Syntheses, Crystal Structures, and Properties of Four Two-Dimensional Network Complexes with Multidentate Bis(Schiff Base) Ligands

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Keywords: Schiff bases / Silver / Cobalt / Crystal engineering

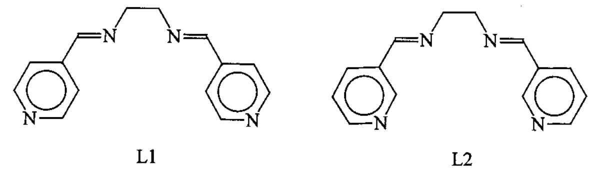
Four novel two-dimensional coordination polymers $[Ag_2(L1)_2](CF_3SO_3)_2\cdot H_2O$ (**1**), $[Ag_3(L1)_2](NO_3)_3\cdot H_2O$ (**2**), $[Co(L1)_2(SCN)_2]\cdot EtOH$ (**3**), and $[Co(L2)_2(SCN)_2]$ (**4**) were obtained by reactions of the bis(Schiff base) ligand 1,2-bis(4′-pyridylmethyleneamino)ethane (L1) with silver(I) trifluoromethanesulfonate, silver(I) nitrate, and cobalt(II) thiocyanate, and 1,2-bis(3′-pyridylmethyleneamino)ethane (L2) with cobalt(II) thiocyanate, respectively. In complex **1**, a 2D network structure was achieved by hydrogen bonding interactions between the two 1D chains, consisting of double-stranded helicates, through solvate water molecules. The 2D network of complex **2** was formed by the coordination to a two-coordinate silver(I) ion instead of hydrogen bonds as in complex **1**. Complex **3** contains molecular square units, which are occupied by disordered ethanol molecules. Complex **4** exhibits a classic square-grid network which is different from that of **3** due to the different terminal pyridyl groups in L1 (4-pyridyl) and L2 (3-pyridyl). These coordination polymers were characterized by X-ray crystallography, electrospray mass spectrometry, cyclic voltammetry and magnetic measurements. The results show a 2D network superstructural diversity by the fine-tuning of construction components.

Introduction

The construction of polymeric coordination complexes has developed rapidly in recent years owing to their structural topologies and interesting catalytic, electronic, magnetic and spectroscopic properties.[1] The "node-and-spacer" approach has been remarkably successful in constructing predictable network architectures, including zero-dimensional polyhedrons, and infinite one- (1D), two- (2D), and three-dimensional (3D) periodic nets.[2−7] In the case of 2D architectures, one would anticipate that the network would possess an inherent ability to include guest molecules. Square grid,[8] rectangular grid,[9] brick wall,[10] herringbone,[11] and bi-layer[12] networks have been reported and can be generated from commonly available metal moieties and linear "spacer" ligands. The square-grid is a simple and well-known 2D metal-organic network.[13] A series of square-grid networks has been obtained by the reaction of bipy spacer ligands with various transition metal ions such as Cd^{II}, Co^{II}, Ni^{II}, and Zn^{II}, with different crystal packing modes.[14] Other commonly used spacer ligands include cyano[15] and pyrazine moieties[16] and longer analogs of bipy.[17]

Although the node-and-spacer approach exerts significant effects on the construction of the network polymers, it can only successfully be applied to the self-assembly of rigid bidentate ligands and metal moieties. An assembly process containing multidentate ligands is usually very complicated and is influenced by various factors such as solvent system, templates, counterions, valences and the geometric needs of the metal ions and sometimes the ratio between the metal salt and the ligand.[18] Therefore it is still difficult at the present time to design and synthesize supermolecular architectures with predicted structures and properties when the number of donor atoms in the ligands is more than two.

To investigate the influence of the nature of multidentate ligands on the construction of 2D network polymers, the tetradentate bis(Schiff base) ligands 1,2-bis(4′-pyridyl)ethylenediamine (L1) and 1,2-bis(3′-pyridyl)ethylenediamine (L2; Scheme 1) − longer analogs of bipyridine − were em-



Scheme 1

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ployed as organic ligands. Self-assembly of these ligands with monovalent silver(I) and divalent cobalt(II) salts as the nodes was carried out.

Schiff bases are an important class of ligands in coordination chemistry and have been studied extensively[19] as they are selective and sensitive toward various metal ions. In our previous work we reported that the assembly of Schiff base ligand L1 with copper(I) salts produced two complexes $[Cu(L1)(CH_3CN)]NO_3$ and $[Cu(L1)(CH_3CN)]ClO_4$ with infinite zigzag chain-like structures;[20] two infinite 2D grid networks were obtained by assembly of reduced L1 ligand, 1,6-bis(4′-pyridyl)-2,5-diazahexane (L), with the same copper(I) salts.[22] This indicates the significant influence of the nature of the ligand on the construction of supramolecular architectures. In this paper, the reaction of L1 with silver(I) salts with different counteranions, is shown to produce two 2D coordination polymers $[Ag_2(L1)_2](CF_3SO_3)_2{\cdot}H_2O$ (**1**) and $[Ag_3(L1)_2](NO_3)_3{\cdot}H_2O$ (**2**) containing double-stranded helicates. In addition, the self-assembly of ligands L1 and L2 with $Co(SCN)_2$ produces two different 2D coordination complexes, $[Co(L1)_2](SCN)_2{\cdot}EtOH$ (**3**) and $[Co(L2)_2](SCN)_2$ (**4**). These coordination complexes were characterized by X-ray crystal diffraction, electrospray mass spectrometry, cyclic voltammetry and magnetic measurements.

Results and Discussion

Crystal Structure Description

Complexes **1** and **2** have the same ligand and metal ion but different anions, while complexes **3** and **4** have different ligands. X-ray crystal structure analyses reveal that complexes **1**−**4** crystallize in different crystal systems with different symmetries, from triclinic to tetragonal. Details of the crystal parameters, data collection and refinement for complexes **1**−**4** are summarized in Table 4, and selected bond lengths and angles with their estimated standard deviations are listed in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] for **1**−**4**

$[Ag_2(L1)_2](CF_3SO_3)_2{\cdot}H_2O$ (**1**)			
Ag(1)−N(1)	2.337(2)	Ag(1)−N(3)	2.328(2)
Ag(1)−N(2)	2.405(2)	Ag(1)−N(4)	2.387(2)
Ag(2)−N(11)	2.176(2)	Ag(2)−N(31)	2.185(2)
N(1)−Ag(1)−N(2)	75.77(8)	N(2)−Ag(1)−N(3)	125.17(8)
N(1)−Ag(1)−N(3)	135.86(8)	N(2)−Ag(1)−N(4)	129.37(8)
N(1)−Ag(1)−N(4)	125.21(8)	N(3)−Ag(1)−N(4)	74.68(8)
N(11)−Ag(2)−N(31)	171.42(9)		
$[Ag_3(L1)_2](NO_3)_3{\cdot}H_2O$ (**2**)			
Ag(1)−N(31)	2.331(4)	Ag(1)−N(21)	2.346(3)
Ag(1)−N(41)	2.402(4)	Ag(1)−N(11)	2.407(3)
Ag(2)−N(12)	2.154(4)	Ag(2)−N(42)	2.155(4)
Ag(3)−N(32)	2.147(4)	Ag(3)−N(22)	2.152(4)
N(31)−Ag(1)−N(21)	138.71(13)	N(31)−Ag(1)−N(41)	74.92(12)
N(21)−Ag(1)−N(41)	122.40(12)	N(31)−Ag(1)−N(11)	128.74(12)
N(21)−Ag(1)−N(11)	73.90(11)	N(41)−Ag(1)−N(11)	127.04(13)
N(12)−Ag(2)−N(42)	167.50(17)	N(32)−Ag(3)−N(22)	177.56(18)
$[Co(L1)_2](SCN)_2{\cdot}EtOH$ (**3**)			
Co(1)−N(1)	2.096(3)	Co(1)−N(2)	2.098(3)
Co(1)−N(12)	2.188(3)	Co(1)−N(22)	2.191(3)
Co(1)−N(32)	2.171(3)	Co(1)−N(42)	2.159(3)
N(1)−Co(1)−N(2)	176.47(12)	N(1)−Co(1)−N(42)	92.43(11)
N(1)−Co(1)−N(32)	91.18(12)	N(1)−Co(1)−N(22)	87.63(11)
N(1)−Co(1)−N(12)	89.13(11)	N(12)−Co(1)−N(22)	89.56(10)
N(42)−Co(1)−N(22)	91.93(10)	N(42)−Co(1)−N(32)	86.54(10)
N(42)−Co(1)−N(12)	177.89(11)	N(32)−Co(1)−N(22)	178.02(10)
N(12)−Co(1)−N(32)	92.01(11)		
$[Co(L2)_2](SCN)_2$ (**4**)			
Co(1)−N(1)	2.051(4)	Co(1)−N(2)	2.053(5)
Co(1)−N(12)	2.1791(15)		
N(1)−Co(1)−N(2)	180.0	N(1)−Co(1)−N(12)	89.92(6)
N(12)−Co(1)−N(12B)	90.0		

Crystallographic analysis indicates that the asymmetric unit of complex **1** consists of two silver(I) ions, two L1 ligands, two $CF_3SO_3^-$ anions and one water molecule, as shown in Figure 1. It is interesting that the Ag^I atoms have two different coordination environments, which is not com-

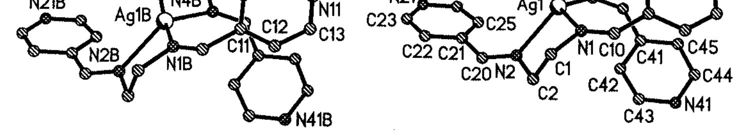
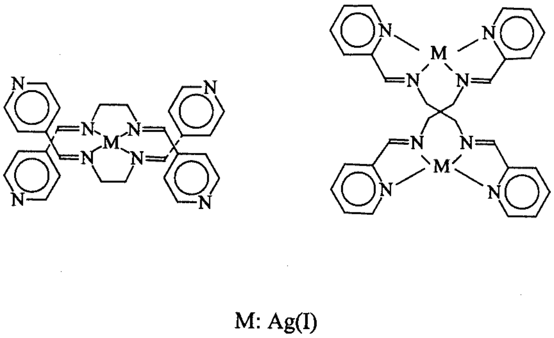


Figure 1. 1D chain structure of $[Ag_2(L1)_2](CF_3SO_3)_2{\cdot}H_2O$ (**1**) with atom numbering scheme; anions, water molecules, and hydrogen atoms have been omitted for clarity

mon in metal complexes with open-chain bis(Schiff base) ligands. In the previously reported silver(I) complex with a flexible reduced bis(Schiff base) ligand, 1,7-bis(4′-pyridyl)-2,6-diazaheptane, the 2D brick-wall network consists of trigonal and linear silver(I) ions.[21] In complex **1**, four imine N atoms from two different L1 ligands bind to the Ag(1) atom to form a double-stranded helicate. The coordination geometry of the four-coordinate Ag(1) is distorted tetrahedral with N−Ag(1)−N coordination angles ranging from 74.68(8) to 135.86(8)° and an average Ag(1)−N bond length of 2.364(2) Å (Table 1). Similar Ag−N bond lengths have been reported for silver(I) complexes with the same AgN_4 binding site, for example $[Ag(L)]NO_3$ has an average Ag−N bond length of 2.360(3) Å.[22] The double-stranded helicates are further linked to the Ag(2) atom through the coordination of two pyridine N(11) and N(31) atoms, as illustrated in Figure 1. The N(31)−Ag(2)−N(11) angle of 171.42(9)° indicates that the Ag(2) has an almost linear coordination geometry with bond lengths of 2.176(2) and 2.185(2) Å. Therefore, each Ag(1) atom in **1** is coordinated by two different L1 ligands and, in turn, each L1 ligand connects two Ag^I ions. Such a coordination mode generates an infinite chain-like structure (Figure 1). The intermetallic distance between Ag(1) and Ag(2) is 7.39 Å. It has been reported that the bis(Schiff base) ligand obtained from pyridine-2-carbaldehye and 1,2-ethanediamine forms a dinuclear double-stranded helical complex with silver(I) tetrafluoroborate.[23,24] This helical complex shows remarkable differences to ours with respect to the coordination mode, as shown schematically in Scheme 2.



Scheme 2

It is noteworthy that one pyridine unit of each L1 ligand remains uncoordinated in complex **1**. This means that the N_4 donor ligand L1 actually serves as a tridentate ligand when it reacts with silver(I) trifluoromethanesulfonate. A similar phenomenon has been observed in the complex $[Cu(L1)(CH_3CN)]NO_3$ with a zigzag chain-like structure.[20] In this complex, one pyridine unit of the L1 ligand is also free from coordination; instead, one acetonitrile molecule coordinates to the copper center to complete the coordination sphere of the copper(I) ion.[20] The uncoordinated pyridine N atom in complex **1** forms an O−H···N hydrogen bond with a solvate water molecule. Each water molecule forms two such O−H···N hydrogen bonds between the two adjacent chains and links the 1D chains to give a 2D network structure as shown in Figure 2. The $CF_3SO_3^-$ anions located at the vacancy of the 2D network form four C−H···O hydrogen bonds. Each cavity contains two $CF_3SO_3^-$ anions. The hydrogen bonding data are summarized in Table 2.

When the self-assembly of ligand L1 with silver(I) nitrate was carried out under the same conditions as **1**, coordination polymer **2** with a similar 2D network structure was obtained. However, the asymmetric unit of complex **2** contains three Ag^I ions (rather than two as in **1**), two L1 ligands, three NO_3^- anions and one water molecule, as shown in Figure 3. The most important difference between **1** and **2** is that the four N atoms of the L1 ligand all participate in the coordination with silver(I) ions in complex **2**, while in **1** only three of the four N atoms coordinate to Ag (vide supra). The four-coordinate Ag(1) has a distorted tetrahedral geometry with coordination angles ranging from 73.90(11) to 138.71(13)° while Ag(2) [N(12)−Ag(2)−N(42) = 167.50(17)°] and Ag(3) [N(32)−Ag(3)−N(22) = 177.56(18)°] are both two-coordinate with an almost linear geometry in complex **2**. As illustrated in Figure 4, the 1D chains containing double-stranded helicates in **2** are connected by the coordination bonds of two-coordinate silver(I) ions with two pyridine ring N donors from two adjacent chains − instead of O−H···N hydrogen bonds as in complex **1** − into a 2D network structure. The NO_3^- anions located at the voids of the network form nine C−H···O hydrogen bonds as listed in Table 2. Each cavity contains three NO_3^- anions with the solvate water molecules located in the cavity between the two layers.

The different linkage mode from 1D chains to 2D network for complexes **1** and **2** may be explained by the different sizes of the $CF_3SO_3^-$ and NO_3^- anions which occupy the vacancies of the 2D network i.e. the size of the anion controls the vacancy size of the 2D networks. In the case of **1** (with the larger $CF_3SO_3^-$ anion) the vacancy has an Ag(2A)−Ag(2B) distance of 14.98 Å and an O(7A)−O(7B) distance of 14.36 Å (Figure 2), while in the case of **2** with the smaller NO_3^- anion, the corresponding distances are Ag(2)−Ag(2A) = Ag(3)−Ag(3B) = 14.09 Å (Figure 4). The distance between two pyridine N atoms [e.g. N(21B) and N(41A) in Figure 2] linked by one water molecule in complex **1** is 5.22 Å, which is longer than the distance of 4.29 Å between two pyridine N atoms [e.g. N(12) and N(42), N(22) and N(32) in Figure 4] coordinated by the two-coordinate silver(I) ion in complex **2**. This result shows that the counteranions have a large effect on the formation of network structures.

The Schiff-base ligand L1 and its reduced form L react with silver(I) nitrate to form the 2D network complex **2** and the 1D hinged-chain complex $[Ag(L)]NO_3$,[22] respectively. It is interesting that each ligand L1 in **2** has a “C” shape while the shape of L in $[Ag(L)]NO_3$ is “Z” due to the flexibility of the ligands. In addition, the imine N atoms and pyridyl N atoms are coordinated to four-coordinate and two-coordinate silver(I) ions, respectively, in **2** while in the case of $[Ag(L)]NO_3$, each silver(I) ion is coordinated by two

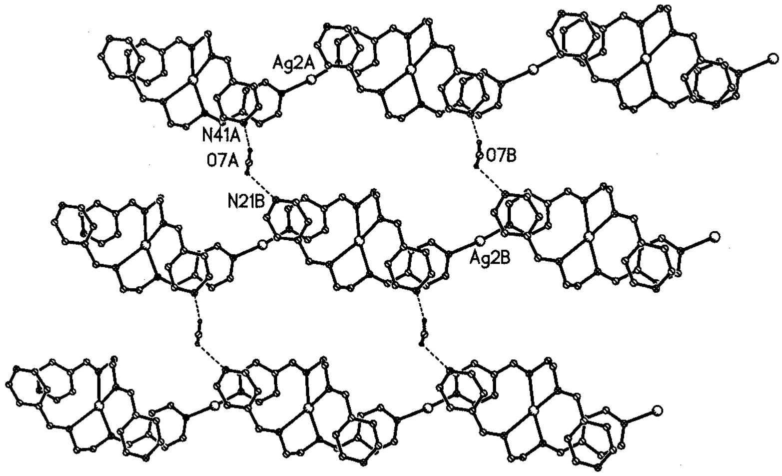


Figure 2. Formation of the 2D network structure of $[Ag_2(L1)_2](CF_3SO_3)_2\cdot H_2O$ (**1**) from 1D chains linked by O−H···N hydrogen bonds

Table 2. Hydrogen bonds data for the complexes **1**−**3**

D−H···A	Distance of D···A [Å]	Angle of D−H−A [°]
$[Ag_2(L1)_2](CF_3SO_3)_2\cdot H_2O$ (**1**)		
O(7)−H(29)···N(21)[a]	2.898(7)	113
O(7)−H(30)···N(41)[b]	3.005(7)	161
C(3)−H(5)···O(5)[c]	3.203(4)	125
C(10)−H(9)···O(4)[d]	3.293(4)	152
C(14)−H(12)···O(6)[e]	3.247(4)	130
C(33)−H(21)···O(6)[e]	3.207(4)	139
$[Ag_3(L1)_2](NO_3)_3\cdot H_2O$ (**2**)		
C(4)−H(7)···O(12)	3.354(9)	137
C(10)−H(9)···O(11)[f]	3.249(7)	141
C(12)−H(10)···O(11)[f]	3.212(7)	130
C(12)−H(10)···O(21)[g]	3.281(6)	132
C(13)−H(11)···O(41)[h]	3.420(11)	154
C(14)−H(12)···O(12)	3.380(7)	161
C(14)−H(12)···O(13)	3.074(7)	124
C(23)−H(16)···O(22)	3.333(8)	171
C(44)−H(27)···O(13)	3.277(8)	137
$[Co(L1)_2](SCN)_2\cdot EtOH$ (**3**)		
O(1)−H(39)···S(2)	3.480(9)	151
O(2)−H(40)···S(2)[i]	3.421(13)	170
C(13)−H(11)···N(2)	3.146(5)	115
C(23)−H(16)···O(1)	3.110(10)	136
C(23)−H(16)···O(1)[j]	3.415(10)	148
C(25)−H(18)···N(41)[k]	3.482(5)	151
C(44)−H(27)···N(21)[i]	3.325(5)	133

[a] Equivalent atoms generated by $2 - x, 1 - y, 1 - z$. [b] Equivalent atoms generated by $1 - x, 1 - y, -z$. [c] Equivalent atoms generated by $1 + x, y, -1 + z$. [d] Equivalent atoms generated by $x, y, -1 + z$. [e] Equivalent atoms generated by $1 + x, y, z$. [f] Equivalent atoms generated by $x, 1 + y, z$. [g] Equivalent atoms generated by $0.5 + x, 0.5 + y, z$. [h] Equivalent atoms generated by $x, 1 - y, -0.5 + z$. [i] Equivalent atoms generated by $1 - x, -y, z$. [j] Equivalent atoms generated by $1 - x, 1 - y, z$. [k] Equivalent atoms generated by $x, 1 - y, 0.5 + z$.

amine N atoms and two pyridyl N atoms from three different L ligands.[22] This suggests that a subtle change in the organic ligand may cause a large change in the assembly products.

In contrast to monovalent metal ions like Cu^I and Ag^I, which require a tetrahedral or linear coordination geometry, a divalent metal ion such as Co^{II} is usually six-coordinate with an octahedral geometry. After several attempts at reactions between the L1 ligand and Co^{II} salts with different anions, we succeeded in the isolation of a complex with the SCN^- anion, $[Co(L1)_2(SCN)_2]\cdot EtOH$ (**3**). The repeat unit of complex **3** is shown in Figure 5. The coordination sphere of the cobalt(II) ion is defined by four pyridine N donors of four different L1 ligands situated in the equatorial plane and two N donors of SCN^- anions at the axial positions, leading to a slightly distorted octahedral coordination environment. The two linear SCN^- anions are not perpendicular to the equatorial plane and the C(2)−N(2)−Co(1) and C(1)−N(1)−Co(1) angles are 147.3(3) and 161.2(3)°, respectively. The four equatorial Co−N bond lengths range from 2.159(3) to 2.191(3) Å and are longer than those of the two axial Co−N bonds [2.096(3) and 2.098(3) Å] (Table 1). Similar bond lengths and angles have been observed in a Co^{II} complex with the tetradentate Schiff-base ligand 1,3-bis(pyridine-2-carboxaldiamino)propane.[25] Surprisingly, the L1 ligand in **3** serves as a bidentate, not a tetradentate, ligand and connects two Co^{II} ions; the N atoms of the imine group do not participate in the coordination to the Co^{II} ion, as shown in Figure 6. The structure of complex **3** consists of many square units interconnected through L1 bridges into a 2D network. Each square unit is composed of two L1 spacers and two cobalt(II) ions and its cavity is occupied by a disordered ethanol molecule (Figure 6). It is obvious that the sheets of **2** have a corrugated and wavy network structure and are linked by C−H···N hydrogen bonds [Figure S1 (for Supporting Information see footnote on the first page of this article) and Table 2]. The disordered ethanol molecules are disposed between the layers by (ethanol) O−H···S and C−H···O (ethanol) hydrogen bonds (Table 2). Similar to the

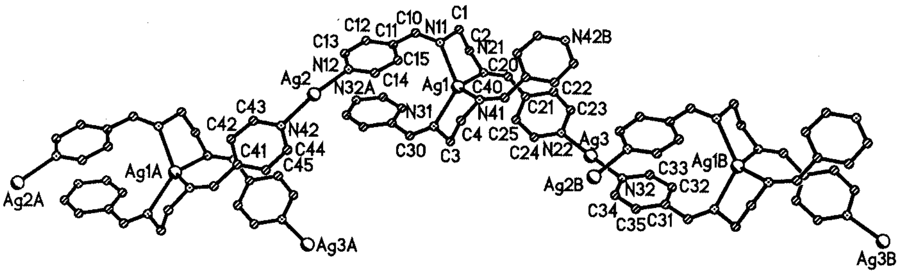


Figure 3. Coordination environment around the silver(I) ions in $[Ag_3(L1)_2](NO_3)_3{\cdot}H_2O$ (**2**) with atom numbering scheme, anions, water molecules, and hydrogen atoms have been omitted for clarity

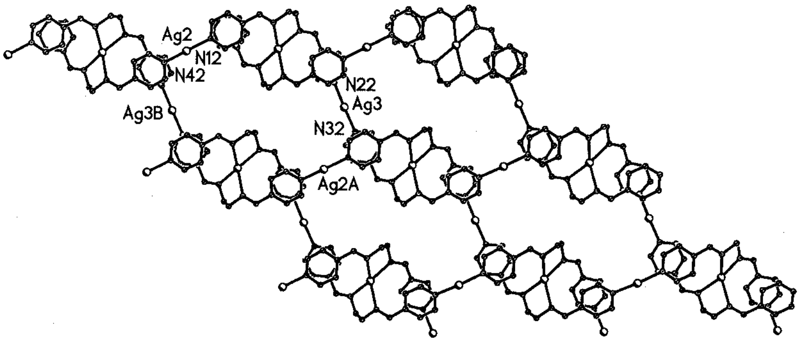


Figure 4. 2D network structure of $[Ag_3(L1)_2](NO_3)_3{\cdot}H_2O$ (**2**) formed by coordination bonds

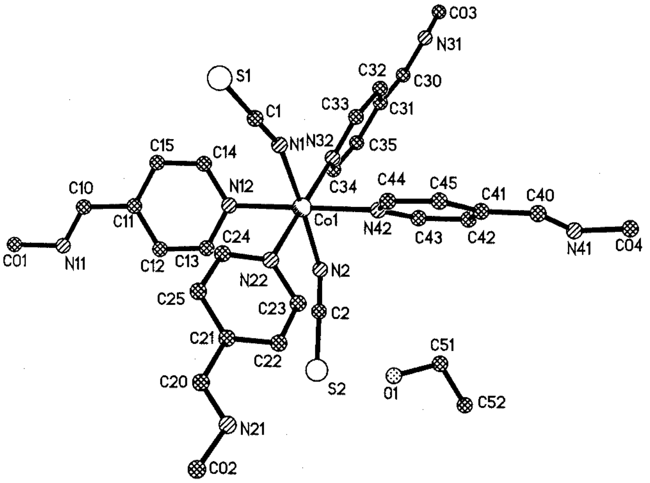


Figure 5. Asymmetric unit structure of complex $[Co(L1)_2](SCN)_2{\cdot}EtOH$ (**3**); hydrogen atoms have been omitted for clarity

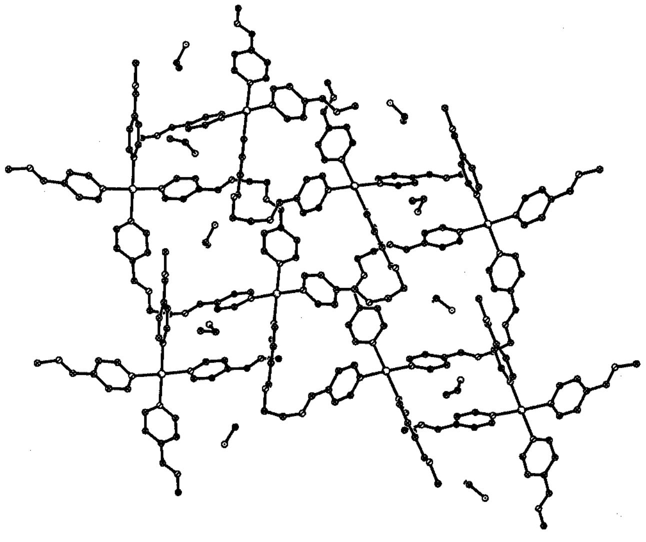


Figure 6. 2D network structure of the complex $[Co(L1)_2(SCN)_2]{\cdot}EtOH$ (**3**) with ethanol molecules filled in the vacancy of 2D sheet; SCN^- ions have been omitted for clarity

extended analog of bipyridine, a metal-organic framework with larger cavity was constructed by reaction of the ligand L1 with the metal moiety.

In order to compare the structures of complexes obtained by reactions of $Co(SCN)_2$ with different ligands L1 and L2, a crystallographic analysis was carried out for complex **4**. It can be seen from Figure 7 that the coordination mode around the Co^{II} ion in complex **4** is similar to that in complex **3** (Figure 5); the N atoms of the imine groups also remain uncoordinated as in complex **3**. However, two SCN^- anions and the Co^{II} ion are in a line, i.e. the SCN^- anions are perpendicular to the equatorial plane in **4**. In addition, each Co^{II} ion is bridged by four L2 ligands to four adjacent Co^{II} centers, resulting in an infinite 2D square grid with dimensions of 11.34 × 11.34 Å (Figure 8, a), near to the value of 11 Å observed in the 1D ladder complex

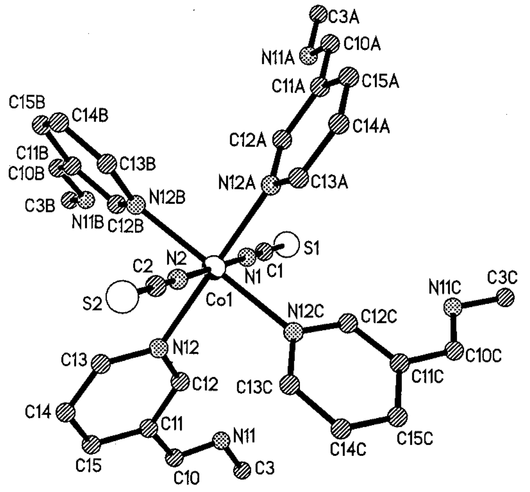
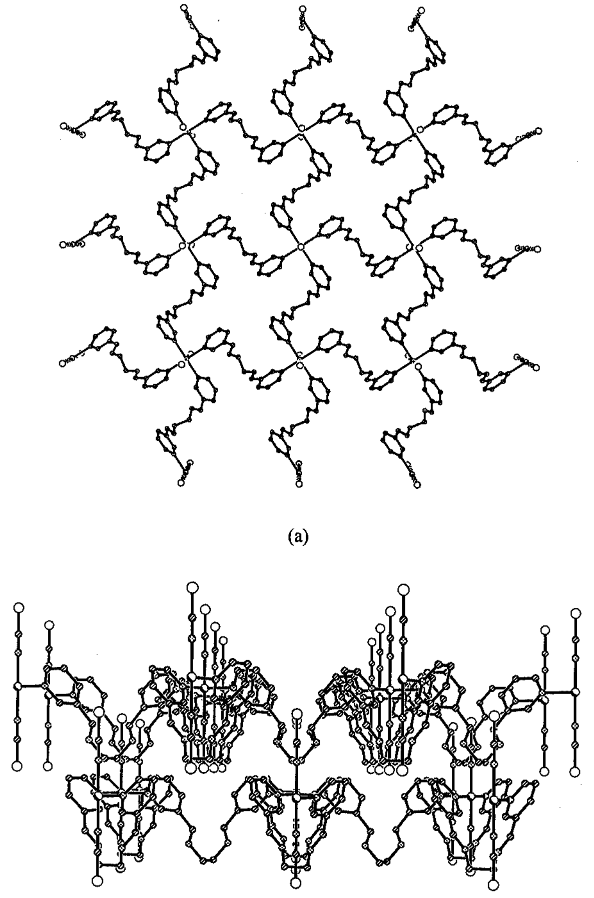


Figure 7. Coordination environment around the Co^{II} ion in the complex $[Co(L2)_2](SCN)_2$ (**4**) with atom numbering scheme; hydrogen atoms have been omitted for clarity


(a)

(b)

Figure 8. (a) Square-grid network of complex **4**; (b) packing diagram of two sheets in **4**

$[Co(bpy)_{1.5}(NO_3)_2]$.[26] The crystal packing diagram of **4**, shown in Figure 8, b, reveals that the 2D sheets repeat in an ---ABAB--- stacking sequence, with the Co atom of one layer located above the center of the grid of the adjacent layer. As a result, there is no open channel and no solvate molecules are found in complex **4**. Ligand L2 is different from L1 as it contains a 3-pyridyl group instead of a 4-pyridyl group and this change results in a completely different metal-organic framework. These results again demonstrate that the nature of the organic ligand plays an important role in the construction of supramolecular architectures.

Properties

Electrospray mass spectrometry (ES-MS) has recently been proved to be a powerful technique in the characterization of assemblies.[27] However, there are few reports on the application of ES-MS to self-assembled coordination polymers. Using this technique our group has successfully characterized coordination polymers and observed cationic mono-, di-, tri-, and tetranuclear metal species under ES-MS conditions.[22,28] Complexes **1**−**4** were also investigated by ES-MS and the spectroscopic data are summarized in Table 3. The ES-MS spectrum of the 2D coordination polymer **1** in acetonitrile solution is shown in Figure 9, a and gives a clear picture of the different species formed. Four main peaks at m/z = 345.2, 376.7, 583.0, and 615.0 are observed corresponding to the mononuclear species $[Ag(L1)]^+$ $[Ag(L1) + CH_3OH]^+$, $[Ag(L1)_2]^+$, and $[Ag(L1)_2 + CH_3OH]^+$ (methanol was used as the mobile phase), respectively. The other four peaks at 840.7, 872.9, 904.7, and 1162.5 originate from the dinuclear species (Table 3). All these assignments were confirmed by good agreement between the observed and calculated isotopic distributions. Figure 9, b shows a typical example of a comparison between the experimental and calculated isotope distributions for the peak at m/z = 872.9, corresponding to the dinuclear species $[Ag_2(L1)_2(CF_3SO_3) + CH_3OH]^+$. The observation of cationic species in the ES-MS spectrum confirms the coordination of L1 to the Ag^I atom under the ES-MS experimental conditions. Similar mono- and dinuclear species were also observed in the complexes **2**−**4** (Table 3). Observation of a peak at m/z = 715.9, corresponding to the $[Co(L1)_2H(SCN)_2 + C_2H_5OH + H_2O]^+$ species, confirms the presence of an ethanol molecule in complex **3**.

The complexes were further investigated by electrochemistry. The cyclic voltammograms for $[Co(L1)_2(SCN)_2]{\cdot}EtOH$ (**3**) and $[Co(L2)_2(SCN)_2]$ (**4**) are shown in Figure 10. It can be seen that the cobalt(II) complexes exhibit similar electrochemical behavior in the positive potential region. Irreversible anodic peaks were observed at +0.76 V for complex **3** and at +0.80 V for complex **4** vs. Ag/AgCl in acetonitrile. The known (Schiff base)cobalt complexes $[Co(DSALPTP)]_2[CoCl_4]$ [$H_2DSALPTP$ = 1,3-bis(*o*-salicylaldiminophenylthio)propane] and [CoSalmbfn] [Salmbfn = bis(salicylaldehyde)methylene-*p*,*p*′-diphenylene] showed a similar irreversible oxidation of Co^{II} to Co^{III} at 0.75 and 0.80 V vs. Ag/AgCl, respectively.[29−31] The more positive oxidation potential of

Table 3. ES-MS data for complexes **1**−**4**

m/*z*	Assignment	*m*/*z*	Assignment
1		**2**	
239.3	$[(L1)H]^+$	239.2	$[(L1)H]^+$
271.2	$[(L1)H+CH_3OH]^+$	271.2	$[(L1)H+CH_3OH]^+$
345.2	$[Ag(L1)]^+$	345.2	$[Ag(L1)]^+$
376.7	$[Ag(L1)+CH_3OH]^+$	566.9	$[Ag_2(L1)(NO_3)+CH_3OH+H_2O]^+$
583.0	$[Ag(L1)_2]^+$	583.0	$[Ag(L1)_2]^+$
615.0	$[Ag(L1)_2+CH_3OH]^+$	615.0	$[Ag(L1)_2+CH_3OH]^+$
840.7	$[Ag_2(L1)_2(CF_3SO_3)]^+$	753.8	$[Ag_2(L1)_2(NO_3)]^+$
872.9	$[Ag_2(L1)_2(CF_3SO_3)+CH_3OH]^+$	785.8	$[Ag_2(L1)_2(NO_3)+CH_3OH]^+$
904.7	$[Ag_2(L1)_2(CF_3SO_3)+2CH_3OH]^+$	818.0	$[Ag_2(L1)_2(NO_3)+2CH_3OH]^+$
1162.5	$[Ag_2(L1)_2(CF_3SO_3)+2CH_3OH+H_2O]^+$		
3		**4**	
239.2	$[(L1)H]^+$	239.3	$[(L2)H]^+$
271.1	$[(L1)H+CH_3OH]^+$	271.2	$[(L2)H+CH_3OH]^+$
386.9	$[Co(L1)SCN+ CH_3OH]^+$	332.7	$[Co_3(L2)(SCN)_4+ H_2O]^{2+}$
562.9	$[Co_2(L1)(SCN)_3 +CH_3OH]^+$	386.9	$[Co(L2)SCN+ CH_3OH]^+$
593.0	$[Co(L1)_2SCN]^+$	579.0	$[Co_2(L2)(SCN)_3+CH_3OH+H_2O]^+$
625.0	$[Co(L1)_2SCN +CH_3OH]^+$	691.9	$[Co(L2)_2H(SCN)_2+CH_3CN]^+$
651.8	$[Co(L1)_2H(SCN)_2]^+$		
684.0	$[Co(L1)_2H(SCN)_2+CH_3OH]^+$		
715.9	$[Co(L1)_2H(SCN)_2 + C_2H_5OH + H_2O]^+$		
768.0	$[Co_2(L1)_2(SCN)_3]^+$		

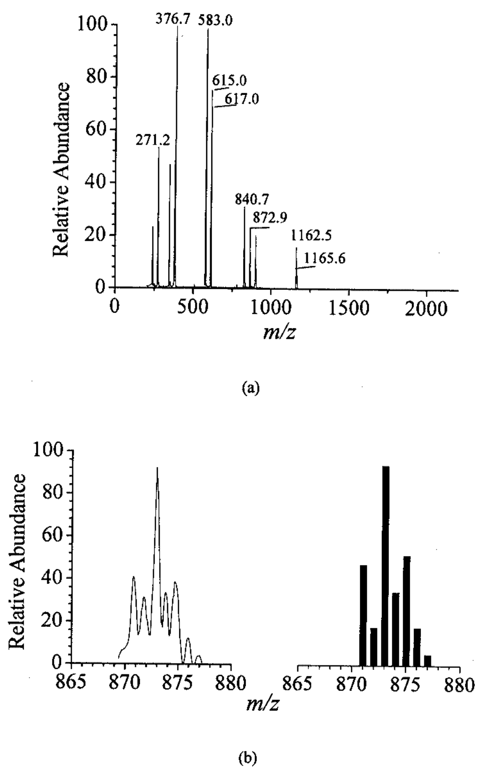


Figure 9. (a) ES mass spectrum of $[Ag_2(L1)_2](CF_3SO_3)_2{\cdot}H_2O$ (**1**) in acetonitrile solution; (b) observed (traces) and calculated (bars) isotopic distributions for the peak at *m*/*z* = 872.9

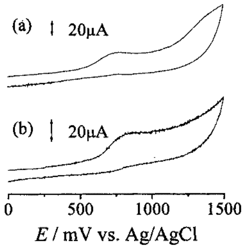


Figure 10. Cyclic voltammograms in acetonitrile with 0.1 M Bu_4NClO_4 as supporting electrolyte: (a) $[Co(L1)_2(SCN)_2]{\cdot}EtOH$ (**3**); (b) $[Co(L2)_2(SCN)_2]$ (**4**); scan rate = 100 mV/s

complex **4** implies that it is more difficult to oxidize than complex **3** under the electrochemical conditions.

The temperature dependence of the magnetic susceptibility of complexes **3** and **4** was measured in the temperature range 75−300 K. It was found that the effective magnetic moment values for **3** and **4** were 5.05 μ_B and 4.85 μ_B ($\mu_B \approx 9.27{\cdot}10^{-24}$ $J{\cdot}T^{-1}$), respectively, at 300 K. These values are within the expected range (4.3−5.2 μ_B) for isolated d^7 high-spin, six-coordinate Co^{II} complexes.[32] Upon lowering the temperature, the effective magnetic moment gradually decreased to 4.32 μ_B for **3** and 4.20 μ_B for **4**. These results indicate that there are only weak antiferromagnetic interactions between the metal centers due to the large Co···Co separations revealed by the crystal structures.

Table 4. Crystallographic data for complexes **1**−**4**

Complex	**1**	**2**	**3**	**4**
Empirical formula	$C_{30}H_{30}Ag_2F_6N_8O_7S_2$	$C_{28}H_{30}Ag_3N_{11}O_{10}$	$C_{32}H_{34}N_{10}CoOS_{.2}$	$C_{30}H_{28}N_{10}CoS_{.2}$
Molecular weight	1008.48	1004.24	697.74	651.67
Crystal system	triclinic	monoclinic	orthorhombic	tetragonal
Space group	$P\bar{1}$	Cc	*Iba*2	*I*4
a [Å]	11.0577(4)	26.2730(13)	29.5151(8)	11.3350(9)
b [Å]	13.9358(12)	10.1924(3)	12.5454(3)	11.3350(9)
c [Å]	14.3642(10)	14.3278(8)	18.8052(5)	13.0035(7)
α [°]	99.538(3)			
β [°]	109.125(3)	119.5780(10)		
γ [°]	108.798(2)			
V [Å^3]	1886.5(2)	3336.8(3)	6963.2(3)	1670.7(2)
Z	2	4	8	2
$D_{calcd.}$ [g·cm^{-3}]	1.775	1.999	1.331	1.295
μ [mm^{-1}]	1.234	1.817	0.654	0.674
Reflections collected	13716	15008	33548	7535
Independent reflections	8564	6516	7983	1915
R_{int}	0.0241	0.0303	0.0746	0.0738
Obsd. reflections [$I > 2\sigma(I)$]	6482	6201	6466	1750
Parameters refined	502	502	432	103
R (obsd. data)	0.0334	0.0314	0.0549	0.0378
wR (obsd. data)	0.0837[a]	0.0802[b]	0.1002[c]	0.0851[d]
Goodness of fit	1.083	1.043	1.030	1.028
Residuals [e·Å^{-3}]	0.602; −0.721	0.853; −0.691	0.375; −0.321	0.317; −0.238

[a] $\omega = 1/[\sigma^2(F_o)^2 + (0.0478P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. [b] $\omega = 1/[\sigma^2(F_o)^2 + (0.0537P)^2 + 3.4468P]$, where $P = (F_o^2 + 2F_c^2)/3$. [c] $\omega = 1/[\sigma^2(F_o)^2 + (0.0483P)^2 + 5.7779P]$, where $P = (F_o^2 + 2F_c^2)/3$. [d] $\omega = 1/[\sigma^2(F_o)^2 + (0.0524P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

Conclusion

From the structure analysis of 2D networks **1** and **2**, it has been found that the anions play a key role in the construction of coordination polymers. In complex **1**, the large $CF_3SO_3^-$ anion lengthens the distances between the 1D chains, so that the formation of 2D network depends on the O−H···N hydrogen bonds formed between the chains and solvate water molecules. In complex **2**, with the small nitrate anion, a 2D structure is obtained by the coordination interactions between two-coordinate silver(I) ions and 1D chains. In addition variation of the terminal coordination group from 4-pydriyl to 3-pyridyl generates two completely different polymers **3** and **4**. These results indicate that a small change in the organic ligand has a significant effect on the self-assembly products.

The present study shows that the multidentate Schiff-base ligands L1 and L2 can offer a different number of N donors according to the coordination requirement of different transition metal ions. The ligand L1 is tridentate in complex **1** and tetradentate in complex **2**, while in the case of complexes **3** and **4**, both L1 and L2 act as bidentate ligands. This also suggests the complexity of multidentate ligands in the self-assembly process with metal salts.

Experimental Section

General: All commercially available chemicals were of reagent grade and used as received without further purification. L1 was prepared by a method reported previously.[20] Solvents were purified according to standard methods. Samples for C, H, N analyses were dried under vacuum and the analyses were performed with a Perkin−Elmer 240C elemental analyzer at the analysis center of Nanjing University. ^{1}H NMR spectra were measured with a Bruker DRX500 MHz NMR spectrometer at room temperature. Electrospray MS measurements were carried out with an LCQ System (Finnigan MAT, USA) using methanol as mobile phase. Variable-temperature magnetic susceptibilities (75−300 K) of complexes **3** and **4** were measured with a CHAN-2000 Faraday magnetometer. A diamagnetic correction was made with Pascal's constants for all the constituent atoms, and the magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_m)^{1/2}$. Cyclic voltammograms (CVs) were recorded with an EG&G M273 potentiostat/galvanostat system using a platinum working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode. The CV measurements were carried out in acetonitrile solution containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte at a scan rate of 100 mV·s^{-1}. Ferrocene was added at the end of the experiment and used as an internal reference.

Preparation of 1,2-Bis(3′-pyridylmethyleneamino)ethane (L2): 1,2-Ethanediamine (0.53 mL, 7.9 mmol) was dissolved in refluxing absolute methanol (30 mL) and pyridine-3-carbaldehyde (1.42 mL, 15.0 mmol) in absolute methanol (30 mL) was added slowly to give a clear yellowish solution. The mixture was refluxed for 3 h and stirred overnight at ambient temperature. The solvents were evaporated to give a yellow solid under reduced pressure. White needle-shaped crystals were obtained by recrystallization of the residue from methanol and deionized water. After washing with diethyl ether and drying under vacuum, 1.52 g of L2 was obtained with a yield of 85%. ES-MS: m/z = 239.1 [L2 + H]$^+$. $C_{14}H_{14}N_4$ (238.29): calcd. C 70.56, H 5.92, N 23.51; found C 70.39, H 5.81, N 23.75.

Synthesis of $[Ag_2(L1)_2](CF_3SO_3)_2 \cdot H_2O$ (1): All procedures for synthesis and recrystallization were carried out in the dark. A deionized aqueous solution (5 mL) of CF_3SO_3Ag (12.8 mg, 0.05 mmol) was added dropwise to a stirred solution of L1 (11.9 mg, 0.05 mmol) in acetonitrile (5 mL) at room temperature. After filtration, the clear filtrate was allowed to stand at 5 °C for several days, and colorless crystals were collected (14.1 mg, 56%). Single crystals suitable for X-ray diffraction analysis were obtained by slow concentration of the filtrate at 5 °C. ^{1}H NMR (D_2O, 25 °C): δ = 3.98 (s, 4 H), 5.97 (s, 2 H), 7.81 (d, 4 H), 8.73 (d, 4 H) ppm. $C_{30}H_{30}Ag_2F_6N_8O_7S_2$ (1008.48): calcd. C 35.73, H 3.00, N 11.11; found C 35.77, H 3.05, N 11.05.

Synthesis of $[Ag_3(L1)_2](NO_3)_3 \cdot H_2O$ (2): The complex was prepared in a manner similar to that for **1** except that CF_3SO_3Ag was replaced by $AgNO_3$. Light-brown block single crystals were obtained (8.4 mg, 50%). $C_{28}H_{30}Ag_3N_{11}O_{10}$ (1004.24): calcd. C 33.49, H 3.01, N 15.34; found C 33.38, H 3.26, N 15.36.

Synthesis of $[Co(L1)_2(SCN)_2] \cdot EtOH$ (3): This complex was prepared by the layering method. A solution of ligand L1 (11.9 mg, 0.05 mmol) in ethanol (5 mL) was added slowly and carefully to a layer of a solution of $Co(SCN)_2$ (11.5 mg, 0.05 mmol) in ethanol (3 mL) in a tube. Red-orange platelet single crystals suitable for X-ray diffraction analysis were obtained after standing for several days (12.6 mg, 72%). $C_{32}H_{34}CoN_{10}OS_{.2}$ (697.74): calcd. C 55.08, H 4.91, N 20.07; found C 55.02, H 5.00, N 20.28.

Synthesis of $[Co(L2)_2(SCN)_2]$ (4): According to the preparation method of complex **3**, pink column single crystals suitable for X-ray diffraction analysis were obtained by reaction of the ligand L2 with $Co(SCN)_2$; yield 11.1 mg, 68%. $C_{30}H_{28}CoN_{10}S_{.2}$ (651.67): calcd. C 55.29, H 4.33, N 21.49; found C 55.12, H 4.49, N 21.47.

X-ray Crystal Structure Analysis for Complexes 1−4: The intensity data for the complexes **1**−**4** (Table 4) were collected with a Rigaku RAXIS-RAPID Imaging Plate diffractometer at 200 K, using graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å). The structures were solved by direct methods with SIR92[33] and expanded using Fourier techniques.[34] All data were refined anisotropically by the full-matrix least-squares method for non-hydrogen atoms. The hydrogen atom positions were generated geometrically except for those of the water molecules, which were found from difference maps. Disordered NO_3^- anions and ethanol molecules were observed in complex **2** and **3**, respectively, although the data collection was performed at low temperature (200 K). All calculations were carried out with an SGI workstation using the teXsan crystallographic software package of Molecular Structure corporation.[35] CCDC-189685 (**1**), -189686 (**2**), -189687 (**3**), and -189688 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by National Natural Science Foundation of China.

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Received July 18, 2002
[I02400]