

萘啶酮的单核和双核银配合物的合成与晶体结构

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摘要: 合成了萘啶酮的单核和双核银配合物 $\text{Ag}_2(\text{L}_1)_2(\text{HL}_1=5,7\text{-二甲基-1,8-萘啶-2-酮})$ (**1**)和 $[\text{Ag}(\text{HL}_2)(\text{PPh}_3)_2]\cdot 2\text{H}_2\text{O}(\text{H}_2\text{L}_2=1,8\text{-萘啶-2,7-二酮})$ (**2**)。并通过元素分析,红外光谱及 X-射线单晶衍射对其进行了结构表征。配合物 **1** 的晶体属单斜晶系, $P\bar{1}$ 空间群。中心金属银为三配位 T 型几何构型, Ag-Ag 间距离为 0.274 8(2) nm, 具有强的 Ag \cdots Ag 作用。配合物 **2** 的晶体属三斜晶系, $P2_1/n$ 空间群。银与 1 个氮原子及 2 个磷原子形成三配位结构。

关键词: 合成; 萘啶酮; 银配合物; 晶体结构

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Synthesis and Structural Characterization of Mononuclear and Dinuclear Silver Complexes of Naphthyridinone

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Abstract: Complex $\text{Ag}_2(\text{L}_1)_2$ ($\text{HL}_1=5,7\text{-dimethyl-1,8-naphthyridin-2-one}$) (**1**) and $[\text{Ag}(\text{HL}_2)(\text{PPh}_3)_2]\cdot 2\text{H}_2\text{O}$ ($\text{H}_2\text{L}_2=1,8\text{-naphthyridin-2,7-dione}$) (**2**) have been prepared and their structures were determined by X-ray diffraction. $\text{Ag}_2(\text{L}_1)_2$ crystallizes in a monoclinic space $P\bar{1}$. The Ag^+ ion features a T-shaped tricoordinated geometry, being coordinated by two nitrogen atoms from two different L_1 ligands and one from Ag \cdots Ag interaction. The Ag \cdots Ag bond distance is 0.274 8(2) nm showing some metallophilic interaction. $[\text{Ag}(\text{HL}_2)(\text{PPh}_3)_2]\cdot 2\text{H}_2\text{O}$ crystallizes in a triclinic space group $P2_1/n$. The Ag^+ ion is tricoordinated by one N atom from L_2 and two triphenylphosphine. CCDC: 608043, **1**; 608044, **2**.

Key words: synthesis; naphthyridinone; silver complex; crystal structure

Electronic communication between atoms or atomic groups is a fundamental process to many complex chemical systems in biochemical and biophysical sciences, and material chemistry^[1]. The direct electronic transfer processes between metal atoms are especially important because this phenomenon is often associated with many potentially useful chemical and physical properties of materials such as catalytic behavior,

magnetic, optical or electronic properties^[2]. Silver-silver interactions between closed-shell heavy metals have been widely recognized and termed as argentophilicity^[3]. Theoretical interest has been sparked by work which shows that silver displays the ability to form attractive nonbonding “metallophilic” interactions that can strongly influence the structures and properties of these materials.

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Molecular structures and chemical properties of transition metal complexes of 1,8-naphthyridine (napy) and its derivatives have received much attention, because the ligands are linked to metals with several coordination modes such as monodentate, chelating bidentate fashion. The 1,8-naphthyridine bridge has similar dimensions to those of carboxylate and formamido bridges, and consequently, metal-metal-bonded units can be spanned by the two nitrogen atoms^[4]. 5,7-dimethyl-1,8-naphthyridin-2-one and 1,8-naphthyridin-2,7-dione (Chart 1) are potentially anionic tridentate and tetradentate ligands and are capable of linking two to four metal atoms together to form metal aggregates having metal-metal interactions^[5]. We have been interested in the chemistry of metal aggregates having metal-metal bonds such as Pt-Pt, Pt-Ag, Pt-Tl bonds^[6]. In this paper, we wish to report the preparation and the crystal structures of mono- and dinuclear Ag(I) complexes, $[\text{Ag}_2(\text{L}_1)_2]$ and $[\text{Ag}(\text{HL}_2)(\text{PPh}_3)_2] \cdot 2\text{H}_2\text{O}$.

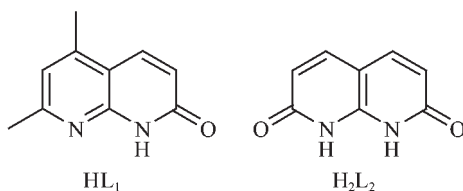


Chart 1

1 Experimental

1.1 Materials and instruments

All starting materials and solvents were used as received without further purification. 5,7-dimethyl-1,8-naphthyridine-2-one (HL_1)^[7] and 1,8-naphthyridin-2,7-dione (H_2L_2)^[8] were prepared by the method described in the literature. Elemental analysis was determined with a Perkin-Elmer 2400C instrument. IR spectra were measured as KBr pellets using a Nicolet 5DX FX-IR spectrophotometer.

1.2 Preparation of silver complexes

1.2.1 Preparation of $\text{Ag}_2(\text{L}_1)_2$ (**1**)

To a solution of HL_1 (0.174 g, 1 mmol) in DMF (10 mL) was added AgNO_3 (0.167 g, 1 mmol) in 3 mL of water. A white precipitate was formed immediately. Then the mixture was treated with a few drops of ammonia until the precipitate dissolved. The filtrate was left to evaporate slowly in dark at room temperature. Colorless needle-like crystals were obtained after a few days. Yield: 0.167 g, 60%. Anal. Calcd. (%) for $\text{C}_{20}\text{H}_{18}\text{Ag}_2\text{N}_4\text{O}_2$: C, 42.73; H, 3.23; N, 9.97. Found (%): C, 42.78; H, 3.26; N, 9.87. IR data (KBr pellet, cm^{-1}): 1 656(m), 1 618(s), 1 559(s), 1 526(m), 1 467(m), 1 448(m), 1 383(m), 1 296(m), 1 194(w), 1 097(w), 1 034(m), 869(w), 824(m), 791(w), 758(m), 625(m), 579(w), 490(w), 441(w).

1.2.2 Preparation of $[\text{Ag}(\text{HL}_2)(\text{PPh}_3)_2] \cdot 2\text{H}_2\text{O}$ (**2**)

To a stirred solution of H_2L_2 (0.199 g, 1 mmol), sodium hydroxide (0.040 g, 2 mmol) in 10 mL of water was added AgNO_3 (0.167 g, 1 mmol). A white precipitate was formed immediately. The mixture was then treated with PPh_3 (0.524 g, 2 mmol) in 10 mL of EtOH. The filtrate was left to evaporate slowly at room temperature. Suitable single crystals were obtained after a few days. Yield: 68%. Anal. Calcd. (%) for $\text{C}_{44}\text{H}_{39}\text{AgN}_2\text{O}_4\text{P}_2$: C, 63.70; H, 4.74; N, 3.38. Found (%): C, 63.61; H, 4.68; N, 3.29.

1.3 Crystal structure determination

Suitable crystals were selected for the structure analysis. The diffraction data were collected on a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 40 mA using Mo $K\alpha$ radiation (0.071 073 nm). Data collection and reduction were performed using the SMART and SAINT softwares^[9]. The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using SHELXTXL package^[10]. The hydrogen atoms were generated geometrically and included in structure factor calculations. Crystal data and refinement details are summarized in Table 1.

CCDC: 608043, **1**; 608044, **2**.

Table 1 Crystal data and structure refinement summary for the compounds **1** and **2**

	1	2
Formula	$\text{C}_{20}\text{H}_{18}\text{Ag}_2\text{N}_4\text{O}_2$	$\text{C}_{44}\text{H}_{39}\text{AgN}_2\text{O}_4\text{P}_2$
Formula weight	562.12	829.58

Continued Table 1

T / K	298(2)	293(2)
Wavelength / nm	0.071 073	0.071 073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a / nm	0.559 2(3)	1.056 2(19)
b / nm	0.897 5(5)	1.293 2(2)
c / nm	1.786 7(10)	1.610 1(3)
$\beta / (^\circ)$	98.661(7)	87.903(3)
V / nm^3	0.886 5(8)	2.032 6(6)
Z	2	2
$D_{\text{calc}} / (\text{Mg} \cdot \text{m}^{-3})$	2.106	1.355
Absorption coefficient / mm^{-1}	2.235	0.618
$F(000)$	552	852
Crystal size / mm	$0.49 \times 0.15 \times 0.10$	$0.12 \times 0.10 \times 0.07$
θ range / $(^\circ)$	2.31~25.01	1.27~25.10
Limiting indices	$-6 \leq h \leq 6, -10 \leq k \leq 10, -15 \leq l \leq 21$	$-12 \leq h \leq 12, -15 \leq k \leq 11, -17 \leq l \leq 19$
Reflections collected	4 518	10 179
Reflections independent	1 566 ($R_{\text{int}}=0.028$ 1)	7 088 ($R_{\text{int}}=0.051$ 6)
Goodness-of-fit on F^2	1.049	1.030
Final R indices [$I > 2\sigma(I)$]	0.029 9, 0.076 1	0.084 1, 0.216 9
R indices (all data)	0.039 6, 0.083 0	0.171 5, 0.268 2
Largest diff. peak and hole / $(\text{e} \cdot \text{nm}^{-3})$	595, -369	2 833, -1 529

2 Results and discussion

2.1 Structural characterization of **1**

Complex **1** was obtained as colorless crystals by reacting AgNO_3 and HL_1 in the presence of ammonia in DMF. The compound is air stable and light insensitive. IR spectrum of **1** shows that there are no stretching vibrations of N-H and O-H bonds. The lack of O-H and N-H stretching bands in the IR region between 3 300 and 3 600 cm^{-1} illustrates the ligand was deprotonated upon complexation. The complex does not dissolve in common organic solvent, but dissolves in DMF and DMSO.

The crystal structure shows that the complex is binuclear. The molecular structure of the compound is shown in Fig.1, and selected bond distances and angles are summarized in Table 2. The asymmetric unit of the structure consists of half of the molecule with a silver atom and a naphthyridine ligand. The two silver atoms are held together by a pair of L_1^- anions to form an eight-membered ring. The Ag^+ ion is

tricoordinated, and each Ag(I) ion features a T -shaped geometry, being coordinated by two nitrogen atoms from two different L_1^- anions. Both two L_1^- anions adopt a bidentate bridging coordination mode. The oxygen atom of 5,7-dimethyl-1,8-naphthyridin-2-one does not coordinate to the silver atoms. The Ag(1)-N(1) bond distance is 0.214 2(4) nm, which is shorter than those of the known silver-naphthyridine complex $[\text{Ag}_2(\text{napy})_2(\text{ONO}_2)_2]$ [0.221 3 (3) nm, $\text{napy}=\text{naphthyridine}$]^[4c] and $[\text{Ag}_2(\text{napy})(\text{ClO}_4)_2]$ [0.221 1(15) nm]^[4b]. The bond angle N(2)-C(1)-N(1) is $116.4(4)^\circ$, which is about 1° smaller than that in the free ligand $[115.5(3)^\circ]$ ^[11] because of the geometry requirement resulted from the formation of the metallocycle upon complexation. The C-O bond distance is 1.258(6) nm, typical for a C=O double bond. There is a remarkably deviation from linearity for the $\text{N(1)-Ag(1)-N(2)\#1}$ angle $[168.64(13)^\circ]$. The distortion may be a consequence of Ag-Ag interaction. The intramolecular Ag(I)-Ag(I) distance is 0.274 8(2) nm, which is significantly shorter than the Ag-Ag separation of 0.288 nm in the metallic state^[12],

Table 2 Selected bond lengths (nm) and bond angles ($^{\circ}$) for **1**

Ag(1)-N(1)	0.214 2(4)	Ag(1)-N(2)#1	0.215 2(4)	Ag(1)-Ag(1)#1	0.274 8(2)
Ag(1)#1-N(2)	0.215 2(4)	C(8)-O(1)	1.25 8(6)		
N(1)-Ag(1)-N(2)#1	168.64(13)	N(1)-Ag(1)-Ag(1)#1	80.22(10)	N(2)#1-Ag(1)-Ag(1)#1	88.48(10)
C(8)-N(1)-Ag(1)	106.8(3)	C(1)-N(1)-Ag(1)	132.4(3)	C(2)-N(2)-Ag(1)#1	119.2(3)
C(1)-N(2)-Ag(1)#1	122.5(3)	N(2)-C(1)-N(1)	116.4(4)	O(1)-C(8)-N(1)	118.3(4)

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

indicating some Ag-Ag interaction. The very close approach of the two metals can be a result of argentophilicity and the geometry requirement by the two bridging naphthyridine. Similar Ag-Ag interactions have been observed in many silver complexes such as catena-bis (4-aminobenzoato)disilver (I) complex (0.2987~0.3297 nm)^[13] and oligomeric and polymeric silver-imidazol-2-ylidene iodide complexes (0.292 ~ 0.307 nm)^[14]. Ligand unsupported silver-silver interact-

ions are also known^[15]. In the crystal of **1**, the adjacent molecules stack via Ag-p π interaction shown in Fig.2. The closest Ag \cdots C contact between adjacent molecules is 0.321 5 nm.

2.2 Structure of **2**

Silver complex **2** was prepared by reaction of in situ formed [Ag(PPh₃)₂NO₃] and disodium 1,8-naphthyridin-2,7-dionate (Na₂L₂) in aqueous solution and obtained as colorless crystals. The compound is air stable and light insensitive. The crystal structure of **2** showed that the complex is mononuclear with one HL₂⁻ anions adopting a monodentate coordination mode. The molecular structure is shown in Fig.3, and selected bond distances are listed in Table 3. The Ag⁺ ion is tricoordinated by one N atom from HL₂⁻ and two P atoms from triphenylphosphine ligands and displays triangle geometry. The oxygen atom does not coordinate to the silver atom. There existed two lattice water molecules. The bond angles of N(1)-Ag(1)-P(1), N(1)-Ag(1)-P(2), and P(1)-Ag(1)-P(2) are 117.1 (2) $^{\circ}$, 117.6 (2) $^{\circ}$, and 124.48(9) $^{\circ}$, respectively, which are all around 120 $^{\circ}$ illustrating the central silver atom and the three coordinating atoms are nearly coplanar. The bond length of Ag(1)-N(1) is 0.227 6(7) nm, which is significantly longer than that in complex **1** as a consequence of the large steric hindrance of PPh₃ ligands. The Ag-P bond distances in **2**, 0.243 1(3) nm and 0.243 8(3) nm lie at the

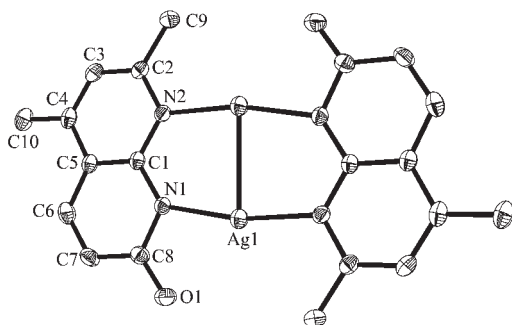


Fig.1 Molecular structure of **1** showing the atomic numbering scheme with thermal ellipsoids at the 50% probability level

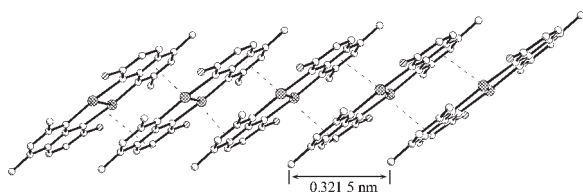


Fig.2 Packing diagram showing the Ag-p π interactions of complex **1**

Table 3 Selected bond lengths (nm) and bond angles ($^{\circ}$) for **2**

Ag(1)-N(1)	0.227 4(8)	Ag(1)-P(1)	0.243 3(3)	Ag(1)-P(2)	0.243 9(3)
C(1)-O(1)	0.125 0(13)	C(6)-O(2)	0.122 7(13)		
N(1)-Ag(1)-P(1)	117.1(2)	N(1)-Ag(1)-P(2)	117.5(2)	P(1)-Ag(1)-P(2)	124.50(9)
O(1)-C(1)-N(1)	118.6(10)	O(2)-C(6)-N(2)	120.3(9)	N(1)-C(7)-N(2)	116.5(9)
C(7)-N(1)-Ag(1)	134.9(7)	C(1)-N(1)-Ag(1)	104.8(7)	C(9)-P(1)-Ag(1)	114.0(4)
C(21)-P(1)-Ag(1)	117.3(3)	C(15)-P(1)-Ag(1)	112.6(3)		

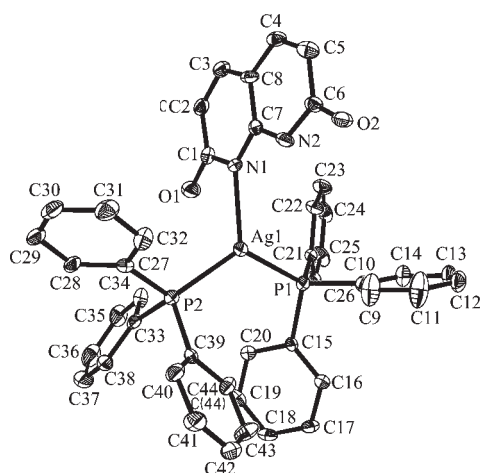


Fig.3 Thermal ellipsoid diagram of the molecular structure of complex **2** with 30% probability level

short end of range for known silver-phosphine complexes^[16]. These distances are comparable to $[\text{Ag}(\text{PPh}_3)_2(\text{ONO}_2)]$ ^[17] and $[\text{Ag}(\text{PPh}_3)_2]\text{BF}_4$ ^[16]. The bond lengths of C(1)-O(1) and C(6)-O(2) are 0.124 8(13) nm and 0.122 0(13) nm, respectively, which is well consistent with C=O bond lengths showing that the ligand exists as its dione form.

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