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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
R factor = 0.037
wR factor = 0.093
Data-to-parameter ratio = 15.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

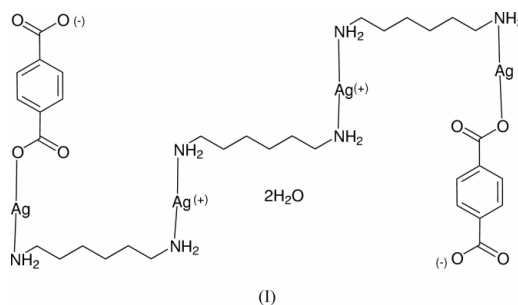
Tris(μ -1,6-diaminohexane)diterephthalato-tetrasilver(I) dihydrate

The title compound, $[\text{Ag}_4(\text{C}_8\text{H}_4\text{O}_4)_2[\text{H}_2\text{N}(\text{CH}_2)_6]_3] \cdot 2\text{H}_2\text{O}$, is an Ag^{I} tetranuclear complex. Four Ag^{I} atoms, three hexamethylenediamine molecules, and two terephthalate dianions constitute a chain-like tetranuclear silver(I) complex. The complex lies on a center of symmetry, located at the mid-point of the central C—C bond. The two different kinds of Ag^{I} atoms are both in a linear environment. One kind of Ag atom is coordinated by two N atoms from different amine ligands, and the other is coordinated by an O atom from a carboxylate group and by a N atom from an amine ligand. Adjacent complexes are joined together by weak $\text{Ag} \cdots \text{Ag}$ interactions to form ladder-like ribbons, which are further linked by hydrogen bonds to form a three-dimensional structure.

Received 3 September 2003
Accepted 15 September 2003
Online 24 September 2003

Comment

The title complex, (I), is a silver(I) tetranuclear complex with two uncoordinated molecules of water of crystallization. Four Ag^{I} atoms, three hexamethylenediamine molecules, and two terephthalate dianions constitute a chain-like tetranuclear silver(I) complex extended along the *b* axis, as shown in Fig. 1. The complex lies on a center of symmetry, located at the mid-point of the central C—C bond.



There are two different kinds of Ag^{I} atoms in the complex, both of which have approximately linear coordination. Atom Ag1 is coordinated by two N atoms from different amine ligands, with average Ag—N distances of 2.129 (4) Å. Atom Ag2 is coordinated by an O atom from a carboxylate group and by an N atom from an amine ligand. The Ag2—O and Ag2—N bond lengths are 2.090 (3) and 2.157 (5) Å, respectively. The angles around the metal atoms are 177.74 (14)° for atom Ag1 and 157.5 (2)° for atom Ag2, indicating that the coordination environment around Ag1 is much closer to linear than that around Ag2. All the amines adopt a 1,6-bridging mode and are fully extended. The terephthalate ligands act as monodentate ligands and are located at the ends of the tetranuclear chains. The length of a chain is about 50 Å. Weak

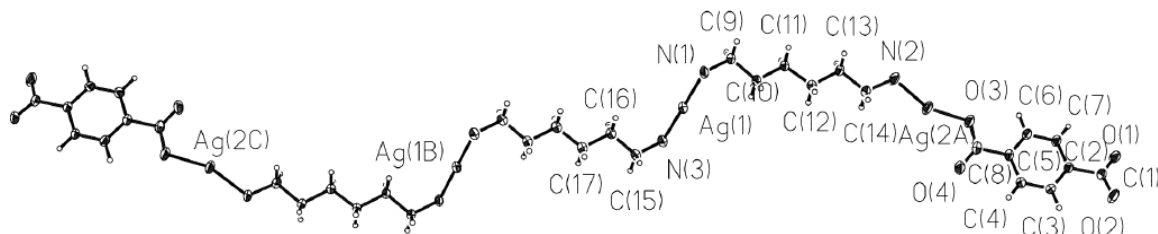


Figure 1

The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. Atom Ag(2A) is related by symmetry to atom Ag(2), which is in the adjacent molecule, weakly linked to atom Ag(1). Atoms Ag(1B) and Ag(2C) are related to atoms Ag(1) and Ag(2A) by inversion symmetry.

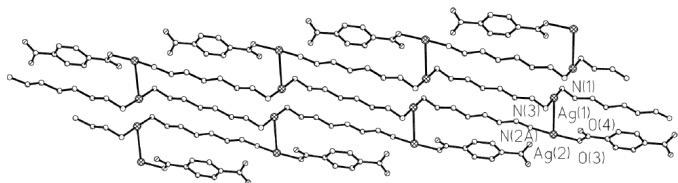


Figure 2

The ribbon structure of (I). H atoms have been omitted for clarity.

Ag \cdots Ag interactions [3.0646 (14) Å] link adjacent chains to give 38-membered macrocycles that share edges in a ladder-like ribbon with a width of *ca* 10 Å. All the N and O atoms, except atom O3, which is bonded to the metal, contribute to the formation of hydrogen bonds, *viz.* N1—H1A \cdots O4ⁱ, N1—H1B \cdots O1ⁱ, N1—H1B \cdots O2ⁱ, N3—H3B \cdots O1Wⁱⁱ, N3—H3C \cdots O2ⁱⁱⁱ, N2—H2B \cdots O1^{iv}, O1W—H1WA \cdots O2 and O1W—H1WB \cdots O4ⁱⁱ (see Table 1 for symmetry codes).

Experimental

All reagents and solvents were used as obtained without further purification. Ag₂O (0.5 mmol, 116 mg), terephthalic acid (0.5 mmol, 83 mg) and 1,6-diaminohexane (1 mmol, 116 mg) were dissolved in ammonia (10 ml). The mixture was stirred for *ca* 10 min to obtain a clear solution. On keeping the solution in air overnight, with release of ammonium gas, large colorless crystals were formed. These were isolated, washed three times with water, and dried in a vacuum desiccator using CaCl₂ (yield 85%).

Crystal data

[Ag₄(C₈H₄O₄)₂(C₆H₁₄N₂)₃] \cdot 2H₂O
M_r = 572.18
 Triclinic, P $\bar{1}$
a = 7.220 (1) Å
b = 10.928 (2) Å
c = 13.919 (3) Å
 α = 110.08 (3) $^\circ$
 β = 98.73 (3) $^\circ$
 γ = 96.31 (3) $^\circ$
V = 1003.9 (3) Å³

Z = 2
D_x = 1.893 Mg m⁻³
 Mo K α radiation
 Cell parameters from 4208 reflections
 θ = 2.8–25.9 $^\circ$
 μ = 1.98 mm⁻¹
T = 293 (2) K
 Rod, colorless
 0.38 \times 0.38 \times 0.30 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.490, *T_{max}* = 0.552
 4537 measured reflections

3814 independent reflections
 3353 reflections with *I* > 2 σ (*I*)
R_{int} = 0.015
 θ_{max} = 26.0 $^\circ$
h = -8 \rightarrow 6
k = -12 \rightarrow 13
l = -17 \rightarrow 17

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.037
wR(*F*²) = 0.093
S = 1.07
 3814 reflections
 245 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 1.1362P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.93 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.95 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0038 (6)

Table 1

Hydrogen-bonding geometry (Å, $^\circ$).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1A \cdots O4 ⁱ	0.90	2.47	3.283 (5)	151
N1—H1B \cdots O1 ⁱⁱ	0.90	2.13	3.023 (5)	172
N1—H1B \cdots O2 ⁱⁱ	0.90	2.55	3.090 (5)	119
N3—H3B \cdots O1W ⁱⁱⁱ	0.90	2.15	2.998 (5)	157
N3—H3C \cdots O2 ^{iv}	0.90	2.13	2.997 (5)	163
N2—H2B \cdots O1 ^v	0.90	2.18	2.924 (6)	140
O1W—H1WA \cdots O2	0.99	1.76	2.749 (5)	177
O1W—H1WB \cdots O4 ⁱⁱⁱ	0.89	1.92	2.751 (5)	155

Symmetry codes: (i) 1 + *x*, *y*, *z*; (ii) 1 + *x*, 1 + *y*, *z*; (iii) -*x*, -*y*, 1 - *z*; (iv) *x*, 1 + *y*, *z*; (v) -*x*, -1 - *y*, -*z*.

All H atoms were placed in idealized positions and constrained to ride on their parent atoms, with N—H and C—H distances of 0.90 and 0.96 Å, respectively. The *U_{eq}* values for H atoms were fixed at 0.08 Å².

Data collection: SMART (Siemens, 1996); cell refinement: SMART; data reduction: SAINT (Siemens, 1996); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXTL.

The authors thank the Education Office of Hubei Province, People's Republic of China, for the research grant No. 2002B29002 and the Natural Science Foundation of Hubei Province, People's Republic of China, for research grant No. 2003ABB010.

References

- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
 Sheldrick, G. M. (1997a). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
 Sheldrick, G. M. (1997b). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
 Siemens (1996). *SMART* and *SAINTE*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.