Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\AA^2$) for (2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ag1	0	0.37973 (11)	0.55732 (9)	0.0703 (6)
P1	1/4	0.3787 (4)	1/4	0.0546 (10)
F1	0.2239 (5)	0.3788 (6)	0.3528 (4)	0.099 (3)
F2	0.1239 (5)	0.3794 (8)	0.2306 (5)	0.135 (4)
F3	1/4	0.2642 (9)	1/4	0.144 (5)
F4	1/4	0.4948 (9)	1/4	0.160 (6)
O1	0	0.4337 (10)	0.3986 (8)	0.077 (4)
N1	0.1766 (6)	0.3646 (7)	0.5688 (5)	0.055 (2)
C1	0.4435 (6)	0.3647 (7)	0.6511 (6)	0.051 (3)
C2	0.3876 (6)	0.3640 (7)	0.5716 (6)	0.041 (2)
C3	0.4426 (7)	0.3649 (7)	0.4923 (7)	0.050 (3)
C4	0.2699 (7)	0.3650 (7)	0.5699 (7)	0.049 (3)

Table 4. *Selected geometric parameters ($\AA$, °) for (2)*

Ag1—N1	2.164 (8)	Ag1—O1^{ii}	2.569 (13)
Ag1—N1^i	2.164 (8)	O1—Ag1^{ii}	2.569 (13)
Ag1—O1	2.513 (13)		
N1—Ag1—N1^i	165.9 (5)	N1—Ag1—O1^{ii}	93.9 (2)
N1—Ag1—O1	96.0 (2)	N1^i—Ag1—O1^{ii}	93.9 (2)
N1^i—Ag1—O1	96.0 (2)	O1—Ag1—O1^{ii}	88.5 (4)

Symmetry codes: (i) $-x, y, z$; (ii) $-x, 1 - y, 1 - z$.

Table 5. *Hydrogen-bonding geometry ($\AA$, °) for compounds (1) and (2)*

	D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
(1)	O4—H1$\cdots$O3^i	0.75 (3)	2.13 (3)	2.866 (4)	169 (3)
(2)	O1—H1$A\cdots$F1	0.96 (10)	1.95 (10)	2.904 (8)	169 (1)

Symmetry code: (i) $\frac{1}{2} + x, -y, z$.

For both structures, the H atoms of the water molecules were located from difference Fourier maps and their coordinates and displacement parameters refined. The H atoms of the benzene ring were added at geometrically calculated positions (C—H = 0.93 $\AA$) and the U values were assigned as $1.2U_{eq}$ of the adjacent non-H atoms.

For both compounds, data collection: *Crystal Logic* (Strouse, 1988); cell refinement: *Crystal Logic* (Strouse, 1988); data reduction: *PROFILE* (Blessing, Coppens & Becker, 1974); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1971); software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: FG1114). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Silver(I) Complex of 4,4'-Dicyanodiphenylacetylene with a Difluorophosphate ($PO_2F_2^-$) Counterion

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Abstract

Crystallization of 1,2-ethynediylbis(4-benzonitrile) with silver(I) hexafluorophosphate results in hydrolysis of the counterion to the difluorophosphate species. The resulting complex, poly[disilver(I)-bis(μ_3-difluorophosphato-*O:O:O'*)-μ-[1,2-ethynediylbis(4-benzonitrile)-*N:N*]], [$Ag_2(F_2O_2P)_2(C_{16}H_8N_2)$]$_\infty$, consists of infinite chains of ligands coordinated to silver(I) which are linked through counterion O atoms to form undulating sheets.

Comment

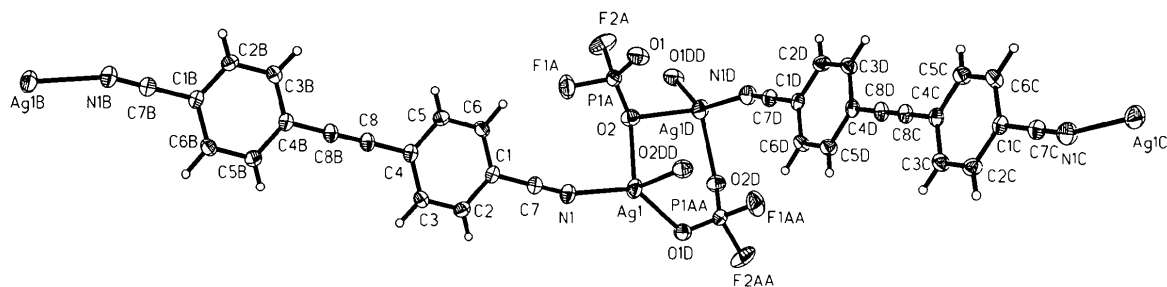The formation of coordination networks through the binary combination of a multitopic organic ligand with

Fig. 1. An *ORTEPII* plot (Johnson, 1971) of (I) showing 35% probability ellipsoids for non-H atoms and circles of arbitrary size for H atoms. Minor site counterion positions have been omitted for clarity.

a transition metal salt is currently an area of intense interest (Hoskins & Robson, 1989; Moore & Lee, 1994). We reported previously the influence of the counterion on network topology in the crystallization of 4,4'-biphenyldicarbonitrile with silver(I) salts (Hirsch, Venkataraman, Wilson, Moore & Lee, 1995). We have extended this study to the use of 4,4'-dicyanodiphenyl-acetylene and report here the results of crystallization with silver(I) hexafluorophosphate ($AgPF_6$), (I).

(I)
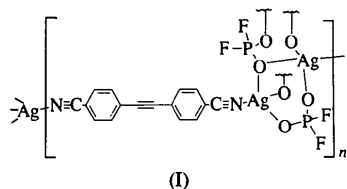
Crystallization of 4,4'-dicyanodiphenylacetylene with $AgPF_6$ in xylenes by heating and slow cooling is accompanied by inadvertent counterion hydrolysis to the rather unusual difluorophosphate ($PO_2F_2^-$) species (Horn & Snow, 1980; Kitagawa, Kawata, Nozaka & Munakata, 1993). As a result of the small amount of adventitious water typically present in xylenes, the likely source is the $AgPF_6$ used which is known to be hygroscopic. The structure obtained is that of infinite chains of 4,4'-dicyanodiphenylacetylene units coordinated to silver(I) ions through the nitrile group (Fig. 1). These chains are bridged by counterion O atoms to form undulating sheets projecting along (102). Bridging occurs so as to allow $\pi-\pi$ stacking between 4,4'-dicyanodiphenylacetylene molecules at a plane-to-plane distance of 3.45 Å with an offset angle of 45.3°. Silver(I) adopts a distorted tetrahedral geometry, bonding to one ligand N atom and three O atoms. Bond angles around silver(I) range from 96.60 (11) to 138.25 (12)°. The Ag—N distance is 2.186 (3) Å and the Ag—O distances are 2.224 (3), 2.411 (3) and 2.488 (3) Å. Aromatic C—C distances range from 1.372 (6) to 1.403 (5) Å [average 1.386 (12) Å]. The acetylenic C≡C bond length is 1.193 (8) Å and the nitrile C≡N bond length is 1.131 (5) Å. Aromatic C—H bond lengths range from 0.83 (4) to 0.98 (4) Å. The H-atom U values range from 0.031 (10) to 0.038 (11).
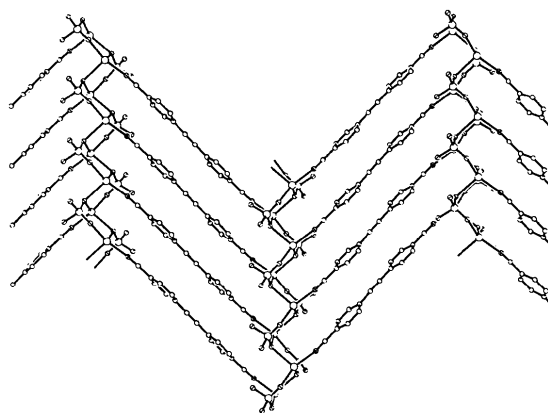

Fig. 2. A portion of an undulating sheet of the title complex in the (102) plane. Face-to-face aromatic stacking of the 4,4'-dicyanodiphenylacetylene molecule is evident.
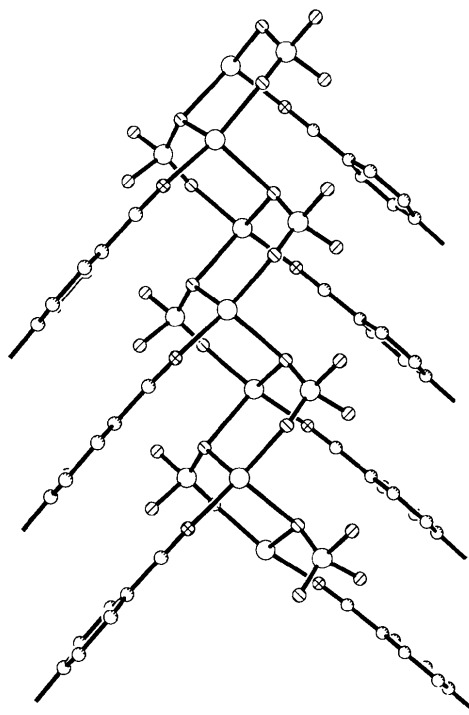

Fig. 3. A portion of the title complex detailing the tetrahedral coordination of silver(I). The metal is bonded to one N atom of the ligand and to three O atoms of the counterion.

The formation of the difluorophosphate counterion has a significant effect on the network topology. It is possible that a diamondoid network would have formed in the presence of hexafluorophosphate, similar to our previous results with 4,4'-biphenyldicarbonitrile (Hirsch, Venkataraman, Wilson, Moore & Lee, 1995). However, in this example, the strong coordinating propensity of difluorophosphate through oxygen allows only one 4,4'-dicyanodiphenylacetylene ligand to enter the coordination sphere of silver(I).

Experimental

For the preparation of (I), a mixture of silver(I) hexafluorophosphate (14 mg, 0.05 mmol) and 4,4'-dicyanodiphenylacetylene (10 mg, 0.05 mmol) in xylenes (4 ml) in a clean vial with a Teflon-lined screw cap was heated in an oil bath to 383 K for 2.5 h. Slow cooling overnight to ambient temperature provided X-ray quality single crystals as colorless needles.

Crystal data

[Ag$_2$(F$_2$O$_2$P)$_2$(C$_{16}$H$_8$N$_2$)]
M_r = 645.92
Monoclinic
$P2_1/c$
a = 9.615 (2) Å
b = 4.9090 (10) Å
c = 21.126 (4) Å
β = 99.02 (3)°
V = 984.8 (3) Å^3
Z = 2
D_x = 2.178 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9.34–11.68°
μ = 2.214 mm^{-1}
T = 198 (2) K
Acicular
0.43 × 0.06 × 0.05 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/θ scans
Absorption correction: by integration from crystal shape
T_{min} = 0.87, T_{max} = 0.90
3638 measured reflections
1722 independent reflections

1421 observed reflections $[I > 2\sigma(I)]$
R_{int} = 0.039
θ_{max} = 24.97°
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 5$
$l = -25 \rightarrow 25$
3 standard reflections frequency: 90 min intensity decay: <0.4%

Refinement

Refinement on F^2
$R(F)$ = 0.030
$wR(F^2)$ = 0.078
S = 1.05
1722 reflections
180 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 1.1277P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.79 e Å^{-3}
$\Delta\rho_{min}$ = −0.61 e Å^{-3}
Extinction correction: none
Atomic scattering factors from International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ag1	0.44674 (3)	0.19991 (8)	0.17816 (2)	0.0481 (2)
N1	0.5480 (3)	0.4595 (8)	0.1147 (2)	0.0455 (9)
C1	0.7108 (4)	0.8124 (8)	0.0738 (2)	0.0307 (8)
C2	0.6821 (4)	0.9035 (9)	0.0108 (2)	0.0364 (8)
C3	0.7654 (4)	1.0994 (9)	−0.0104 (2)	0.0360 (8)
C4	0.8797 (4)	1.2046 (8)	0.0308 (2)	0.0306 (8)
C5	0.9111 (4)	1.1053 (9)	0.0937 (2)	0.0352 (8)
C6	0.8268 (4)	0.9103 (9)	0.1148 (2)	0.0347 (8)
C7	0.6203 (4)	0.6125 (9)	0.0965 (2)	0.0362 (8)
C8	0.9653 (4)	1.4122 (8)	0.0092 (2)	0.0337 (8)
O1	0.7304 (3)	0.4043 (8)	0.32937 (13)	0.0528 (8)
O2	0.6480 (3)	0.0270 (6)	0.24933 (13)	0.0454 (7)
P1A†	0.7574 (3)	0.2146 (7)	0.28044 (15)	0.0356 (6)
F1A†	0.8182 (5)	0.3755 (10)	0.2285 (2)	0.0657 (13)
F2A†	0.8888 (3)	0.0481 (8)	0.3053 (3)	0.0711 (14)
P1B‡	0.756 (3)	0.176 (4)	0.2910 (10)	0.043 (5)
F1B‡	0.871 (3)	0.244 (6)	0.2504 (13)	0.068 (5)
F2B‡	0.843 (3)	−0.015 (4)	0.3381 (14)	0.077 (5)

† Occupancy of 0.874 (9).   ‡ Occupancy of 0.126 (9).

Table 2. *Selected geometric parameters (Å, °)*

Ag1—N1	2.186 (3)	O1—Ag1^{iii}	2.224 (3)
Ag1—O1^i	2.224 (3)	O2—P1A	1.473 (4)
Ag1—O2	2.411 (3)	O2—Ag1^i	2.488 (3)
Ag1—O2^{ii}	2.488 (3)	P1A—F2A	1.527 (4)
N1—C7	1.131 (5)	P1A—F1A	1.539 (5)
O1—P1A	1.445 (4)		
N1—Ag1—O1^i	138.24 (12)	P1A—O2—Ag1	120.3 (2)
N1—Ag1—O2	101.35 (11)	P1A—O2—Ag1^i	115.7 (2)
O1^i—Ag1—O2	110.22 (11)	O1—P1A—O2	121.7 (3)
N1—Ag1—O2^{ii}	104.05 (13)	O1—P1A—F2A	109.3 (3)
O1^i—Ag1—O2^{ii}	96.60 (11)	O2—P1A—F2A	108.3 (3)
O2—Ag1—O2^{ii}	100.30 (7)	O1—P1A—F1A	108.1 (3)
C7—N1—Ag1	162.2 (3)	O2—P1A—F1A	109.1 (2)
N1—C7—C1	178.8 (4)	F2A—P1A—F1A	97.7 (3)
P1A—O1—Ag1^{iii}	126.2 (2)		

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

Systematic absences unambiguously suggested the space group $P2_1/c$. The P and F atoms of the difluorophosphate counterion were modeled as being disordered over two sites with a relative site occupancy of 0.874 (9). All H atoms were located from the Fourier difference map and refined. The data crystal was mounted using oil (Paratone-N, Exxon) onto a thin glass fiber. The data crystal was bound by the (010), (0$\bar{1}$0), (001), (00$\bar{1}$), (100) and ($\bar{1}$00) faces. The distances from the crystal center to these facial boundaries were 0.43, 0.43, 0.05, 0.05, 0.05 and 0.05 mm, respectively. Step-scanned intensity data were reduced by profile analysis (*PROFILE*; Blessing, Coppens & Becker, 1974) and corrected for Lorentz–polarization effects and absorption (*SHELX*76; Sheldrick, 1976). Scattering factors and anomalous dispersion terms were taken from standard tables (Wilson, 1992). The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1990); correct positions for 11 atoms were deduced from an E map. One cycle of isotropic least-squares refinement followed by an unweighted difference Fourier synthesis revealed positions for the remaining atoms. Disordered difluorophosphate counterions were restrained to have equivalent geometry with an effective standard deviation of 0.03 Å. Disordered P and F sites separated by less than 1.1 Å were restrained (e.s.d. = 0.01) to have similar displace-

ment parameters. Successful convergence of the full-matrix least-squares refinement on F^2 (SHELXL93; Sheldrick, 1993) was indicated by the maximum shift/error for the last cycle. The highest peaks in the final difference Fourier map were in the vicinity of the Ag atom; the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude or resolution.

Data collection: CAD-4 Software (Enraf–Nonius, 1989). Cell refinement: CAD-4 Software. Molecular graphics: OR-TEPII (Johnson, 1971). Software used to prepare material for publication: CIFTAB in SHELXL93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BK1228). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,2'-Biphenylbis(η-cyclopentadienyl)titanium

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Abstract

The Ti atom in the title compound, [Ti(η-C$_5$H$_5$)$_2$-(C$_{12}$H$_8$)], has a distorted tetrahedral coordination and is attached to two cyclopentadienyl rings and to two C atoms in the 2 and 2' positions of the biphenyl ligand. The two eclipsed cyclopentadienyl (Cp) rings are bent back to make room for the σ-bonded biphenyl ligand. The Cp(centroid)—Ti—Cp(centroid) angles are in the range 135.7 (2)–137.3 (2)° for the three independent molecules in the asymmetric unit.

Comment

In recent years, the number of studies of cyclic organometallic compounds of transition metals has increased because of their special activation of C—H bonds and also because of their action in cycloaddition reactions and the disproportionation of alkenes. Compounds of type [Cp$_2$TiR$_2$] (where Cp is cyclopentadienyl and R is alkyl or aryl) have been studied extensively (Rausch & Klemann, 1971; Sonogashira & Hagihara, 1966; Atwood, Hunter, Alt & Rausch, 1976; Fachinetti, Floriani, Marchetti & Mellini, 1978; Bristow, Lappert, Martin, Atwood & Hunter, 1984; Engelhardt, Leung, Papasergino, Raston, Twiss & White, 1987).

The crystal structure of the title compound, (I), comprises three neutral molecules (A, B and C) per asymmetric unit. The molecular geometries of these three independent molecules are quite similar.
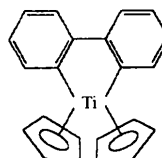
(I)

The coordination geometry of the Ti atom can be described as a distorted tetrahedron involving two C atoms of biphenyl and two Cp rings, if the centroid of each Cp ring is considered to occupy one coordination site (Fig. 1). The Ti atom forms an unstrained five-