85%); m.p.: 75~77 ℃. ^{1}H NMR (300 MH_Z, $CDCl_3$): δ 7.95~7.87(m, 3H), 7.61(s, 1H), 7.58~7.54(m, 2H), 7.46 (t, 1H), 7.19(d, 1H), 7.12(s, 1H), 6.95(s, 1H), 5.61(s, 2H).

1.3 Synthesis of L·HCl (1)

Ligand (L) (2.000 g, 9.6 mmol) was reacted with hydrochloric acid (8 mL, 6 mol·L^{-1}) to afford L·HCl (**1**) as a pale yellow solid. Yield: 2.618 g (94%); m.p.: 141~143 ℃. Anal. Calcd for $C_{14}H_{13}N_2Cl$ (%): C 68.71, H 5.35, N 11.45. Found (%): C 68.43, H 5.64, N 11.76. ^{1}H NMR (300 MH_Z, $CDCl_3$): δ 8.72 (s, 1H, 2-imiH), 8.00~8.11 (m, 3H, NpH), 7.50~7.95 (m, 5H, NpH or imiH), 7.27(s, 1H, 4 or 5-imiH), 5.06(s, 2H, CH_2), 3.45 (s, 1H, NH).

1.4 Synthesis of $[L]_2AgPF_6$ (2)

A methanol solution (10 mL) containing (L) (100 mg, 0.48 mmol) was added to a methanol solution (10 mL) of $AgPF_6$ (61 mg, 0.24 mmol). After ca. 30 min of vigorous mixing, the filtrate was allowed stand at room temperature. Colorless block-shaped crystals were deposited slowly with the evaporation of the solvent within one week. Yield: 170 mg (53%); m.p.: 204~206 ℃. Anal. Calcd for $C_{28}H_{24}AgF_6N_4P$ (%): C 50.24, H 3.61, N 8.37. Found(%): C 50.73, H 3.86, N 8.45. IR (KBr, cm^{-1}): 3 424bm, 3 146m, 1 599m, 1 506m, 1 441m, 1 362 m, 1 239m, 1 096m, 833s, 779m, 654m, 557m.

1.5 Structure determinations

For compounds **1** and **2**, selected single crystals were mounted on a Bruker SMART 1000 CCD single crystal diffractometer operating at 50 kV and 20 mA using monochromatic Mo $K\alpha$ radiation (0.071 073 nm). Data collection and reduction were performed using the SMART and SAINT software [12] with frames of 0.6° oscillation in the θ range $1.8° < \theta < 25°$. An empirical absorption correction was applied using the SADABS program[13]. The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELXTL package[14]. All hydrogen atoms were generated geometrically (C-H bond lengths fixed at 0.096 nm), assigned appropriated isotropic thermal parameters and included in structure factor calculations. Crystal data and structure refinement and selected bond lengths (nm) and angles (°) for **1** and **2** are presented in Table 1 and 2, respectively.

CCDC: 648611, **1**; 648610, **2**.

Table 1 Crystal data and structure refinements for 1 and 2

	1	2
Chemical formula	$C_{14}H_{13}ClN_2$	$C_{28}H_{24}AgF_6N_4P$
Formula weight	244.71	669.35
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a / nm	1.103(1)	0.924(9)
b / nm	1.028(1)	1.068(1)
c / nm	1.077(1)	1.451 (1)
α / (°)		72.981(1)
β / (°)	94.363(11)	87.917(1)
γ / (°)		82.561(1)
V / nm^3	1.218(2)	1.357(2)
Z	4	2
D_c / (Mg·m^{-3})	1.334	1.639
Abs coeff / mm^{-1}	0.291	0.869
F(000)	512	672
Crystal size / mm	0.24 × 0.20 × 0.18	0.28 × 0.22 × 0.16
θ_{min}, θ_{max} / (°)	1.85, 25.02	2.01, 25.03
T / K	293(2)	293(2)
No. of data collected	6 294	7 427
No. of unique data (R_{int})	2 150 (0.038 0)	4 731 (0.015 9)
Reflections observed	1 750	3 619
No. of refined params	154	364
Goodness-of-fit on F^2*	1.097	1.034
Final R indices** [$I>2\sigma(I)$]	R_1=0.0355, wR_2=0.100 4	R_1=0.039, wR_2=0.097
R indices (all data)	R_1=0.043 8, wR_2=0.104 4	R_1=0.055 8, wR_2=0.104 6

* Goof=$[\Sigma\omega(F_o^2-F_c^2)^2/(n-p)]^{1/2}$, where n is the number of reflection and p is the number of parameters refined;

** $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$; $wR_2=1/[\sigma^2(F_o^2)+(0.069\,1P)+1.410\,0P]$ where $P=(F_o^2+2F_c^2)/3$.

Table 2 Selected bond lengths (nm) and angles (°) for 1 and 2

		1			
N(1)-C(1)	0.135(2)	N(2)-C(1)	0.135(2)	C(1)-H(1)	0.093
N(1)-C(2)	0.131(2)	N(2)-C(3)	0.132(2)	N(1)-H(1A)	0.086
N(1)-C(1)-N(2)	10.73(1)	C(1)-N(1)-C(2)	10.92(1)	C(1)-N(2)-C(3)	10.84(1)
N(1)-C(1)-H(3)	12.63	C(1)-N(1)-H(1A)	12.54		
N(2)-C(1)-H(3)	12.63	C(2)-N(1)-H(1A)	12.54		
		2			
Ag(1)-N(1)	0.209(3)	N(1)-C(2)	0.135(5)	N(2)-C(4)	0.148(5)
Ag(1)-N(3)	0.209(3)	N(2)-C(1)	0.132(5)		
N(1)-C(1)	0.131(5)	N(2)-C(3)	0.135(5)		
N(1)-Ag(1)-N(3)	17.35(1)	C(2)-N(1)-Ag(1)	12.79(3)	C(3)-N(2)-C(4)	12.69(3)
C(1)-N(1)-C(2)	10.55(3)	C(1)-N(2)-C(3)	10.66(3)		
C(1)-N(1)-Ag(1)	12.59(3)	C(1)-N(2)-C(4)	12.64(3)		

2 Results and discussion

2.1 Crystal structure of 1

1-(1-Naphthylmethyl)imidazole (L) was prepared from imidazole by alkylation with 1-chloromethylnaphthalene, and obtained as a pale yellow solid[15]. The ligand L is very soluble in common organic solvents (such as CH_2Cl_2, CH_3OH, CH_3CN and DMF etc.), therefore, crystallization of its complexes with inorganic metal salts occurs readily.

The ligand L was reacted with hydrochloride acid to form salt L·HCl (**1**). Analysis of the crystal packing of **1** shows the existence of both types of intermolecular hydrogen bonds (Fig.1a), namely, N1–H1A···Cl2^{i} and C3′–H3′···Cl2^{ii} hydrogen bonds (symmetry code ^{i} −1+x, y, z; ^{ii} 1−x, −y, 1−z; see Table 3)[5]. Two L·H$^+$ parts are connected by two bridging chlorines through above both types of hydrogen bonds to form a dimeric unit with a 10-membered ring, and all atoms forming the 10-membered ring are almost coplanar. The dimeric units of **1** are further extended into 2D supramolecular layers throuth the face-to-face π-π interactions from naphthalene rings with the inter-planar separation of 0.362 nm (center-to-center separation: 0.389 nm) (Fig.1b)[7]. Thus aromatic π-π stacking interactions play an important role in the forming 2D supramolecular layers.

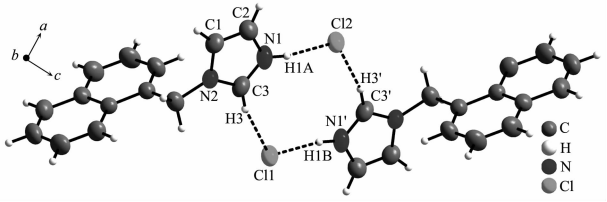


Fig.1a　Dimeric unit formed through H-bonding interactions in **1**

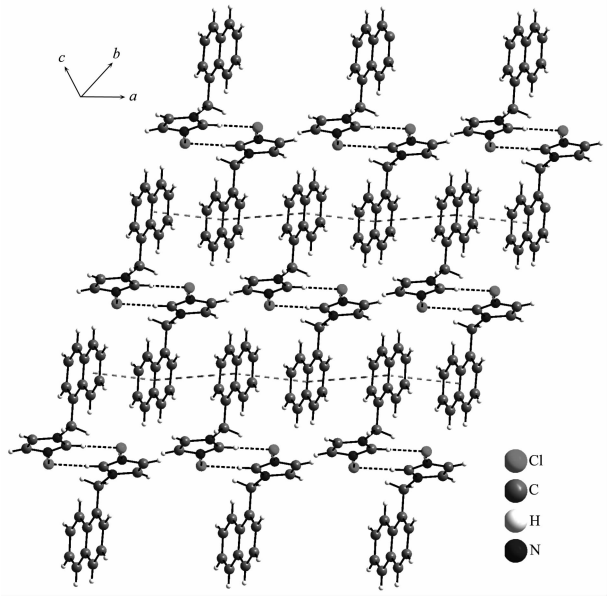


Fig.1b　2D supramolecular layers formed through H-bonding and aromatic π-π interactions in **1**

Table 3　H-bonding geometry for 1

	D–H···A	D-H / nm	H···A / nm	D···A / nm	D–H···A / (°)
1	N1–H1A···Cl2^{i}	0.086	0.220	0.304	16.6
	C3′–H3′···Cl2^{ii}	0.009	0.244	0.334	16.3

Symmetry code: ^{i} −1+x, y, z; ^{ii} 1−x, −y, 1−z.

2.2 Crystal structure of 2

Complex **2** was prepared via the reaction of ligand L with $AgPF_6$ in methanol solution. The crystals of **2** suitable for X-ray diffraction were grown by evaporating slowly its CH_3OH solution at room temperature. The complex **2** is air stable, and soluble in chloroform and DMSO and insoluble in diethyl ether, hydrocarbon solvents and water. As depicted in Fig.2a, the coordination geometry on the silver atom is approximately linear with the bond angle (N1-Ag-N3) of 173.5°. The Ag-N bond distance of 0.209(3) nm is a normal Ag-N coordination bond[16]. Two imidazole rings around metal center are trans conformation with the dihedral angle of 23.2. The dihedral angle between the naphthalene ring and adjacent imidazole ring is 102.9°, and the dihedral angle between two naphthalene rings is 85.4°.

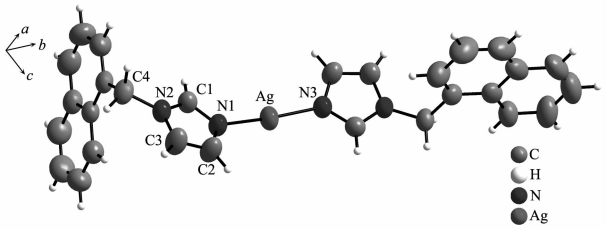
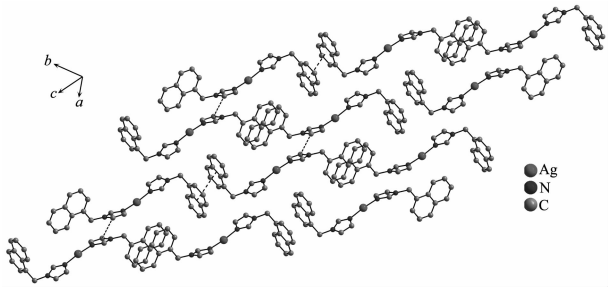


Fig.2a　Perspective view of **2** and anisotropic displacement parameters depicting at 30% probability

An interesting feature in the packing diagrams of **2** is that both types of aromatic π-π stacking interactions are observed[7] as shown in Fig.2b. One type is the face-to-face π-π stacking interactions from inter-unit naphthalene rings with the inter-planar separation of 0.363 nm (center-to-center separation: 0.391 nm), which forms 1D infinite chains. Another type is the head to tail π-π interactions from inter-chain imidazole rings with the inter-planar separation of 0.323 nm (center-to-center separation: 0.482 nm), which extends the above 1D infinite chains into 2D supramolecular layers. Thus aromatic π-π stacking interactions are mainly responsible for expanding the 1D polymeric chains to 2D supramolecular layers in **2**.



Hydrogen atoms have been omitted for clarity

Fig.2b 2D supramolecular layers formed throughboth types of π-π stacking interactions in **2**

2.3 Fluorescent emission spectra of L, 1 and 2

The fluorescent emission spectra of L, **1** and **2** in the solid state at room temperature are indicated in Fig. 3. The maximum emission bands of these compounds are at 330 ~340 nm, and the fluorescence emission spectra of compounds **1** and **2** are stronger than that of ligand L, which may be assigned to the result of the incorporation of cation-ligand interactions. These results show that thus the compounds might be good candidates for potential photoactive materials[17].

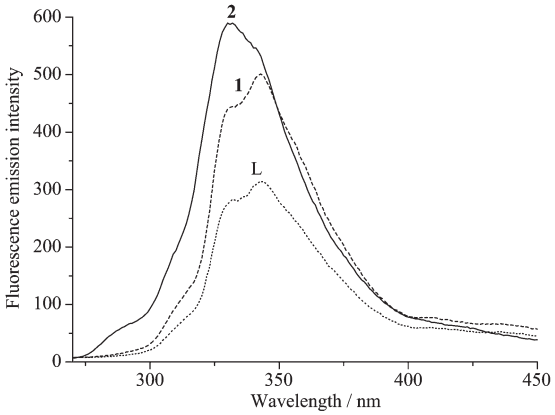


Fig.3 Emission spectra of L (···), **1** (–––) and **2** (—) at 298 K in solid state

2.4 Thermogravimetric analysis of complex 2

Complex **2** is air stable at ambient conditions and the thermogravimetric experiments were performed to explore its thermal stability. The TGA curve of **2** reveals that the complex starts to decompose beyond 280 ℃ with two steps of weight losses (peaks at 310 ℃ and 340 ℃) and does not stop until heating ends at 750 ℃.

3 Conclusion

In summary, Two new compounds **1** and **2** have been prepared by reactions of 1-(1-naphthylmethyl)imidazole with HCl or $AgPF_6$, and structurally characterized by X-ray diffraction structure analyses. In the packing diagrams of **1** and **2** 2D supramolecular layers are observed, but 2D layers of **1** are formed through hydrogen bonds and π-π stacking interactions, and 2D layers of **2** are formed through both types of π-π stacking interactions. Thermogravimetric analysis of **2** suggests that it has good thermal stability. The fluorescence emission spectra of L, **1** and **2** are described. The resultant structures of these compounds will provide interesting experimental data for supramolecular chemistry and crystal engineering. Further studies on new metal complexes from ligand L and analogous ligands are under way.

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