The First Silver(I) Side-On η^2-Coordination Network Formed by Self-Assembly of Bis(pyrrol-2-ylmethylene)hydrazine

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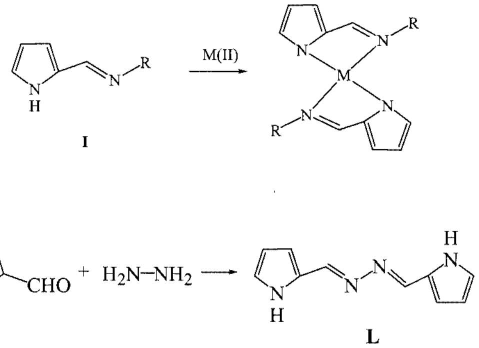
This paper reports the first silver(I) network polymer formed by the self-assembly of bis(pyrrol-2-ylmethylene)hydrazine with silver nitrate, in which the silver centers are bonded to the C–N bonds of the pyrrole rings in an η^2-fashion. An X-ray crystal structure analysis revealed that the self-assembly of the bis(pyrrol-2-ylmethylene)hydrazine ligand with Ag^I gives a 2D sheet, which is further assembled to form a 3D network through weak intermolecular hydrogen bonding between the protons of the pyrrole rings and the oxygen atoms of the nitrate ions.

Introduction

The design and synthesis of supramolecular coordination polymers has attracted increasing attention during the last decade due to their potential applications as functional materials.[1,2] Multidimensional networks based on ligands with a rigid bridging spacer[3] or a flexible bridging spacer[4] have been reported. Coordination networks containing π-sandwiched silver(I) complexes with polycyclic aromatic compounds,[5] cyclopentadienyl rings,[6] and phenyl rings,[7] have been described. Small π-sandwiched silver(I) complexes have been reported recently[8] in which the silver centers are doubly sandwiched. In this paper we report a novel three-dimensional silver(I) coordination network formed by self-assembly of bis(pyrrol-2-ylmethylene)hydrazine with silver nitrate, in which the silver center, unlike its more common sandwich coordination, is side-on η^2-coordinated to the pyrrole ring. To the best of our knowledge, this is the first example of a silver(I) side-on η^2-complex with pyrrole.

Our group is currently exploring the use of pyrrole-based Schiff bases, such as the (pyrrol-2-ylmethylene)amine ligands **I**, as building blocks for supramolecular architectures. By varying the length and geometric arrangement of the bridging spacer, the bis(pyrrol-2-ylmethylene)hydrazines could form dinuclear double-stranded helicates,[9] trimeric triangles, or tetrameric squares.[10] To further explore the application of the (pyrrol-2-ylmethylene)amine ligand **I** in supramolecular self-assembly, we are interested in investigating the self-assembly of bis(pyrrol-2-ylmethylene)hydrazine (**L**), in which two (pyrrol-2-ylmethylene)amine units are directly linked between two imine N atoms. Bis(pyrrol-2-ylmethylene)hydrazine was synthesized by a simple condensation of 2-formylpyrrole with hydrazine, as shown in Scheme 1. Among the many metal ions attempted, Ag^I was found to form complex **1** with ligand **L**, which was stable enough to allow successful isolation and crystallization.



Scheme 1

Results and Discussion

Complex Analysis

The polymer **1**, prepared by simply treating ligand **L** with silver nitrate, has a melting point of 140 °C (dec.), and is insoluble in most common solvents, such as $CHCl_3$, CH_2Cl_2, THF, acetone, ethyl acetate and CH_3OH. The IR analysis confirms the formation of complex **1**, in which the

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peak for nitrate is at 1382 cm^{-1} and is more intense than in **L**, the peak for ν_{N-H} is slightly shifted to a higher frequency (3222 cm^{-1}) with less intensity, while the peak for $\nu_{C=N}$ is not shifted (1631 cm^{-1}) but becomes much weaker than in the free ligand **L**. Attempts to analyze the polymer **1** by ^{1}H NMR spectroscopy in [D$_6$]DMSO or [D$_5$]pyridine failed since **1** decomposed.

X-ray Crystallographic Characterization

Complex **1** has the chemical formula $[Ag_2\mathbf{L}(NO_3)_2]_n$, indicating that two N−H protons remain in the ligand **L**, which is unique and surprising because the protons of pyrrolic NH groups in the (pyrrol-2-ylmethylene)amine ligands are usually removed upon coordinating to metal ions such as Zn^{II}, Ni^{II}, Cu^{II}, Co^{III}, Hg^{II}, Mn^{II} and Mn^{II}.[9−12]

The crystallographic study revealed that each ligand interacts symmetrically above and below the ligand plane in a di-η^2-fashion with two Ag^I ions, which coordinate to two imine-N atoms of two nearby ligands, resulting in an infinite one-dimensional (1D) stair-like polymeric structure as shown in Figure 1 (bottom). Due to an interaction between Ag^I and the five-membered rings in an η^2-fashion, the C5−N3 bond is found to be longer (1.413 Å) than the other four bonds (1.327−1.395 Å) in the pyrrole ring. The Ag1−N3 and Ag1−C5 (2.631 and 2.690 Å, respectively) bond lengths are within the normal range found in silver(I) sandwich complexes (2.47−2.92 Å),[5−8] indicating a moderate interaction between Ag^I and the pyrrole ring.

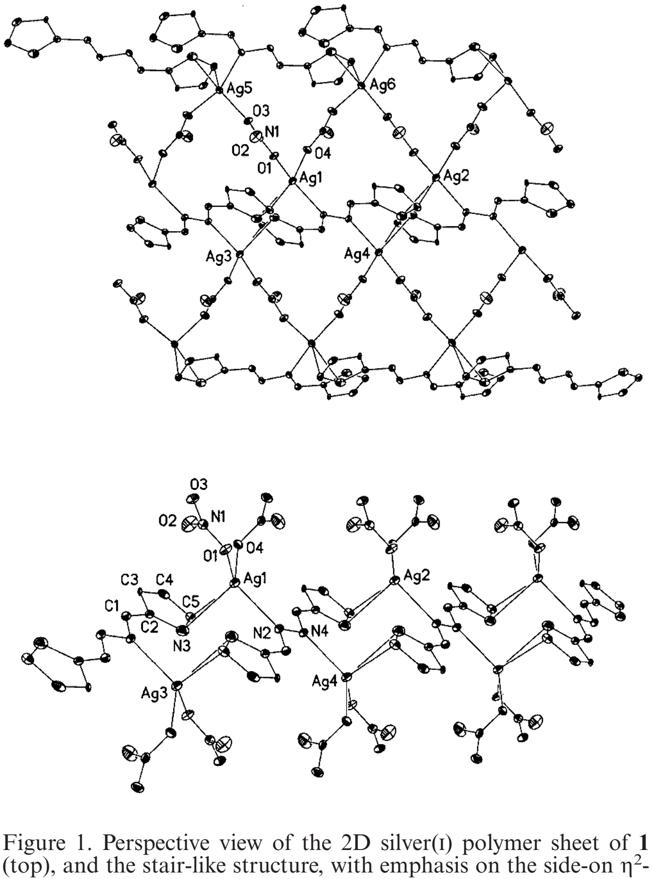

Figure 1. Perspective view of the 2D silver(I) polymer sheet of **1** (top), and the stair-like structure, with emphasis on the side-on η^2-coordination (bottom); hydrogen atoms are omitted for clarity

The adjacent 1D structures are assembled into a two-dimensional (2D) polymeric structure through the linkage of two silver atoms bridged by one nitrate group, with an Ag···Ag separation of 5.639 Å (Figure 1, top). In the 2D polymer sheet of **1**, the bis(pyrrol-2-ylmethylene)hydrazine ligands are arranged in rows in two directions, and the dihedral angle defined by the planes of the ligands in the two adjacent rows is 37.6°.

Each Ag^I center is four-coordinate to a nitrogen donor from the imine group of ligand **L**, a pyrrole ring of another ligand **L** in a side-on η^2-fashion, specifically with the C5−N3 bond (see Figure 1, bottom), and two oxygen atoms of two distinct nitrate ions. In turn, each nitrate ion is bound to two distinct Ag^I centers, while each ligand links four distinct Ag^I centers. This forms a unique stair-like Ag^I coordination polymer, in which the ligand **L** remains neutral, similar to the situation in silver(I) complexes with polycyclic aromatic compounds.[5]

The two (pyrrol-2-ylmethylene)amine units in ligand **L** adopt a *trans* arrangement about the N2−N4 bond, and are coplanar (σ = 0.019 Å). Ag1 and Ag4, bonded to two imine-N atoms of the ligand, are coplanar with ligand **L**. The Ag^I ions in **2** are also arranged into rows with a separation of 6.946 Å for the same row (e.g. Ag1−Ag2), and 4.828 Å for the adjacent separation (e.g. Ag1−Ag3).

The 2D sheets are further assembled to form a three-dimensional (3D) network through weak hydrogen bonding between the H atoms in the C3 and C4 positions of the pyrrole ring and the oxygen atoms of the nitrate ions in the two adjacent sheets (Figure 2). The C(pyrrole)−H···O(nitrate) angles are 154.2 and 142.1°, with an H···O separation (*d*) of 2.379 and 2.108 Å, respectively. These data fall in the range associated with weak hydrogen bonding.[13]

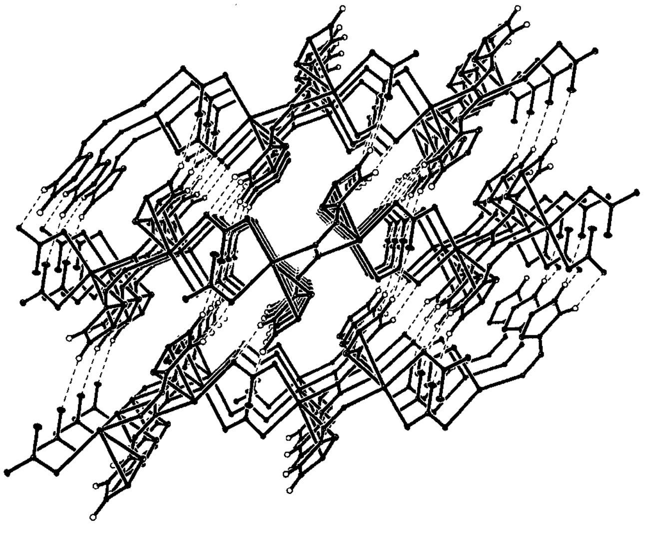

Figure 2. Perspective view of the three-dimensional network of **1** formed by weak intermolecular hydrogen bonding, viewed along the crystallographic *b* axis

In conclusion, a 2D polymer sheet of **2** is formed through self-assembly of bis(pyrrol-2-ylmethylene)hydrazine with silver nitrate. This is the first example of a 2D network polymer where the Ag^I center is side-on coordinated with a pyrrole ring in an η^2-fashion. The 2D sheet polymer is further assembled to form a 3D network through weak intermolecular hydrogen bonding of the type C(pyrrole)−H···O(nitrate).

Experimental Section

General Methods: Pyrrole-2-carbaldehyde was synthesized according to a literature method.[14] All reagents for syntheses and analyses were of analytical grade and used as received. Melting points were determined with a Yanaco MP-500 micro-melting point apparatus and are uncorrected. IR spectra were recorded with a Tensor 27 spectrometer. Raman spectra were recorded with an RFS100 spectrometer. ^{1}H NMR spectra were recorded with a Bruker Avance dpx 400 MHz instrument using TMS as internal standard. Elemental analyses were performed with Carlo Erba-120 elemental analyzer.

Preparation of Bis(pyrrol-2-ylmethylene)hydrazine (L): Pyrrole-2-carbaldehyde (0.95 g, 10 mmol) and hydrazine hydrate (0.25 g, 5 mmol) were dissolved in ethanol (15 mL). The mixture was stirred while a few drops of glacial acetic acid were added. After a few seconds, a yellow precipitate was observed. The suspension was stirred at room temperature for 1 h. The yellow solid was collected by suction filtration, washed with cold ethanol and dried under vacuum to give the expected product. An analytical sample was purified by recrystallization from ethanol. Yield: 0.56 g (60%). Mp. 186−187 °C. Selected FT-IR peaks (KBr pellets): $\tilde{\nu}$ = 3217s cm^{-1} (NH), 3105w (=CH), 3066w (=CH), 1632s (C=N), 1541w (ring), 1409s (ring), 1132m (ring CH), 1029m (ring CH). Raman: $\tilde{\nu}$ = 1584s cm^{-1} (C=N), 1532m (C=N), 1422m (ring), 1347m (ring), 1017s (ring). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ = 6.30 (s, 2 H, pyrrole-H), 6.62 (s, 2 H, pyrrole-H), 6.98 (s, 2 H, pyrrole-H), 8.37 (s, 2 H, imine-H), 9.33 (br., 2 H, NH) ppm. UV/Vis (DMSO): λ = 357 nm (ε = 46500). $C_{10}H_{10}N_4$ (186.09): calcd. C 64.50, H 5.41, N 30.09; found C 64.72, H 5.55, N 30.47.

Preparation of [Ag$_2$L(NO$_3$)$_2$]$_n$ (1): Crystals of **1** were prepared by slow diffusion of a solution of AgNO$_3$ (34 mg, 0.2 mmol) in CH$_3$OH (6 mL) into a solution of **L** (18.6 mg, 0.1 mmol) in CHCl$_3$ (10 mL) in a sealed tube. After one week, light-yellow crystals of **1** suitable for X-ray analysis were obtained. Yield: 29 mg (55%). M.p. > 140 °C (decomp.). Selected FT-IR peaks (KBr pellet): $\tilde{\nu}$ = 3221m cm^{-1} (NH), 3138w (=CH), 3108w (=CH), 1630s (C=N), 1541w (ring), 1410sh (ring), 1382vs (NO$_3^-$), 1361s (ring), 1129m (ring CH), 1032m (ring CH). Raman: $\tilde{\nu}$ = 1576s cm^{-1} (C=N), 1441w (ring), 1362w (ring), 1012w (ring). $C_{10}H_{10}Ag_2N_6O_6$ (525.98): calcd. C 22.84, H 1.92, N 15.98; found C 22.75, H 1.87, N 15.68.

X-ray Data Collection and Structure Solution and Refinements: Single-crystal X-ray diffraction measurements were carried out with a Rigaku R-axis RAPID IP diffractometer. Determination of the unit-cell parameters and data collection were performed with Mo-K_α radiation (λ = 0.71073 Å) and unit-cell dimensions were obtained by least-squares refinement. The structure was solved by direct methods and empirical absorption corrections were applied using the ψ-scan method. The final refinement was carried out by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen positions were calculated and refined as riding on the concerned atoms with fixed thermal factors. A total of 2754 reflections were measured in the range 2.52° ≤ θ ≤ 27.48° (*hkl* range indices: $-12 \le h \le 12$, $-8 \le k \le 8$, $-14 \le l \le 14$) with 1638 unique reflections [R(int) = 0.0303]. The structure was solved with SHELX-97[15] and refined with SHELX-97.[16] The details for structure analysis are summarized in Table 1. Selected bond lengths and angles are given in Table 2. CCDC-208538 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at 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].

Table 1. Crystallographic data for complex **1**

Empirical formula	$C_{10}H_{10}Ag_2N_6O_6$
Formula mass	525.98
Cryst color, habit	light yellow, needle
Crystal size [mm]	0.55 × 0.30 × 0.16
Crystal system	monoclinic
Space group	$P2_1/n$
T [K]	293(2)
a [Å]	9.8332(12)
b [Å]	6.9461(7)
c [Å]	10.8710(8)
β [°]	103.486(6)
V [Å^3]	722.04(13)
$D_{\text{calcd.}}$ [Mg/m^3]	2.419
Z	4
λ(Mo-K_α) [Å]	0.71073
μ(Mo-K_α) [mm^{-1}]	2.757
F(000)	508
R_1 [a]	0.0325
wR_2 [b]	0.0761
GOF	0.940

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o||$. [b] $wR_2 = \Sigma||F_o| - |F_c||w^{1/2}/\Sigma|F_o|w^{1/2}$.

Table 2. Selected bond lengths [Å] and bond angles for the Ag^I network polymer **1**; symmetry transformations used to generate equivalent atoms: ^{i} $-x + 1/2$, $y - 1/2$, $-z + 3/2$; ^{ii} $-x + 1$, $-y$, $-z + 1$; see Figure 2 (bottom) for atom labeling

Bond lengths			
Ag1−N3	2.631(4)	Ag1−C5	2.690(4)
Ag1−N2	2.338(3)	Ag1−O4	2.494(3)
Ag1−O1	2.398(3)		

Bond angles			
N2−Ag1−O1	112.23(11)	N2−Ag1−O4	116.89(11)
O4−Ag1−O1	113.65(10)	N2−Ag1−N3	92.36(12)
O1^{i}−Ag1−N3^{ii}	111.06(12)	O4−Ag1−N3^{ii}	108.55(12)
N2−Ag1−C5^{ii}	97.66(12)	O1^{i}−Ag1−C5^{ii}	134.04(13)
O4−Ag1−C5^{ii}	79.22(11)	N3^{ii}−Ag1−C5^{ii}	30.78(13)

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