1-D cyano-bridged heterometallic complexes consisting of 1,4,8,11-tetraazacyclotetradecanesilver(II) and tetracyanopalladium(II) or tetracyanoplatinum(II)

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Abstract

Two unprecedented bimetallic Ag(II) coordination polymers were synthesized and characterized in this paper. Treatment of $[Ag(cyclam)](ClO_4)_2$ and $K_2[Pd(CN)_4]\cdot 3H_2O$ generated $[Ag(cyclam)Pd(CN)_2(\mu\text{-}CN)_2]_n$ (**1**). Reaction of $[Ag(cyclam)](ClO_4)_2$ with $K_2[Pt(CN)_4]\cdot 3H_2O$ afforded $[Ag(cyclam)Pt(CN)_2(\mu\text{-}CN)_2]_n$ (**2**). The structures of **1** and **2** are similar and consist of 1-D zigzag chains which are linked via intermolecular hydrogen bonding interactions to give rise to 3-D networks. The structural features, IR, ESR and magnetic properties are discussed, respectively. To our knowledge, the complexes reported here are the first example of bimetallic Ag(II) coordination polymers with weak antiferromagnetic spin coupling. The primary results presented here can give an insight into the assembly of Ag(II) coordination polymers. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structures; Magnetic properties; Silver(II) complexes; Bimetallic complexes; Cyano-bridged complexes

1. Introduction

Since the early 1960s, considerable endeavors have been devoted to the synthesis of metallated heterocycles owing to the fact that these metal complexes with macrocyclic ligands have potential applications in many areas, such as biological chemistry, metal ion catalysis, metal ion discrimination and molecule based magnets [1]. Of these macrocyclic ligands, cyclam (1,4,8,11-tetraazacyclotetradecane) and its derivatives give a variety of metal complexes $[M(cyclam)]^{n+}$ in which the metal ion usually possesses one or two available coordination sites besides the four coordination ones occupied by the nitrogen atoms from the ligands [2]. On the other hand, in the last few years, extended bimetallic arrays constructed from different metal ion units or mixed-valence metal ion building blocks have received intensive attention, mainly because they exhibit some particular physicochemical properties, such as photo-physical [3], magnetic [4] and conductive [5] ones. In order to build extended bimetallic networks, a good strategy is to use a metal complex with empty coordination sites, which can then be completed by another ligand capable of bridging two different metal ions. As a result, one potential candidate to this is the square-planar cyclam metal complexes. Moreover, the rich supramolecular chemistry of the metal derivatives of bridging cyano ligand [6] has spurred the development of assembling extended bimetallic arrays due to the cyanide bridges affording a variety of interactions between the two metal ion units to give rise to physico-chemical properties.

Only one simple binary compound of silver(II), AgF_2, can be obtained owing to the powerful oxidizing nature of divalent silver, the propensity of silver(II) to act as an oxidizing agent is well documented [7]. However, silver(II) can be stabilized in nitrogen-containing unsaturated heterocycles, such as pyridines, polypyri-

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dines and related compounds [8], and synthetic macrocyclic ligands, such as cyclam and its derativites [9]. The coordination mode of the silver(II) ions reported in the literature is usually four coordinate and generally approximates to square planar, only a few examples exhibit a six coordination fashion [8,9]. On the other hand, the majority of the Ag(II) complexes reported are monomers and much less attention was paid to the coordination polymers of Ag(II). As an extension to our interest in the coordination chemistry of silver(I) [10a–c] and copper(II) [10d,e] with a d^9 electron configuration, we therefore target our studies on the synthesis of Ag(II) coordination polymers with the aim to explore the assembling process of these polymeric networks. From the self-assembly of some bimetallic complexes with cyanide bridges [4,11], we envisaged that Ag(II) bimetallic arrays may be a good candidate for this purpose, we herein report on two novel 1-D heterometallic Ag(II) polymeric chains constructed from an Ag(II) complex of cyclam and tetracyanopalladium(II) or tetracyanoplatnium(II) ions, respectively.
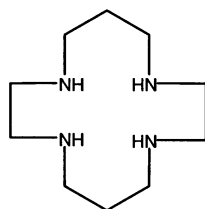
cyclam

2. Experimental

2.1. General considerations

All reactions were carried out under an atmosphere of argon by using the standard Schlenk vacuum line techniques. Solvents were dried and distilled by using standard methods prior to use. Reagent grade $AgClO_4 \cdot H_2O$, $K_2[Pd(CN)_4] \cdot 3H_2O$ and $K_2[Pt(CN)_4] \cdot 3H_2O$ were purchased from Aldrich, while 1,4,8,11-tetraazacyclotetradecane was obtained from Tokyo Kasei Kogyou Co. Ltd. All chemicals were used as received without further purification. IR spectra were recorded as KBr disks on JASCO 8000 FT-IR spectrometer. ESR spectra were measured by JEOL JES-TE200 ESR spectrometer. Variable temperature magnetic data (4–270 K) were obtained using a SQUID magnetometer. Caution: perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of materials should be prepared and handled with great care.

2.2. Preparations

2.2.1. [Ag(cyclam)](ClO₄)₂ [9b]

Silver perchlorate (1.05 g, 5 mmol) was added to 50 ml of distilled water under stirring and to the solution was then added cyclam (0.5 g, 0.25 mmol). After stirring for 1 h, the solution was filtered and acidified to pH 2 using perchloric acid. The orange crystals appeared in it and were collected by filtration, washed with THF, and dried in vacuum for the synthesis purpose of the Ag(II) polymers. IR (KBr, cm^{-1}): 3159–3202 (v_{NH}), 2858–2928 (v_{CH2}), 1377–1458 (δ_{CH2}), 1089 and 626 (v_{OCl}).

2.2.2. [Ag(cyclam)Pd(CN)₂(μ-CN)₂]ₙ (1)

Complex **1** was synthesized by using an interface method at room temperature (r.t.). [Ag(cyclam)](ClO₄)₂ (12.6 mg, 0.025 mmol) and K₂[Pd(CN)₄]·3H₂O (8.6 mg, 0.025 mmol) were added to reactors A and B, respectively. Then, acetonitrile (10 ml) was introduced to the reactor A and methanol (10 ml) to the reactor B. With being stirred for a while, the resultant solution of [Ag(cyclam)](ClO₄)₂ was transferred to a 7 mm glass tube and layered with ethanol as a diffusion solvent, finally covered with the solution of K₂[Pd(CN)₄]. After the solution was allowed to stand for 7 days at r.t., orange brick crystals were collected for X-ray analysis. *Anal.* Calc. for $AgPdN_8C_{14}H_{24}$: C, 32.39; H, 4.63; N, 21.59. Found: C, 32.70; H, 4.55; N, 21.43%. IR (KBr, cm^{-1}): 3196–3242 (v_{NH}), 2856–2926 (v_{CH2}), 2129 ($v_{C≡N}$), 1377–1460 (δ_{CH2}), 1099 (v_{C-N}).

2.2.3. [Ag(cyclam)Pt(CN)₂(μ-CN)₂]ₙ (2)

Similar to the synthesis of **1**, [Ag(cyclam)](ClO₄)₂ (6.3 mg, 0.0125 mmol) and acetonitrile (5 ml) were added to reactor A, while K₂[Pt(CN)₄]·3H₂O (5.4 mg, 0.0125 mmol) and methanol (5 ml) were introduced to reactor B, respectively. After being stirred for a while, the solution of [Ag(cyclam)](ClO₄)₂ was first introduced into a 7 mm glass tube, and then layered with the solution of K₂[Pt(CN)₄]. The glass tube was sealed under Ar and stood at r.t. for two weeks, purple prismatic crystals of **2** were obtained in a lower yield. *Anal.* Calc. for $AgPtN_8C_{14}H_{24}$: C, 27.66; H, 3.95; N, 18.44. Found: C, 27.60; H, 3.82; N, 18.65%. IR (KBr, cm^{-1}): 3186–3246 (v_{NH}), 2855–2926 (v_{CH2}), 2127 ($v_{C≡N}$), 1377–1462 (δ_{CH2}), 1028–1099 (v_{C-N}).

2.3. X-ray determination, structure solution and refinement

A single crystal suitable for X-ray measurement was mounted on a glass fiber. The data for **1** and **2** were collected at 23°C on a Qantum CCD area detector coupled with a Rigaku AFC7 diffractometer with graphite monochromated Mo Kα radiation, and a

Table 1
Crystal data for complexes **1** and **2**

	1	**2**
Formula	$AgPdN_8C_{14}H_{24}$	$AgPtN_8C_{14}H_{24}$
Formula weight	518.67	607.36
T (K)	296(1)	296(1)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	10.238(3)	10.2531(8)
b (Å)	9.247(3)	9.263(1)
c (Å)	10.3418(9)	10.3018(9)
β (°)	95.393(3)	95.479(7)
V (Å^3)	974.8(3)	974.0(2)
Z	2	2
D_{calc} (g cm^{-3})	1.767	2.071
μ (mm^{-1})	19.38	81.60
Reflections collected	2163	2495
Independent reflections	2163	2227
Final $R[I > 3.00\sigma(I)]$	R [a] $= 0.061$, wR [b] $= 0.101$	
Final $R[I > 2\sigma(I)]$		R [a] $= 0.065$, wR [c] $= 0.191$

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

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

1

Bond lengths

Ag(1)–N(1)	2.067(7)	Ag(1)–N(2)	2.055(7)
Ag(1)–N(3)	2.567(9)	Pd(1)–C(6)	1.96(1)
Pd(1)–C(7)	1.95(1)	N(3)–C(6)	1.17(1)
N(4)–C(7)	1.15(1)		

Bond angles

N(1)–Ag(1)–N(1)	180.0	N(3)–Ag(1)–N(3)	180.0
N(2)–Ag(1)–N(2)	180.0	C(6)–Pd(1)–C(6)	180.0
C(7)–Pd(1)–C(7)	180.0	N(1)–Ag(1)–N(2)	86.2(3)
N(1)–Ag(1)–N(2)	93.8(3)	N(2)–Ag(1)–N(3)	89.1(3)
N(1)–Ag(1)–N(3)	88.3(3)	C(6)–Pd(1)–C(7)	87.5(4)
Ag(1)–N(3)–C(6)	134.4(8)		

2

Bond lengths

Ag(1)–N(1)	2.029(8)	Ag(1)–N(2)	2.010(8)
Ag(1)–N(4)	2.529(9)	Pt(1)–C(6)	1.98(1)
Pt(1)–C(7)	1.99(1)	N(4)–C(7)	1.13(1)
N(3)–C(6)	1.14(2)		

Bond angles

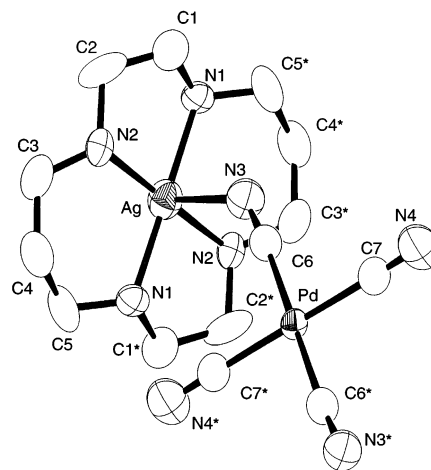|			
N(1)–Ag(1)–N(1)	180.0	N(4)–Ag(1)–N(4)	180.0
N(2)–Ag(1)–N(2)	180.0	C(6)–Pt(1)–C(6)	180.0
C(7)–Pt(1)–C(7)	180.0	N(1)–Ag(1)–N(2)	85.8(3)
N(1)–Ag(1)–N(2)	94.2(3)	N(1)–Ag(1)–N(4)	88.1(3)
N(2)–Ag(1)–N(4)	88.0(3)	C(6)–Pt(1)–C(7)	86.6(4)
Ag(1)–N(4)–C(7)	133.7(9)		

Fig. 1. ORTEP view of the structure for complex **1** showing 50% thermal ellipsoid.

Rigaku AFC7R diffractometer with graphite mono-chromated Mo Kα radiation and a rotating anode generator, respectively. For complexes **1** and **2**, the intensity data were corrected for Loreutz polarization effects and a correction for secondary extinction was applied. An empirical absorption correction based on azmuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.54 to 1.00 for complex **2**.

The structures were solved by direct methods, expanded using Fourier techniques and refined by a full-matrix least-squares analysis based on F^2, with using the TEXAN package [12]. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the two structures were included but no refined. The details of the X-ray experiments and crystal data are summarized in Table 1. The selected bond distances and angles for the two complexes are listed in Table 2.

3. Results and discussion

3.1. Description and features of structures

X-ray analysis has revealed that the crystal structure of **1** consists of 1-D zigzag chains. An ORTEP view of complex **1** is depicted in Fig. 1 with the atomic numbering scheme, both Ag(II) and Pd(II) ions sit on inversion centers. The Ag(II) ion is six-coordinate, complexed with the four nitrogen atoms of a cyclam ligand on the equatorial plane and the two nitrogen atoms from different bridging cyano groups in the axial positions, respectively. The Ag–N bond distances on the equatorial plane have an average value of 2.061(7) Å, while weak axial interactions, a characteristic of d^9 systems, give rise to an Ag–N bond length of 2.567(9) Å and the Ag–N(3) bonds in the axial positions are slightly tilted

from the normal to the AgN_4 plane, forming a slightly distorted and tetragonally elongated octahedral geometry. All N—Ag—N bond angles formed by two face to face nitrogen atoms, no matter where they locate on the equatorial plane or in the axial positions, are 180.0°. By contrast, the Pd(II) ion possesses a square planar coordination surrounding in which it is coordinated to the four carbon atoms from four different cyanide groups. The Pd—C bonds can be divided into two pairs, one has a value of 1.96(1) Å (bridging CN) and the other 1.95(1) Å (terminal CN). Similar to the Ag(II) ion, the
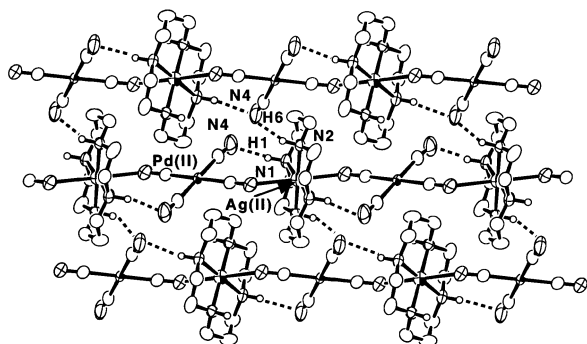

Fig. 2. 1-D chain structure of **1** with hydrogen bonding interactions within and between the chains (N4—H1 distance 2.270 Å and N4—H6 one 2.112 Å).
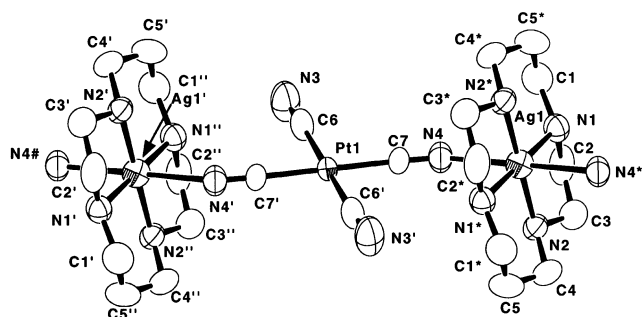

Fig. 3. ORTEP drawing of polymer **2** showing 50% thermal ellipsoid.
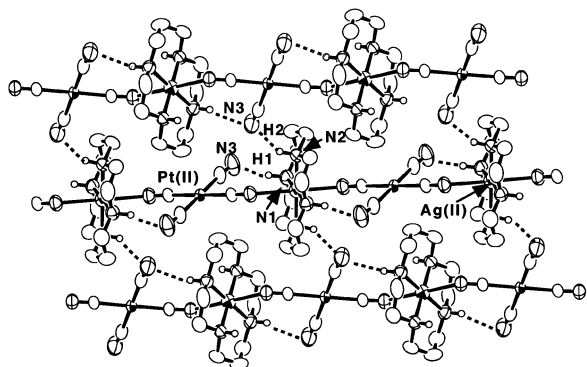

Fig. 4. 1-D chain structure in **2** with hydrogen bonding interactions (N3—H1 distance 2.329 Å and N3—H2 one 2.153 Å).

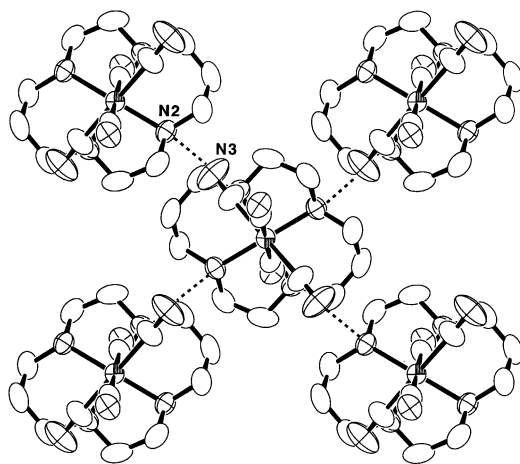Fig. 5. 3-D structure formed by hydrogen bonds for polymer **2** (N2—N3 distance 3.00(1) Å).

C—Pd—C bond angles resulted from two face to face carbon atoms are also 180.0°. Two of the four cyano groups for a tetracyanopalladium(II) ion are connected to two different Ag(II) moieties in a *trans* mode and lead to a zigzag chain owing to a bond angle of 134.4(8)° for the Ag—N(3)—C(6). In the structure, each cyclam ligand contains two six-membered and two five-membered rings in chair and *gauche* configurations, respectively, and the nitrogen atoms in the ligand caclam adopt a *trans*-III configuration [13]. In addition, the intrachain N(4)—N(1) and interchain N(4)—N(2) distances are 3.12(1) and 2.98(1) Å, respectively, indicating there existing hydrogen bonding interactions within and between the chains [14] (Fig. 2) and resulting in a 3-D network.

Complex **2** is an isomorphous compound of complex **1** and an ORTEP view of an asymmetrical unit of **2** is given in Fig. 3. The Ag(II) ion also exhibits a tetragonally elongated octahedral coordination geometry and the average Ag—N bond distances on the equatorial plane and in the apical positions are 2.020(8) and 2.529(9) Å, respectively. Parallel to the Pd(II) ion in **1**, the Pt(II) ion here has the same coordination environment with the Pt—C bond lengths of 1.99(1) and 1.98(1) Å, respectively. The macrocyclic cyclam ligand in complex **2** includes two five-membered and two six-membered rings in chair and *gauche* forms, respectively, and also exhibits the *trans*-III configuration of the nitrogen atoms. The molecular structure of **2** is the same as that of **1** and consists of 1-D zigzag chains with an Ag—N—C bond angle of 133.7(9)° (Fig. 4). The intrachain N(1)—N(3) (3.16(1) Å) and interchain N(2)—N(3) (3.00(1) Å) distances imply that there are also hydrogen bonding interactions within and between the chains, generating a 3-D network (Fig. 5).

Compared with the monomeric Ag(II) complexes of cyclam and its derivatives, one of the most remarkable features for the two Ag(II) coordination polymers described here is that the Ag–N bond distances on the equatorial plane are obviously much shorter than the values of 2.158(2) Å in [Ag(cyclam)](ClO$_4$)$_2$ [9c], 2.160(3) Å in [Ag(tet a)](NO$_3$)$_2$ [9d] and 2.162(5) Å in [Ag(tet b)](ClO$_4$)$_2$ [9f]. The phenomenon reflects that the strains of the *endo* conformation with the coplanar donor nitrogen atoms in the two Ag(II) polymers are different from those in these monomeric complexes reported previously. For cyclam, the center-nitrogen distance for the least strained conformation with the approximately coplanar donor nitrogen atoms is 2.07 Å which has been calculated [15], and this result is consistent with the value of 2.06 Å in the structure of free cyclam [1b]. Hence, when a metal ion is coordinated to cyclam, the increase or decrease for the M–N bond distances implies that there exists compressive strain or tensive strain in the ligand. Only one Ag–N bond length (2.063(5) Å), comparable to such short Ag–N bond distances of 2.061(7) and 2.02(8) Å in the polymers, was reported in a (tetraphenylporphine) silver(II)–tetraphenylporphine molecular solid solution [16]. The reasons for the strain difference might arise

from the configuration of the N-donors, for example, [Ag(tet b)](ClO$_4$)$_2$ having the nitrogen atoms in a *trans*-I configuration, or the steric effects of the six methyl groups in tet a and tet b which elongate the Ag–N coordinate bonds. The Ag–N bond distances previously reported in related complexes are listed in Table 3. In contrast to the Ag–N bond lengths on the equatorial plane, the axial Ag–N bond lengths (2.567(9) and 2.529(9) Å) in the two polymers seem to be longer despite no constraints, indicative of weak interactions. Weak axial interactions of this type, a representative characteristic of d^9 systems, also exist in [Cu(cyclam)-(CH$_3$CN)$_2$][Ni(dmit)$_2$]$_2$ (the axial Cu–N bond distance 2.491(6) Å), [Cu(cyclam)]$_2$[2,5-DM–DCNQI]$_5$ (the axial Cu–N bond distances 2.410(3) and 2.502(3) Å) [2b] and the two isomers of [Cu(cyclam)(TCNQ)$_2$](TCNQ) (the axial Cu–N bond distances 2.536(5) and 2.598(3) Å, respectively) [17]. For complexes **1** and **2**, the comparison of Pd–C and Pt–C bond distances between the title polymers and other similar complexes is summarized in Table 3 [14,18–24].

Though some Ag(II) complexes were reported in the past decades [9e,f,25], to our knowledge, only three Ag(II) coordination polymers were unambiguously described in [Ag(2,2′-bipy)(NO$_3$)$_2$] [8c] and [Ag(2,2′-bipy)2](NO$_3$)·H$_2$O [8f] which have been characterized, and poly(ETPP)Ag(II) [26] where ETPP represents 5-(4-ethynylphenyl)-10,15,20-triphenylporphyrin. In [Ag(2,2′-bipy)(NO$_3$)$_2$], the Ag(II) ion adopts a distorted octahedral geometry in which its coordination sites on the basal plane are occupied by two nitrogen atoms of a dipyridine molecule (Ag–N: 2.124(16)–2.207(16) Å) and two oxygen atoms from two different nitrate anions (Ag–O: 2.148(15)–2.136(15) Å), while the apical coordination ones are completed by two oxygen atoms from the bridging nitrate anions(Ag–O: 2.753(13)–2.763(16) Å), generating a 1-D chain with alternate square grids and hexagon ones. Similarly, the Ag(II) ion in [Ag(2,2′-bipy)2](NO$_3$)$_2$·H$_2$O also possesses an octahedral coordination which has shown the presence of a distorted (~28°) from planar AgN$_4$ unit (Ag–N bond distances: 2.14, 2.15, 2.16, 2.18 Å) and the bridging nitrates linking the two different [Ag(2.2′-bipy)$_2$]$^{2+}$ moieties, with weak axial interaction, to form a chain structure. However, the Ag(II) ions in poly(ETPP)-Ag(II) are coordinated to the four nitrogen atoms for porphyrin moieties and the polymerization of the side arm ethynyl groups in ETPP gives rise to a 1-D chain with paramagnetic metalloporphyrin side chains. In a strict sense, the latter can not be assigned to a coordination polymer because it is formed via the polymerization of the ethynyl groups by means of catalyst instead of the molecular self-recognition and assembly. In contrast to these 1-D chain structures of the reported Ag(II) polymers, the two Ag(II) arrays presented here are extended via bridging cyano groups to link another
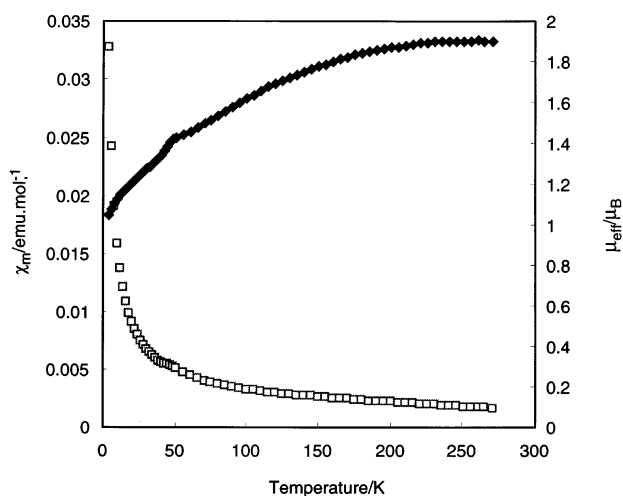
Table 3
The comparison of metal–N(C) bond distances between the title polymers and related complexes

No.	Metal	Metal–N(C) bond distances (Å)	Reference
1	Ag(II)	2.067(7), 2.055(7)	this work
2	Ag(II)	2.029(8), 2.010(1)	this work
3	Ag(II)	2.158(2)	[9c]
4	Ag(II)	2.160(3)	[9d]
5	Ag(II)	2.162(5)	[9f]
6	Ag(II)	2.124(16), 2.207(16)	[8c]
7	Ag(II)	2.09(2), 2.21(2)	[8d]
8	Ag(II)	2.118(10)	[8e]
9	Ag(II)	2.063(5)	[16]
10	Pd(bridged)	1.96(1)	this work
	Pd(terminal)	1.95(1)	this work
11	Pt(bridged)	1.99(1)	this work
	Pt(terminal)	1.98(1)	this work
12	Pd(bridged)	1.943(8)	[14]
	Pd(terminal)	1.994(8)	[14]
13	Pd(terminal)	2.007(8), 2.034(8)	[18]
14	Pd(terminal)	2.028(3), 2.030(3)	[19]
	Pt(terminal)	2.002(5), 2.018(5)	[19]
15	Pd(terminal)	2.12(1)	[20]
	Pt(terminal)	2.01(2)	[20]
16	Pt(bridged)	1.90(1), 1.91(1), 1.980(6), 1.993(6)	[21]
	Pt(terminal)	1.990(8)	[21]
17	Pt(bridged)	1.96(2), 1.99(1)	[22]
	Pt(terminal)	1.97(1)	[22]
18	Pt(terminal)	1.987(5), 1.989(5)	[23]
19	Pt(terminal)	1.997(4), 2.009(4)	[24]

Fig. 6. The temperature dependence of the molar magnetic susceptibility χ_m and effective magnetic moment μ_{eff} for **1**.

metal ion unit, giving rise to 1-D zigzag chains of bimetallic arrays with weak antiferromagnetic interactions.

3.2. IR spectra

The IR spectra of the two coordination polymers and their starting materials ([Ag(cyclam)](ClO₄)₂, K₂[Pd-(CN)₄]·3H₂O and K₂[Pt(CN)₄]·3H₂O) were recorded in the range 4000–400 cm⁻¹ on KBr disks at room temperature, respectively. For complexes **1** and **2**, several significant bands appear in their IR spectra, including the $\nu(CH_2)$, $\delta(CH_2)$, $\nu(NH)$, $\nu(C-N)$ and $\nu(C\equiv N)$ which are also found in the free [Ag(cyclam)](ClO₄)₂, K₂[Pd(CN)₄]·3H₂O and K₂[Pt(CN)₄]·3H₂O respectively, but the $\nu(OCl)$ of the ClO₄⁻ anions, $\nu(OH)$ and $\delta(HOH)$ of the lattice water molecules, which are observed in the free starting materials, vanish in the IR spectra. These results suggest that new compounds be formed. Generally, if the M−C≡N group forms an M−C≡N−M′ type bridge, the $\nu(C\equiv N)$ band shifts to a higher frequency [27a], and a single $\nu(C\equiv N)$ band can be split into two bands due to the presence of the terminal and bridging CN groups in the complex [3,27b]. However, these effects were not observed in **1** and **2** mainly because of weak interactions between the Ag(II) ions and the nitrogen atoms of the cyano groups. The $\nu(N-H)$ bands in the IR spectra of **1**–**2** at 3196 and 3242, 3186 and 3246 cm⁻¹, respectively, are slightly shifted toward higher frequencies with respect to those for the free [Ag(cyclam)] at 3159 and 3202 cm⁻¹, indicative of weak N−H···N hydrogen bonds in the two polymers [14,19].

3.3. Magnetic properties

The room temperature ESR spectra of the two Ag(II) complexes in the microcrystalline state were measured and exhibit a d⁹ axial symmetry ($g_\parallel > g_\perp$) which is consistent with the tetragonally elongated octahedral coordination geometry of the Ag(II) ions in these polymers [28,29]. The ESR parameters $g_\parallel$ and $g_\perp$ are 2.095 and 2.031 for complex **1**, 2.083 and 2.045 for complex **2**, respectively. The observed g tensors are in good agreement with the assignment that the unpaired electron resides in the $d_{x^2-y^2}$ orbit. The g values of axial symmetry in the two polymers resemble those observed in [Ag(tet a)](ClO₄)₂ ($g_\parallel = 2.11$ and $g_\perp = 2.058$) and [Ag-(cyclam)](ClO₄)₂ ($g\parallel = 2.095$ and $g_\perp = 2.038$) [9b], implying that the electron configuration of the Ag(II) ions in the two polymers is similar to that in these reported complexes and indicating weak axial interactions. No ESR signal for the Pd(II) and Pt(II) ions was observed owing to both of them adopting low spin in the square planar coordination.

The variable-temperature magnetic susceptibility of polymer **1** was obtained in the temperature range of 4–270 K. The temperature dependence of the molar magnetic susceptibility (χ_m) and effective magnetic moment (μ_{eff}) per Ag(II) ion is shown in Fig. 6. At 270 K, the μ_{eff} is $1.91\mu_B$ which is slightly larger than the spin-only value of $1.73\mu_B$ and similar to those observed in the Ag(II) complexes of cyclam and its derivatives [9b], and nitrogen-containing heterocycles [8a]. This result also demonstrates that the Pd(II) ion in the polymer has a spin value $S = 0$ which is in agreement with the ESR spectrum. As the temperature is lowered, the μ_{eff} decreases gradually and reaches a value of $1.05\mu_B$ at 4 K. Such magnetic behavior suggests that magnetic interactions exist between and within the chains through CN bridges and hydrogen bonds, giving rise to weak antiferromagnetic spin coupling presumably due to the longer bridging distances between the Ag(II) ions. In contrast to the two Ag(II) polymers, the μ_{eff} values of the Ag(II) complexes reported previously are generally temperature independent, except for silver(II) nicotinate [8a] and Ag(pyz)₂S₂O₈ [30], with the ranges of $1.7–2.1\mu_B$ for the complexes of nitrogen-containing heterocyclic ligands and $1.81–2.2\mu_B$ for ones of cyclam and its derivatives [7,8a,9b]. The values of μ_{eff} at room temperature for these Ag(II) complexes lie appreciably above the spin-only value due to mixing-in of some orbital angular momentum from excited states via spin-orbit coupling [29]. In addition, it is noteworthy that there is a discontinuity in the magnetic susceptibility curve at about 50 K presumably due to there existing a phase transformation.

In conclusion, the assembly of extended bimetallic arrays can give rise to a variety of networks and afford potential magnetic interactions between different metal ion units via bridging groups. The two bimetallic coordination polymers reported here, to our knowledge, are the first example of extended bimetallic arrays for Ag(II) and exhibit weak antiferromagnetic spin coupling, though they consist of simple 1-D zigzag chains. The Ag(II) ions adopt a tetragonally elongated octahe-

dral coordination, demonstrating a typical characteristic of d^9 metal ions, in the two polymers. The further studies will be focused on the effects of different metal units and bridging groups on the assembly and properties of Ag(II) coordination polymeric networks.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 156573 for **1** and 156574 for **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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