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**Crystal Structure
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Tetrakis(μ_2-1,8-naphthyridine)-1:2κ^4*N*:*N*′;3:4κ^4*N*:*N*′-bis(μ_2-salicylato)-1:4κ^2*O*:*O*′;2:3κ^2*O*:*O*′-tetrakis(salicylic acid)-1κ*O*,2κ*O*,3κ*O*,4κ*O*-tetrasilver(**I**)(4 *Ag—Ag*)

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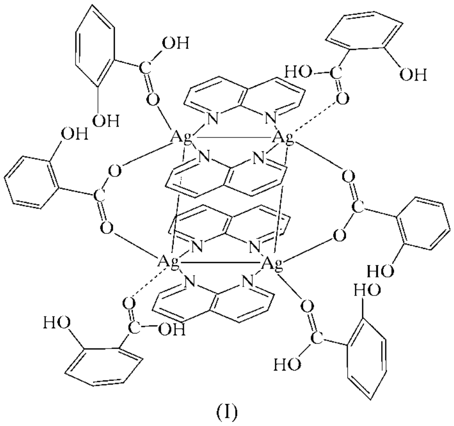
The title complex, $[Ag_4(C_7H_5O_3)_2(C_8H_6N_2)_4(C_7H_6O_3)_4]$, lies about an inversion centre and has a unique tetranuclear structure consisting of four Ag^I atoms bridged by four N atoms from two 1,8-naphthyridine (napy) ligands to form an *N*:*N*′-bridge and four O atoms from two salicylate (SA) ligands to form an *O*:*O*′-bridge. The Ag atoms have distorted octahedral coordination geometry. The centrosymmetric Ag_4 ring has Ag—Ag separations of 2.772 (2) and 3.127 (2) Å, and Ag—Ag—Ag angles of 107.70 (4) and 72.30 (4)°. All SA hydroxy groups take part in intramolecular O—H···O hydrogen bonding. In the crystal packing, the napy rings are oriented parallel and overlap one another. These π–π interactions, together with weak intermolecular C—H···O contacts, stabilize the crystal structure.

Comment

The two active N-donor atoms in 1,8-naphthyridine (napy) can act in different coordination modes, such as monodentate (Dewer *et al.*, 1975; Enwall & Emerson, 1979) and bidentate (Bodner & Hendricker, 1973; Epstein *et al.*, 1974; Munakata *et al.*, 1990). In the case of Ag(napy-*N*) type complexes, napy always acts as a bridging ligand to form planar binuclear complexes (Tsuda *et al.*, 1989; Griffith *et al.*, 1995; Koizumi & Tanaka, 2004). It is also known that silver complexes with salicylic acid (SA) are also based on a bis(carboxylato-κ^2*O*:*O*′)-bridged disilver nucleus (Movsumov *et al.*, 1990).

In the present study, we designed a mixed-ligand silver complex using napy and SA ligands, and synthesized the unique title tetrasilver complex, (I). Complex (I) is the first example in which there are two kinds of Ag—Ag bridges, *i.e.* *O*:*O*′- and *N*:*N*′-bridges, co-existing in one complex molecule.

The structure of (I) is shown in Fig. 1, with principal dimensions given in Table 1. Four Ag^I atoms lie about an inversion centre and, as a consequence, are perfectly planar. Atom Ag1 has a distorted octahedral coordination, being bonded to two N atoms [N3 and N2^i; symmetry code: (i) $1 - x$, $1 - y$, $-z$] from two napy ligands, to one carboxylate O atom (O1) from a bidentate salicylate ligand, to two adjacent Ag2 atoms, and (weakly) to a carboxyl atom (O7) of a salicylic acid molecule. Atom Ag2 also has a distorted octahedral coordination geometry, in which Ag1^i, N1, N4^i and the salicylate O2 atoms form the equatorial plane, and Ag1 and salicylate O4 atoms complete the octahedron. As can be seen in Fig. 1, all salicylic acid hydroxy groups participate in intramolecular O—H···O hydrogen bonds (Table 2).



(I)

Each napy molecule acts as a bidentate ligand and pairs form a rigid bis(napy-*N*:*N*′)-bridged disilver unit. In this unit, the eight-membered bis-chelate ring (–Ag—N—C—N—Ag—N—C—N–) is almost planar but is slightly folded [6.97 (10)°] about the Ag—Ag axis. Two inversion-related salicylate

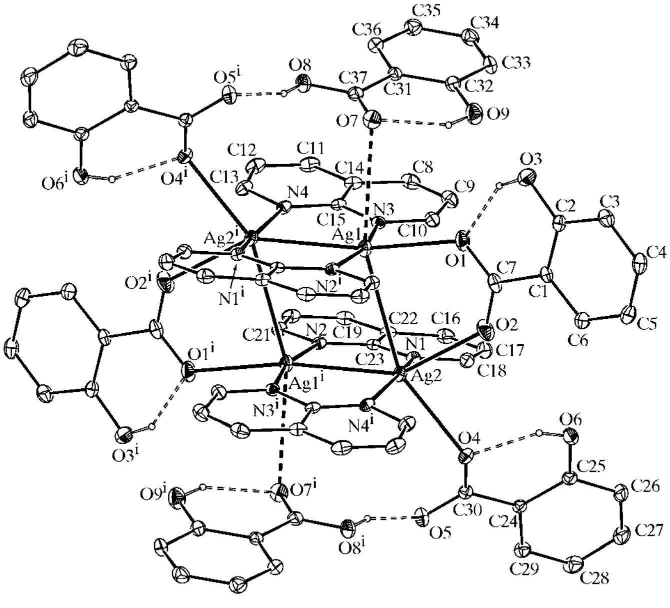


Figure 1
A view of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 10% probability level. All H atoms except those involved in O—H···O hydrogen bonds have been omitted. [Symmetry code: (i) $1 - x$, $1 - y$, $-z$.]

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moieties act as bidentate bridging ligands to form a ten-membered chelate ring (–Ag—Ag—O—C—O—Ag—Ag—O—C—O–). As shown in Fig. 2, the two bridging salicylate aromatic rings are tilted away from the ten-membered chelate ring plane by 18.86 (10)°. The eight-membered chelate rings and the ten-membered chelate rings are essentially orthogonal.

In (I), the average Ag—O [bridged O; 2.413 (2) Å] and Ag—N [2.228 (6) Å] distances are both longer than the corresponding values in complexes with only one kind of bridge unit within an *O*:*O*′- or *N*:*N*′-bridge, *e.g.* 2.180 (4) and 2.196 (5) Å for the Ag—O distance in an *O*:*O*′-bridged silver–salicylate complex (Movsumov *et al.*, 1990) and 2.187 (3)–2.213 (4) Å for the Ag—N distances in *N*:*N*′-bridged napy complexes (Tsuda *et al.*, 1989; Munakata *et al.*, 1990; Griffith *et al.*, 1995; Koizumi & Tanaka, 2004). This suggests that the coordination interaction of Ag with the ligand atoms (O and N) in the mixed-bridged complex, (I), may be weakened.

There are two types of Ag—Ag interaction in (I). One is a weaker Ag1—Ag2 interaction [3.127 (2) Å] formed by the carboxylate-*O*:*O*′ bridge. The other is a relatively stronger Ag1—Ag2^i interaction [2.773 (2) Å] formed by the napy-*N*:*N*′ bridge. Compared with analogous complexes, the carboxylate-bridged value is much larger than the values in the literature, for example, 2.855 (1) Å in disilver(I) disalicylate (Movsumov *et al.*, 1990), 2.953 (1) Å in *catena*-bis(4-aminobenzoato)-disilver(I) (Kristiansson, 2001) and 2.761 (2) Å in diaquabis(μ-4-hydroxybenzenecarboxylato)disilver(I) tetrahydrate (Wang & Okabe, 2005). On the other hand, the napy-bridged Ag—Ag separation is almost within the reported ranges, *viz*. from 2.748 (2) Å in [Ag$_2$(μ-napy)$_2$](ClO$_4$)$_2$ (Tsuda *et al.*, 1989) to 2.779 (1) Å in [Ag$_2$(μ-napy)$_2$](PF$_6$)$_2$ (Koizumi & Tanaka, 2004) to 2.780 (1) Å in [Ag$_2$(μ-napy)$_2$](NO$_3$)$_2$ (Griffith *et al.*, 1995).

The pairs of napy rings are oriented almost parallel and overlap to form π–π stacking, with centroid–centroid distances of 3.376 (4) and 3.343 (4) Å for rings N1/C16–C18/C22/C23 and N3/C8–C10/C14/C15, and rings N2/C19–C23 and N4/C11–C15. Intermolecular stacking between the napy rings is also present. Ring N2/C19–C23 overlaps with the inversion-related ring at ($-x$, $1 - y$, $-z$), with an interplanar distance of 3.368 (2) Å and a centroid–centroid separation of 3.514 Å. There are also C—H$\cdots$O interactions (Table 2) between translation-related and screw-axis-related complexes, which link them along the *a* and *b* directions

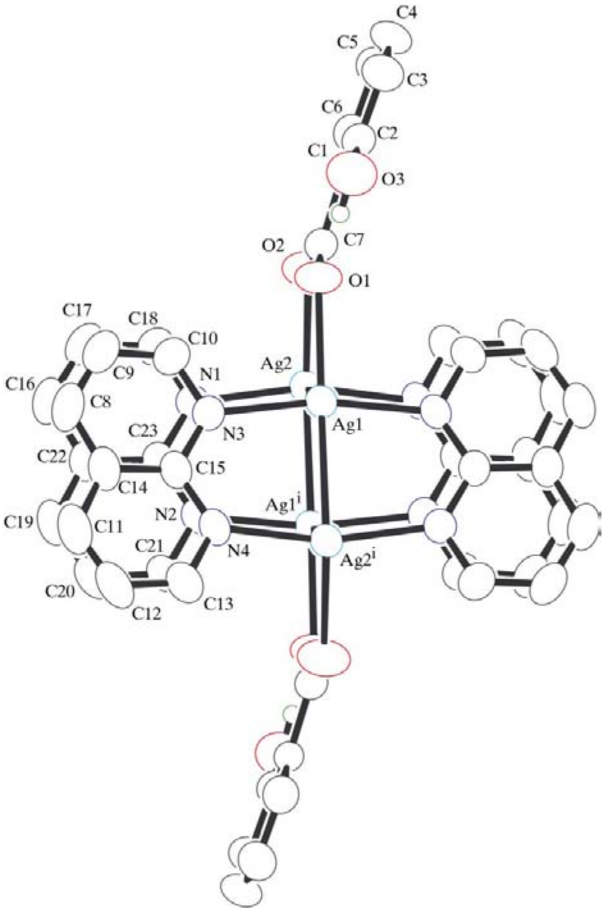

Figure 2
A view of the packing in the tetrasilver unit of (I). The weakly coordinated SA ligands have been omitted for clarity. [Symmetry code: (i) $1 - x$, $1 - y$, $-z$.]

Experimental

Brown platelet-shaped crystals of (I) were obtained by slow evaporation of an 80% methanol solution of a mixture of 1,8-naphthyridine, salicylic acid and AgNO$_3$ (molar ratio 4:4:1) at room temperature.

Crystal data

[Ag$_4$(C$_7$H$_5$O$_3$)$_2$(C$_8$H$_6$N$_2$)$_4$-(C$_7$H$_6$O$_3$)$_4$]
M_r = 1776.75
Monoclinic, $P2_1/c$
a = 10.205 (12) Å
b = 13.129 (10) Å
c = 25.82 (2) Å
β = 99.26 (4)°
V = 3414 (5) Å^3
Z = 2
D_x = 1.728 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 21 592 reflections
θ = 3.1–27.5°
μ = 1.21 mm^{-1}
T = 296.1 K
Platelet, brown
0.3 × 0.3 × 0.03 mm

Table 1
Selected geometric parameters (Å, °).

Ag1—N3	2.227 (2)	Ag2—N4^i	2.219 (2)
Ag1—N2^i	2.237 (2)	Ag2—N1	2.228 (3)
Ag1—O1	2.412 (2)	Ag2—O2	2.414 (3)
Ag1—Ag2^i	2.772 (2)	Ag2—O4	2.498 (2)
Ag1—Ag2	3.127 (2)	Ag2—Ag1^i	2.7725 (16)
N3—Ag1—N2^i	167.87 (7)	N4^i—Ag2—O4	87.58 (8)
N3—Ag1—O1	95.04 (9)	N1—Ag2—O4	92.72 (8)
N2^i—Ag1—O1	96.25 (9)	O2—Ag2—O4	78.90 (8)
N3—Ag1—Ag2^i	84.47 (7)	N4^i—Ag2—Ag1^i	83.53 (7)
N2^i—Ag1—Ag2^i	83.66 (7)	N1—Ag2—Ag1^i	84.43 (7)
O1—Ag1—Ag2^i	170.27 (6)	O2—Ag2—Ag1^i	148.42 (7)
N3—Ag1—Ag2	93.57 (8)	O4—Ag2—Ag1^i	132.63 (5)
N2^i—Ag1—Ag2	92.36 (8)	N4^i—Ag2—Ag1	94.12 (8)
O1—Ag1—Ag2	82.04 (7)	N1—Ag2—Ag1	92.40 (8)
Ag2^i—Ag1—Ag2	107.69 (5)	O2—Ag2—Ag1	76.12 (7)
N4^i—Ag2—N1	163.87 (8)	O4—Ag2—Ag1	154.95 (5)
N4^i—Ag2—O2	98.53 (10)	Ag1^i—Ag2—Ag1	72.30 (5)
N1—Ag2—O2	97.34 (10)		

Symmetry code: (i) $-x + 1$, $-y + 1$, $-z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H31···O1	0.82	1.81	2.531 (4)	147
O6—H61···O4	0.82	1.81	2.540 (4)	147
O8—H81···O5$^{\rm i}$	0.82	1.70	2.484 (4)	159
O9—H91···O7	0.82	1.86	2.589 (4)	147
C16—H16···O3$^{\rm ii}$	0.93	2.82	3.396 (5)	121
C27—H27···O3$^{\rm iii}$	0.93	2.91	3.596 (6)	132

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

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\rm min} = 0.646$, $T_{\rm max} = 0.956$
32 278 measured reflections
7793 independent reflections
4718 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\rm max} = 27.5°$
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 17$
$l = -33 \rightarrow 33$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.054$
$S = 0.80$
7793 reflections
474 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0275P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.61$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.46$ e Å^{-3}

All H atoms were located from difference Fourier maps; they were then regenerated in their ideal positions and treated as riding, with C—H = 0.93 Å and O—H = 0.82 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,O).

Data collection: *RAPID-AUTO* (Rigaku, 2003); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004) and *CRYSTALS* (Watkin *et al.*, 1996); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999) and *DIRDIF99* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *CrystalStructure*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1829). Services for accessing these data are described at the back of the journal.

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