

**catena-Poly[[disilver(I)(Ag—Ag)-bis-  
 $\mu$ -1,1'-(butane-1,4-diyl)diimidazole-  
 $\kappa^2N^3:N^{3'}$ ]] bis(perchlorate)]: a double  
 helix stabilized by ligand-unsupported  
 argentophilic interactions**

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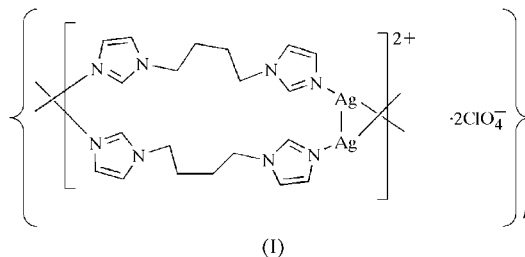
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The title compound,  $\{[Ag_2(C_{10}H_{14}N_4)_2](ClO_4)_2\}_n$ , is a one-dimensional coordination polymer formed by  $Ag^I$  atoms linearly bridged by 1,1'-(butane-1,4-diyl)diimidazole molecules. The chains have a helical arrangement and pairs of chains are held together by the rarely reported ligand-unsupported  $Ag—Ag$  interaction [2.966 (1) Å], which results in a double-helix structure. The double helix contains twisted 24-membered metallomacrocycles, which are composed of four  $Ag$  atoms and two ligands. The  $Ag$  atoms lie on twofold axes.

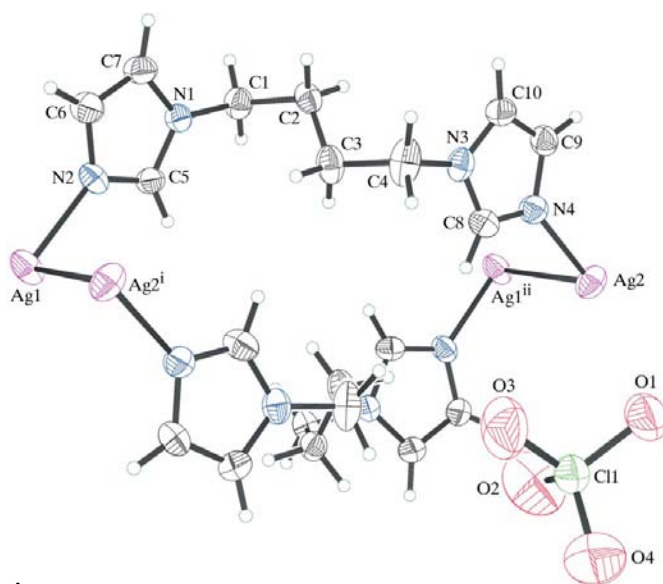
**Comment**

It is well known that weak interatomic interactions, such as hydrogen bonding and  $\pi-\pi$  stacking, have presented a synthetic paradigm for the rational design and synthesis of functional materials in supramolecular chemistry. The metallophilic attractions between the closed-shell  $d^{10}$  coinage metals also promote aggregation, as supported by spectroscopic and structural evidence (Codina *et al.*, 2002). Such compounds are often associated with many potentially useful chemical and physical properties of materials, such as optical or electronic properties or catalytic behaviour, so the synthesis and properties of these metallophilic aggregates have attracted an ever-increasing level of attention. Compared with  $Au—Au$  interactions,  $Ag—Ag$  interactions have been reported as argentophilicity and are calculated to be relatively weak. They can also be used to control the conformation and topology of metallic aggregates. There are many examples of argentophilic interactions; most are ligand supported (Wang & Mak, 2001; Huang *et al.*, 2006), while a few are reported to be ligand unsupported (Liu *et al.*, 2006; Singh *et al.*, 1997). We are interested in the synthesis of coordination polymers organized

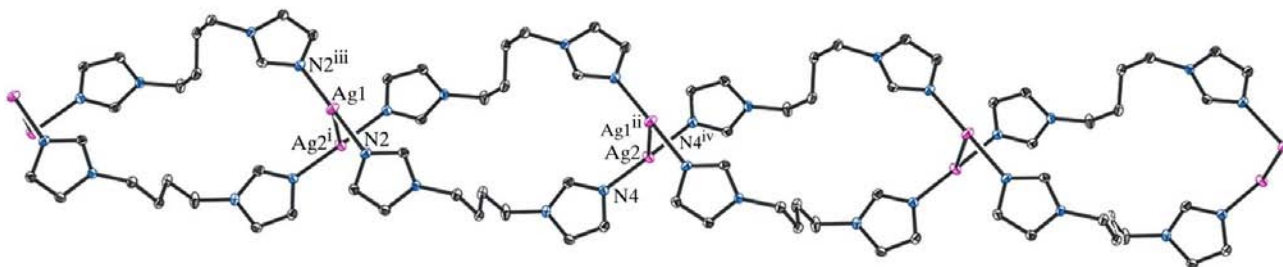
by means of  $N$ -donor ligands (Lou *et al.*, 2006; Li & Lou, 2007). In this paper, we report the synthesis and characterization of the title compound, (I), an interesting silver complex of double-helix chains stabilized by ligand-unsupported argentophilic interactions based on 1,1'-(butane-1,4-diyl)diimidazole (hereinafter abbreviated to bdim).



Compound (I) is a one-dimensional coordination polymer. As shown in Fig. 1, the asymmetric unit consists of two symmetry-independent  $Ag^I$  ions, which lie on twofold axes, one bdim ligand and one perchlorate anion. As shown in Fig. 2, the two crystallographically unique  $Ag^I$  ions are bridged by the bdim ligands to form a one-dimensional infinite polymeric chain structure. Within a single strand of the chain, the coordination around each  $Ag^I$  ion is made up of two symmetry-related  $N$  atoms from different bdim ligands in a linear geometry, and the  $Ag—N$  distances are consistent with other reported  $Ag^I$  complexes of  $N$ -donor ligands (Singh *et al.*, 1997; Carlucci *et al.*, 1998). Interestingly, pairs of chains are held together by ligand-unsupported argentophilic interactions between symmetry-independent  $Ag$  atoms on the same twofold axis. The individual strands of the paired chains intertwine in a helical fashion to give a double-helix motif (Fig. 2). The  $Ag—Ag$  distance is 2.966 (1) Å, which is slightly longer than the  $Ag—Ag$  separation in metallic silver (2.889 Å;



**Figure 1**  
 One metallomacrocycle in the double-helix chain of (I), showing the atom-numbering scheme of the asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $x + 1, y, z$ .]



**Figure 2**

The double-helix structure in (I). H atoms and perchlorate anions have been omitted. [Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $x + 1, y, z$ ; (iii)  $-x, y, -z + \frac{3}{2}$ ; (iv)  $-x + 2, y, -z + \frac{3}{2}$ .]

Bondi, 1964), but much shorter than the sum of the van der Waals radii (3.44 Å; Bondi, 1964). As a result of the Ag—Ag interactions, the total coordination geometry at each Ag<sup>I</sup> atom is T-shaped.

Although Ag—Ag interactions are widely reported in silver coordination compounds, only a few examples of ligand-unsupported Ag<sup>I</sup> aggregates are known and ligand-unsupported Ag<sup>I</sup> coordination polymers are rare (Ming & Mak, 1991; Omary *et al.*, 1998; Liu *et al.*, 2006, 2005). The structural characterization of silver complexes having ligand-unsupported Ag—Ag interactions is of importance, because this has been a matter of some debate due to the scarcity of unambiguous experimental evidence of argentophilicity being stable in the absence of stabilizing ligands. The Ag—Ag contact in compound (I) is consistent with those of the known silver complexes having ligand-unsupported Ag—Ag bonds.

The development of the double-helical strands containing the Ag—Ag interactions results in the formation of 24-membered metallacycles containing four Ag atoms and two bdim ligands (Fig. 1). Each of these metallacycles occupies one half of a turn of the helix. Helicity is a fundamental structural feature of great current interest in inorganic and coordination chemistry (Shang *et al.*, 2007; Berti *et al.*, 2005; Erxleben, 2001; Carlucci *et al.*, 1998). It has a fundamental role in biology, and potential applications in the fields of supramolecular chemistry, asymmetric catalysis and nonlinear optical materials. Ag<sup>I</sup> complexes containing infinite double helices are interesting but have been investigated only rarely (Lee *et al.*, 2005; Erxleben, 2001). The twisted 24-membered metallomacrocyclic ring and the T-shaped Ag coordination environment in (I) lead to chains with an almost rectangular cross-section. Coordination compounds having specially shaped metallomacrocyclic rings show promise in various applications, such as selective sensors, gas storage, sorters, catalysis and luminescent materials.

## Experimental

All reagents were of analytical grade and used without further purification. Bdim was prepared by the general procedure of Ma *et al.* (2003). A solution of pymim (0.4 mmol, 76 mg) in MeOH (4 ml) was added dropwise to a stirred solution of AgClO<sub>4</sub> (0.8 mmol, 167 mg) in MeOH (8 ml). The white precipitate that formed immediately was collected, washed with MeOH and dried. Colourless single crystals of (I) were grown by vapour diffusion of diethyl ether into a

dimethylformamide solution containing the silver complex [yield 38%; m.p. 540–543 K (decomposition)]. Analysis found: C 30.11, H 3.69, N 14.23%; calculated for C<sub>10</sub>H<sub>14</sub>AgClN<sub>4</sub>O<sub>4</sub>: C 30.21, H 3.55, N 14.09%.

### Crystal data

[Ag <sub>2</sub> (C <sub>10</sub> H <sub>14</sub> N <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	$V = 2799.3 (8) \text{ \AA}^3$
$M_r = 397.57$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 11.090 (2) \text{ \AA}$	$\mu = 1.65 \text{ mm}^{-1}$
$b = 13.293 (2) \text{ \AA}$	$T = 298 (2) \text{ K}$
$c = 18.989 (3) \text{ \AA}$	$0.40 \times 0.22 \times 0.11 \text{ mm}$
$\beta = 90.488 (3)^\circ$	

### Data collection

Bruker SMART 1K CCD area-detector diffractometer	7211 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	2520 independent reflections
$T_{\min} = 0.558, T_{\max} = 0.839$	1733 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.037$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	100 restraints
$wR(F^2) = 0.141$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.78 \text{ e \AA}^{-3}$
2520 reflections	$\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$
183 parameters	

**Table 1**

Selected geometric parameters (Å, °).

Ag1—N2	2.110 (5)	Ag2—N4	2.115 (5)
Ag1—Ag2 <sup>i</sup>	2.966 (1)		
N2 <sup>ii</sup> —Ag1—N2	179.2 (3)	N4 <sup>iii</sup> —Ag2—N4	177.2 (3)
N2—Ag1—Ag2 <sup>i</sup>	89.62 (15)	N4—Ag2—Ag1 <sup>iv</sup>	88.62 (16)

Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $-x, y, -z + \frac{3}{2}$ ; (iii)  $-x + 2, y, -z + \frac{3}{2}$ ; (iv)  $x + 1, y, z$ .

The Cl—O bond lengths and O···O separations in the perchlorate anion were restrained to 1.44 (1) and 2.35 (2) Å, respectively. The  $U^{ij}$  components for these atoms were also restrained using similarity and approximate isotropic restraints. The H atoms were positioned geometrically and treated as riding, with C—H bond lengths constrained to 0.93 (aromatic CH) or 0.97 Å (methylene CH<sub>2</sub>), and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and publCIF (Westrip, 2007).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3066). Services for accessing these data are described at the back of the journal.

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