Self-assembly of a Novel Three-dimensional Silver(I) Supramolecular Framework from Cationic Chains and Anionic Sheets

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A new three-dimensional (3D) supramolecular framework, $[Ag_2(bipy)_2(bdc)\cdot 4H_2O]_n$ **1**, has been synthesized by the ultrasonic reaction of Ag_2O, bipy and H_2bdc (H_2bdc = 1,4-benzenedicarboxylic acid; bipy = 4,4′-bipyridine) at room temperature. It exhibits a new 3D supramolecular framework which is built from cationic Ag-bipy chains and anionic bdc-H_2O sheets through hydrogen bonds, $\pi\cdots\pi$ stacking and C–H$\cdots\pi$ interactions. Additionally, the photoluminescent and thermal properties of **1** were investigated.

Key words: Silver, 4,4′-Bipyridine, Hydrogen Bond, $\pi\cdots\pi$ Interactions, Photoluminescence Properties

Introduction

The construction of coordination polymers and supramolecular compounds based on multitopic ligands and metal centers represents one of the most rapidly developing fields in current coordination chemistry owing to their potential as functional materials [1 – 6]. In the past few years, the development of supramolecular self-assembly chemistry allows to rationally design and prepare supramolecular architectures through non-covalent interactions, in which it is crucial to meet both geometric as well as energetic prerequisites [7]. Doubtless, the hydrogen bond is the most familiar secondary force in supramolecular assemblies due to its moderately directional intermolecular interaction that may control molecular packing [8, 9], and thus many studies have focused on the investigation of hydrogen bonds [10 – 13]. Compared to the hydrogen bonds, $\pi\cdots\pi$ and C–H$\cdots\pi$ interactions have been somewhat less considered, and only few examples generated by combination of multi-supramolecular interactions have been reported [14]. Bipy and its analogs are neutral linear ligands widely used as excellent spacers in the construction of novel supramolecular compounds by diverse supramolecular interactions [15, 16]. Recently, we have undertaken a series of investigations into the assembly of Ag(I) ions with different angular and linear bipodal N-donor ligands, such as aminopyrimidines and aminopyrazines [17 – 19], with the principal aim to obtain supramolecular compounds or multifunctional coordination polymers. In an attempt to exploit the Ag-bipy/dicarboxylate system under ammoniacal conditions, we successfully synthesized the supramolecular coordination polymer **1**.

Experimental Section

All reagents and solvents employed were commercially available and used as received without further purification. Infrared spectra were recorded on a Nicolet Avatat FT-IR360 spectrometer from KBr pellets in the frequency range 4000 – 400 cm^{-1}. The elemental analysis (C, H, N contents) was carried out on a CE instruments EA 1110 analyzer. Photoluminescence measurements were performed on a Hitachi F-4500 fluorescence spectrophotometer with solid powder on a 1 cm quartz round plate.

Synthesis of $[Ag_2(bipy)_2(bdc)\cdot 4H_2O]_n$ *(**1**)*

A mixture of Ag_2O (116 mg, 0.5 mmol), bipy·$2H_2O$ (194 mg, 1 mmol) and H_2bdc (166 mg, 1 mmol) was stirred in CH_3OH-H_2O mixed solvent (8 mL, v/v: 3/1). Then aqueous NH_3 solution (25 %) was dropped into the mixture to give a clear solution under ultrasonic treatment. The resulting solution was allowed to evaporate slowly in the dark at r. t. for several days to give colorless crystals of **1** (yield, 51 %). They were washed with small volumes of cold CH_3OH and diethyl ether. Anal. for $AgC_{14}H_{14}N_2O_4$: calcd. C 44.00, H 3.69, N 7.33; found C 43.95, H 3.64, N 7.38. – IR (KBr): ν = 3431

Table 1. Crystal structure data for **1**.

	1
Formula	$C_{14}H_{14}AgN_2O_4$
M_r	382.14
Crystal size, mm^3	0.24 × 0.21 × 0.18
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	7.2014(14)
b, Å	9.3868(19)
c, Å	11.354(2)
α, deg	75.34(3)
β, deg	81.51(3)
γ, deg	69.41(3)
V, Å^3	693.6(2)
Z	2
D_{calcd}, g cm^{-3}	1.83
μ(MoK_α), cm^{-1}	1.5
$F(000)$, e	382
hkl range	±8, ±11, ±13
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.6168
Refl. measured	5348
Refl. unique	2681
R_{int}	0.0260
Param. refined	190
$R1(F)/wR2(F^2)$^{a} (all refl.)	0.0250 / 0.0652
GoF (F^2)^{b}	1.041
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.54 / −0.70

^{a} $R1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2(F^2) = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (0.0399P)^2 + 0.0920P]^{-1}$, where $P = (\mathrm{Max}(F_o{}^2, 0) + 2F_c{}^2)/3$; ^{b} GoF $= [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{obs} - n_{param})]^{1/2}$.

(s), 3046(w), 2925(w), 2855 (w), 1606(s), 1559(s), 1483(w), 1428(w), 1381(s), 1220(m), 1071 (w), 804 (w), 735 (w), 619(w), 501 (w) cm^{-1}.

X-Ray structure determination

The reflection intensities of the crystal of **1** were collected at 298(3) K using a Bruker-AXS CCD area detector single-crystal diffractometer, with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å), using the $\psi/2\vartheta$ scan mode. An absorption correction was applied using the program SADABS [20]. The structure was solved by Direct Methods using SHELXS-97 [21] and refined by full-matrix least-squares methods on F^2 (SHELXL-97 [22]). All hydrogen atoms attached to the carbon atoms were generated geometrically, and the hydrogen atoms of the water molecules were located from difference Fourier syntheses. All non-hydrogen atoms were finally refined with anisotropic displacement parameters. H atoms attached to C atoms were treated as riding, with C–H = 0.93 Å. The H atoms of the water molecules were refined with $U_{iso}(H)$ = 1.2 $U_{eq}(O)$. The positions of the water H atoms were refined with the O–H distances restrained to 0.85 Å. Crystal data and further information on the structure determination are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2.

Table 2. Selected bond lengths (Å), angles (deg) and hydrogen bonding parameters for **1**^{a}.

Distances and angles			
Ag1-N2^{i}	2.1374(19)	Ag1-O2W	2.5401(19)
Ag1-N1	2.1417(18)		
N2^{i}-Ag1-N1	171.31(7)	N1-Ag1-O2W	93.62(7)
N2^{i}-Ag1-O2W	95.06(7)		
C4-C3-C6-C7	23.1(3)	O2-C15-C13-C12	5.2(3)

Hydrogen bonds				
D-H···A	D-H	H···A	D···A	D-H···A
O1W-H1WA-O2^{iv}	0.85	2.02	2.856(2)	170
O1W-H1WB-O2^{v}	0.85	1.95	2.783(3)	168
O2W-H2WA-O1^{vi}	0.85	1.91	2.755(2)	176
O2W-H2WB-O1W^{vi}	0.85	1.92	2.760(3)	169

^{a} Symmetry codes: ^{i} $x, y, -1+z$; ^{iv} $1-x, -y, -z$; ^{v} $-1+x, y, z$; ^{vi} $x, 1+y, z$.

CCDC 749432 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Synthesis and IR spectra

It is common knowledge that silver complexes are not stable in the light. So we placed the reaction mixtures in the dark to protect them from photodecomposition. The formation of the products is not significantly affected by changes of the molar ratio of organic ligands to metal ions, and the resultant crystals are insoluble in water and common organic solvents. During the synthesis, precipitates were quickly formed when mixing the reactants. Therefore, our solution to the problem of precipitates was dropping ammonia solution (25 %) into the reaction mixture under ultrasonic treatment until it was almost completely dissolved, and then filtering to get a clear solution to evaporate in air. Ag_2O was used instead of $AgNO_3$ or other common silver(I) salts in order to promote the carboxylates instead of small anions to coordinate to the silver(I) centers. The infrared spectra and the elemental analysis of **1** are fully consistent with the formulation. The IR spectra exhibit strong characteristic bands of carboxylic groups in the range from ~1606 to ~1559 cm^{-1} for the asymmetric vibrations and from ~1483 to ~1381 cm^{-1} for the symmetric vibrations. The absence of the characteristic bands at around 1700 cm^{-1} attributed to the carboxylic groups indicate complete deprotonation of all carboxylate groups in **1** [23].

Structure description

As shown in Fig. 1, the asymmetric unit of **1** consists of one Ag(I) ion, one half of the bdc dianion located at an inversion center, one bipy ligand and two water molecules. Each Ag(I) ion is coordinated by two nitrogen atoms from two different bipy ligands and one water molecule in a

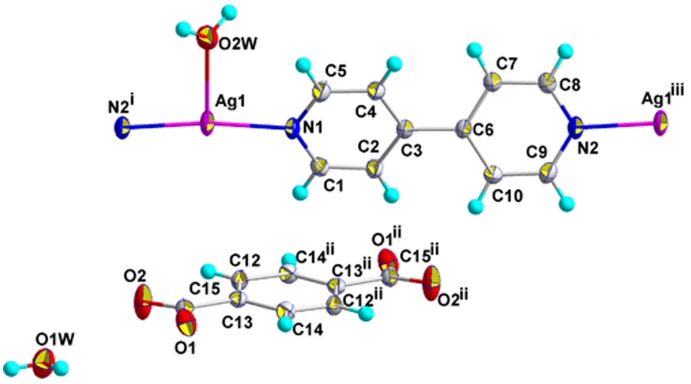

Fig. 1. The molecular structure and atom labeling of **1**, showing the coordination environment of the silver centers (symmetry codes: ^{i} $x, y, -1+z$; ^{ii} $2-x, -y, 1-z$; ^{iii} $x, y, 1+z$).

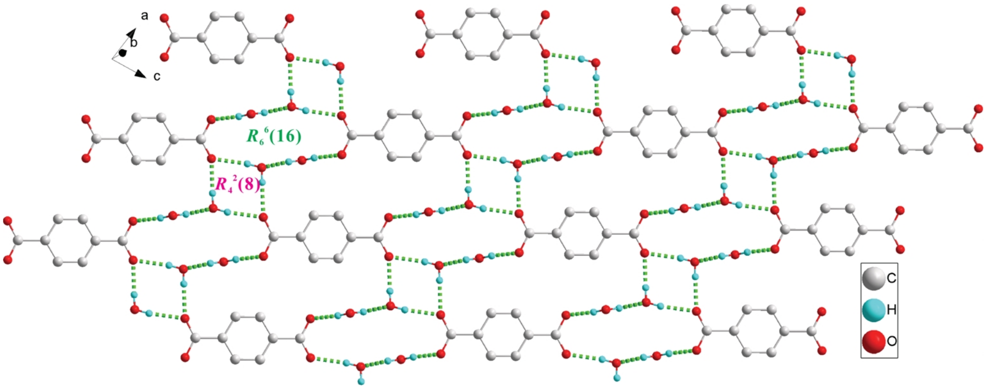

Fig. 2. The ball-stick perspective view of an anionic sheet incorporating $R_6{}^6(16)$ and $R_4{}^2(8)$ hydrogen bond motifs (dashed lines).

T-shaped fashion to form a linear chain with alternating Ag(I) and bipy units [Ag1–N2^{i} = 2.1374(19), Ag1–N1 = 2.1417(18) Å]. The N1–Ag1–N2 bond angle of 171.31(7)° indicates a distortion from linearity, which may be assigned to the coordinative interaction between Ag(I) and the water molecule [Ag–O2W = 2.5401(19) Å]. The bipy ligand has a twist conformation with the dihedral angle between the two pyridine rings at 23.1(3)°. Each pair of parallel Ag-bipy chains shows a "head-to-tail" packing motif where the cationic repulsion is minimized [24]. The shortest Ag···Ag distance between neighboring chains is 6.224 Å indicating no direct Ag···Ag interaction [25]. Weak aromatic $\pi\cdots\pi$ stacking interactions [$Cg1\cdots Cg1(2-x, 1-y, 1-z)$ = 3.7608(16) Å, offset distance = 1.486 Å; $Cg2\cdots Cg2(1-x, 1-y, 2-z)$ = 3.7985(17) Å, offset distance = 1.257 Å; $Cg1$ and $Cg2$ are the centroids of the N1/C1/C2/C3/C4/C5 and N2/C6/C7/C8/C9/C10 ring, respectively] also exist between the pyridine rings of neighboring bipy ligands.

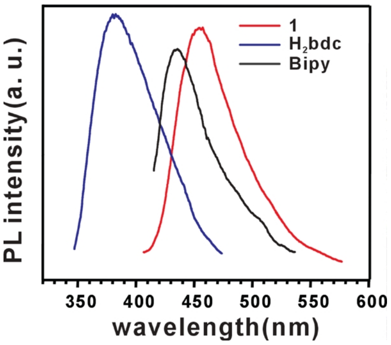

Fig. 3. Emission spectra of compound **1** and its free ligands.

In addition, the ancillary ligand H_2bdc is deprotonated to balance the charge, but does not participate in coordinating to the Ag(I) ion. Each O1W acts as a donor to two O atoms from two different carboxylate groups, forming centrosymmetric $R_4{}^2(8)$ water-bridged carboxylate rings with the D-A (donor-acceptor) distances being 2.783(3) and 2.856(2) Å. These $R_4{}^2(8)$ rings are centered at $(n{+}0, 0, 0)$ where n represents an integer. On the other hand, the coordinating H_2O molecules (O2W) act as donors incorporating H_2O molecules (O1W) and carboxylic groups to form another hydrogen bonding motif [26]: $R_6{}^6(16)$, with centers at $(n{+}0.5, 0, 0)$ where n again represents an integer, and sharing edges with $R_4{}^2(8)$ rings. Combination of these two hydrogen bond motifs constructs the bdc-H_2O anionic sheets (Fig. 2). Along with classical hydrogen bonds, nonclassical C–H···O hydrogen bonds also exist between the cationic chains and anionic sheets with an average C–H···O distance of 3.34 Å. The $\pi\cdots\pi$ stacking interactions and O–H···O and C–H···O hydrogen bonds combine with the C–H···π interactions [C1–H1–*C*g3 = 151°, H1···*C*g3 = 2.62 Å, C1···*C*g3 = 3.465(3) Å; *C*g3 is the centroid of the C12/C13/C14/C12$^{\text{ii}}$/C13$^{\text{ii}}$/C14$^{\text{ii}}$ ring, symmetry code: (ii) $2-x$, $-y$, $1-z$] to give a 3D supramolecular framework.

Photoluminescence properties

The solid-state photoluminescence data for both free ligands and for complex **1** at r. t. are shown in Fig. 3. Complex **1** exhibits photoluminescence in the solid state, with an emission maximum at 456 nm upon excitation at 330 nm at r. t. To understand the nature of the emission bands, we analyzed the photoluminescence properties of the corresponding free ligands and found that free bipy and H_2bdc ligands emit photoluminescence at 436 and 383 nm, respectively [27]. Therefore, the emission band of **1** is probably due to $\pi^* \rightarrow$ n or $\pi^* \rightarrow \pi$ transitions.

Thermal analyses

Over the temperature range 20 – 600 °C, the title complex dissociates in three steps in a flowing N_2 atmosphere. The dehydration is found to be completed at 97 °C, at which temperature the weight loss reaches 9.3 % in good agreement with the calculated value of 9.4 % for four water molecules per two formula units. The second weight loss of 20.9 % from 123 to 212 °C corresponds to the decomposition of one uncoordinated bdc per two formula units (calcd. 21.5 %). The decomposition of bdc indicates that decarboxylation may occur. Above 212 °C, the Ag-bipy chain starts to decompose, and the decomposition ends above 300 °C.

Conclusion

The crystal structure of **1** features Ag-bipy cationic chains and bdc-H_2O anionic sheets, constructed by coordination bonds and supramolecular interactions, respectively.

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