

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0774P)^2 + 0.3972P]$
$R[F^2 > 2\sigma(F^2)] = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.162$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.006$	$\Delta\rho_{\max} = 0.468 \text{ e } \text{\AA}^{-3}$
2470 reflections	$\Delta\rho_{\min} = -0.244 \text{ e } \text{\AA}^{-3}$
160 parameters	Extinction correction: none
H atoms riding with $U(H) = 1.2U_{\text{eq}}(C)$	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

C1—O1	1.302 (5)	N1—Ni1	1.889 (4)
C11—N1	1.309 (5)	O1—Ni1	1.823 (3)
C12—N1	1.506 (5)		
O1—C1—C10	123.8 (4)	C11—N1—Ni1	126.2 (3)
O1—C1—C2	116.8 (4)	C12—N1—Ni1	120.3 (3)
N1—C11—C10	126.4 (4)	C1—O1—Ni1	131.3 (3)
N1—C12—C13	110.6 (4)	O1 <sup>1</sup> —Ni1—N1	88.00 (15)
C11—N1—C12	113.5 (4)		
O1—C1—C10—C11	0.4 (6)	C10—C1—O1—Ni1	4.1 (7)
C1—C10—C11—N1	-3.1 (7)	C1—O1—Ni1—N1	-4.5 (4)
C10—C11—N1—Ni1	1.5 (6)	C11—N1—Ni1—O1	1.7 (4)

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

Data collection: *CAD-4 Diffractometer Control Software* (Enraf-Nonius, 1993). Cell refinement: *CAD-4 Diffractometer Control Software*. Data reduction: *REDU4* (Stoe & Cie, 1991). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1237). Services for accessing these data are described at the back of the journal.

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## A Silver(I) Complex of a Tube-Shaped Hydrocarbon†

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### Abstract

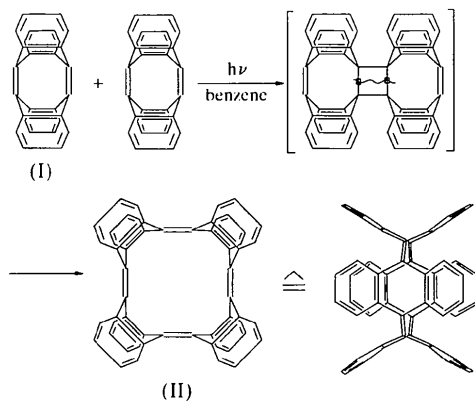
The bis[silver(I) trifluoromethanesulfonate] complex of the fully conjugated tubelike hydrocarbon 5,24:6,11:12,17:18,23-tetra[1,2]benzenotetrabenzo[*a,e,i,m*]cyclohexadecene crystallizes with two molecules of water and two of toluene, and thus has the formula  $[\text{Ag}_2(\text{C}_{56}\text{H}_{32})(\text{C}_7\text{H}_8)_2(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_2$ . The formula unit of the latter displays inversion symmetry, while the ligand itself displays approximate  $D_{4h}$  symmetry. Each  $\text{Ag}^+$  ion is coordinated by one C atom of each of two adjacent rings of the ligand, one water oxygen and one toluene C—C bond.

### Comment

We recently reported (Herges *et al.*, 1996) on the photochemically induced ring-expanding metathesis of tetrahydrodianthracene, (I) (Cheung *et al.*, 1974), forming the tubular hydrocarbon 5,24:6,11:12,17:18,23-tetra[1,2]benzenotetrabenzo[*a,e,i,m*]cyclohexadecene, (II)

† Systematic name:  $[\mu-(4,7-\eta:16,19-\eta)-5,24:6,11:12,17:18,23\text{-tetra}[1,2]\text{-benzenotetrabenzo}[a,e,i,m]\text{cyclohexadecene}]\text{bis}\{\text{aqua}[(2,3-\eta)\text{-toluene}]\text{-silver(I)}\}$  bis(trifluoromethanesulfonate).

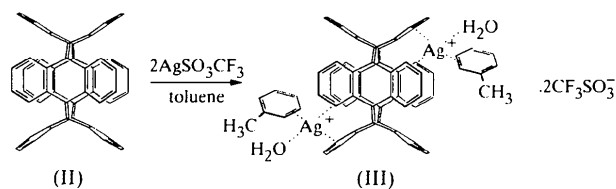
(Scheme 1; Herges & Kammermeier, 1996). The 'picotube', (II), consists of four 9,10-anthracenyldiene units linked by double bonds, and is the first conventionally synthesized and completely conjugated tubelike hydrocarbon besides the carbon nanotubes obtained by vaporization of carbon (Iijima, 1991).



Scheme 1

We expected the  $D_{4h}$  symmetrical hydrocarbon (II) to act as a  $\pi$ -spherand (Gloe *et al.*, 1995), since all  $p$ -orbitals point approximately towards the interior of the cavity. At the 'waist' of the structure, the four quinoid double bonds should provide an environment acting as an eight-electron square-planar ligand (Clardy

*et al.*, 1986) with a diameter of 5.4 Å.  $\pi$ -Complexes of this kind with  $\text{Ag}^+$  ions are known (Boekelheide *et al.*, 1985; Armand *et al.*, 1981; Cohen-Addad *et al.*, 1983; Bubenitschek *et al.*, 1995; Jones, Bubenitschek *et al.*, 1996; Jones, Heirtzler & Hopf, 1996). However, the structure of the title silver(I) complex, (III), did not correspond to our expectations.



Scheme 2

Crystals of complex (III) contain one molecule of (II), two  $\text{Ag}^+$  ions, two trifluoromethanesulfonate ions, two molecules of toluene and two molecules of water per formula unit (Fig. 1); there is one formula unit, with crystallographic inversion symmetry, in each unit cell. The one independent  $\text{Ag}^+$  ion is not bound at the centre of (II), but is instead coordinated to one C atom of each of two adjacent benzene rings at the rim of (II) [ $\text{Ag}-\text{C}7$  2.536 (3) and  $\text{Ag}-\text{C}24$  2.548 (3) Å; contacts to adjacent C atoms > 2.8 Å], and additionally to one of the aromatic C—C bonds of toluene [ $\text{Ag}-\text{C}102$  2.458 (3) and  $\text{Ag}-\text{C}101$  2.509 (3) Å]. Finally,

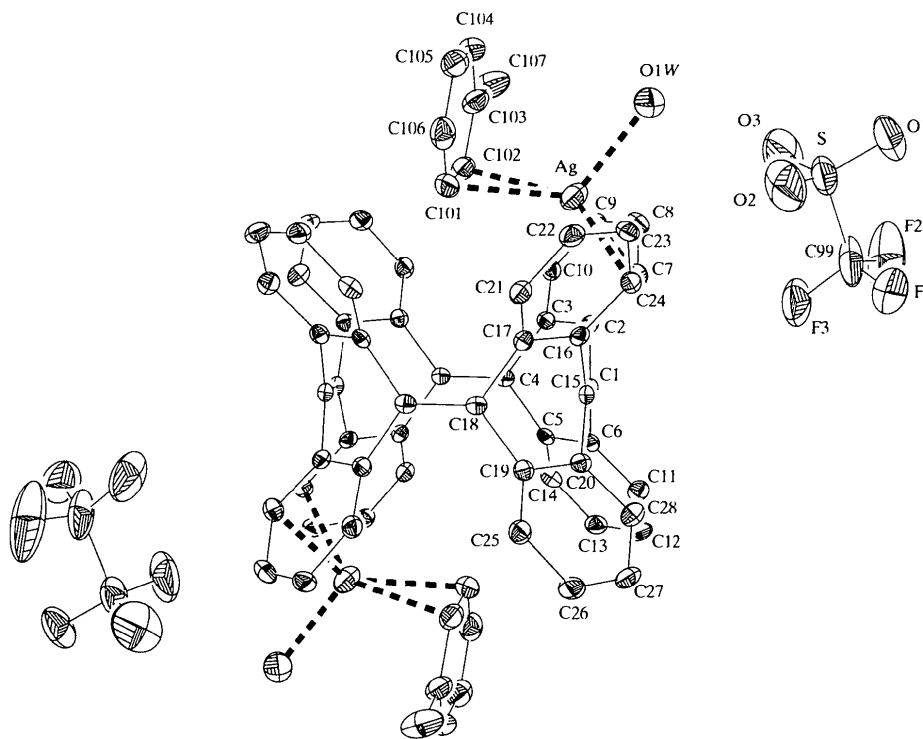


Fig. 1. The formula unit of complex (III) in the crystal. Ellipsoids are plotted at the 50% probability level and H atoms have been omitted for clarity. Only the asymmetric unit is labelled.

there is an Ag—O<sub>water</sub> interaction of 2.328 (3) Å. Thus, the complete coordination sphere of Ag<sup>+</sup> involves four C atoms and one water. The coordinated water forms hydrogen bonds to trifluoromethanesulfonate ions, the effect of which is to produce 12-membered rings centred on  $\frac{1}{2}, \frac{1}{2}, 0$  (Fig. 2).

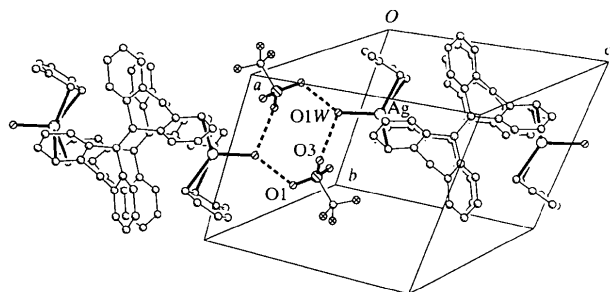


Fig. 2. Dimer formation in (III) via hydrogen bonds (dashed lines).

The ligand in (III) displays the approximate  $D_{4h}$  symmetry that was inferred from the NMR spectra of the free ligand, (II). The diameter of the central ring of (II) is probably too large for square-planar complexation of Ag<sup>+</sup>, which is achieved in the structurally related pentacyclo[12.2.2.2<sup>2,5</sup>.2<sup>6,9</sup>.2<sup>10,13</sup>]tetracos-1,5,9,13-tetraene, with a diameter of 5.1 Å (Clardy *et al.*, 1986). We are currently investigating the coordination of other metal ions by (II) and its dianion.

The olefinic double bonds in tetrahydrodianthracene, (I), are highly strained. The distance of the opposing bridgehead C atoms, at only 2.436 Å, is far below the sum of their van der Waals radii, and the pyramidalization angle is 35.6° (Herges *et al.*, 1996) (the pyramidalization angle of an olefinic C atom is defined as the angle between the C=C bond and the plane defined by the two single bonds of the  $sp^2$ -C atom). From the X-ray data of (III) it is seen that in the complexed ligand, (II), the distance between the quinoid double bonds is about 5.3 Å [C4...C18 5.292 (4) Å] and the pyramidalization of the olefinic C atoms only 5.1 and 4.5°, respectively, for C4 and C18. Assuming that the structure of the free ligand is not greatly different, it is most probable that reduction of strain is the main driving force for the metathetic dimerization of (I) (Scheme 1). This also explains the much lower reactivity of (II) compared with (I), towards electrophiles and nucleophiles, and in cycloadditions, and its subsequent metathesis with (I) to form higher cyclic oligomers.

## Experimental

Compound (II) was prepared by photolysis of a suspension of tetrahydrodianthracene in benzene with a high-pressure mercury lamp in a quartz reactor, then isolated by flash chromatography with hexane-dichloromethane on silica gel, and finally recrystallized from toluene. Crystallization experiments with (II) and silver trifluoromethanesulfonate were performed

in several solvents. A first indication of coordination was provided by the fact that a suspension of sparingly soluble (II) in tetrahydrofuran (THF) can be dissolved by adding silver(I) trifluoromethanesulfonate. However, upon crystallization, THF successfully competes with (II) as a ligand for Ag<sup>+</sup>, and (II) precipitates without the metal cation. From a saturated solution of (II) in toluene (which is a weaker ligand than THF) and silver(I) trifluoromethanesulfonate (ratio 1:2), single crystals of the silver(I) complex, (III) [(II)<sub>2</sub>Ag<sup>+</sup>·2CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>·2C<sub>7</sub>H<sub>8</sub>·2H<sub>2</sub>O], were obtained (Scheme 2).

### Crystal data

[Ag<sub>2</sub>(C<sub>56</sub>H<sub>32</sub>)(C<sub>7</sub>H<sub>8</sub>)<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>

$M_r = 1439.00$

Triclinic

$P\bar{1}$

$a = 10.9634 (8) \text{ \AA}$

$b = 11.1491 (8) \text{ \AA}$

$c = 13.2319 (10) \text{ \AA}$

$\alpha = 114.161 (6)^\circ$

$\beta = 95.894 (4)^\circ$

$\gamma = 92.468 (6)^\circ$

$V = 1461.4 (2) \text{ \AA}^3$

$Z = 1$

$D_x = 1.635 \text{ Mg m}^{-3}$

$D_m$  not measured

### Data collection

Siemens P4 diffractometer

$\omega$  scans

Absorption correction:

$\psi$  scan (XEMP;

Siemens, 1994a)

$T_{\min} = 0.793$ ,  $T_{\max} = 0.835$

5254 measured reflections

4967 independent reflections

4133 reflections with

$I > 2\sigma(I)$

### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.080$

$S = 1.051$

4967 reflections

415 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0385P)^2$

$+ 1.0074P]$

where  $P = (F_o^2 + 2F_c^2)/3$

Mo K $\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 63

reflections

$\theta = 4.3\text{--}12.5^\circ$

$\mu = 0.822 \text{ mm}^{-1}$

$T = 173 (2) \text{ K}$

Prism

$0.40 \times 0.28 \times 0.22 \text{ mm}$

Colourless

$R_{\text{int}} = 0.014$

$\theta_{\text{max}} = 25.00^\circ$

$h = -13 \rightarrow 13$

$k = 0 \rightarrow 12$

$l = -15 \rightarrow 14$

3 standard reflections

every 247 reflections

intensity decay: none

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.973 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.720 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Ag—O1W	2.328 (3)	Ag—C24	2.548 (3)
Ag—C102	2.458 (3)	C1—C15	1.354 (4)
Ag—C101	2.509 (3)	C4—C18'	1.356 (4)
Ag—C7	2.536 (3)		
O1W—Ag—C102	114.69 (11)	C101—Ag—C7	130.55 (10)
O1W—Ag—C101	122.50 (11)	O1W—Ag—C24	100.43 (11)
C102—Ag—C101	32.62 (11)	C102—Ag—C24	139.71 (10)
O1W—Ag—C7	102.51 (10)	C101—Ag—C24	111.13 (10)
C102—Ag—C7	112.56 (10)	C7—Ag—C24	76.12 (9)

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

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

D—H...A	D—H	H...A	D...A	D—H...A
O1W—H11'...O1'	0.76 (3)	2.14 (3)	2.895 (4)	172 (5)
O1W—H12'...O3	0.74 (3)	2.37 (4)	3.061 (6)	157 (5)

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

Water H atoms were refined with O—H distance restraints (command *SADI* in *SHELXL93*; Sheldrick, 1993) and methyls were refined as rigid groups, with other H atoms riding.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *XP* (Siemens, 1994b). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1410). Services for accessing these data are described at the back of the journal.

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## Manganese(II) Triphenylacetate Hydrate, a Manganese(II) Complex with a Chain Structure

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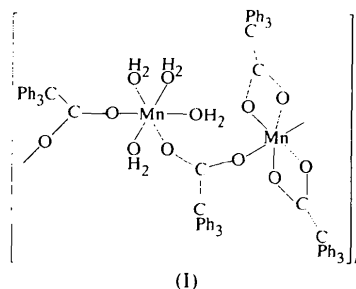
## Abstract

The crystal structure of *catena*-poly[[tetraaqua-2κ<sup>4</sup>O-μ-triphenylacetato-1:2κ<sup>2</sup>O:O'-bis(triphenylacetato)-1κ<sup>4</sup>O,O'-dimanganese(II)]-μ-triphenylacetato-2κO:1'κO'], [Mn<sub>2</sub>(C<sub>20</sub>H<sub>15</sub>O<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>]<sub>n</sub>, was determined at 294 K by single-crystal X-ray diffraction. This compound has a chain structure with repeating dimeric units containing two crystallographically independent Mn<sup>II</sup> atoms bridged by *sym-sym*-(μ-triphenylacetato-O,O') groups *via cis* positions.

## Comment

Bridged metal carboxylates are of interest since the reactive site in many enzyme systems contain these structural features (Holm *et al.*, 1996).

Manganese(II) triphenylacetate hydrate, (I), has a chain structure. The repeating dimeric unit contains two crystallographically independent Mn<sup>II</sup> atoms bridged by *sym-sym*-(μ-triphenylacetato-O,O') groups *via cis* positions; the Mn1 atom is bonded to two chelating



triphenylacetato groups, while Mn2 is bonded to four aqua ligands. The H atoms of the aqua ligands were located on structural refinement (Fig. 1). The Mn...Mn distances are Mn1...Mn2 4.5275 (7) and Mn1...Mn2' 4.7210 (7) Å. There are no inter-chain O...O distances less than 3.313 (5) Å. The only important intra-chain distance where a hydrogen bond almost certainly occurs is between the O4 atom of a chelating acetato ligand and the O9 atom of a ligated water molecule [2.693 (3) Å].