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金和银氮杂环卡宾原子簇化合物的合成结构与细胞毒性研究

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摘要：由$[Ag_3L_2(CH_3CN)_2](PF_6)_3$(**1**,L=bis(*N*-pyridylimidazoliumyl)methane)通过金属转移反应合成了含有氮杂环卡宾配体的金银混合原子簇化合物,$[Au_2AgL_2(CH_3CN)_2](PF_6)_3$ (**2**)和$[Au_4AgL_4](PF_6)_5$ (**3**),用 X-射线单晶衍射确定了 **2** 和 **3** 的晶体结构。化合物 **1** 和 **2** 结构相同,3 个金属原子三角形排列。化合物 **3** 中 5 个金属原子呈链状排列,其中银原子居于中间。这些化合物在室温下分别在 417,415 和 457 cm^{-1} 处表现荧光。用 MTT 实验方法研究了对 HuH7,C6 和 A375 肿瘤细胞的毒性,其毒性顺序为 **1**>**2**>**3** 与这些化合物中银含量顺序相一致。

关键词：金；银；咪唑盐；*N*-杂环卡宾；原子簇；细胞毒性

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Mixed Gold-Silver Clusters Possessing *N*-Heterocyclic Carbenes: Synthesis, Structural Characterization, and Cytotoxicity

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Abstract: Gold and silver clusters, $[Au_2AgL_2(CH_3CN)_2](PF_6)_3$ (**2**, L=bis(*N*-pyridylimidazoliumyl)methane) and $[Au_4AgL_4](PF_6)_5$ (**3**), have been synthesized from $[Ag_3L_2(CH_3CN)_2](PF_6)_3$ (**1**) via transmetallation reactions, and their structures were determined by X-ray diffraction analysis. Complexes **1** and **2** are isostructural with each other consisting of triangular metallic rings showing weak metal-metal interaction. Complex **3** is a chain compound with the silver atom located in between two Au_2 units. All the complexes are luminescent in their solid states at room temperature. The cytotoxicities of the complexes were investigated by MTT assay. The results show that all these complexes are toxic to HuH7, C6, and A375 tumor cells, and the toxicity order is **1** > **2** > **3** consistent with the silver content in these complexes. CCDC: 724081, **2**; 724083, **3**.

Key words: gold; silver; cluster; *N*-heterocyclic carbene; cytotoxicity

0 Introduction

N-Heterocyclic carbene (NHC) complexes of coinage metals have attracted considerable interest in recent years because they exhibit intriguing structural diversities and have shown potential applications in material science and medicine[1-4]. Silver-NHC complexes can be easily prepared and are widely used as carbene transfer reagents for the preparation of many other transition metal complexes[5-6]. Silver and gold complexes of NHCs are emissive in their solid states and in solutions, and they are potentially useful

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luminescent materials and sensors[7-14]. Gold and silver complexes have shown their potential as anti-cancer, anti-arthritis, and anti-bacterial drugs[15-21]. Gold and silver complexes are also useful catalysts for a number of organic transformations involving double and triple bonds such as hydrosilylation[22], alkyne hydration[23], and hydroamination[24]. Although a large number of coinage metal complexes and homonuclear clusters containing *N*-heterocyclic carbenes have been reported in recent years, the heteronuclear coinage metal clusters of NHC have only been scarcely studied[14,25-26].

Our work in this area primarily concerns the chemistry of coinage metal complexes supported by functionalized multidentate *N*-heterocyclic carbenes such as 3,5-bis(*N*-methylimidazolylidenyl) methyl) pyrazolate[27-28], naphthyridine-linked NHCs[29] etc. These studies led to several interesting findings including the isolation and structural characterization of new silver clusters like linear Ag_3, triangular Ag_3, square-planar Ag_4, and Au_4 complexes. These multinuclear silver and gold complexes display short Ag-Ag or Au-Au interactions and interesting luminescence properties. As a continuation, here we describe the synthesis and structural characterization of mixed Au_2Ag and Au_4Ag complexes supported by bis (*N*-pyridylimidazolylidenyl)methane. Their luminescence properties and cytotoxicity were also studied.

1 Experimental

1.1 General procedures

All the chemicals were obtained from commercial suppliers and used without further purification. $Au(Et_2S)Cl$ was prepared according to the known procedure[30]. The C, H, and N elemental analyses were carried out with a Flash EA 1112 elemental analyzer. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield to TMS at $\delta=0$ ppm and coupling constants (J) are expressed in Hz. The photoluminescence study was carried out on powdered samples in the solid state at room temperature using a Hitachi 850 spectrometer.

1.2 Synthesis of metal complexes

1.2.1 Synthesis of $[Au_2AgL_2(CH_3CN)_2](PF_6)_3$ (**2**)

$Au(Et_2S)Cl$ (193.5 mg, 0.6 mmol) was added to the colorless solution of **1** (432.6 mg, 0.30 mmol) in 10 mL of CH_3CN. The mixture was protected from light and stirred at room temperature overnight. The resulting mixture was filtered through Celite to remove AgCl, and the filtrate was reduced to about 2 mL. A colorless solid obtained after addition of 20 mL of Et_2O to the filtrate. Yield: 381.1 mg (76%). ^1H NMR (400 MHz, DMSO-d_6): δ 8.29 (d, J=4 Hz, *o*-C_6H_5, 4H), 8.24 (br, *m*-C_6H_5, 4H), 8.23, 7.79 (both s, NCHCHN, each 4H), 7.83 (t, J=7.4 Hz, *m*-C_6H_5, 4H), 7.51 (t, J= 6.0 Hz, *p*-C_6H_5, 4H), 7.54 (d, J=14 Hz, CH_2, 2H), 6.67 (d, J=14 Hz, CH_2, 2H). ^{13}C NMR (100 MHz, CD_3CN): δ 180.9 (Au-C), 149.9, 149.8, 140.6, 125.4, 123.7, 123.6, 118.8, 118.5 (CH_3CN), 64.07, 1.53 (CH_3CN). Calcd. (%) for $C_{38}H_{34}N_{14}Au_2AgF_{18}P_3$ ($[Au_2AgL_2(CH_3CN)_2](PF_6)_3$): C, 28.11; H, 2.11; N, 12.08. Found (%): C, 28.36; H, 2.28; N, 12.44.

1.2.2 Synthesis of $[Au_4AgL_4](PF_6)_5$ (**3**)

$Au(Et_2S)Cl$ (96.8 mg, 0.30 mmol) was added to the colorless solution of **1** (432.6 mg, 0.3 mmol) in 20 mL of CH_3CN. The mixture was protected from light and stirred at room temperature overnight. The resulting mixture was filtered through Celite to remove AgCl, and the filtrate was reduced to about 2 mL. A colorless solid was obtained by adding 20 mL of Et_2O. Yield: 225.6 mg (53%). ^1H NMR (400 MHz, DMSO-d_6): δ 8.25 (d, J=2.0 Hz, NCHCHN, 4H), 8.11 (d, J=2.0 Hz, NCHCHN, 4H), 7.95 (d, J=3.6 Hz, *o*-C_6H_5, 4H), 7.85~7.78 (m, J=7.8, *m*-C_6H_5, 8H), 7.31~7.28 (dd, J= 1.5, 6.4 Hz, *p*-C_6H_5, 4H), 6.84 (br, CH_2, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 181.0 (Au-C), 149.9, 149.1, 140.7, 124.7, 123.8, 121.9, 118.4 (CH_3CN), 116.3, 65.62 (CH_2), 1.37 (CH_3CN). Anal. Calcd. (%) for $C_{68}H_{56}N_{24}Au_4AgF_{30}P_5$ ($[Au_4AgL_4](PF_6)_5$): C, 28.86 ; H, 1.99 ; N, 11.88. Found(%): C, 28.86; H, 2.21; N, 11.54.

1.3 X-ray diffraction analysis

Single-crystal X-ray diffraction data for the complexes were collected at 298(2) K on a Siemens Smart/CCD 1K area-detector diffractometer with a Mo $K\alpha$ radiation (λ=0.071 073 nm) by using a ω-2θ

scan mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the SMART and SAINT software[31]. All structures were solved by direct methods and refined against F^2 by the full-matrix least squares techniques[32]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in their calculated positions. Details of the X-ray experiments and crystal data are summarized in Table 1.

CCDC: 724081, **2**; 724083, **3**.

Table 1　Summary of X-ray crystallographic data for complexes 2 and 3

	2	**3**
Formula	$C_{42}H_{40}AgAu_2F_{18}N_{16}P_3$	$C_{72}H_{62}AgAu_4F_{30}N_{26}P_5$
Formula weight	1 705.61	2 912.06
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a / nm	1.375 17(15)	1.393 42(17)
b / nm	1.389 15(16)	1.425 98(18)
c / nm	1.506 76(18)	1.436 10(19)
α / (°)	97.538(2)	104.520 0(10)
β / (°)	92.813 0(10)	109.403(2)
γ / (°)	91.511 0(10)	93.921 0(10)
V / nm^3	2.848 5(6)	2.569 3(6)
Z	2	1
D_c / (g·cm^{-3})	1.989	1.882
Cryst size / mm	0.32×0.29×0.18	0.26×0.24×0.16
Reflns collected	14 749	13 135
Ind reflns, R_{int}	9 813, 0.035 6	8 787, 0.024 3
Goodness-of-fit on F^2	1.143	1.487
R_1, wR_2 ($I>2\sigma(I)$)	0.060 5, 0.157 0	0.107 2, 0.318 9
R_1, wR_2 (all data)	0.092, 0.186 2	0.146 4, 0.354 4

1.4　Cell culture and cytotoxicity assay

HuH7, C6, and A375 cells were grown in DMEM (GIBCO, China) supplemented with 10% *V*/*V* fetal calf serum (FCS) (GIBCO, China), incubated at 37 ℃ in a humidified atmosphere containing 5% CO_2. Three cell lines (HuH7, C6, and A375 cells) were cultured in DMEM medium supplemented with 10% FBS at 37 ℃, 5% CO_2, and 95% relative humidity. For cell viability assay, the cells (10,000 cells/well for HuH7 and A375, and 8 000 cells/well for C6) were seeded into 96-well microtiter plates (Costar, Corning Corp. USA). After 24 h, culture media were replaced with serum-supplemented culture media containing serial dilutions of complexes and the cells were incubated for 4 h; 10 μL sterile filtered MTT (5 mg·mL^{-1}) stock solution in PBS was added to each well, reaching a final concentration of 0.5 mg MTT·mL^{-1}. After 4 h, unrelated dye was removed by aspiration. The complexes in crystal form were dissolved in 100 μL/well DMSO and measured spectrophotometrically in a microplate reader (Spectra Plus, TECAN) at a wavelength of 570 nm. Six wells were treated together as a group. The relative cell growth (%) related to control cells cultured in media without polymer was calculated by $c(A)_{test}/c(A)_{control}\times100\%$.

1.5　Microscopy

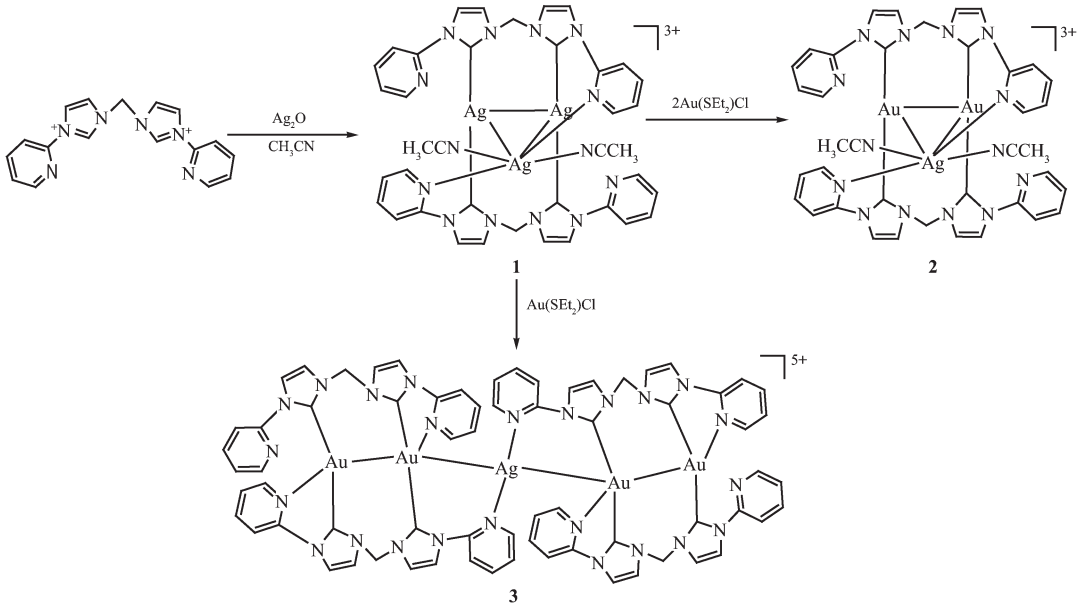
C6 cell lines were plated at 25,000 cells per well in 24-well plates. Compounds **1**, **2** and **3** were dissolved in DMSO to a concentration of 25 μg·mL^{-1}, and diluted into cell culture medium to the desired testing concentration. Medium in each well was removed and replaced with the fresh medium containing test compounds. The test compounds were incubated for 4 h and cells were rinsed with PBS. All

images were captured by using Nikon (ECLIPSE Ti-S).

2 Results and discussion

2.1 Synthesis and spectral characterization

We previously reported that treatment of bis(*N*-pyridylimidazoliumyl)methane hexafluorophosphate with Ag_2O in acetonitrile afforded $[Ag_3L_2(CH_3CN)_2](PF_6)_3$ (**1**, L=bis(*N*-pyridylimidazolylidenyl)methane)[33]. The compound consists of a triangular Ag_3 ring and short Ag-Ag interactions. As shown in Scheme 1, treatment of **1** with two equivalent of $Au(SEt_2)Cl$ in acetonitrile results in incomplete metal-exchange affording a mixed gold-silver complex $[Au_2AgL_2(CH_3CN)_2](PF_6)_3$ (**2**) as a white solid. Attempts to prepare $AuAg_2$ complex were not successful by variation of the ratio of $Au(SEt_2)Cl$ and **1**. Reaction of **1** with one equivalent of $Au(SEt_2)Cl$ affords $[Au_4AgL_4](PF_6)_5$ (**3**) as a white solid in 53% yield other than the expected $AuAg_2$ complex. The compositions of these complexes were identified by elemental analysis and later confirmed by X-ray crystallography.



Scheme 1 Synthesis of complexes

^{1}H NMR spectra of **2** shows expected resonance peaks assignable to imidazolylidene and pyridine groups. In the ^{1}H NMR spectra of **2**, two doublets ascribed to CH_2 moieties are observed because the methylene protons become magnetically inequivalent upon complexation of bis(*N*-pyridylimidazolylidenyl)methane. In the ^{1}H NMR spectra of **3** there is only a broad singlet ascribed to CH_2 moieties. It should be noted that although the imidazolylidenes in both **2** and **3** are coordinated to gold atoms, the ^{13}C chemical shifts are much closer to that of the trisilver complex **1**. All of them appear in the range of 160~195 ppm, consistent with those of the known gold and silver-NHC complexes depending on the ancillary ligands[1-4,34-36].

2.2 Structure description

Single crystals of **2** suitable for X-ray diffraction analysis were grown by slow evaporation of diethyl ether into an acetonitrile solution of **2**. As shown in Fig.1, X-ray diffraction analysis reveals that the trinuclear complex contains two $[Au(NHC)_2]^+$ and one $[Ag(CH_3CN)_2]^+$ bonded together by two bis(*N*-pyridylimidazolylidenyl)methane ligands. The three metal atoms form a unsymmetrical triangular Au_2Ag ring because of metal-metal interaction. The gold-silver interaction has been observed for a few mixed Au-Ag complexes supported by NHC ligands[25-26]. The Au-Ag bond distances are 0.297 4 (1) and 0.293 3 (1) nm, whereas Au-Au distance is 0.345 4 (1) nm, indica-ting weak metal-metal interaction. The two Au(I) ions display linear coordination geometry with C-Au-C angles of *ca.* 175°. The imidazolylidene rings coordinated to the same gold ion are bisected with dihedral

angles of 40.81° and 43.38°. The Au-C bond distances of *ca.* 0.202 nm are normal for gold complexes containing NHC ligands[8,25-27]. The silver ion is tertacoordinated by two pyridine and two acetonitrile molecules, displaying a severely distorted octahedral geometry provided that two Au-Ag bonds are also counted. The Ag-$N_{pyridine}$ and Ag-$N_{acetonitrile}$ distances are significantly longer than normal Ag-N distances at about 0.20 nm illustrating that both pyridine and acetonitrile are loosely coordinated. The most important bond distances and bond angles are listed in Table 2.

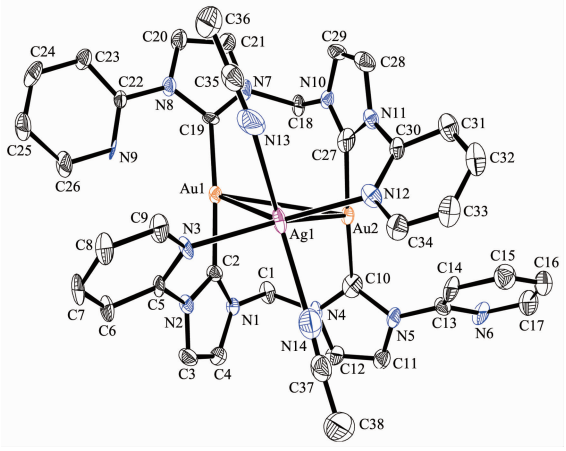


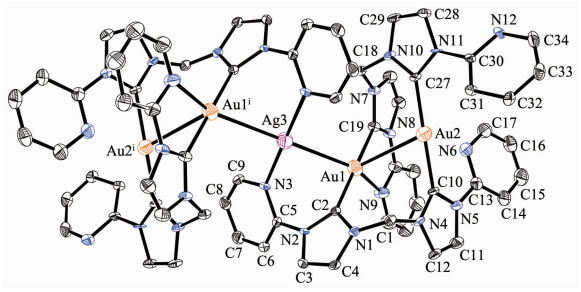
Fig.1　Molecular structure of **2**, thermal ellipsoids are drawn at 30% probability level

Colorless single crystals of **3** were grown by slow diffusion of diethyl ether into its acetonitrile solution. The structure of **3** is depicted in Fig.2. X-ray diffraction analysis reveals that the compound is pentanuclear containing four gold atoms and one silver atom located at the center of the molecule. The five metal ions are held together by four bis (*N*-picolylimidazolylidenyl)methane molecules. The asymmetric unit consists of one half of the molecule, and the whole molecule is generated by symmetry operation (symmetry code: $-x$, $-y+1$, $-z$). Each gold atom is linearly bicoordinated by two imidazolylidene ligands, and the central silver ion is coordinated by two pyridine groups in linear coordination geometry. Each bis(*N*-picolylimidazolylidenyl)methane is bonded to two gold atoms and one silver atom in tridentate fashion with one pyridine uncoordinated. In the metallic chain compound, both Au-Au and Au-Ag interactions are observed. The Au-Au and Au-Ag bond distances are comparable to those in **2** and other gold and silver clusters supported by N-heterocyclic carbenes[25-27]. The Au-Ag-Au axis is perfectly linear due to geometric requirement, but the Au-Au-Ag is bent with a bond angle of 109.61(3)°.

Table 2　Important bond distances (nm) and angles (°) for complexes 2 and 3

Complex **2**					
Au(2)-Ag(1)	0.297 4(1)	Au(1)-Ag(1)	0.293 3(1)	Au(1)-Au(2)	0.345 4(1)
Au(1)-C(19)	0.202 8(11)	Au(1)-C(2)	0.203 0(14)	Au(2)-C(10)	0.201 2(14)
Au(2)-C(27)	0.203 2(14)	Ag(1)-N(3)	0.238 8(12)	Ag(1)-N(12)	0.238 6(11)
Ag(1)-N(13)	0.256 8(13)	Ag(1)-N(14)	0.257 4(18)		
C(19)-Au(1)-C(2)	174.1(5)	C(10)-Au(2)-C(27)	176.6(5)	N(3)-Ag(1)-N(12)	144.0(4)
N(3)-Ag(1)-N(13)	85.1(4)	N(12)-Ag(1)-N(13)	84.0(4)	N(3)-Ag(1)-N(14)	89.3(5)
N(12)-Ag(1)-N(14)	86.8(4)	N(13)-Ag(1)-N(14)	156.0(5)	Au(1)-Ag(1)-Au(2)	71.57(3)
Ag(1)-Au(2)-Au(1)	53.66(2)	Ag(1)-Au(1)-Au(2)	54.76(2)		
Complex **3**					
Au(1)-Ag(3)	0.310 3(1)	Au(1)-Au(2)	0.303 7(1)	Au(1)-C(2)	0.208 1(13)
Au(1)-C(19)	0.211 4(13)	Au(1)-N(9)	0.259 0(15)	Au(2)-C(27)	0.208 0(14)
Au(2)-C(10)	0.210 0(13)	Ag(3)-N(3)	0.228 9(12)		
C(2)-Au(1)-C(19)	179.4(5)	C(2)-Au(1)-N(9)	110.4(5)	C(19)-Au(1)-N(9)	69.6(5)
C(27)-Au(2)-C(10)	175.1(5)	N(3i)-Ag(3)-N(3)	180.0	Au(2)-Au(1)-Ag(3)	109.61(3)
Au(1i)-Ag(3)-Au(1)	180.0				

Symmetry code: **3**: ^{i} $-x$, $-y+1$, $-z$.



Symmetry code: i $-x, -y+1, -z$

Fig.2 Molecular structure of **3**, thermal ellipsoids are drawn at 30% probability level

2.3 Luminescence properties

Several mononuclear Au(I)-NHC complexes have been reported containing short Au···Au contacts less than the sum of the van der Waals radii (0.36 nm) in their solid state, and these aurophilic interactions are often associated with strong solid-state luminescence[7-9]. The luminescent properties of a few binuclear Au(I)-NHC complexes have also been explored recently[10-13]. However, so far only a few gold complexes with higher nuclearity have been investi-gated[25-27]. The gold and silver complexes presented above with metallophilic interaction are expected to be emissive in their solid state. As shown in Fig.3, the trisilver complex displays emission band at 417 nm upon excitation at 349 nm. Interestingly, $[Au_2AgL_2(CH_3CN)_2](PF_6)_3$ shows emissive band at 415 nm when it is irradiated at 339 nm. We assumed that this is because complexes **1** and **2** share analogous structure and M-M interaction (M =Au, Ag). The pentanuclear complex $[Au_4AgL_4](PF_6)_5$ containing both Au-Ag and Au-Au interaction is intensely luminescent in the solid state. It exhibits a symmetrical broad emission band centered at 457 nm when irradiated at 378 nm. The luminescent property of the pentanuclear complex is similar to the polymeric gold-silver complex reported by Catalano et al. [14]. The intense emission of the Au(I)-NHC complexes can be originated from intraligand states or metal-centered states. We are unable to assign the nature of the excited states at present due to the complexity brought by metallophilic attractions existing in the complexes.

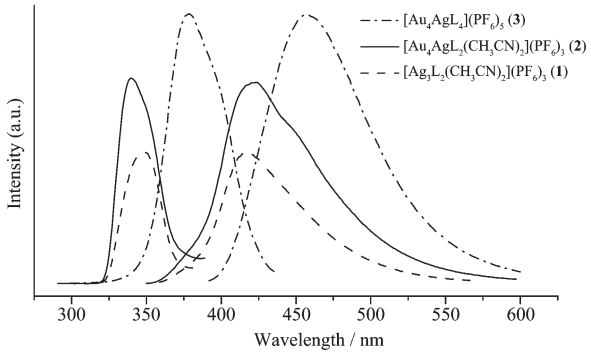


Fig.3 Emission (right) and excitation (left) spectra of complexes **1**, **2** and **3**

2.4 Cell viability assay

The medicinal application of various transition metal-NHC complexes including silver, gold, rhodium, ruthenium, and palladium has been gaining interest over the past decade. Recent advances in the studies of the antimicrobial, antitumor, and resistance properties of metal-NHCs have been reviewed[37-38]. For cell viability issue the cytotoxicities of compounds **1**, **2** and **3** were evaluated in HuH7 tumor liver cell, C6 (glioma), and A375 (human malignant melanoma) cell lines by MTT assay. The antitumor activities against concentration variations of **1**, **2** and **3** are shown in Fig.4. The HuH7 cell line does not survive upon exposure of 25 $\mu g \cdot mL^{-1}$ of **1**, **2** and **3**. The MTT assay against C6 and A375 cell lines also shows that these silver and gold complexes have significant effect on cell viability. The MTT assay illustrats that the cell viability is less sensitive to the concentration of **2**.

Half inhibitory concentrations (IC_{50}) were determined on three cell lines. The IC_{50} of these three compounds are listed in Table 3. The silver cluster **1** has the lowest IC_{50} for the cells examined, and complex **2** has the highest IC_{50} value, whereas chain complex **3** is in between **1** and **2**. These data may suggest that the toxicity of the complex is related with the silver content in the complex. Higher gold content complexes is less toxic towards three tumor cells

Table 3 IC_{50} for compounds 1, 2 and 3 in HuH7, C6, and A375 cell lines

($\mu g \cdot mL^{-1}$)

	1	2	3
HuH7	5.0	8.0	7.0
C6	10.6	28.9	4.3
A375	6.7	12.7	7.9

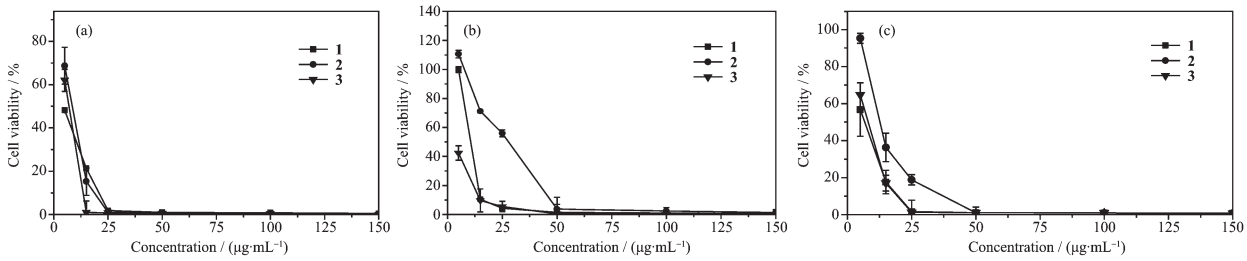
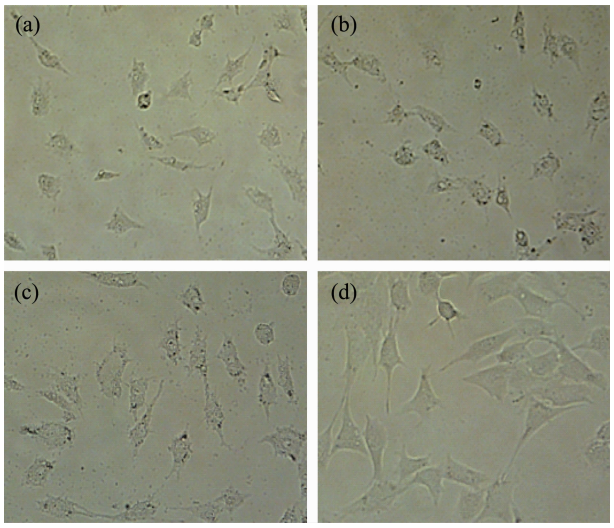


Fig.4　Cell viability assay of compounds **1**, **2** and **3** in (a) HuH7, (b) C6, and (c) A375 cell lines

probably because gold-NHC complex is more stable than silver-NHC complexes[16].

Fig.5 shows the images of the morphology of compounds **1**, **2** and **3** in C6 cell lines after 4 h incubation at the concentration of 25 $\mu g \cdot mL^{-1}$. From the comparation of Fig.5a~c with 5 d we can see that compounds **1**, **2** and **3** have significant effect on cell viability, and over 60% cells died at the concentration examined. Fig.5d is a control group with cells under the same experimental conditions. Obviously, these results show that compounds **1**, **2** and **3** have good toxic effect on cell viability.



(a) **1**; (b) **2**; (c) **3**; (d) Control

Fig.5　Cell morphology after incubation with complexes for 4 h in C6 cell lines

3　Conclusions

In summary, we described the synthesis of gold and silver clusters, $[Au_2AgL_2(CH_3CN)_2](PF_6)_3$, and $[Au_4AgL_4](PF_6)_5$, from $[Ag_3L_2(CH_3CN)_2](PF_6)_3$ (L=bis(*N*-pyridylimidazoliumyl)methane) via incomplete transmetallation reactions. Their structures have been identified by X-ray diffraction analysis. The gold and mixed gold/silver complexes exhibit luminescence at room temperature. The cytotoxicity investigation for these complexes shows that they are all toxic to HuH7, C6, and A375 cells and the toxicity order is **1** > **2** > **3** consistent with the silver content in these complexes.

References:

[1] Garrison J C, Youngs W J. *Chem. Rev.*, **2005**,**105**:3978-4008

[2] Lin I J B, Vasam C S. *Coord. Chem. Rev.*, **2007**,**251**:642-670

[3] Marion N, Nolan S P. *Chem. Soc. Rev.*, **2008**,**37**:1776-1782

[4] Lin J C Y, Huang R T W, Lee C S, et al. *Chem. Rev.*, **2009**, **109**:3561-3598

[5] Zhang X, Liu B, Liu A, et al. *Organometallics*, **2009**,**28**:1336-1349

[6] Liu A, Zhang X, Chen W. *Organometallics*, **2009**,**28**:4868-4871

[7] Wang H M J, Chen C Y L, Lin I J B. *Organometallics*, **1999**, **18**:1216-1223

[8] Wang H M J, Vasam C S, Tsai T Y R, et al. *Organometallics*, **2005**,**24**:486-493

[9] Jothibasu R, Huynh H V, Koh L L. *J. Organomet. Chem.*, **2008**,**693**:374-380

[10]Liu B, Chen W, Jin S. *Organometallics*, **2007**,**26**:3660-3667

[11]Samantaray M K, Pang K, Shaikh M M, et al. *Inorg. Chem.*, **2008**,**47**:4153-4165

[12]Barnard P J, Wedlock L E, Baker M V, et al. *Angew. Chem.*, **2006**,**118**:6112-6116

[13]Barnard P J, Baker M V, Berners-Price S J, et al. *Dalton Trans.*, **2004**:1038-1047

[14]Catalano V J, Etogo A O. *Inorg. Chem.*, **2007**,**46**:5608-5615

[15]Kascatan-Nebioglu A, Panzner M J, Tessier C A, et al. *Coord. Chem. Rev.*, **2007**,**251**:884-895

[16]Ray S, Mohan R, Singh J K, et al. *J. Am. Chem. Soc.*, **2007**, **129**:15042-15053

[17]Hickey J L, Ruhayel R A, Barnard P J, et al. *J. Am. Chem.*

Soc., **2008**,**130**:12570-1257

[18]Melaiye A, Simons R S, Milsted A, et al. *J. Med. Chem.*, **2004**,**47**:973-977

[19]Krishnamurthy D, Karver M R, Fiorillo E, et al. *J. Med. Chem.*, **2008**,**51**:4790-4795

[20]Horvath U E I, Bentivoglio G, Hummel M, et al. *New J. Chem.*, **2008**,**32**:533-539

[21]Barnard P J, Baker M V, Berners-Price S J. *J. Inorg. Biochem.*, **2004**,**98**:1642-1647

[22]Díez-González S, Nolan S P. *Acc. Chem. Res.*, **2008**,**41**:349-358

[23]Marion N, Ramón R S, Nolan S P. *J. Am. Chem. Soc.*, **2009**,**131**:448-449

[24]Bender C F, Widenhoefer R A. *Org. Lett.*, **2006**,**8**:5303-5305

[25]Catalano V J, Malwitz M A, Etogo A O. *Inorg. Chem.*, **2004**, **43**:5714-5724

[26]Catalano V J, Moore A L. *Inorg. Chem.*, **2005**,**44**:6558-6566

[27]Zhou Y, Chen W. *Organometallics*, **2007**,**26**:2742-2746

[28]Zhou Y, Zhang X, Chen W, et al. *J. Organomet. Chem.*, **2008**, **693**:205-215

[29]Ye J, Jin S, Chen W, et al. *Inorg. Chem. Commun.*, **2008**, **11**:404-408

[30]Usón R, Laguna A, Laguna M. *Inorg. Synth.*, **1989**,**26**:85-86

[31]*SMART-CCD Software*, *Version* 4.05, Siemens Analytical X-ray Instruments, Madison, WI, **1996**.

[32]Sheldrick G M. *SHELXS*-97 *and SHELXL*-97, *Program for X-ray Crystal Structure Refinement*, University of Götingen, Götingen, Germany, **1997**.

[33]Xi Z, Zhang X, Chen W, et al. *Organometallics*, **2007**,**26**: 6636-6642

[34]de Frémont P, Stevens E D, Eelman M D, et al. *Organometallics*, **2006**,**25**:5824-5828

[35]de Frémont P, Stevens E D, Fructos M R, et al. *Chem. Commun.*, **2006**:2045-2047

[36]Hahn F E, Radloff C, Pape T, et al. *Chem. Eur. J.*, **2008**,**14**: 10900-10904

[37]Hindi K M, Panzner M J, Tessier C A, et al. *Chem. Rev.*, **2009**,**109**:3859-3884

[38]Teyssot M L, Jarrousse A S, Manin M, et al. *Dalton Trans.*, **2009**:6894-6902