

Financial support was provided by CEE grant CH1*CT91-0913, FONDECYT grant 1930024, DICYT grant 02-9542CHM and DGICYT grant PB92-0594.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1230). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Churchill, M. R. & Lin, K.-K. G. (1973). *Inorg. Chem.* **12**, 2274–2279.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Katz, T. J. & Rosenberger, M. (1963). *J. Am. Chem. Soc.* **85**, 2030–2031.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Oelckers, B., Chávez, I., Manríquez, J. M. & Román, E. (1993). *Organometallics*, **12**, 3396–3397.
- Seiler, P. & Dunitz, J. D. (1979). *Acta Cryst.* **B35**, 1068–1074.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Spek, A. L. (1995a). *PLATON. Program for Analysis of Derived Crystal Structure Results*. Version of October 1995. University of Utrecht, The Netherlands.
- Spek, A. L. (1995b). *PLUTON. Molecular Graphics Program*. Version of August 1995. University of Utrecht, The Netherlands.

Acta Cryst. (1996). **C52**, 2416–2419

Silver(I) Complexes of 1,4-Dicyanobenzene

D. VENKATARAMAN,^a GEOFFREY B. GARDNER,^b AARON C. COVEY,^b STEPHEN LEE^b AND JEFFREY S. MOORE^c

^aDepartment of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801, USA,

^bDepartment of Chemistry, Willard H. Dow Laboratory, University of Michigan, Ann Arbor, Michigan 48109-1055, USA, and ^cDepartments of Chemistry and Materials Science & Engineering, University of Illinois, Urbana, Illinois 61801, USA. E-mail: moore@aries.scs.uiuc.edu

(Received 14 August 1995; accepted 13 May 1996)

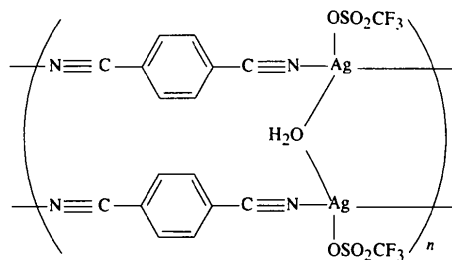
Abstract

The crystal structures of the complexes of 1,4-benzenedinitrile with silver(I) trifluoromethanesulfonate, *catena*-poly[$\{\mu$ -(*aqua-O,O*)-bis[(trifluoromethanesulfonato-*O*)]silver(I)]-di- μ -(1,4-benzenedinitrile-*N:N'*)], [Ag₂(CF₃O₃S)₂(C₈H₄N₂)₂(H₂O)]_n, and *catena*-poly[[di-

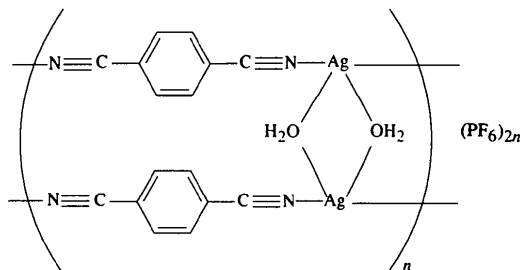
μ -(*aqua-O,O*)-disilver(I)]- μ -(1,4-benzenedinitrile-*N:N'*) bis(hexafluorophosphate)], [Ag₂(C₈H₄N₂)₂(H₂O)₂]_n(PF₆)_{2n}, show that irrespective of the counterion, the basic network formed is that of a chain structure. Water molecules located in the unit cell of these structures bridge a pair of adjacent chains by coordinating to silver(I) resulting in ladder-type motifs.

Comment

The use of coordination bonds in the construction of supramolecular networks has received much attention (Carlucci, Ciani, Proserpio & Sironi, 1995; Fujita, Kwon, Washizu & Ogura, 1994; Gardner, Venkataraman, Moore & Lee, 1995; Hoskins & Robson, 1990; Moore & Lee, 1994; Yaghi & Li, 1995). As part of a continuing study on the use of Ag—N bonds for the construction of coordination networks, we were interested in the role of the counterion on the final network motif and hence crystallized the 1,4-dicyanobenzene.AgOTf, (1) (OTf is trifluoromethanesulfonate), and 1,4-dicyanobenzene.AgPF₆, (2), complexes. The basic network in these structures is a one-dimensional chain. Water molecules located in the unit cell bridge a pair of adjacent chains by coordinating to silver(I), forming ladder-type motifs.



(1)



(2)

In the structure of 1,4-dicyanobenzene.AgOTf, (1), silver(I) is four-coordinate and adopts a trigonal pyramidal geometry (Fig. 1). Two nitrile groups of 1,4-dicyanobenzene and an O atom of a water molecule are in the basal plane, with the apical position occupied by an O atom of the trifluoromethanesulfonate anion. The O atom of the water molecule lies on

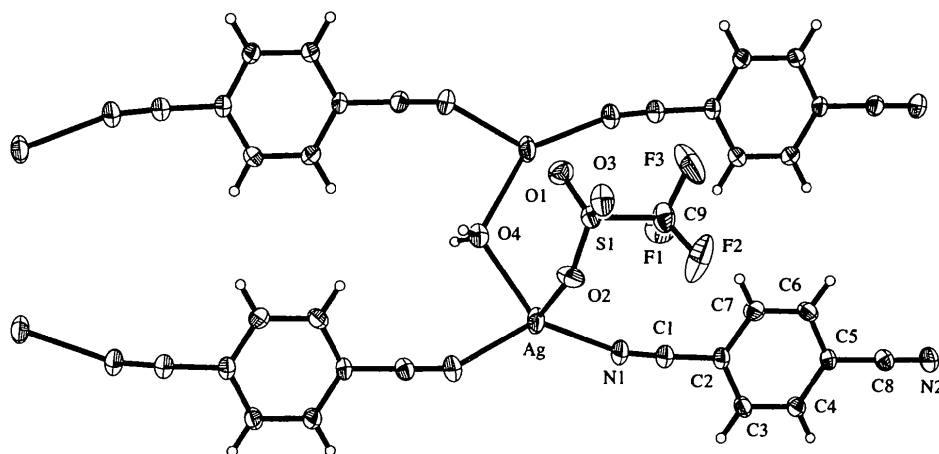


Fig. 1. An *ORTEP* (Johnson, 1971) plot (35% probability ellipsoids) showing the ladder-type motif in the complex of 1,4-dicyanobenzene with silver(I) trifluoromethanesulfonate. Silver(I) adopts a trigonal pyramidal coordination in this complex and is coordinated to two nitrile groups of 1,4-dicyanobenzene, an O atom of a water molecule and an O atom of the trifluoromethanesulfonate anion.

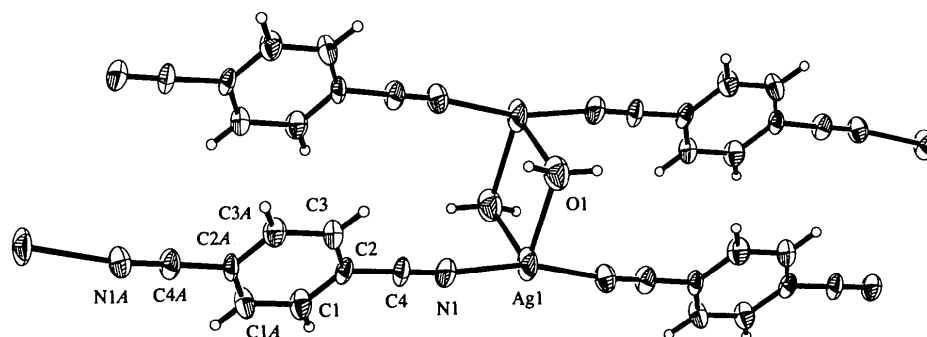


Fig. 2. An *ORTEP* (Johnson, 1971) plot (35% probability ellipsoids) showing the double-rung ladder motif in the complex of 1,4-dicyanobenzene with silver(I) hexafluorophosphate. Silver(I) adopts a saw-horse coordination in this complex and is coordinated to two nitrile groups of 1,4-dicyanobenzene and the O atoms of two water molecules. For clarity, the hexafluorophosphate counterion has not been shown. [Symmetry code: (A) $1 - x, y, z$].

a crystallographic twofold axis. The N—Ag distances are 2.211 (3) and 2.286 (3) Å and the N—Ag—N bond angle is 130.61 (11)°. The Ag—O bond distances for trifluoromethanesulfonate and water are 2.595 (3) and 2.449 (2) Å, respectively. The chains of molecules are cross-linked by O—H···O hydrogen bonds between the water O—H group and the sulfonate O3 atom of a neighboring chain (Table 5).

In the structure of 1,4-dicyanobenzene.AgPF₆, (2), silver(I) adopts a four-coordinate saw-horse geometry (Fig. 2) bonding to two nitrile groups of 1,4-dicyanobenzene and the O atoms of two water molecules. The Ag atom lies on a site of *m* symmetry, while the PF₆[−] anion lies on a crystallographic twofold axis. The aromatic ring lies across a mirror plane and the structural motif lies about sites with *2/m* crystallographic symmetry. The O atom of the water molecule lies on a site with *m* symmetry. The N—Ag bond distance is 2.164 (8) Å. The Ag—O bond distances are 2.513 (13) and 2.569 (13) Å. The N—Ag—N bond angle is 165.9 (5)° and the O—Ag—N

bond angles are 93.9 (2) and 96.0 (2)°. The hexafluorophosphate counterion occupies the space between the chains (Fig. 2). The polymeric cation chains are cross-linked by the PF₆[−] ions *via* pairs of O—H···F hydrogen bonds between the water O—H groups and F1 atoms of adjacent anions (Table 5).

Experimental

For the synthesis of complex (1), a solution of silver(I) trifluoromethanesulfonate (40 mg, 0.15 mmol) in benzene (2 ml) was added slowly to a solution of 1,4-dicyanobenzene (20 mg, 0.156 mmol) in benzene (3 ml) in a clean vial fitted with a Teflon-lined cap. The resulting solution, on standing at ambient temperature overnight, yielded crystals suitable for X-ray analysis. Systematic conditions suggested the space group to be *I2/a* or *Ia*. The space group *I2/a* was chosen and confirmed by refinement. For the synthesis of complex (2), a solution of silver(I) hexafluorophosphate (12.9 mg, 0.051 mmol) in toluene (1 ml) was added to a solution of 1,4-dicyanobenzene (10 mg, 0.078 mmol) in toluene (2 ml) in a clean vial fitted with a Teflon-lined cap. The resulting white precipitate was

then redissolved by the slow addition of ethanol (1 ml). The solution was allowed to evaporate slowly on the bench top. After a week, crystals suitable for X-ray analysis appeared. Systematic conditions suggested the space group to be *Cmca* or *C2cb*. The space group *Cmca* was chosen and confirmed by refinement.

Complex (1)

Crystal data

[Ag₂(CF₃O₃S)₂(C₈H₄N₂)₂(H₂O)]

$M_r = 788.14$

Monoclinic

$I2/a$

$a = 13.032$ (4) Å

$b = 11.948$ (4) Å

$c = 16.295$ (5) Å

$\beta = 103.83$ (2)°

$V = 2463.8$ (13) Å³

$Z = 4$

$D_x = 2.125$ Mg m⁻³

D_m not measured

Data collection

Syntex P2₁ diffractometer

$\omega/2\theta$ scans

Absorption correction:

ψ scan (Siemens, 1995)

$T_{\min} = 0.531$, $T_{\max} =$

0.671

5939 measured reflections

2841 independent reflections

2236 observed reflections

$[I > 2\sigma(I)]$

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 16.29$ – 30.38 °

$\mu = 1.853$ mm⁻¹

$T = 293$ (2) K

Needle

$0.42 \times 0.12 \times 0.05$ mm

Colorless

O3	-0.0909 (2)	0.1635 (2)	0.0194 (2)	0.0475 (6)
O4	1/4	0.0065 (3)	0	0.0396 (7)
N1	0.3263 (2)	0.2879 (2)	0.1786 (2)	0.0465 (7)
N2	0.3423 (2)	0.9469 (2)	0.1964 (2)	0.0459 (7)
C1	0.3327 (3)	0.3821 (2)	0.1854 (2)	0.0387 (7)
C2	0.3391 (2)	0.5021 (2)	0.1890 (2)	0.0334 (6)
C3	0.4051 (2)	0.5559 (2)	0.2574 (2)	0.0364 (6)
C4	0.4087 (2)	0.6711 (2)	0.2591 (2)	0.0352 (6)
C5	0.3451 (2)	0.7314 (2)	0.1931 (2)	0.0308 (6)
C6	0.2781 (2)	0.6769 (3)	0.1254 (2)	0.0380 (7)
C7	0.2749 (3)	0.5631 (3)	0.1235 (2)	0.0411 (7)
C8	0.3458 (2)	0.8518 (3)	0.1953 (2)	0.0362 (6)
C9	0.0399 (3)	0.3216 (3)	0.0175 (3)	0.0502 (9)

Table 2. Selected geometric parameters (Å, °) for (1)

Ag—N1	2.211 (3)	Ag—O4	2.449 (2)
Ag—N2 ⁱ	2.286 (3)	Ag—O2	2.595 (3)
N1—Ag—N2 ⁱ	130.61 (11)	N1—Ag—O2	94.04 (10)
N1—Ag—O4	141.59 (10)	N2 ⁱ —Ag—O2	110.18 (9)
N2 ⁱ —Ag—O4	85.54 (10)		

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

Complex (2)

Crystal data

[Ag₂(C₈H₄N₂)₂(H₂O)₂](PF₆)₂

$M_r = 797.96$

Orthorhombic

Cmca

$a = 12.165$ (3) Å

$b = 13.296$ (9) Å

$c = 15.175$ (8) Å

$V = 2454.7$ (21) Å³

$Z = 4$

$D_x = 2.159$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 9.50$ – 28.95 °

$\mu = 1.840$ mm⁻¹

$T = 293$ (2) K

Needle

$0.29 \times 0.05 \times 0.03$ mm

Colorless

Refinement

Refinement on F^2

$R(F) = 0.0318$

$wR(F^2) = 0.0801$

$S = 1.065$

2841 reflections

183 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0349P)^2 + 3.2994P]$

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

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

$\Delta\rho_{\max} = 0.629$ e Å⁻³

$\Delta\rho_{\min} = -0.986$ e Å⁻³

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0012 (2)

Atomic scattering factors

from *International Tables for Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Data collection

Syntex P2₁ diffractometer

$\omega/2\theta$ scans

Absorption correction:

ψ scan (Siemens, 1995)

$T_{\min} = 0.744$, $T_{\max} =$

0.798

4347 measured reflections

1142 independent reflections

607 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0994$

$\theta_{\max} = 25.05$ °

$h = 0 \rightarrow 14$

$k = -15 \rightarrow 15$

$l = -18 \rightarrow 18$

3 standard reflections

monitored every 97

reflections

intensity decay: 0.3%

Refinement

Refinement on F^2

$R(F) = 0.0674$

$wR(F^2) = 0.1669$

$S = 1.085$

1142 reflections

100 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0653P)^2]$

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

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

$\Delta\rho_{\max} = 0.533$ e Å⁻³

$\Delta\rho_{\min} = -0.543$ e Å⁻³

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0005 (2)

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 (Å²) for (1)

	x	y	z	U_{eq}
Ag	0.29399 (2)	0.11486 (2)	0.13134 (2)	0.04814 (12)
S1	0.01956 (6)	0.17163 (6)	0.02077 (5)	0.0323 (2)
F1	0.1376 (2)	0.3460 (2)	0.0132 (2)	0.0655 (6)
F2	0.0249 (3)	0.3726 (2)	0.0846 (2)	0.1073 (12)
F3	-0.0227 (2)	0.3663 (2)	-0.0513 (2)	0.1009 (12)
O1	0.0470 (2)	0.1324 (2)	-0.05436 (15)	0.0476 (6)
O2	0.0903 (2)	0.1384 (2)	0.0988 (2)	0.0513 (6)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	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 , $^\circ$) 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 , $^\circ$) for compounds (1) and (2)

	D—H...A	D—H	H...A	D...A	D—H...A
(1)	O4—H1...O3 ⁱ	0.75 (3)	2.13 (3)	2.866 (4)	169 (3)
(2)	O1—H1A...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 ($C-H = 0.93 \text{\AA}$) and the U values were assigned as $1.2U_{\text{eq}}$ 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: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1971); software used to prepare material for publication: *CIFTAB* in *SHELXL93*.

We thank the School of Chemical Sciences Materials Characterization Laboratory at the University of Illinois for X-ray data collection and the National Science Foundation (grant CHE-94-23121) for financial assistance. JSM gratefully acknowledges additional support from the 3M Company and the Camille Dreyfus Teacher-Scholar Awards Program. SL thanks the A. P. Sloan Foundation (1993–1995) and the J. D. and C. T. MacArthur Foundation (1993–1997) for fellowships.

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.

References

- Blessing, R. H., Coppens, P. & Becker, P. (1974). *J. Appl. Cryst.* **7**, 488–492.
- Carlucci, L., Ciani, G., Proserpio, D. M. & Sironi, A. (1995). *J. Am. Chem. Soc.* **117**, 4562–4569.
- Fujita, M., Kwon, Y. J., Washizu, S. & Ogura, J. (1994). *J. Am. Chem. Soc.* **116**, 1151–1152.
- Gardner, G. B., Venkataraman, D., Moore, J. S. & Lee, S. (1995). *Nature*, **374**, 792–795.
- Hoskins, B. F. & Robson, R. (1990). *J. Am. Chem. Soc.* **112**, 1546–1554.
- Johnson, C. K. (1971). *ORTEPII*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
- Moore, J. S. & Lee, S. (1994). *Chem. Ind.* pp. 556–560.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1995). *SHELXTL*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Strouse, C. E. (1988). *Crystal Logic. Programs for Automated Collection of Step-Scan Data*. University of California at Los Angeles, California, USA.
- Yaghi, O. M. & Li, G. M. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 207–209.

Acta Cryst. (1996). **C52**, 2419–2422

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

KEITH A. HIRSCH,^a SCOTT R. WILSON^a AND JEFFREY S. MOORE^b

^aDepartment of Chemistry, University of Illinois, Urbana, Illinois 61801, USA, and ^bDepartments of Chemistry and Materials Science & Engineering, University of Illinois, Urbana, Illinois 61801, USA. E-mail: moore@aries.scs.uiuc.edu

(Received 8 January 1996; accepted 22 April 1996)

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*]], $[\text{Ag}_2(\text{F}_2\text{O}_2\text{P})_2(\text{C}_{16}\text{H}_8\text{N}_2)]_\infty$, 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