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Formation of novel discrete silver(I) coordination architectures with quinoline-based monothioethers: adjusting the intramolecular Ag···Ag distances and complex structures by ligands modifications and variations of counter anions

Rui-Feng Song,[a] **Ya-Bo Xie,**[a] **Jian-Rong Li**[a] **and Xian-He Bu** *[a,b]
[a] *Department of Chemistry, Nankai University, Tianjin 300071, China.*
E-mail: buxh@nankai.edu.cn
[b] *The State Key Lab of Coordination Chemistry, Nanjing University, Nanjing 210093, China*

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In our efforts to design discrete polynuclear metal complexes with tailored structures, four structurally related quinoline-based new monothioether ligands, 8-(2-pyridylsulfanylmethyl)quinoline (**L**^{1}), 8-(4-pyridyl- sulfanyl-methyl)quinoline (**L**^{2}), 8-(2-pyrimidylsulfanylmethyl)quinoline (**L**^{3}), 5-methyl-2-(8-quinolylmethyl- sulfanyl)-1,3,4-thiadiazole (**L**^{4}) have been designed, and six new Ag^I complexes with these ligands, $\{[AgL^1](ClO_4)(CHCl_3)\}_2$ **1**, $[Ag_2L^1(NO_3)_2]_2$ **2**, $\{[AgL^1(CH_3CN)](PF_6)\}_2$ **3**, $[AgL^2(NO_3)]_2$ **4**, $\{[AgL^3(CH_3OH)](ClO_4)\}_2$ **5** and $\{[AgL^4](ClO_4)\}_2$ **6** have been synthesized and characterized by single-crystal X-ray diffraction analysis. All six complexes adopt discrete structures, with **1**,**3**,**4**,**5** and **6** being dinuclear and **2** being tetranuclear, and Ag–Ag interactions were found to exist in complexes **1**,**2**,**3** and **6**, as well as π–π stacking in **1**–**4**. Furthermore, the Ag ··· Ag distances in **1**–**6** were compared. In the six complexes, the sulfur atoms of the ligands adopt quite different coordination modes: bridging in **1**,**2** and **3**, chelating in **5** and non-coordination in **4** and **6**. In addition, the structural differences of **1**,**2** and **3** indicate that the change in the counter anion greatly influences the coordination modes of the ligands and the coordination geometries of Ag^I ion, which consequently affects the resulting frameworks of such complexes.

Introduction

The design and synthesis of multi-nuclear discrete coordination architectures[1] and polymeric coordination networks[2,3] is a rapidly developing field in current coordination and supramolecular chemistry. In recent years, much attention has been focused on the synthetic approach and the structural control of coordination architectures, and great progress has been achieved, especially for those with multi-dimensional structures. However, the rational design and controlled formation of discrete molecular architectures rather than extended infinite coordination polymers still remains a great challenge.[4]

The design of suitable organic ligands favoring structure-specific self-assembly is crucial for the construction of discrete coordination architectures. Heterocyclic flexible thioether ligands containing nitrogen donors possess rich structural information, and reports on Ag^I complexes with such ligands have increased in recent years.[5–11] However, most of the reported work on such complexes are polymeric coordination networks, and those with discrete structures are comparatively less reported.

In our attempts to synthesize discrete coordination architectures, we designed a series of asymmetric monothioether ligands containing the large quinoline ring, and some discrete dinuclear or polynuclear Ag^I complexes with these ligands have been obtained. We report herein the design of four new quinoline-based monothioether ligands, 8-(2-pyridylsulfanylmethyl)quinoline (**L**^{1}), 8-(4-pyridylsulfanylmethyl)quinoline (**L**^{2}), 8-(2-pyrimidylsulfanylmethyl)quinoline (**L**^{3}), 5-methyl-2-(8-quinolylmethylsulfanyl)-1,3,4-thiadiazole (**L**^{4}) (Chart 1) and the synthesis and crystal structures of six discrete Ag^I complexes with these ligands. Crystallographic data and experimental details for structural analyses of the six complexes are summarized in Table 1.

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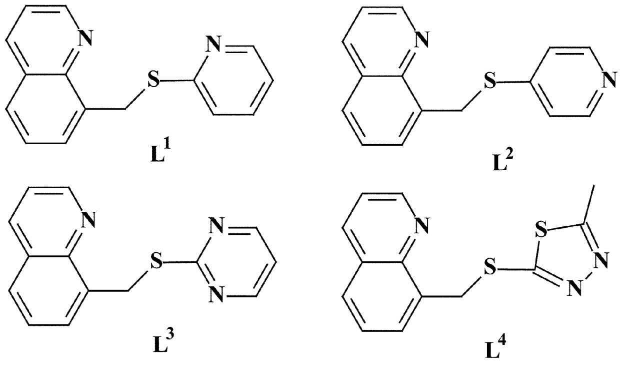

Chart 1

Results and discussion

Dinuclear complex $\{[AgL^1](ClO_4)(CHCl_3)\}_2$ (1), tetranuclear complex $[Ag_2L^1(NO_3)_2]_2$ (2) and dinuclear complex $\{[AgL^1(CH_3CN)](PF_6)\}_2$ (3), effects of counter anions

The crystal structure of **1** consists of a discrete dinuclear $[Ag_2(L^1)_2]^{2+}$ cation, two ClO_4^- anions and two $CHCl_3$ solvent molecules. The $[Ag_2(L^1)_2]^{2+}$ dinuclear cation comprises two **L**^{1} ligands and two Ag^I ions, and possesses a crystallographic center of symmetry located at the midpoint of two Ag^I centers (Fig. 1a). Each Ag^I ion adopts a distorted trigonal planar geometry formed by two N donors (a pyridine nitrogen and a quinoline nitrogen) from one **L**^{1} ligand and an S donor from another **L**^{1} ligand. All three Ag–donor bond distances are within the range expected for such coordination bonds (see Table 2).[6,11] The Ag^I center deviates from the coordination plane by *ca.* 0.2748 Å, and the bond angles around each Ag^I center are 122.6(2), 137.3(1) and 95.8(1)°, respectively.

Table 1 Crystallographic data and structure refinement summary for complexes **1**–**6**

	1	**2**	**3**
Chemical formula	$C_{16}H_{13}AgCl_4N_2O_4S$	$C_{15}H_{12}Ag_2N_4O_6S$	$C_{17}H_{15}AgF_6N_3PS$
Formula weight	579.01	592.09	546.22
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	8.809(5)	8.621(4)	10.890(4)
b/Å	9.550(5)	10.408(5)	13.577(5)
c/Å	12.505(7)	10.829(5)	14.816(6)
a/°	86.91(1)	107.237(6)	90
β/°	85.99(1)	100.105(7)	107.046(7)
γ/°	79.31(1)	97.077(7)	90
V/Å^3	1030(1)	897.7(7)	2094(1)
Z	2	2	4
D_c/g cm^{-3}	1.866	2.191	1.732
μ/mm^{-1}	1.624	2.341	1.198
T/K	293(2)	293(2)	293(2)
Reflections collected	3689	4197	9591
Unique reflections (R_{int})	3389 (0.0192)	3344 (0.0206)	4253 (0.0457)
R^a/wR^b	0.0407/0.1243	0.0457/0.1056	0.0448/0.0802
	4	**5**	**6**
Chemical formula	$C_{15}H_{12}AgN_3O_3S$	$C_{15}H_{15}AgClN_3O_5S$	$C_{13}H_{11}AgClN_3O_4S_2$
Formula weight	422.21	492.68	480.69
Crystal system	Triclinic	Tetragonal	Monoclinic
Space group	$P\bar{1}$	$I4_1/a$	$P2_1/c$
a/Å	9.733(4)	22.068(4)	12.327(1)
b/Å	9.753(3)	22.068(4)	10.276(1)
c/Å	10.233(4)	14.406(5)	12.847(1)
a/°	116.611(6)	90	90
β/°	112.350(6)	90	102.681(2)
γ/°	96.984(6)	90	90
V/Å^3	751.5(5)	7016(3)	1587.7(4)
Z	2	16	4
D_c/g cm^{-3}	1.866	1.866	2.011
μ/mm^{-1}	1.498	1.453	1.725
T/K	293(2)	293(2)	184(2)
Reflections collected	4322	16362	7206
Unique reflections (R_{int})	3022 (0.0282)	3595 (0.0537)	3330 (0.0206)
R^a/wR^b	0.0416/0.0988	0.0396/0.0953	0.0256/0.0615

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

Table 2 Selected bond lengths (Å) and angles (degrees) for complex **1**

Ag(1)–N(2)^a	2.252(4)	Ag(1)–N(1)^a	2.436(4)
Ag(1)–S(1)	2.533(2)	Ag(1)–Ag(1)^a	2.944(1)
N(2)^a–Ag(1)–N(1)^a	122.6(2)	N(2)^a–Ag(1)–S(1)	137.3(1)
N(1)^a–Ag(1)–S(1)	95.8(1)	N(2)^a–Ag(1)–Ag(1)^a	88.5(1)
N(1)^a–Ag(1)–Ag(1)^a	88.2(1)	S(1)–Ag(1)–Ag(1)^a	73.60(5)
C(11)–S(1)–C(10)	101.0(2)	C(11)–S(1)–Ag(1)	109.1(1)
C(10)–S(1)–Ag(1)	108.5(1)		

^{a} Symmetry code: $-x + 1, -y, -z + 1$.

Each ligand adopts tridentate coordination mode with two N donors chelating an Ag^I ion to form an 8-membered ring which adopts a chair conformation, and with an S donor bridging another Ag^I ion. In the chelating ring, the distance between Ag and S is 3.297 Å, which is out of the range expected for such coordination bonds.[9,11] In the dinuclear unit of **1**, the Ag ··· Ag separation of 2.944(1) Å is longer than that in metallic silver (2.889(6) Å), but is shorter that the sum of their van der Waals radii (3.44 Å),[12] indicating the existence of some Ag–Ag weak interaction as observed in some analogous systems.[7] Such short Ag ··· Ag separations have often been observed in some bi- and polynuclear complexes,[7,14] however, no d^{10} metal–metal bond is considered to exist when the Ag ··· Ag distance is longer than 2.705(1) Å.[14b,15] In addition, in **1**, all the aromatic ring planes are almost parallel to each other, and the dihedral angle between the pyridine and quinoline ring is 5.6°. The centroid–centroid separation (3.664 Å) and the offset distance (0.824 Å) between the pyridine ring and the pyridine moiety of the quinoline ring indicate the presence of intramolecular face-to-face π–π stacking interactions.[8,11] The co-effects of Ag–Ag and π–π interactions further stabilize the binuclear unit.

One oxygen atom of ClO_4^- accepts a hydrogen atom of a quinoline ring to form C–H ··· O hydrogen bond (C ··· O 3.326 Å, H ··· O 2.555Å, C–H ··· O 140.5°). Meanwhile, ClO_4^- ions weakly interact with Ag^I centers to form a quasi 1D chain, and a quasi 2D network is further formed by π–π stacking interactions of the intermolecular parallel quinoline rings (the centroid–centroid separation is *ca* 3.67 Å and the offset distance is *ca* 1.23 Å) (Fig. 1b).

Complex **2** is a discrete neutral tetranuclear molecule with an inversion center, and Fig. 2a shows a perspective view of the structure with atom labeling. In the tetranuclear unit, there are two independent Ag^I centers. The Ag(1) center is coordinated to two N donors of a **L^1** ligand and an S donor from another ligand taking a distorted trigonal planar geometry with the Ag(1) atom deviating from the coordination plane by *ca.* 0.4252 Å. The bond angles around Ag(1) are 127.5(2), 130.4(2) and 92.2(1)°, respectively. The Ag(1)–S distance (2.611(2) Å) in **2** is slightly longer than that in **1** (2.533(2) Å). The Ag(2) center adopts tetrahedral coordination geometry composed of an S donor and three oxygen atoms of two nitrate anions. All Ag–donor bond distances are in the normal range for such coordination bonds (see Table 3).[6,11]

In **2**, each S atom of **L^1** coordinates to two Ag^I centers in μ_2 mode resulting in the formation of the tetranuclear structure, in

Table 3 Selected bond lengths (Å) and angles (degrees) for complex **2**

Ag(1)–N(2)	2.265(5)	Ag(1)–N(1)	2.422(5)
Ag(1)–S(1)^a	2.611(2)	Ag(1)–Ag(1)^a	3.109(1)
Ag(2)–O(1)	2.464(7)	Ag(2)–O(4)	2.514(7)
Ag(2)–S(1)	2.551(2)	Ag(2)–O(5)	2.596(6)
Ag(1)^a–S(1)	2.611(2)		
N(2)–Ag(1)–N(1)	127.5(2)	N(2)–Ag(1)–S(1)^a	130.4(2)
N(1)–Ag(1)–S(1)^a	92.2(1)	N(2)–Ag(1)–Ag(1)^a	86.7(1)
N(1)–Ag(1)–Ag(1)^a	83.1(1)	S(1)^a–Ag(1)–Ag(1)^a	67.97(5)
O(1)–Ag(2)–O(4)	86.1(2)	O(1)–Ag(2)–S(1)	142.8(1)
O(4)–Ag(2)–S(1)	131.0(1)	O(1)–Ag(2)–O(5)	109.1(2)
O(4)–Ag(2)–O(5)	48.9(1)	S(1)–Ag(2)–O(5)	96.6(1)

^{a} Symmetry code: $-x$, $-y$, $-z$.

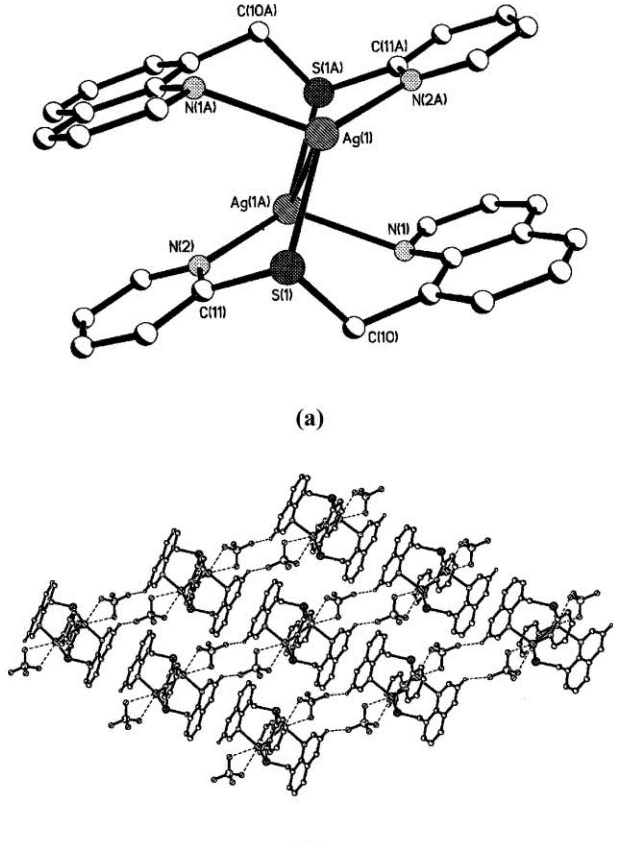

Fig. 1 (a) Perspective view of the $[Ag_2(\mathbf{L}^1)_2]^{2+}$ cation of **1**, and (b) the quasi 2D network formed through intermolecular C–H $\cdots$ O hydrogen bonds and intermolecular π–π interactions.

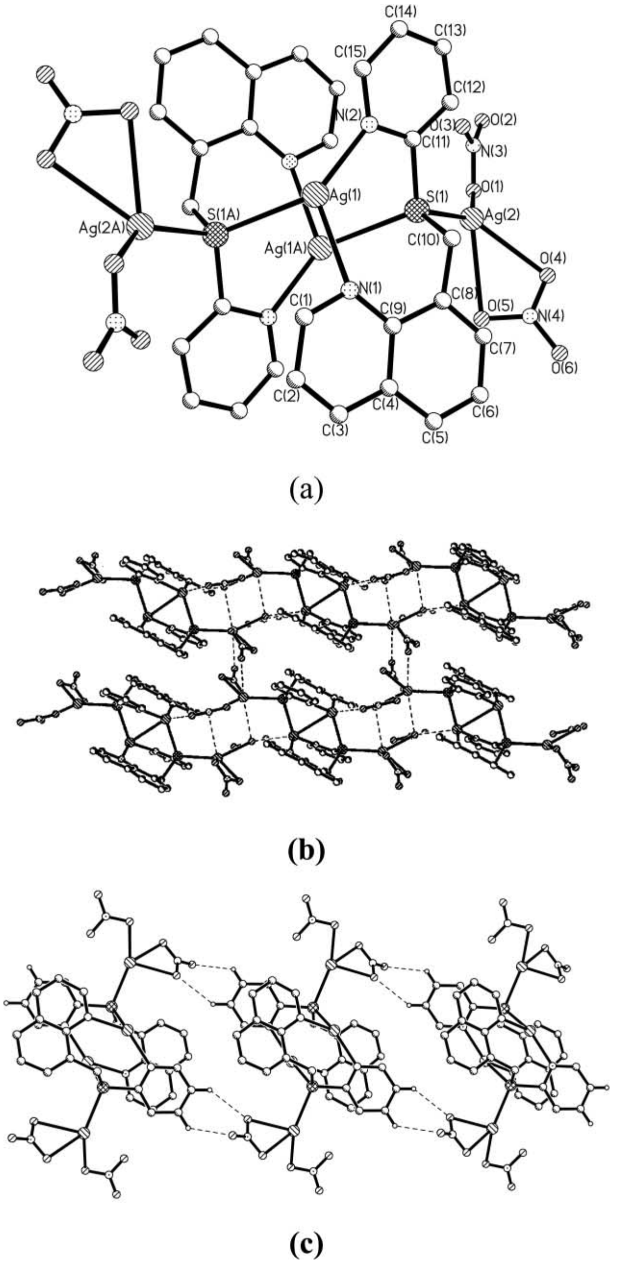

Fig. 2 (a) Perspective view of complex **2**, (b) the quasi 2D network formed through intermolecular Ag $\cdots$ O weak interactions, and (c) a view of two kinds of intermolecular C–H $\cdots$ O hydrogen bonds.

which, the Ag $\cdots$ Ag distance of 3.109(1) Å is longer than that of 2.944(1) Å in **1**, but also being within the summed van der Waals radii of two Ag atoms (3.44 Å),[12] indicating the presence of ligand-supported weak Ag–Ag interaction.[7,14] The dihedral angle of 12.6° between the pyridine and quinoline rings is greater than that of 5.6° in **1**. A centroid–centroid separation (*ca.* 3.63 Å) and the offset distance (1.155 Å) between the pyridine ring and the pyridine moiety of the quinoline ring indicate the presence of intramolecular face-to-face π–π stacking interaction.[8,11] The Ag(2) centers of one tetranuclear unit show weak interactions with the oxygen atoms of NO_3^- from adjacent tetranuclear units (the Ag $\cdots$ O distances are 2.716, 2.816, 2.986 and 2.750 Å). These weak interactions link the tetranuclear units into a quasi 2D network (Fig. 2b), which are further packed into a quasi 3D structure through two kinds of C–H $\cdots$ O hydrogen bonds (Fig. 2c) (C $\cdots$ O 3.225 Å, H $\cdots$ O 2.537 Å, C–H $\cdots$ O 147.9°; C $\cdots$ O 3.294 Å, H $\cdots$ O 2.510Å, C–H $\cdots$ O 142.1°).

The reaction of $\mathbf{L}^1$ with $AgPF_6$ produces a centrosymmetric dinuclear complex **3** consisting of $[Ag\mathbf{L}^1(CH_3CN)]_2^{2+}$ cation and two uncoordinated PF_6^- (Fig. 3). The local geometry of the Ag^I center is a distorted tetrahedron comprised of three N donors from an $\mathbf{L}^1$ ligand and an acetonitrile, and an S donor from another $\mathbf{L}^1$. The bond angles around Ag^I center range from 92.2(2) to 133.54(9)°. All Ag–donor bond distances are within the normal range expected for such coordination bonds (see Table 4).[6,11] In **3**, $\mathbf{L}^1$ adopts a similar coordination mode as that in **1**. There also exists weak Ag–Ag interactions (the distance is 2.988(1) Å).[7,14] Intramolecular face-to-face π–π stacking is also observed between the pyridine ring and the quinoline ring (the dihedral angle is 12.5°, the centroid–centroid separation is 3.635 Å and the offset distance is 0.741 Å).[8,11]

The structural differences between **1**,**2** and **3** exhibit the influences of counter anions on the framework formation of such complexes, and may mainly be attributed to the differences in their coordination abilities.[13] In **1**, ClO_4^- ions show weak interactions with Ag^I, and in **2**, the NO_3^- ions show stronger coordination to Ag^I ions, but in **3**, the PF_6^- ions only serve as counter anions. The coordination of NO_3^- and S donor to Ag(2) in **2** completes the tetrahedral coordination of Ag^I to

Table 4 Selected bond lengths (Å) and angles (degrees) of complex **3**

Ag(1)–N(1)	2.295(4)	Ag(1)–N(3)	2.338(5)
Ag(1)–N(2)	2.476(4)	Ag(1)–S(1)[a]	2.541(1)
Ag(1)–Ag(1)[a]	2.988(1)		
N(1)–Ag(1)–N(3)	97.3(2)	N(1)–Ag(1)–N(2)	122.2(1)
N(3)–Ag(1)–N(2)	92.2(2)	N(1)–Ag(1)–S(1)[a]	133.54(9)
N(3)–Ag(1)–S(1)[a]	104.4(1)	N(2)–Ag(1)–S(1)[a]	97.74(9)
N(1)–Ag(1)–Ag(1)[a]	84.43(9)	N(3)–Ag(1)–Ag(1)[a]	178.2(1)
N(2)–Ag(1)–Ag(1)[a]	87.41(9)	S(1)–Ag(1)–Ag(1)[a]	73.84(4)
C(5)–S(1)–C(6)	99.9(1)	C(5)–S(1)–Ag(1)[a]	103.6(1)
C(6)–S(1)–Ag(1)[a]	113.3(1)		

[a] Symmetry code: $-x + 1, -y + 1, -z$.

Table 5 Selected bond lengths (Å) and angles (degrees) of complex **4**

Ag(1)–N(2)[a]	2.228(4)	Ag(1)–N(1)	2.263(4)
Ag(1)–O(1)	2.565(5)		
N(2)[a]–Ag(1)–N(1)	154.7(1)	N(2)[a]–Ag(1)–O(1)	102.3(1)
N(1)–Ag(1)–O(1)	98.2(1)		

[a] Symmetry code: $-x + 2, -y, -z + 1$.

Table 6 Selected bond lengths (Å) and angles (degrees) of complex **5**

Ag(1)–N(2)	2.208(3)	Ag(1)–N(1)[a]	2.373(3)
Ag(1)–O(5)	2.518(3)	Ag(1)–S(1)[a]	2.527(1)
N(2)–Ag(1)–N(1)[a]	128.0(1)	N(2)–Ag(1)–O(5)	91.9(1)
N(1)[a]–Ag(1)–O(5)	87.0(1)	N(2)–Ag(1)–S(1)[a]	140.32(8)
N(1)[a]–Ag(1)–S(1)[a]	91.55(8)	O(5)–Ag(1)–S(1)[a]	93.71(9)
C(11)–S(1)–C(10)	100.5(1)	C(11)–S(1)–Ag(1)[a]	103.1(1)
C(10)–S(1)–Ag(1)[a]	93.8(1)		

[a] Symmetry code: $-x + 1, -y + 1/2, z$.

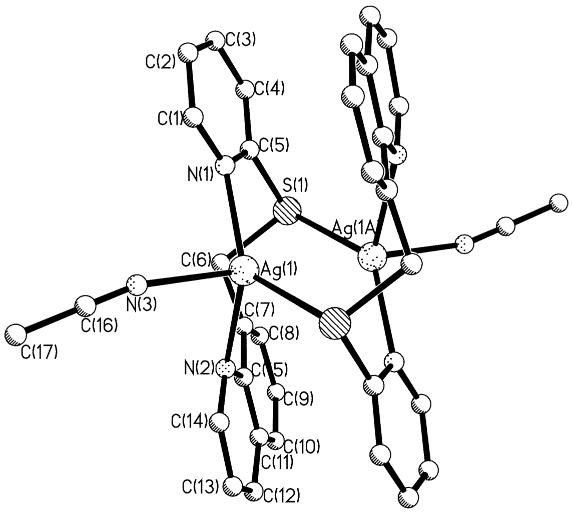

Fig. 3 Perspective view of the $[Ag_2(\mathbf{L}^1)_2(CH_3CN)_2]^{2+}$ cation of **3**.

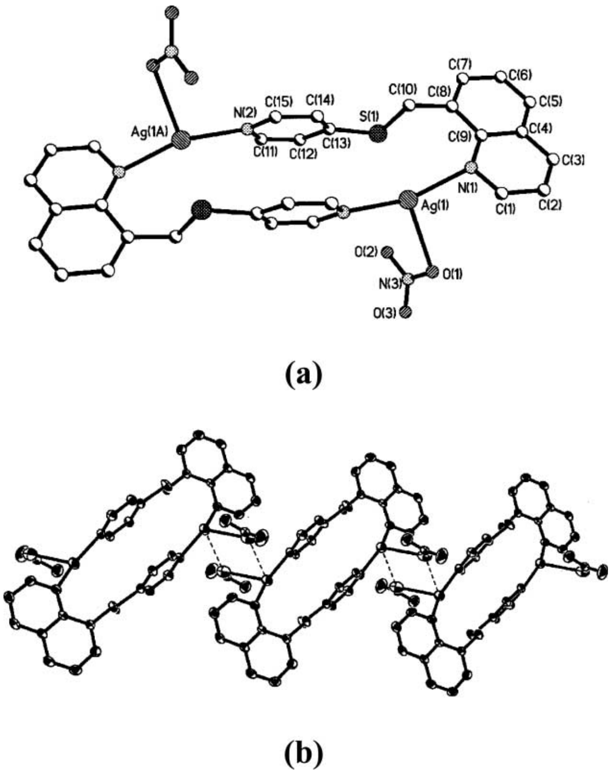

Fig. 4 (a) Perspective view of the complex **4**, and (b) the quasi 1D structure formed through intermolecular Ag ··· O weak interactions.

result in the tetranuclear structure, and the intermolecular Ag ··· O weak interactions further stabilize the structure.

$[AgL^2(NO_3)]_2$ (4), $\{[AgL^3(CH_3OH)](ClO_4)\}_2$ (5) and $\{[AgL^4](ClO_4)\}_2$ (6), three dinuclear complexes

Complex **4** is a centrosymmetric macrometallacycle composed of two Ag^I ions, two $\mathbf{L}^2$ ligands and two NO_3^- ions. Fig. 4a shows a perspective view of the structure with atom numbering, and selected bond distances and angles are listed in Table 5. Each Ag^I center has a distorted T-shaped geometry comprised of a pyridine nitrogen, a quinoline nitrogen from distinct ligands and an oxygen atom from NO_3^-. The three bond angles around Ag^I center are 154.7(1), 102.3(1) and 98.2(1)°, respectively. All the three Ag–donor bond distances are within the normal range expected for such coordination bonds.[6,11] The shortest Ag ··· S distance is 3.11 Å.

In **4**, $\mathbf{L}^2$ adopts a bidentate bridging coordination mode using its two N atoms, and two $\mathbf{L}^2$ ligands bridge two Ag^I ions to form a 20-membered macrometallacycle. In each ligand, the pyridine and quinoline rings are inclined at an angle of 72.1°. In the macrometallacycle, two pyridine rings are parallel to each other with the centroid–centroid separation of 3.526 Å and the offset distance of 1.291 Å, indicating significant intramolecular face-to-face π–π stacking,[8,11] which further enhances the stability of this structure. In addition, the coordinated O atoms of NO_3^- ions show weak interactions with Ag^I centers of adjacent macrometallacycles with the Ag ··· O distance of 2.819 Å, and these Ag ··· O weak interactions link the dinuclear units into a quasi 1D structure (Fig. 4b).

Complex **5** consists of C_2 symmetric $[Ag_2(\mathbf{L}^3)_2(CH_3OH)_2]^{2+}$ cations (Fig. 5a) and uncoordinated ClO_4^-. Each Ag^I center is coordinated to a quinoline N and a pyrimidine N from two distinct $\mathbf{L}^3$ ligands, an S donor and an O donor from MeOH. The *cis*-bond angles around Ag^I center range from 87.0(1) to 140.32(8)°. The geometry of the Ag^I center can best be described as a trigonal pyramid with two N donors and an S donor in the equatorial plane and an O at apical position. All Ag–donor bond distances are within the normal range expected for such coordination bonds (see Table 6).[6,11]

Each ligand adopts tridentate chelating and bridging coordination mode with the quinoline N and S atom chelating Ag^I center forming a 6-membered coordination ring which adopts a boat conformation, and one of the pyrimidine nitrogen atoms of this ligand bridging another Ag^I center. Two pyrimidylsulfanyl groups bridging two Ag^I centers to form an 8-membered dinuclear ring with boat conformation. In the dinuclear cation, two Ag^I centers are related by a C_2 axis with the Ag ··· Ag separation of 3.611 Å, which is longer than the summed van der Waals radii, implying the absence of Ag–Ag interaction.[12] Neither Ag–Ag nor π–π stacking interactions were observed in **5**, which is different from that of complexes **1**–**4**. An interesting feature of the overall topology of **5** is the saddle-shaped structure, in which two pyrimidine rings and two quinoline rings are located up and down, respectively (Fig. 5b).

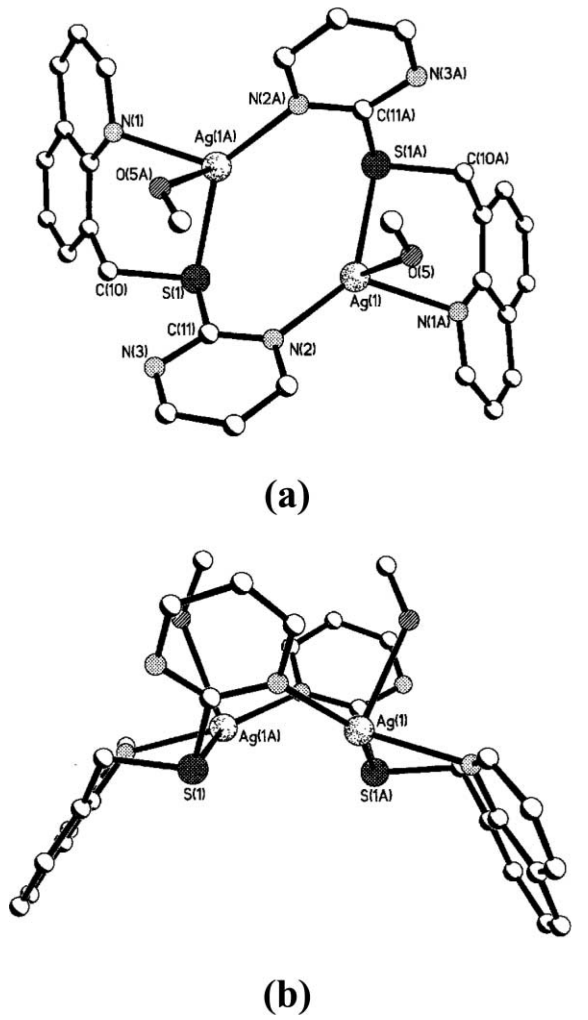

Fig. 5 A saddle-shaped structure of the $[Ag_2(\mathbf{L}^3)_2(CH_3OH)_2]^{2+}$ cation of **5**: (a) a top view and (b) a side view.

Complex **6** is comprised of a centrosymmetric $[Ag_2(\mathbf{L}^4)_2]^{2+}$ dinuclear cation and two uncoordinated ClO_4^- (Fig. 6). Each Ag^I center adopts a trigonal planar geometry formed by a quinoline N donor and two thiadiazole N donors from different ligands with the Ag^I center deviating from the coordination plane by 0.1961 Å. All the three Ag–N bond distances are within the normal range expected for such coordination bonds (Table 7),[6,11] and the three bond angles around Ag^I center are 127.13(7), 117.70(7) and 112.95(7)°, respectively.

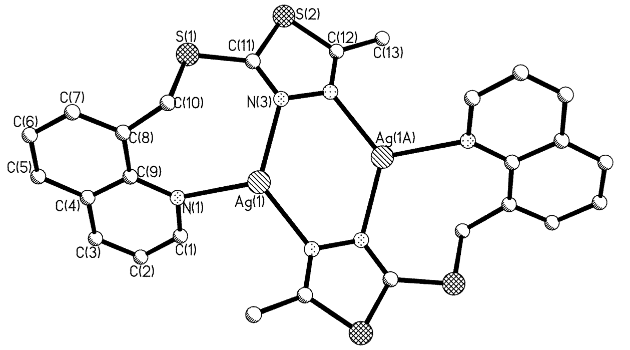

Fig. 6 Perspective view of the $[Ag_2(\mathbf{L}^4)_2]^{2+}$ cation of **6**.

In **6**, each $\mathbf{L}^4$ chelates an Ag^I center with a quinoline N and a thiadiazole N to form an 8-membered coordination ring which adopts a chair conformation with an Ag ··· S nonbonding distance of 3.855 Å. At the same time, two thiadiazole rings from distinct ligands bridge two Ag^I centers to form a centrosymmetric 6-membered dinuclear ring, which adopts flat chair conformation with two thiadiazoles parallel to each other. The Ag–Ag distance of 3.3638(5) Å is significantly longer than those in **1**–**3**, but still within the summed van der Waals radii of two Ag atoms (3.44 Å),[12] and this indicates the $Ag^I \cdots Ag^I$ interaction in **6** is very weak.[14–16] In addition, the planes of two quinoline rings located at the symmetric sites are parallel to each other.

Table 7 Selected bond lengths (Å) and angles (degrees) of complex **6**

Ag(1)–N(2)	2.237(1)	Ag(1)–N(3)	2.279(2)
Ag(1)–N(1)	2.324(2)	Ag(1)–Ag(1)[a]	3.3638(5)
N(2)–Ag(1)–N(3)	127.13(7)	N(2)–Ag(1)–N(1)	117.70(7)
N(3)–Ag(1)–N(1)	112.95(7)	N(2)–Ag(1)–Ag(1)[a]	64.11(5)
N(3)–Ag(1)–Ag(1)[a]	63.43(5)	N(1)–Ag(1)–Ag(1)[a]	156.79(5)

[a] Symmetry code: $-x + 1, -y, -z$.

The common feature of the four ligands is that each contains a large quinoline group. The only difference between $\mathbf{L}^1$ and $\mathbf{L}^2$ is the position of the pyridine nitrogen, but this makes complex **4** form a box-like dinuclear structure with strong intramolecular π–π interaction, while **2** has a tetranuclear structure in which intramolecular π–π stacking is observed. This may be attributed to the differences of the "bite angle" of the two ligands. In **5**, $\mathbf{L}^3$ acts as an N_2S tridentate ligand like $\mathbf{L}^1$, but $\mathbf{L}^3$ shows different coordination modes and forms a complex with a different framework. Although one of the two pyrimidine nitrogens does not adopt part in coordination, the non-coordinated nitrogen atom plays an important role in the formation of **5**. The pyrimidine nitrogen is a weaker donor atom than the pyridine nitrogen, and $\mathbf{L}^3$ may be regarded as one C of $\mathbf{L}^1$ being replaced by an N atom, therefore the pyrimidine ring of $\mathbf{L}^3$ shows more flexible coordination property than $\mathbf{L}^1$ due to the absence of the steric hindrance of H in the C atom in $\mathbf{L}^1$. In **6**, two thiadiazole rings from different $\mathbf{L}^4$ ligands preferentially bridge two Ag^I centers to form a very stable 6-membered cycle, which probably helps the formation of the dinuclear structure.

In the six complexes, the coordination modes of S atom are different and changed with the variation of the terminal groups of ligands. In **1** and **3**, each S donor bridges an Ag^I center, while in **2**, each bridges two Ag^I centers. In **5**, the S donors adopt chelating coordination mode combining with quinoline N donors. However, in **4** and **6**, only the N donors of the ligands coordinated to Ag^I ions indicating that geometrical effects may play more important roles than electric effects in controlling the formation of such complexes. These differences may be attributed to the differences of the configurations and coordination properties of terminal groups in these ligands.

Comparison of the intramolecular Ag ··· Ag distances in 1–6

In **1**–**6**, the intramolecular Ag ··· Ag distances changed with the ligands modifications [the Ag ··· Ag separations are 2.944(1), 3.109(1), 2.988(1), 7.560(1), 3.611(1) and 3.363(9) Å for **1**–**6**, respectively]. Similar cyclic skeletons were formed in **1**–**3** [Fig. 1a, Fig. 2a, and Fig. 3], however the Ag ··· Ag distances are different in these complexes. The longer Ag ··· Ag distance in **2** may result from the formation of the Ag–S coordination bond, and the small difference in **1** and **3** is probably due to the coordination of CH_3CN molecule in complex **3**. In **5**, an 8-membered Ag–N–C–S–Ag–N–C–S ring was formed with the intramolecular Ag ··· Ag distance of 3.611(1) Å being longer than those in **1**–**3**. This is probably attributed to chelation of the Ag^I centers with the quinoline N and S atoms which pulls the Ag^I atoms apart from each other (Fig. 5a). Complex **6** contains a 6-membered Ag–N–N–Ag–N–N ring in which the Ag ··· Ag distance is 3.3638(5) Å, which is longer in the 6-membered ring systems, and this is probably due to the coordination of the quinoline N (Fig. 6). In **4**, the intramolecular Ag $\cdots$ Ag distance is 7.560 Å being longer than those in the other five complexes. These differences in distance are mainly attributed to the differences in terminal groups of such ligands, which have different coordination abilities.

In summary, four quinoline-based monothioether ligands have been designed and synthesized, and the self-assembly of these ligands with Ag^I salts yields six new discrete complexes. The changes of terminal groups of the ligands and counterions can greatly influence the coordination modes of S atom and the complex architectures, as well as the intramolecular Ag $\cdots$ Ag distances and π–π stacking. These results indicate that discrete complexes may be obtained by the self-assembly of such well designed N/S-containing ligands with suitable metal ions.

Experimental

Materials and general methods

8-Bromomethyl quinoline was prepared by reported procedures.[17] All the other reagents for synthesis were commercially available and employed as received or purified by standard methods prior to use. Elemental analyses were performed on a Perkin-Elemer 240C analyzer and IR spectra on a 170SX (Nicolet) FT-IR spectrometer with KBr pellets. ^1H NMR spectra were recorded on a Bruker AC-P500 spectrometer (300 MHz) at 25 °C in $CDCl_3$ with tetramethylsilane as the internal reference.

Caution: Although we have met no problems in handling perchlorate salts and their complexes during this work, these should be treated with great caution owing to their potential explosive nature.

Syntheses of ligands

8-(2-Pyridylsulfanylmethyl)quinoline (L^1). 8-Bromomethyl quinoline (450 mg, 2 mmol) was added to an ice-cooled solution of 2-mercaptopyridine (220 mg, 2 mmol) and KOH (82%, 136 mg, 2 mmol) in ethanol (30 mL) under stirring. The mixture was stirred for 5 h at room temperature, and then filtered and concentrated to give crude **L^1** as a brown solid, which was washed with water and dried in air. Recrystallization from ethanol gave pale brown crystals (480 mg, 95%). Mp 98–99 °C. IR (KBr pellet, cm^{-1}): 3035m, 2938m, 1572s, 1552s, 1497s, 1453vs, 1413s, 1273m, 1117vs, 1028m, 985m, 763s, 720m, 636w. ^1H NMR ($CDCl_3$): δ 5.13 (2H, s, $–CH_2S$), 8.99 (1H, d, H2), 7.41 (1H, t, H3), 8.14 (1H, d, H4), 7.89 (1H, d, H5), 7.45 (1H, t, H6), 7.72 (1H, d, H7), 7.16 (1H, d, H3′), 7.46 (1H, t, H4′), 6.98 (1H, t, H5′), 8.49 (1H, d, H6′). Anal. Found: C, 71.01; H, 4.71; N, 11.17. Calc. for $C_{15}H_{12}N_2S$: C, 71.40; H, 4.79; N, 11.10.

8-(4-Pyridylsulfanylmethyl)quinoline (L^2). The reaction of 4-mercaptopyridine (220 mg, 2 mmol) with 8-bromomethylquinoline (450 mg, 2 mmol) in a similar procedure for **L^1** gave **L^2** as a pale yellow powder in 71% yield. Mp 117–118 °C. IR (KBr pellet, cm^{-1}): 3028w, 2925w, 1576s, 1497m, 1408m, 1108w, 1022w, 979w, 833w, 798s, 636w. ^1H NMR ($CDCl_3$): δ 4.95 (2H, s, CH_2S), 8.99 (1H, d, H2), 7.46 (1H, t, H3), 8.18 (1H, d, H4), 7.83 (1H, d, H5), 7.50 (1H, t, H6), 7.77 (1H, d, H7), 8.35 (2H, d, H2′, 6′), 7.21 (2H, d, H3′, 5′). Anal. Found: C, 71.07; H, 4.72; N, 11.01. Calc. for $C_{15}H_{12}N_2S$: C, 71.40; H, 4.79; N, 11.10.

8-(2-Pyrimidylsulfanylmethyl)quinoline (L^3). The reaction of 2-mercaptopyrimidine (224 mg, 2 mmol) with 8-bromomethylquinoline (450 mg, 2 mmol) in a similar procedure used for **L^1** gave **L^3** as a white powder in 92% yield. Mp 135–137 °C. IR (KBr pellet, cm^{-1}): 3034w, 2943w, 1561s, 1548s, 1497m, 1377vs, 1200m, 1172m, 829m, 795s, 629w. ^1HNMR ($CDCl_3$): δ 5.11 (2H, s, CH_2S), 8.98 (1H, d, H2), 7.42 (1H, t, H3), 8.15 (1H, d, H4), 7.93 (1H, d, H5), 7.47 (1H, t, H6), 7.74 (1H, d, H7), 8.54 (2H, d, H4′, H6′), 6.95 (1H, t, H5′). Anal. Found: C, 66.69; H, 4.47; N, 16.36. Calc. for $C_{14}H_{11}N_3S$: C, 66.35; H, 4.38; N, 16.59.

5-Methyl-2-(8-quinolylmethylsulfanyl)-1,3,4-thiadiazole (L^4). The reaction of 5-methyl-2-sulfanyl-1,3,4-thiadiazole (264 mg, 2 mmol) with 8-bromomethylquinoline (450 mg, 2 mmol) in a similar procedure used for **L^1** gave **L^4** as a white powder in 81% yield. Mp 54–56 °C. IR (KBr pellet, cm^{-1}): 2986w, 1593m, 1577m, 1497s, 1471w, 1381s, 1258m, 1069s, 1028m, 797s, 633w, 586m. ^1H NMR ($CDCl_3$): δ 5.20 (2H, s, CH_2S), 2.71 (3H, s, CH_3), 8.96 (1H, d, H2), 7.43 (1H, t, H3), 8.16 (1H, d, H4), 7.92 (1H, d, H5), 7.47 (1H, t, H6), 7.78 (1H, d, H7). Anal. Found: C, 57.46; H, 4.15; N, 15.42. Calc. for $C_{13}H_{11}N_3S_2$: C, 57.12; H, 4.06; N, 15.37.

Syntheses of complexes 1–6

$\{[AgL^1](ClO_4)(CHCl_3)\}_2$ (1). A solution of $AgClO_4{\cdot}H_2O$ (23 mg, 0.1 mmol) in CH_3CN (3 mL) was slowly added to a solution of **L^1** (25 mg, 0.1 mmol) in $CHCl_3$ (3 mL). Slow diffusion of acetone into the resulting solution yielded colorless single crystals **1** suitable for X-ray analysis in 30% yield. IR (KBr pellet, cm^{-1}): 3089w, 2999w, 1578m, 1560w, 1503m, 1454m, 1427m, 1397w, 1098vs, 1010m, 834m, 800m, 757s, 623s. Anal. Found: C, 33.48; H, 2.09; N, 4.95. Calc. for $C_{16}H_{13}AgCl_4N_2O_4S$: C, 33.19; H, 2.26; N, 4.84.

$[Ag_2L^1(NO_3)_2]_2$ (2). A solution of $AgNO_3$ (17 mg, 0.1 mmol) in CH_3CN (3 mL) was added to a solution of **L^1** (25 mg, 0.1 mmol) in $CHCl_3$ (3 mL). Slow diffusion of acetone into the resulting solution yielded colorless single crystals **2** in 25% yield based on **L^1**. IR (KBr pellet, cm^{-1}): 3071w, 2939w, 1579m, 1558w, 1504m, 1455m, 1414s, 1284s, 1351vs, 1281s, 1120m, 1029w, 1007w, 838w, 799m, 769m, 723w, 634w. Anal. Found: C, 30.69; H, 2.13; N, 9.62. Calc. for $C_{15}H_{12}Ag_2N_4O_6S$: C, 30.43; H, 2.04; N, 9.46.

$\{[AgL^1(CH_3CN)](PF_6)\}_2$ (3). A solution of $AgPF_6$ (25 mg, 0.1 mmol) in CH_3CN (6 mL) was added to a solution of **L^1** (25 mg, 0.1 mmol) in $CHCl_3$ (3 mL). Slow diffusion of acetone into the resulting solution yielded colorless single crystals **3** in 28% yield. IR (KBr pellet, cm^{-1}): 3069w, 2959m, 2924m, 1582s, 1562m, 1500m, 1454s, 1425m, 1392w, 1298s, 1147s, 1096m, 831vs, 796s, 756m. Anal. Found: C, 37.09; H, 2.96; N, 7.87. Calc. for $C_{17}H_{15}AgF_6N_3PS$: C, 37.38; H, 2.77; N, 7.69.

$[AgL^2(NO_3)]_2$ (4). Colorless crystals of **4** suitable for X-ray analysis were obtained by a similar method described for **2**. Yield: 32%. IR (KBr pellet, cm^{-1}): 3054w, 2923w, 1587vs, 1508m, 1422s, 1386vs, 1299vs, 1110m, 838m, 796s, 634w. Anal. Found: C, 42.32; H, 2.94; N, 9.79. Calc. for $C_{15}H_{12}AgN_3O_3S$: C, 42.67; H, 2.86; N, 9.95.

$\{[AgL^3(CH_3OH)](ClO_4)\}_2$ (5). A solution of $AgClO_4{\cdot}H_2O$ (23 mg, 0.1 mmol) in CH_3OH (10 mL) was slowly added to a solution of **L^3** (25 mg, 0.1 mmol) in $CHCl_3$ (5 mL). The reaction mixture was kept in the dark and was allowed to evaporate slowly and colorless single crystals of **5** were obtained suitable for X-ray analysis in 27% yield. IR (KBr pellet, cm^{-1}): 3461m, 3074w, 2944w, 1837w, 1561m, 1549s, 1502m, 1380vs, 1105vs, 830w, 798m, 626s. Anal. Found: C, 36.35; H, 3.16; N, 8.48. Calc. for $C_{15}H_{15}AgClN_3O_5S$: C, 36.57; H, 3.07; N, 8.53.

$\{[AgL^4](ClO_4)\}_2$ (6). Colorless crystals of **6** suitable for X-ray analysis was obtained by a similar method used for **1**. Yield: 26%. IR (KBr pellet, cm^{-1}): 2979w, 2927w, 1595w, 1576w, 1499s, 1466w, 1381m, 1259w, 1089vs, 884w, 795s, 766w, 635m, 621s, 584w. Anal. Found: C, 32.76; H, 2.41; N, 8.57. Calc. for $C_{13}H_{11}AgClN_3O_4S_2$: C, 32.48; H, 2.31; N, 8.74.

X-Ray crystallography

Single-crystal X-ray diffraction measurements of **1**–**5** were carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite monochromator at room temperature, and **6** was on a Rigaku Mercury CCD area detector at 184 K. The determination of unit cell parameters and data collections were performed with Mo-Kα radiation (λ = 0.71073 Å). Unit cell dimensions were obtained with least-squares refinements and all structures were solved by direct methods.[18] Ag atoms in each complex were located from *E*-maps. The other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2.[19] Hydrogen atoms were added theoretically and riding on the concerned atoms.

CCDC reference numbers 211351–211356.

See http://www.rsc.org/suppdata/dt/b3/b309176g/ for crystallographic data in CIF or other electronic format.

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