Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A two-dimensional undulating Ag^I coordination polymer constructed of Ag—C and Ag—O bonds: poly[[[μ_3-(5,6-η):κO^2:κO^2-(±)-(1*S*,2*S*,3*R*,4*R*)-3-carboxy-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylato]silver(I)] monohydrate]

Feng-Yan Wang,[a] Xue-Bing Jiang,[b,c] Xue-Jie Tan[a]* and Dian-Xiang Xing[a]

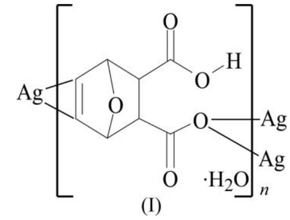
[a]School of Chemical and Pharmaceutical Engineering, Shandong Institute of Light Industry, Jinan 250353, People's Republic of China, [b]School Hospital, Shandong Institute of Light Industry, Jinan 250353, People's Republic of China, and [c]Institute of Immunology, School of Medicine, Shandong University, Number 44 Wenhua Xi Road, Jinan 250012, People's Republic of China
Correspondence e-mail: tanxuejie@163.com

Received 22 April 2011
Accepted 23 May 2011
Online 4 June 2011

The title coordination polymer, $\{[Ag(C_8H_7O_5)]\cdot H_2O\}_n$, is built from Ag^+ cations and singly protonated dehydronorcantharidin (SP-DNC) anions, with a distorted trigonal-planar geometry at the metal centre. The coordination number of Ag^I is three (with one Ag—π bond and two Ag—O bonds, one from each of three different SP-DNC ligands), if only formal Ag–ligand bonds are considered, but can be regarded as five if longer weak Ag$\cdots$O interactions are also included. The two-dimensional corrugated-sheet coordination polymer forms a non-interpenetrating framework with (4.8^2) topology. Disordered water molecules are sandwiched between the sheets.

Comment

As an important derivative of cantharidin, 7-oxabicyclo-[2.2.1]hept-5-ene-2,3-*exo*-dicarboxylic anhydride (dehydronorcantharidin, hereinafter DNC) is effective in inhibiting the growth of tumour cells (Xian *et al.*, 2005; Shimi *et al.*, 1982) and sensitizing tumours to chemotherapy (Li *et al.*, 2008). The crystal structure of DNC has been reported three times so far (Baggio *et al.*, 1972; Ramírez *et al.*, 1998; Goh *et al.*, 2008), but the structures of its metal complexes have not yet been reported. Many metal complexes are known to have antimicrobial or antineoplastic activities. We have synthesized some such complexes based on DNC, and this article describes the crystal structure of the title silver complex, (Ag–SP-DNC)$_\infty$, (I), which is a coordination polymer built from Ag^+ cations and singly protonated DNC anions (abbreviated as SP-DNC) with a novel two-dimensional ($4,8^2$) noninterpenetrating framework.



(I)

As shown in Fig. 1, each SP-DNC anion binds one Ag^+ cation *via* the C=C group at one end and two other Ag^+ cations *via* carboxylate atom O5 at the other end. Meanwhile, each Ag^+ cation is coordinated to three SP-DNC anions which results in a two-dimensional network. The coordination of the C=C group to the Ag^+ ion results in Ag—C distances of 2.377 (3) and 2.381 (3) Å; these are short and nearly equal, suggesting a strong interaction between the Ag^+ cation and the π orbital of the double bond (Fig. 2*a*). Customarily, the Ag—π interaction is considered as a single coordination site (Cottram & Steel, 2006), so the coordination number is three. Rather than a severely distorted triangular pyramidal geometry, the coordination environment of Ag^+ is more like a distorted trigonal-planar geometry, for the distance between the Ag^+ cation and the least-squares plane through the coordinated atoms C5, C6, O5($x + \frac{1}{2}$, $-y + \frac{1}{2}$, $z + \frac{1}{2}$) and O5($-x + \frac{1}{2}$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$) is only 0.3993 (5) Å.

Apart from the three-membered ring constructed by Ag^+ and C=C, there are two types of chelating rings around the Ag^+ cations. Two SP-DNC-bridged Ag^+ cations, together with the two bridging O5 atoms, form a four-membered ring with an Ag$\cdots$Ag nonbonding distance of 3.7035 (8) Å. Four Ag^+ cations and four SP-DNC anions link together to form 24-membered rings. If each SP-DNC anion around the Ag^+ cation is simplified as a node, then the Ag^+ cation can be simplified as a 3-connecting node, and the coordination polymer has a two-dimensional ($4,8^2$) net that extends along the *bc* plane of the unit cell (Fig. 2*b*). This type of net consists of 3-connected nodes shared by one rhomboidal unit and two octagons, as predicted by Wells (1984) and first observed by Schröder and co-workers in 2000 (Long *et al.*, 2000).

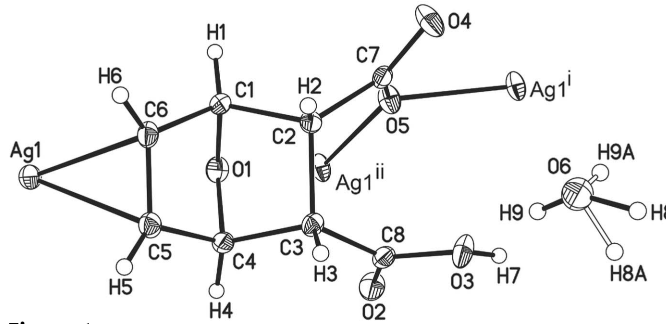


Figure 1
The crystal structure of (I), showing the atom-numbering scheme and the disordered water molecule. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $x - \frac{1}{2}$, $-y + \frac{1}{2}$, $z - \frac{1}{2}$; (ii) $-x + \frac{1}{2}$, $y - \frac{1}{2}$, $-z + \frac{3}{2}$.]

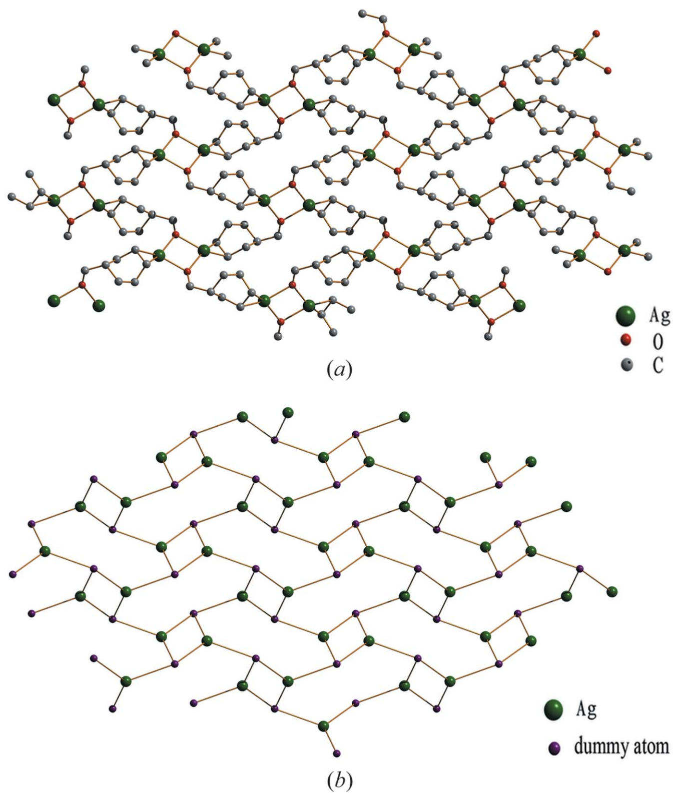


Figure 2
(*a*) A portion of an infinite two-dimensional sheet framework in (I), viewed along the *a* axis. All H atoms, water molecules, C8 atoms and noncoordinated O atoms have been omitted for clarity. (*b*) A two-dimensional $(4,8^2)$ topological diagram of (I) where the SP-DNC anions have been abstracted into dummy atoms.

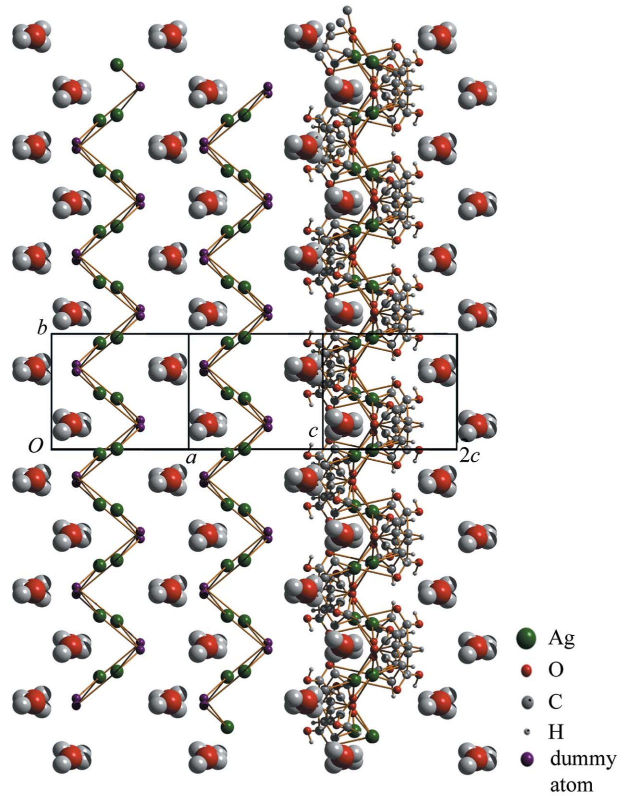


Figure 3
A view of the overlapping undulating tapes, viewed along the [101] axis. The two tapes on the left have been simplified by abstracting SP-DNC anions into dummy atoms, and all of the water molecules are shown in space-filling mode.

In the above analysis we described a three-coordinated Ag^+ cation in which the Ag—μ-O (to a pair of symmetry-related O5 atoms) bond lengths are 2.2985 (19) and 2.4149 (19) Å. However, we could also include longer, weaker, interactions between Ag and O (Huang *et al.*, 2004; Young & Hanton, 2008; Steed *et al.*, 2003; Novitchi *et al.*, 2010; Dean *et al.*, 2004) and regard both O1 and O2 as also being coordinated to Ag^+, with bond lengths of 2.7529 (18) and 2.744 (2) Å, respectively. Thus, the coordination number of Ag^+ would become five, but still involving just three SP-DNC anions: one coordinates through its C═C group, the second coordinates *via* atoms O1, O2 and O5, and the third coordinates through atom O5. This kind of coordination mode was predicted by Casida and co-workers in 1987 (Matsuzawa *et al.*, 1987) and this is the first example, to the best of our knowledge. The two-dimensional net has a vertex symbol (3.20.6.7.9.20), but is still (4.8^2) if the SP-DNC anion is simplified as a node, as mentioned above.

The coordination polymer produces an extended two-dimensional zigzag-type architecture in which water molecules are sandwiched between two undulating sheets (Fig. 3). The distance between two adjacent sheets is 12.746 (3) Å and the water molecules occupy the centre of the void space between these sheets. The two sheets are held together *via* hydrogen bonds between them and the water molecules (Table 2). The water H atoms were found to be disordered over two positions, which were determined from the difference Fourier map and modelled with refined site-occupancy factors of 0.84 (4) (for H8 and H9) and 0.16 (4) (for H8*A* and H9*A*). Splitting the occupancies of the H atoms reduced the final R and U_{iso} values.

Experimental

Crystals of $(Ag\text{–SP-DNC})_\infty$, (I), were obtained from the reaction of DNC and $AgNO_3$ (1:1 molar ratio) in water at room temperature. Elemental analysis for (I) calculated: C 31.09, H 2.94, O 31.06%; found: C 31.01, H 3.05, O 31.24%.

Crystal data

$[Ag(C_8H_7O_5)]\cdot H_2O$
M_r = 309.02
Monoclinic, $P2_1/n$
a = 9.885 (2) Å
b = 7.0011 (15) Å
c = 12.746 (3) Å
β = 97.280 (3)°
V = 874.9 (3) $Å^3$
Z = 4
Mo $K\alpha$ radiation
μ = 2.31 mm^{-1}
T = 298 K
0.32 × 0.27 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.482, T_{max} = 0.758
4990 measured reflections
1995 independent reflections
1868 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Table 1
Selected geometric parameters (Å, °).

Ag1—O5^{i}	2.2985 (19)	Ag1—O5^{ii}	2.4149 (19)
Ag1—C5	2.377 (3)	Ag1—O2^{ii}	2.744 (2)
Ag1—C6	2.381 (3)	Ag1—O1^{ii}	2.7529 (18)
O5^{i}—Ag1—C5	110.88 (8)	O5^{ii}—Ag1—O1^{ii}	71.55 (6)
O5^{i}—Ag1—C6	143.47 (8)	O2^{ii}—Ag1—O1^{ii}	70.70 (6)
C5—Ag1—C6	32.91 (9)	C1—O1—Ag1^{iii}	120.41 (14)
O5^{i}—Ag1—O5^{ii}	76.45 (7)	C4—O1—Ag1^{iii}	115.61 (14)
C5—Ag1—O5^{ii}	153.66 (8)	C8—O2—Ag1^{iii}	106.90 (17)
C6—Ag1—O5^{ii}	132.53 (8)	C7—O5—Ag1^{iv}	114.34 (16)
O5^{i}—Ag1—O2^{ii}	90.23 (7)	C7—O5—Ag1^{iii}	141.10 (17)
C5—Ag1—O2^{ii}	130.65 (8)	Ag1^{iv}—O5—Ag1^{iii}	103.55 (7)
C6—Ag1—O2^{ii}	117.07 (8)	C6—C5—Ag1	73.70 (16)
O5^{ii}—Ag1—O2^{ii}	72.76 (6)	C4—C5—Ag1	107.46 (16)
O5^{i}—Ag1—O1^{ii}	146.34 (6)	C5—C6—Ag1	73.39 (16)
C5—Ag1—O1^{ii}	102.47 (8)	C1—C6—Ag1	107.33 (17)
C6—Ag1—O1^{ii}	69.58 (8)		

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.080$
$S = 1.05$
1995 reflections
164 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.87$ e Å^{-3}
$\Delta\rho_{min} = -0.95$ e Å^{-3}

All H atoms were found in a difference map and refined isotropically. The water H atoms were disordered over two positions, which were determined from the difference Fourier map and modelled with refined site-occupancy factors of 0.84 (4) (for H8 and H9) and 0.16 (4) (for H8*A* and H9*A*).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXL97*.

This work was supported by the Natural Science Foundation of Shandong Province (grant No. ZR2009BM040).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H7···O6^{v}	0.88	1.67	2.540 (3)	170
C6—H6···O2^{vi}	0.93 (3)	2.40 (3)	3.087 (3)	130 (2)
C1—H1···O4^{vii}	0.91	2.53	3.400 (4)	159

Symmetry codes: (v) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (vi) $x, y+1, z$; (vii) $-x, -y+1, -z+1$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: WQ3003). Services for accessing these data are described at the back of the journal.

References

Baggio, S., Barriola, A. & de Perazzo, P. K. (1972). *J. Chem. Soc. Perkin Trans. 2*, pp. 934–937.
Bruker (2000). *SMART*, *SAINT*, *SADABS* and *XPREP*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cottram, J. R. A. & Steel, P. J. (2006). *J. Organomet. Chem.* **691**, 2286–2290.
Dean, P. A. W., Craig, D., Dance, I., Russell, V. & Scudder, M. (2004). *Inorg. Chem.* **43**, 443–449.
Goh, Y. W., Pool, B. R. & White, J. M. (2008). *J. Org. Chem.* **73**, 151–156.
Huang, Z., Du, M., Song, H. B. & Bu, X. H. (2004). *Cryst. Growth Des.* **4**, 71–78.
Li, Y.-X., Bao, Y.-L., Zheng, L.-H., Wu, Y., Yu, Ch.-L. & Meng, X.-Y. (2008). Chinese Patent CN101317835.
Long, D. L., Blake, A. J., Champness, N. R. & Schröder, M. (2000). *Chem. Commun.* pp. 1369–1370.
Matsuzawa, M., Graziano, M. J. & Casida, J. E. (1987). *J. Agric. Food Chem.* **35**, 823–829.
Novitchi, G., Ciornea, V., Costes, J.-P., Gulea, A., Kazheva, O. N., Shova, S. & Arion, V. B. (2010). *Polyhedron*, **29**, 2258–2261.
Ramírez, B. M., Díaz de Delgado, G., Velásquez, W. O. & Perdomo, G. M. (1998). *Z. Kristallogr. New Cryst. Struct.* **213**, 197–198.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Shimi, I. R., Zaki, Z., Shoukry, S. & Medhat, A. M. (1982). *Eur. J. Cancer Clin. Oncol.* **18**, 785–793.
Steed, J. W., Johnson, K., Legido, C. & Junk, P. C. (2003). *Polyhedron*, **22**, 769–774.
Wells, A. F. (1984). In *Structural Inorganic Chemistry*, 5th ed. Oxford: Clarendon Press.
Xian, L. J., Wang, B., Cai, Y. Ch., Liu, Y., Shan, H. B., Zeng, W. N., Chen, H. X., Xu, Z. L. & Liu, X. H. (2005). Chinese Patent CN1686109.
Young, A. G. & Hanton, L. R. (2008). *Coord. Chem. Rev.* **252**, 1346–1386.