Metal–Metal Interactions

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A Stair-Shaped Molecular Silver(0) Chain**

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Compounds formed by metal–metal interactions, such as metal clusters[1,2] and extended metal–atom chains,[3,4] are important for the development of new electrical and electronic devices. In particular, silver-containing compounds are interesting because silver has one of the highest electric conductivities of all metals. However, no extended chains of Ag^0 or Ag^I centers formed purely by Ag–Ag interactions without any bridging ligands have been reported to date. Silver clusters of several (2–23) Ag^0 atoms have been reported, but their structures were derived only from theoretical calculations.[5,6] Surprisingly, there has been no report of the isolation of an Ag^0 coordination compound, although the Ag^0 species $[Ag_2(\mu\text{-}(Bzim)Ph_2P)_3]$ ((Bzim)Ph_2P = 1-benzyl-2-imidazolyldiphenylphosphine) was observed as a transient species during the electrochemical reduction of Ag^I compounds,[7] and some Ag^0 complexes of π-donor ligands were trapped in various matrices and characterized by EPR spectroscopy.[8]

Herein we report the X-ray single crystal structure of a stair-shaped infinite silver atom chain, $[Ag_4py_2]_n$ (**1**; py = C_5H_5N), as the first Ag^0 coordination compound without bridging ligands. It is formed from two covalently linked 1D zigzag Ag chains, with alternating long and short Ag–Ag bonds. Theoretical calculations indicate that partially positively (+0.35) and negatively (−0.30) charged Ag atoms are also alternately located and that **1** has a HOMO–LUMO gap of 4.1 eV (HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital).

We have been interested in coordination polymers and their inclusion of metal nanoparticles.[9,10] During the synthesis of silver carboxylate frameworks, we unexpectedly obtained crystals that were found to be **1**. This compound was originally prepared by the addition of an aqueous solution of Na_2C_6DC (C_6DC = 1,6-hexanedicarboxylate) or Na_2BPDC (BPDC = 4,4′- biphenyldicarboxylate) to AgX (X = NO_3 or CF_3SO_3) in a water/pyridine solution. However, this method gave an extremely poor yield and it took several months to obtain crystals. Therefore, we have modified the synthetic procedure to obtain the crystals in a shorter period of time with higher yields.

Colorless flat parallelepiped crystals of $[Ag_4py_2]_n$ (**1**) were prepared by slow diffusion of NaOH solution into the water/pyridine solution of $AgNO_3$ in a refrigerator for three weeks. In this context, NaOH appears to reduce Ag^I to Ag^0. NaOH is known to reduce, or promote reduction of, Ag, Pd, and Pt ions to result in metallic clusters; stabilizers or alcoholic solvents should be additionally used to obtain monodispersed nanoparticles.[11] To obtain crystals of **1**, a small reaction scale, the correct amount of NaOH, and a slow diffusion rate are very important, otherwise significant amounts of a brown precipitate of Ag nanoparticles form, as confirmed by high-resolution transmission electron microscopy (HRTEM).

The crystals of **1** are stable only in their mother liquor, and they instantly lose pyridine molecules upon exposure to air, which results in the formation of yellowish $[Ag_4]_n$, as shown by elemental analysis data. Therefore, except the X-ray structure, no characterization data was obtained for **1**. The X-ray structure of $[Ag_4]_n$ could not be determined because it does not form single crystals, even though the crystal morphology was retained. The EPR spectrum of **1**, which is likely to be that of $[Ag_4]_n$ because **1** loses pyridine molecules as soon as it is removed from the mother liquor, was silent (see the Supporting Information). This indicates that an unpaired electron of each Ag^0 atom is coupled with an electron from an adjacent Ag^0 atom.

The X-ray single crystal structure of **1** is shown in Figure 1. The diffraction data were collected in the presence of the mother liquor in a glass capillary. The asymmetric unit of **1** consists of four crystallographically independent silver atoms (Ag1–Ag4). These are linked by covalent bonds to form a rhombic tetranuclear Ag_4 cluster unit, as well as two pyridine molecules coordinating to the Ag3 and Ag4 atoms (see the Supporting Information). The observed structure of the tetranuclear Ag_4 cluster unit is similar to that derived from theoretical calculations,[6] although the bond distances and angles of the observed cluster unit are much larger. The Ag_4 units are further linked with those of the adjacent Ag_4 cluster units by Ag–Ag bonds, with the inversion center in the middle of two units. This gives rise to a stair-shaped molecular silver chain formed from two infinite 1D zigzag Ag chains. The angles between the adjacent Ag_4 planes are in the range of 126–127°. The Ag–Ag bond lengths along the infinite 1D chain alternate between long (2.876–2.897 Å) and short (2.827–2.830 Å), with an average Ag–Ag distance of 2.858(1) Å. The average Ag–Ag separation between the two Ag chains is 2.890(1) Å. These Ag–Ag distances are well below the sum of the van der Waals radii of silver atoms (3.44 Å), and are close to the Ag–Ag separation in bulk metallic silver (2.89 Å). Ag–Ag bonds are also formed

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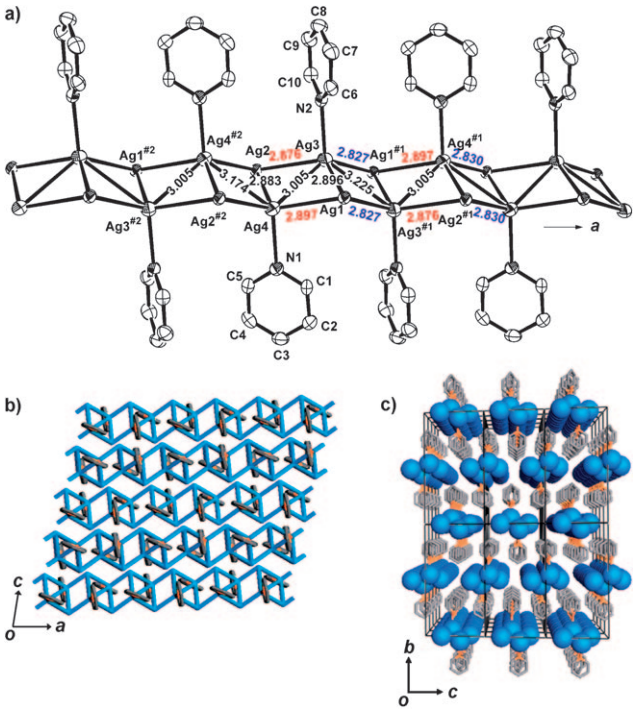

Figure 1. The X-ray structure of $[Ag_4py_2]_n$ (**1**). a) ORTEP drawing of **1** with atomic numbering scheme (thermal ellipsoids at 30% probability). Symmetry operations: #1, $-x+2$, $-y$, $-z+1$; #2, $-x+1$, $-y$, $-z+1$. b) View seen along the *bc* plane. c) View seen along the *ab* plane, showing the stair-shaped molecular silver chain running along the *a* direction. Blue Ag, gray C, orange N.

between the pyridine-coordinated Ag atoms (Ag3 and Ag4), with an average bond length of 3.135(1) Å. Therefore, Ag1 and Ag2 are bound to three Ag atoms, and Ag3 and Ag4 are bound to five Ag atoms and a pyridine molecule. The average Ag–N(py) distances are 2.349(6) Å and the dihedral angle between the two pyridine rings coordinated to Ag3 and Ag4 is 57.4(3)°, whilst the dihedral angles between the Ag_4 plane and the pyridine molecules coordinated to Ag3 and Ag4 are 66.2(2)° and 66.7(3)°, respectively. Each pyridine molecule interacts with six adjacent pyridine molecules, two from its own chain and four from two neighboring chains, by edge-to-face π–π interactions (see the Supporting Information). The thickness of the stair-shaped silver chain is 0.46 nm × 0.58 nm and each chain extends along the [100] direction. The axis-to-axis distances between the neighboring molecular chains are 17.0 Å along the [010] direction, and 9.50 Å along the [001] direction (Figure 1 b and c). The shortest molecular chain-to-chain distance is 9.74 Å along the [011] direction.

The X-ray structure of $[Ag_2I_2py_2]_n$, which was obtained from recrystallization of AgI in pyridine, has been reported previously. Surprisingly, the structure of $[Ag_2I_2py_2]_n$ was very similar to that of **1**.[12] To check if $[Ag_2I_2py_2]_n$ was the same as **1**, we independently prepared colorless rectangular prismatic crystals of $[Ag_2I_2py_2]_n$ and determined its X-ray crystal structure (see the Supporting Information).[13] Although the X-ray crystal structure is identical to that of **1**, $[Ag_2I_2py_2]_n$ is different from **1** in terms of energy dispersive X-ray spectroscopy (EDS) data and crystal properties. The EDS data (Figure 2) indicate that **1**, after the release of pyridine molecules in a vacuum chamber, contains only silver; in contrast, $[Ag_2I_2py_2]_n$ on release of pyridine molecules contains a 1:1 ratio of silver and iodine atoms. The Ag L_α and Ag L_β

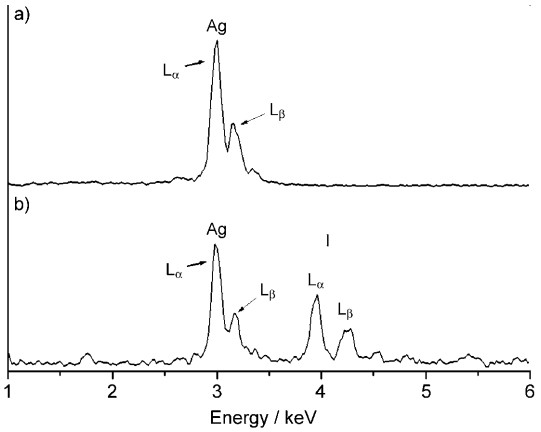

Figure 2. Energy dispersive X-ray spectroscopy (EDS) data for a) $[Ag_4]_n$ (**1**) showing that silver is the only chemical element present and b) $[Ag_2I_2]_n$ showing that silver and iodine elements coexist. During the measurement in the vacuum chamber, pyridine molecules are released from **1** and $[Ag_2I_2py_2]_n$.

peaks for **1** are found at 2.98 keV and 3.15 keV, respectively, but those for $[Ag_2I_2py_2]_n$ appear at 3.00 keV and 3.16 keV, respectively. The EDS data for $[Ag_2I_2py_2]_n$ show additional L_α and L_β peaks for iodine at 3.94 keV and 4.24 keV, respectively. On heating at 500 °C, **1** has a metallic silver luster while $[Ag_2I_2py_2]_n$ becomes a yellowish powder (see the Supporting Information). Although mass spectrometry would show any differences between the two compounds, mass spectra could not be recorded because of the nonvolatile nature of the samples. It seems that **1** and $[Ag_2I_2py_2]_n$ have very similar structures because silver and iodine atoms have similar covalent radii, 1.34 Å and 1.33 Å, respectively.

We have performed ab initio energy calculations on $[Ag_4py_2]_n$ (**1**) ($n=2$–5) by the HF/SBKJC(d) method,[14] employing the general atomic and molecular electronic structure system (GAMESS).[15] The geometries of **1** were taken from the X-ray crystal data. Mulliken population analysis of **1** (Figure 3 a) clearly indicates that the pyridine-coordinated Ag atoms (Ag3 and Ag4) have partial positive charges and the uncoordinated Ag atoms (Ag1 and Ag2) have partial negative charges. The calculated atomic charges for the Ag atoms are a function of model cluster size ($n=2$–5), and the limiting values are obtained by extrapolating to a system where $n=$ infinity ($1/n=0$), which gives charges of $+0.35$ and -0.30. Such alternating charge pattern, together with the alternating long and short Ag–Ag distances, can be attributed to structural dimerizations along the chain, which could arise from Peierls instability of one-dimensional chains.[16] The limiting value of the HOMO–LUMO gap in the $[Ag_4py_2]_n$ model cluster is 4.1 eV (Figure 3 b). It is noted, however, that the estimated gap value should be considered qualitatively because the theoretical methods adopted here tend to overestimate the HOMO–LUMO gap. In any case, it

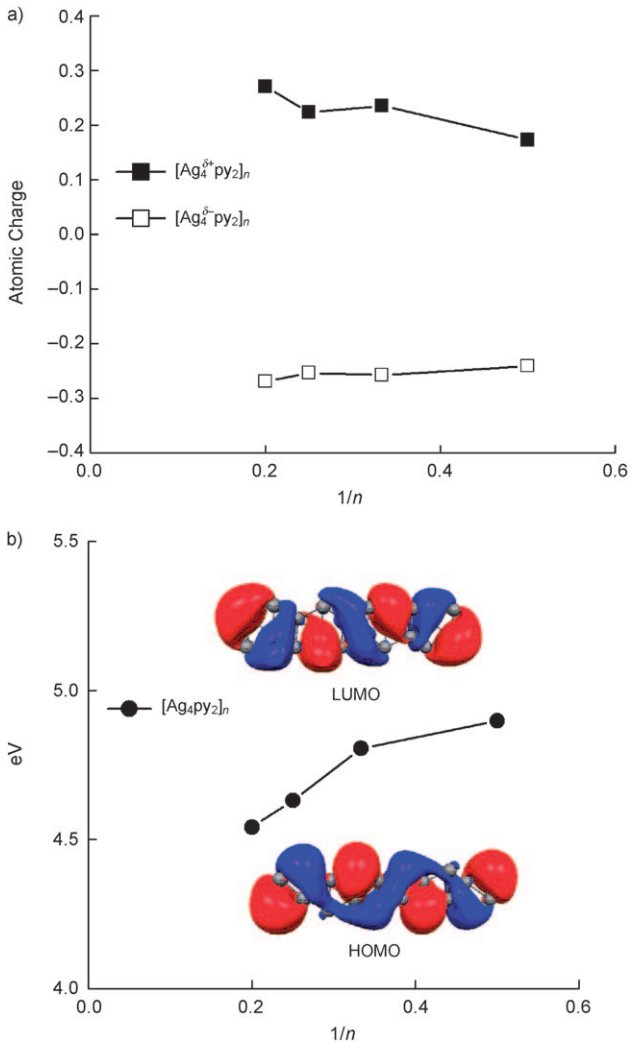

Figure 3. Theoretical calculations on $[Ag_4py_2]_n$ (**1**). a) The calculated atomic charges for the Ag atoms as a function of model cluster size (n = 2–5). The limiting values are obtained by extrapolation to $1/n$ = zero. b) The calculated HOMO–LUMO gaps as a function of model cluster size (n = 2–5). The limiting values are obtained by extrapolation to $1/n$ = zero.

is clear that the limiting values for **1** deviate from a bandgap value of zero, which suggests that the silver chain has a semiconducting character.

In conclusion, we have reported the X-ray single crystal structure of a molecular silver chain as the first Ag^0 coordination compound. The chain is formed from rhombic tetranuclear Ag_4 cluster units that are linked linearly by Ag–Ag bonds to give a stair-shaped infinite chain of Ag atoms comprising two 1D zigzag chains. The Ag–Ag covalent bonds have partially ionic character with charges of +0.35 and −0.30, and the chain has a HOMO–LUMO gap of 4.1 eV, according to theoretical calculations. Since the compound releases pyridine molecules easily and loses its single-crystal nature on exposure to air, the X-ray structure of $[Ag_4]_n$ could not be determined. Further studies will focus on the investigation of the electronic properties and structure of $[Ag_4]_n$ as well as the synthesis of molecular chains formed from other metallic elements.

Experimental Section

1: An aqueous solution (3 mL) of NaOH (0.004 g, 0.057 mmol) was added dropwise to a solution of $AgNO_3$ (0.021 g, 0.059 mmol) in H_2O/pyridine (1:3 v/v, 4 mL). The solution was allowed to stand in a refrigerator for approximately three weeks until colorless flat parallelepiped crystals formed. The crystals were filtered and briefly washed with the mother liquor. On exposure to air the crystal lost single crystallinity and became a yellowish solid. FTIR (KBr pellet): $\tilde{\nu}$ = 1591(s), 1482(s), 1441(s), 1213(s) cm^{-1}. Yield: 1.98 mg (27%). Elemental anal. calcd for $Ag_4C_{10}H_{10}N_2$: C, 20.37; H, 1.71; N, 4.75. Found: C, 0.1159; H, 0.0; N, 0.0. The elemental analysis data indicates that **1** lost pyridine molecules as soon as it was exposed to air.

Crystal data for **1**: $Ag_4C_{10}H_{10}N_2$, M_r = 589.50, crystal size 0.3 × 0.1 × 0.1 mm^3, monoclinic, space group $P2_1/n$, a = 9.2810(3), b = 17.0351(10), c = 9.5013(5) Å, β = 106.346(3)°, V = 1441.46(12) $Å^3$, Z = 4, ρ_{calcd} = 2.717 $g\,cm^{-3}$, λ = 0.71073 Å, T = 293(2) K, $2\theta_{max}$ = 27.46°, R_1 = 0.0597 ($I > 2\sigma(I)$, 3271 reflections), wR_2 = 0.2396 [all data, 5655 reflections], GOF = 1.083. CCDC 633448 (**1**) 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

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[13] We prepared $[Ag_2I_2py_2]_n$ according to the method described in Ref. [12] and obtained an X-ray single crystal structure and EDS data. The X-ray crystallographic data are provided in the Supporting Information.

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