Organic–inorganic hybrid cyclic aggregate or 2D network assembled by silver(I) 3,5-dinitrobenzoate with 2-methylimidazole or 2-aminopyrimidine

An-Wu Xu,[a] Cheng-Yong Su,*[a] Ze-Fu Zhang,[b] Yue-Peng Cai[a] and Chun-Long Chen[a]

[a] *School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275, China. E-mail: cesscy@zsu.edu.cn*
[b] *Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China*

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Silver(I) 3,5-dinitrobenzoate (DNB) reacts with 2-methylimidazole (MeIm), producing a linearly coordinated $[Ag(MeIm)_2]^+$ cation that is further assembled with 3,5-dinitrobenzoate anion *via* N–H···O hydrogen bonding to give the cyclic aggregate $\{[Ag(MeIm)_2](DNB)\}_2$ **1**; whereas with 2-aminopyrimidine (APym) it affords the coordination polymer $[Ag(Apym)(DNB)]_\infty$ **2**, which is assembled into a two-dimensional network sustained by weak C–H···O hydrogen bonds.

The controlled design of solid-state architectures, so-called crystal engineering, is currently recognized as one of the most important research areas due to its close relation to biomimetics, catalysis and materials science.[1,2] It is also expected to throw light upon the understanding of how molecules can be organized and how functions can be revealed. Two main synthetic branches have drawn much attention according to their different synthetic strategies, namely "coordination polymers" achieved primarily through the assembly of metal complexes and "organic solids" formed from the assembly of organic molecules or ions.[3–5] The versatile metal–ligand bonds promote quick growth of inorganic crystal engineering,[6] while the variety of intermolecular forces, such as halogen···halogen, N···halogen, S···S, π···π contacts and various types of weak hydrogen bonds (C–H···O, C–H···N, O–H···π, C–H···π), in contrast to the traditional hydrogen bonds (X–H···Y; X, Y = F, O and N), play important roles in the construction of ordered organic networks.[7] Recently, a combination of the two aforementioned strategies has become increasingly prominent due to easier access to unique structures and properties not readily available in individual inorganic or organic solids.

This new strategy often relies on the deliberate selection of ligands that can simultaneously coordinate metal ions and provide potential intermolecular interaction sites.[8–10] The angular disposition of N atoms in pyrimidine has led to the formation of various supramolecular isomers in its metal complexes[11,12] in which discrete macrocycles, 1D, 2D and 3D architectures have been generated. 2-Aminopyrimidine was selected here because of its potential amino donor besides the two exodentate imino nitrogen atoms.[13] Similarly, the imidazolate anion, easily obtained by deprotonation of imidazole, is capable of acting as a bridging ligand. The 1,3-arrangement of the nitrogen atoms imposes geometrical constraints such that only one imidazolate bridge is possible between two metal centers. Accordingly, imidazolate-bridged transition metal complexes show higher linearity[14] and many oligomeric and polymeric complexes have been fabricated,[15–18] though few of them are silver(I)-containing and only a handful of single crystal structures determined.[19–21] On the other hand, non-deprotonated imidazole itself is monodentate and is found to linearly coordinate to silver(I) ions in bis(imidazole)silver(I) nitrate.[22] Interestingly, a novel Ag_6 cluster has been obtained from reaction of silver(I) perchlorate and imidazole in which no other bridging force but Ag···Ag contacts contributes to clustering.[23] We are interested in utilizing the potential hydrogen bond donor NH group, and in this paper, efforts are focused on the assembly of organic–inorganic hybrid aggregates following the above-mentioned new strategy. A cyclic aggregate and a two-dimensional network have been constructed from 2-methylimidazole and 2-aminopyrimidine ligands of somewhat similar donor arrangements with silver(I) 3,5-dinitrobenzoate, suggesting different crystal engineering assembly pathways from different intermolecular interactions.

Experimental

Materials and methods

All starting materials were reagent grade obtained from commercial sources and used without further purification. Silver(I) 3,5-dinitrobenzoate was prepared from reaction of silver(I) nitrate with 3,5-dinitrobenzoic acid. The elemental analyses for C, H and N were carried out with a Varian EL elemental analyzer. ^1H NMR spectra were measured on a Varian INOAN 500 instrument using DMSO-d_6 as solvent with TMS as internal standard at room temperature.

Preparation

$\{[Ag(MeIm)_2](DNB)\}_2\cdot H_2O$, $1\cdot H_2O$. A solution of silver(I) 3,5-dinitrobenzoate (0.32 g, 1 mmol) in MeCN (5 cm^3) was added to a stirred solution of 2-methylimdazole (0.16 g, 2 mmol) in MeOH (2 cm^3). The resulting mixture was filtered and slow diffusion of diethyl ether for 24 h produced pale yellow prismatic crystals, which were collected by filtration, washed with MeCN and MeOH and dried in a vacuum desiccator over silica gel. Yield: 60%. Elem. anal. found: C, 36.46; H, 3.55; N, 17.22; calc. for $C_{30}H_{32}N_{12}Ag_2O_{13}$: C, 36.60; H, 3.28; N, 17.07%. ^1H NMR (500 MHz, DMSO-d_6): δ 2.45 (6H,

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

	1	**2**
Formula	$C_{30}H_{32}N_{12}O_{13}Ag_2$	$C_{11}H_8N_5O_6Ag$
Formula weight	984.42	414.09
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/c$
a/Å	8.9218(11)	9.038(6)
b/Å	11.9058(14)	6.373(3)
c/Å	18.795(2)	23.946(16)
α/°	71.592(2)	
β/°	76.372(2)	100.79(2)
γ/°	88.482(2)	
U/Å^3	1838.4(4)	1354.9(14)
Z	2	4
μ/mm^{-1}	1.147	1.531
T/K	293(2)	293(2)
Unique reflections	9809	2396
Observed reflections $I > 2\sigma(I)$	6621	1457
R^a	0.0318	0.0494
wR^b	0.0784	0.0927

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

methyl), 7.07 (4H, imidazole), 8.79 (1H, NDB_{4H}) and 8.91 (2H, $NDB_{2,6H}$).

[Ag(Apym)(DNB)]$_\infty$, 2. This was prepared in a similar way using the procedure described for complex **1** with 2-aminopyrimidine (0.19 g, 2 mmol) instead of 2-methylimidazole. Yield: 65%. Elem. anal. found: C, 31.66; H, 1.87; N, 17.21; calc. for $C_{11}H_8N_5AgO_6$: C, 31.91; H, 1.95; N, 16.91%.

X-Ray crystallographic studies

The diffraction intensities of complex $\mathbf{1}\cdot H_2O$ were collected (hemisphere technique) on a Bruker SMART 1K diffractometer with a CCD area detector. Absorption corrections were performed using the SADABS program.[24] Data collection for **2** was performed on a Siemens R3m four-circle diffractometer. An empirical absorption correction based on psi scans of several reflections was applied. All the structures were solved by direct methods and refined by full-matrix least-squares against F^2 of all data using SHELXTL software.[25] Anisotropical thermal factors were assigned to all of the non-hydrogen atoms while the hydrogen atoms were included in the calculations isotropically but not refined. A summary of parameters for the data collections and refinements is given in Table 1. Selected bond distances and bond angles are listed in Tables 2 and 3.

Table 2 Selected bond distances (Å) and angles (°) for complex **1**. Symmetry transformation used to generate equivalent atoms: (a) $2 - x, 1 - y, -z$

Ag1–N3	2.1139(18)	Ag1–N1	2.1194(19)
Ag2–N7	2.1211(19)	Ag2–N5	2.1239(18)
N2···O11	2.742(3)	N6···O5	2.768(3)
N4···O6	2.767(2)	N8···O12	2.703(2)
O1W···O5	2.956(3)	O1W···O6a	2.880(3)
N3–Ag1–N1	161.37(8)	N7–Ag2–N5	159.94(8)
N2–H2···O11	165.9	N4–H4···O6	171.7
N8–H8···O12	173.3	N6–H6···O5	167.5
O1W–H1W···O5	174.0	O1W–H2W···O6a	174.2

Table 3 Selected bond distances (Å) and angles (°) for complex **2**. Symmetry transformations used to generate equivalent atoms: (a) $x, y - 1, z$; (b) $1 - x, 1 - y, 2 - z$; (c) $1 + x, 1/2 - y, 1/2 + z$; (d) $1 + x, 3/2 - y, 1/2 + z$

Ag1–N4a	2.215(5)	Ag1–O1	2.274(4)
Ag1–N3	2.363(5)	Ag1–N5b	2.658(5)
C8···O3	3.379(6)	C10···O3	3.363(6)
N4a–Ag1–O1	132.37(18)	N4a–Ag1–N3	121.50(17)
O1–Ag1–N3	98.79(18)	N4a–Ag1–N5b	117.03(18)
O1–Ag1–N5b	82.71(16)	N3–Ag1–N5b	91.91(18),
C8–H8a···O3c	146.5	C10–H10a–O3d	147.7

CCDC reference number 440/250. See http://www.rsc.org/suppdata/nj/b0/b008383f/ for crystallographic files in .cif format.

Results and discussion

Single-crystal X-ray analysis reveals that the complex $\mathbf{1}\cdot H_2O$ consists of two $[Ag(MeIm)_2]^+$ cations, two 3,5-dinitrobenzoate anions and one water molecule. Each silver(I) ion is coordinated to two imino nitrogen atoms of two monodentate 2-methylimidazole ligands, showing four similar Ag–N bonds [Ag1–N3 2.1139(18), Ag1–N1 2.1194(19), Ag2–N7 2.1211(19), Ag2–N5 2.1239(18), average 2.1196 Å], which are slightly longer than those in the $[Ag(imidazole)_2](ClO_4)$ complex (2.082 Å)[23] but shorter than those in other heterocyclic nitrogen coordination complexes ($Ag–N_{pyridine}$ 2.135, $Ag–N_{benzimidazole}$ 2.184, $Ag–N_{quinoline}$ 2.263–2.444 Å).[26–28] The N–Ag–N angles [N3–Ag1–N1 161.37(8)°, N7–Ag2–N5 159.94(8)°] deviate from linearity, indicating that the coordination geometry of the silver(I) ion may be best described as bent.[12] The 3,5-dinitrobenzoate anion does not directly bind to silver(I) but is involved in the formation of intermolecular interactions through its acetate group. As shown in Fig. 1, each 3,5-dinitrobenzoate anion forms two N–H···O acceptor hydrogen bonds with the NH groups of 2-methylimidazole belonging to two different $[Ag(MeIm)_2]^+$ cations, thus assembling two $[Ag(MeIm)_2]^+$ cations and two 3,5-dinitrobenzoate anions into a neutral four-component ring structure[29] in which four N–H···O hydrogen bonds are involved (N2–H2···O11, N6–H6···O5, N4–H4···O6 and N8–H8···O12). In addition, the solvate water molecules form weak O–H···O donor hydrogen bonds with the O5 atom of one 3,5-dinitrobenzoate anion [O1W···O5 2.956(3) Å, O1W–H1W···O5 174.0°] and the O6a atom of another anion belonging to the adjacent cyclic aggregate [O1W···O6a 2.880(3), Å, O1W–H2W···O6 174.2°], linking two such cyclic aggregates to form a hydrogen bonded dimer. The shortest silver(I) ion separation between two molecules is 4.837 Å, indicating no Ag···Ag interaction.

As shown in Fig. 2, complex **2** is a one-dimensional staircase polymer linked by 1,3-bridging 2-aminopyrimidine molecules. The silver(I) ion is three coordinated by one oxygen atom of the 3,5-dinitrobenzoate anion and two nitrogen atoms belonging to two 2-aminopyrimidine ligands. The Ag–N

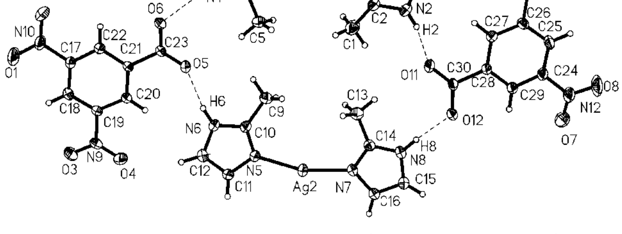

Fig. 1 The neutral cyclic aggregate $\{[Ag(MeIm)_2](NDB)\}_2$ in **1** linked *via* N–H···O hydrogen bonding.

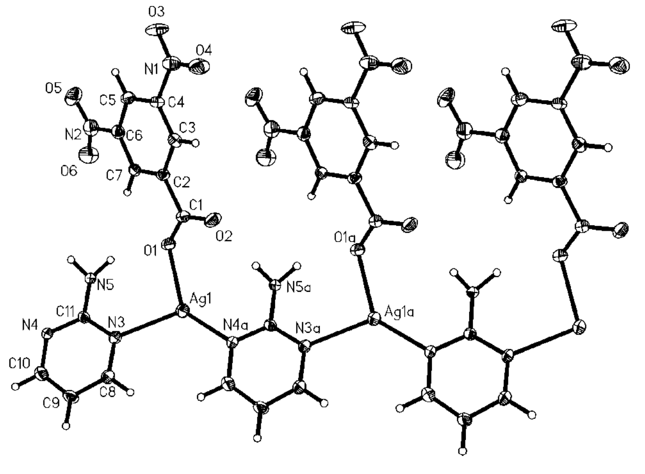

Fig. 2 Extended 1D coordination polymer $[Ag(APym)(DNB)]_\infty$ in **2** bridged by 2-aminopyrimidine.

bonds [Ag1–N4 2.215(5), Ag1–N3 2.363(5) Å] are somewhat longer than those in **1**, while the Ag–O bond [Ag1–O1 2.274(4) Å] is comparable with those in nitrate coordination complexes.[27,28] It is interesting that two of the ring pyrimidine hydrogen atoms are engaged in C–H···O hydrogen bonding with the O3 atom belonging to the neighboring coordination polymer. The ordered two-dimensional network is thus assembled as shown in Fig. 3. The topology of the network can be simplified to regard Apym as a four-connecting node, with DNB and the Ag(I) as three-connecting nodes. Therefore, two pyrimidine rings are connected by two Ag–N coordination bonds and two C–H···O hydrogen bonds to compose a tetragon. Such tetragons share vertices to form one-dimensional arrays that are further linked by 3,5-dinitrobenzoate anions through the remaining vertices. So the network is composed of equal numbers of tetragons sharing vertices and hexagons sharing edges with tetragons. The NH_2 group of 2-aminopyrimidine in **2** is not involved in coordination, but significantly interacts with the silver(I) ion of the adjacent network [Ag1···N5b 2.658(5) Å]. Therefore, a ribbon double layer architecture is constructed and the whole crystal structure is stacked up by such double layers.

Comparison of the present two structures may provide clues to the design of new solid materials. Both 2-methylimidazole and 2-aminopyrimidine have 1,3-positioned nitrogen donors, and a similar bridging coordination mode is rationally expected once the NH group of imidazole is deprotonated.[11–18] However, when 2-methylimidazole retains its NH group to act as a hydrogen bond donor, significant differences may result. In complex $\mathbf{1}\cdot H_2O$ linear $[Ag(MeIm)_2]^+$ coordination motifs are joined with 3,5-dinitrobenzoate anions by N–H···O hydrogen bonds, while in **2** a one-dimensional coordination polymer is formed *via* aminopyrimidine bridging. The 3,5-dinitrobenzoate anion behaves as a versatile connector: in $\mathbf{1}\cdot H_2O$ only the CO_2 groups are involved in intermolecular interactions, while in **2** one of the NO_2 groups is engaged in C–H···O hydrogen bonding and the CO_2 group is weakly bonded to the silver(I) ion. This difference is obviously related to the different donating behaviors of methylimidazole and aminopyrimidine mentioned above: in **1** the uncoordinated NH groups of the $[Ag(MeIm)_2]^+$ cation make it possible to form N–H···O hydrogen bonds with the acetate group of dinitrobenzoate anions, therefore generating a ring structure. But in **2** aminopyrimidine acts as a bridging ligand to connect two Ag(I) ions, so the dinitobenzoate anion prefers to interact with the Ag(I) ion *via* its acetate group and to form intramolecular N–H···O hydrogen bonds with the NH_2 group [N5···O1a 2.913(4), N5···O2 2.903(4) Å].

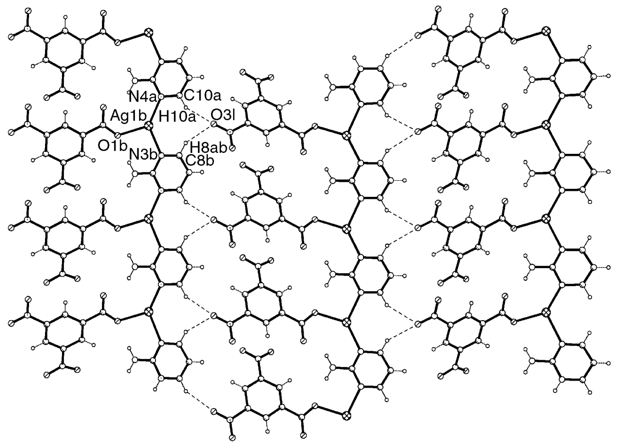

Fig. 3 Top view of the 2D network consisting of 1D chains consolidated by C–H···O hydrogen bonds in **2**.

In summary, assembly of an organic–inorganic hybrid cyclic aggregate and a two-dimensional network have been investigated by selecting the same silver(I) 3,5-dinitrobenzoate moiety and comparable 2-methylimdazole and 2-aminopyrimidine ligands. The different intermolecular interactions play an important role in the assembly process and the final structures are controlled by the donating behaviors of the ligands. This may be an example for the creation of ordered solid materials by utilizing coordination bonds as well as various intermolecular interactions, based on the strategy incorporating both techniques used in organic and inorganic systems.

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