A Binuclear Monofluoro-Bridged Tricoordinate Silver(I) Complex. The X-ray Molecular Structure of μ-Fluorobis{2,11-bis(diphenylphosphinomethyl)benzo[*c*]-phenanthrene}disilver(I) Tetrafluoroborate

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Single-crystal X-ray diffraction studies have been completed on the binuclear complex μ-fluorobis{2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene}disilver(I) tetrafluoroborate, $[(1)Ag(\mu_2\text{-}F)Ag(1)]BF_4$. *Crystal data are:* $a = 12.555(2)$, $b = 13.322(2)$, $c = 13.949(3)$ Å, $\alpha = 97.97(1)$, $\beta = 109.31(2)$, $\gamma = 117.32(1)^\circ$; *space group P1;* $R = 6.9\%$ *for 4747 reflections. The cationic binuclear complex consists of two* $Ag(1)^+$ *units, formed by chelation of the bidentate ligand 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene, 1, through its P donor atoms, held together by a* F^- *anion.*

Introduction

Complexes Ag(*1*)X, in which *1* is the bidentate diphosphine 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene [1] and X an anionic ligand, have simple monomeric structures [2]. During the study of the molecular structure of some of these complexes, we intended to determine the crystal structure of the complex Ag(*1*)(BF_4) for which the ionic form $Ag(1)^+BF_4^-$ with a linear 2-coordinate species for the cation would be expected.

Several crystallization attempts using various solvents were made to obtain single crystals, suitable for X-ray analysis, starting from the product which was supplied by Professor L. M. Venanzi, ETH, Zurich.

Very few colourless, well-formed crystals were obtained only from acetone, and the X-ray analysis was undertaken using these crystals. After the resolution it became evident that the compound under examination was the species $[(1)Ag(\mu_2\text{-}F)Ag(1)]BF_4$.

Decomposition of the BF_4^- ion into F^- and BF_3 can occur in many reactions of transition metal tetrafluoroborate with sterically hindered ligands [3].

During the attempts of crystallization the reaction

$$2Ag(1)(BF_4) \rightarrow [(1)Ag(\mu_2\text{-}F)Ag(1)]BF_4$$

probably has occurred, giving rise to the first example of a fluoro-bridged binuclear complex of silver. The BF_3 freed in this reaction is probably coordinated to solvent molecules.

The structure of the fluorobridged binuclear complex of silver is reported here.

Experimental

Crystals of $[(1)Ag(\mu_2\text{-}F)Ag(1)]BF_4$ are triclinic, as indicated by a preliminary photographic study. Measurement of cell constant and data collection proceeded on a Syntex $P2_1$ computer-controlled diffractometer. A summary of crystal parameters, with various details concerning the experimental data, are given in Table I.

TABLE I. Summary of Crystal Data and Intensity Collection Details.

Compd	$[(1)Ag(\mu_2\text{-}F)Ag(1)]BF_4$
Formula	$C_{88}H_{68}Ag_2BF_5P_2$
Fw	1570.950
a, Å	12.555(2)
b, Å	13.322(2)
c, Å	13.949(3)
α, deg	97.97(1)
β, deg	109.31(2)
γ, deg	117.32(1)
V, $Å^3$	1835.2(6)
Z	1
Density, g cm^{-3} (calcd)	1.421
Space group	$P1$
Crystal dimensions (mm^3)	0.20 × 0.25 × 0.25
Radiation	CuKα (graphite monochromatized)
μ, cm^{-1}	56.7
Scan mode	ω-scan
Scan range (deg)	0.85
Bkd counts	0.5 the scan time at ±0.47°
2ϑ limits (deg)	3–116
Observations, total no.	5307
No. unique data $F_0^2 > 3\sigma(F_0^2)$	4747
Final no. of variables	343
Final R, R_w	0.069, 0.078

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TABLE II. Final Positional Parameters.[a]

	x	*y*	*z*		*x*	*y*	*z*
AG(1)	0	0	0	C(44)	-2665(10)	-16(9)	2759(10)
AG(2)	583(1)	-3136(1)	-1747(1)	C(45)	-2696(10)	-1066(9)	2415(10)
F	-79(7)	-1684(7)	-1203(5)	C(46)	-1692(11)	-1016(8)	2164(9)
P(1)	600(5)	134(4)	1870(3)	C(47)	890(16)	-963(12)	2303(12)
P(2)	-486(4)	979(3)	-1269(3)	C(48)	730(16)	-1895(14)	1558(9)
P(3)	-1097(4)	-4545(4)	-3545(3)	C(49)	905(16)	-2773(12)	1883(11)
P(4)	2940(3)	-2179(3)	-388(3)	C(50)	1240(16)	-2718(12)	2953(12)
C(1)	3623(17)	2409(15)	1889(13)	C(51)	1401(16)	-1786(14)	3698(9)
C(2)	3349(15)	1827(14)	2570(12)	C(52)	1226(16)	-908(12)	3373(11)
C(3)	4269(21)	1550(19)	3180(17)	C(53)	-430(14)	2311(10)	-720(10)
C(4)	5514(19)	2024(17)	3095(15)	C(54)	-300(14)	2613(11)	327(10)
C(5)	7181(20)	3397(18)	2643(16)	C(55)	-353(14)	3594(12)	737(8)
C(6)	7533(20)	4204(18)	2196(16)	C(56)	-536(14)	4273(10)	101(10)
C(7)	7007(21)	5239(19)	950(17)	C(57)	-666(14)	3971(11)	-945(10)
C(8)	6106(21)	5304(19)	205(17)	C(58)	-613(14)	2990(12)	-1356(8)
C(9)	3754(18)	4433(16)	-1168(14)	C(59)	-2154(10)	-3(10)	-2398(9)
C(10)	2421(18)	3473(16)	-1691(15)	C(60)	-2365(9)	-919(11)	-3199(10)
C(11)	1978(14)	2498(13)	-1332(11)	C(61)	-3632(12)	-1699(10)	-4068(8)
C(12)	2875(15)	2511(13)	-410(12)	C(62)	-4687(10)	-1564(10)	-4136(9)
C(13)	4872(16)	2865(15)	1803(13)	C(63)	-4475(9)	-648(11)	-3334(10)
C(14)	5798(18)	2662(16)	2487(14)	C(64)	-3209(12)	133(10)	-2465(8)
C(15)	4216(16)	3513(14)	158(13)	C(65)	-2703(16)	-4734(34)	-3916(10)
C(16)	4677(18)	4411(17)	-255(15)	C(66)	-2987(15)	-4471(28)	-3066(9)
C(17)	5181(16)	3535(14)	1112(13)	C(67)	-4232(13)	-4637(14)	-3281(8)
C(18)	6605(17)	4368(16)	1415(14)	C(68)	-5194(16)	-5067(34)	-4347(10)
C(19)	2148(18)	1598(16)	2816(12)	C(69)	-4909(15)	-5331(28)	-5197(9)
C(20)	601(16)	1432(15)	-1978(11)	C(70)	-3664(13)	-5165(14)	-4982(8)
C(21)	901(15)	-1728(14)	-3748(12)	C(71)	-1470(10)	-6084(7)	-3913(9)
C(22)	-288(16)	-2763(14)	-4459(13)	C(72)	-595(9)	-6325(9)	-4141(9)
C(23)	-1328(18)	-2658(16)	-5216(14)	C(73)	-891(9)	-7499(9)	-4421(9)
C(24)	-1079(22)	-1570(20)	-5233(18)	C(74)	-2062(10)	-8432(7)	-4473(9)
C(25)	543(19)	609(17)	-4755(15)	C(75)	-2937(9)	-8191(9)	-4246(9)
C(26)	1771(21)	1504(19)	-4287(17)	C(76)	-2641(9)	-7017(9)	-3965(9)
C(27)	4219(27)	2526(25)	-2946(22)	C(77)	4041(9)	-2285(12)	-944(7)
C(28)	5104(25)	2529(23)	-2222(20)	C(78)	3494(7)	-2983(16)	-2021(7)
C(29)	5782(24)	1780(21)	-709(19)	C(79)	4326(9)	-3056(11)	-2447(7)
C(30)	5490(22)	1086(20)	-113(18)	C(80)	5703(9)	-2430(12)	-1796(7)
C(31)	4115(17)	149(15)	-472(14)	C(81)	6249(7)	-1732(16)	-719(7)
C(32)	3181(16)	-34(15)	-1432(13)	C(82)	5418(9)	-1659(11)	-293(7)
C(33)	1181(15)	-573(14)	-3740(12)	C(83)	3269(15)	-2740(12)	724(9)
C(34)	174(17)	-520(16)	-4574(14)	C(84)	3709(15)	-2054(10)	1780(11)
C(35)	3456(16)	655(14)	-2100(13)	C(85)	3943(15)	-2511(12)	2612(9)
C(36)	4844(19)	1650(17)	-1643(15)	C(86)	3737(15)	-3654(12)	2387(9)
C(37)	2496(18)	522(16)	-3088(14)	C(87)	3296(15)	-4341(10)	1331(11)
C(38)	2811(19)	1529(17)	-3444(16)	C(88)	3062(15)	-3884(12)	499(9)
C(39)	-501(16)	-3987(14)	-4528(12)	B	1488(21)	4673(24)	4200(17)
C(40)	3769(18)	-553(16)	253(14)	F(1)	257(13)	4341(19)	3582(15)
C(41)	-658(10)	82(9)	2256(10)	F(2)	1901(25)	4270(29)	3485(21)
C(42)	-627(10)	1131(9)	2599(10)	F(3)	2342(26)	5740(17)	4591(25)
C(43)	-1631(11)	1082(8)	2850(9)	F(4)	1591(17)	4062(21)	4853(18)

[a] For the rigid group atoms the derived parameters are tabulated. Rigid group parameters and thermal parameters have been deposited.

Three standard reflections were re-measured after every 100 reflections. Their intensities were constant throughout the run. The 5307 collected reflections were processed as previously described [4] using factor $p = 0.011$. 4774 reflections had $F_0^2 > 3\sigma(F_0^2)$ and were used in subsequent calculations.

The structure was solved by the heavy atom method and refined by least-squares procedures. The isotropic refinement converged at $R = 0.101$. The refinement was continued allowing the non-hydrogen non-sp^2 carbon atoms to vibrate anisotropically. Each phenyl ring was treated as a rigid body restricted to its idealized geometry ($6/mmm$ symmetry, d(C–C) = 1.392, d(C–H) = 1.0 Å) with one overall isotropic thermal parameter per ring. The fixed contribution of the hydrogen atoms was included into the calculations with idealized positions and isotropic temperature factors of the nearest carbon atoms. Convergence was reached at $R = 0.069$ ($R_w = 0.078$). A block-diagonal approximation of the equation matrix was adopted during the refinement and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = \sin\vartheta/\lambda$.

Scattering factors and anomalous dispersion terms were taken from *International Tables for X-ray Crystallography* [5]. All calculations were performed using local programs on the Univac 1110 of the University of Rome [6] and on the HP 21MX minicomputer of the CNR Research Area of Rome [7]. Final positional parameters are tabulated in Table II. Listings of the observed and calculated amplitudes are available on request from the authors.

Results and Discussion

Description of the Structure of [(1)Ag(μ_2-F)Ag(1)]-BF_4

The crystal structure of this complex consists of the packing of monofluorobridged binuclear silver cations and non-interacting tetrafluoroborate anions. A perspective drawing with atom labelling of the cation is shown in Fig. 1. A listing of selected bond distances and angles in the $[(1)\mathrm{Ag}(\mu_2\text{-F})\mathrm{Ag}(1)]^+$ moiety is given in Table III.

The two silver atoms have distorted trigonal coordination, being bonded to two phosphorus and one fluorine atoms.

In each $\mathrm{Ag}(1)^+$ moiety the chelated ligand *1* has almost identical conformation, as indicated by the values of the internal torsion angles of the twelve-membered ring generated by chelation of *1* on the metal centre, Table IV. Such conformation is characteristic for those complexes of *1* in which the P–M–P angle is far from 180° [8], and was observed for other silver complexes of the type Ag(*1*)X (X = Cl^- $\mathrm{NO_3}^-$, $\mathrm{ClO_4}^-$) [9, 10], all having the P–Ag–P angle near to 150°.

The two independent $\mathrm{Ag}(1)^+$ moieties are held together by a F^- anion which is bonded to the two Ag atoms, giving rise to the binuclear fluoro-bridged complex $[(1)\mathrm{Ag}(\mu_2\text{-F})\mathrm{Ag}(1)]^+$ with a Ag···Ag separation of 5.009(1) Å.

In the binuclear complex the two ligands *1* are faced but rotated by ~50° one with respect to the other. No short contacts between atoms of the two units are observed.

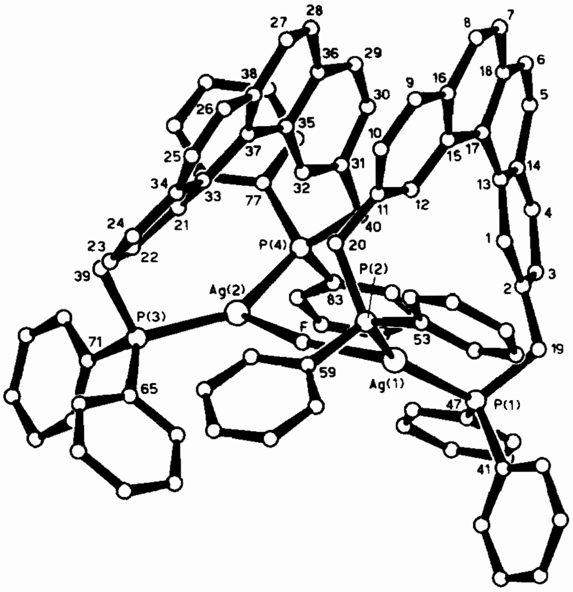

Fig. 1. Perspective view of the cation $[(1)\mathrm{Ag}(\mu_2\text{-F})\mathrm{Ag}(1)]^+$.

TABLE III. Selection of Interatomic Distances and Interbond Angles in the $[(1)\mathrm{Ag}(\mu_2\text{-F})\mathrm{Ag}(1)]^+$ Cation.

	Å		°
Ag(1)···Ag(2)	5.009(1)	P(1)–Ag(1)–P(2)	143.5(2)
Ag(1)–P(1)	2.419(5)	P(1)–Ag(1)–F	116.1(2)
Ag(1)–P(2)	2.422(4)	P(2)–Ag(1)–F	100.3(2)
Ag(1)–F	2.549(9)	Ag(1)–F–Ag(2)	158.6(5)
Ag(2)–F	2.548(8)	P(3)–Ag(2)–P(4)	144.9(1)
Ag(2)–P(3)	2.413(7)	P(3)–Ag(2)–F	108.2(3)
Ag(2)–P(4)	2.477(7)	P(4)–Ag(2)–F	104.3(3)
P(1)–C(19)	1.85(4)	Ag(1)–P(1)–C(19)	112.0(6)
P(1)–C(41)	1.81(1)	Ag(1)–P(1)–C(41)	111.4(6)
P(1)–C(47)	1.80(2)	Ag(1)–P(1)–C(47)	119.1(7)
P(2)–C(20)	1.87(2)	C(19)–P(1)–C(41)	104.0(9)
P(2)–C(53)	1.79(2)	C(19)–P(1)–C(47)	104.1(12)
P(2)–C(59)	1.82(2)	C(41)–P(1)–C(47)	104.9(8)
P(3)–C(39)	1.86(2)	Ag(1)–P(2)–C(20)	115.9(6)
P(3)–C(65)	1.79(3)	Ag(1)–P(2)–C(53)	115.4(6)
P(3)–C(71)	1.83(1)	Ag(1)–P(2)–C(59)	112.2(9)
P(4)–C(40)	1.83(3)	C(20)–P(2)–C(53)	104.9(10)
P(4)–C(77)	1.84(1)	C(20)–P(2)–C(59)	102.1(10)
P(4)–C(83)	1.82(1)	C(53)–P(2)–C(59)	104.8(9)
C(2)–C(19)	1.56(3)	Ag(2)–P(3)–C(39)	108.2(10)
C(11)–C(20)	1.48(4)	Ag(2)–P(3)–C(65)	114.4(12)
C(22)–C(39)	1.51(3)	Ag(2)–P(3)–C(71)	119.0(6)
C(31)–C(40)	1.51(3)	C(39)–P(3)–C(65)	107.4(10)
		C(39)–P(3)–C(71)	102.4(8)
		C(65)–P(3)–C(71)	104.4(19)
		Ag(2)–P(4)–C(40)	112.4(9)
		Ag(2)–P(4)–C(77)	114.5(6)
		Ag(2)–P(4)–C(83)	118.2(9)
		C(40)–P(4)–C(77)	103.0(10)
		C(40)–P(4)–C(83)	105.4(11)
		C(77)–P(4)–C(83)	101.7(6)
		C(2)–C(19)–P(1)	111.4(16)
		C(11)–C(20)–P(2)	116.5(14)
		C(22)–C(39)–P(3)	111.5(12)
		C(31)–C(40)–P(4)	113.6(18)

TABLE IV. Parameters Defining the Conformation of *1* in the Binuclear Complex $[(1)Ag(\mu_2\text{-}F)Ag(1)]^+$.

Relevant torsion angles (deg) internal at the twelve membered rings			
C(1)–C(2)–C(19)–P(1)	91	C(21)–C(22)–C(39)–P(3)	87
C(2)–C(19)–P(1)–Ag(1)	−57	C(22)–C(39)–P(3)–Ag(2)	−60
C(12)–C(11)–C(20)–P(2)	61	C(32(–C(31)–C(40)–P(4)	60
C(11)–C(20)–P(2)–Ag(1)	−75	C(31)–C(40)–P(4)–Ag(2)	−74
Dihedral angles			
C(19)–P(1)···P(2)–C(20)	62	C(39)–P(3)···P(4)–C(40)	70

The coordination planes of the two silver atoms, defined by P(1), P(2), F and P(3), P(4), F respectively, make a dihedral angle of 53.60°. While Ag(1) almost lies on both planes (it is 0.05 Å out from the former and 0.03 Å from the latter), Ag(2) is 0.63 and 0.22 Å respectively out from the two planes.

The Ag···Ag separation in $[(1)Ag(\mu_2\text{-}F)Ag(1)]^+$ is very large: it has the maximum value observed in polynuclear silver complexes [11–14].

The Ag–F bonds have the same length [2.549(9) and 2.548(8) Å]. They exceed (by 0.57 Å) the standard distance given by the sum of the single bond covalent radii (1.979 Å) [15], and are only 0.07 Å shorter than the sum of the ionic radii (2.62 Å) [15]. The character of the Ag–F bonds can be described as prevailingly ionic.

The Ag–F–Ag angle [158.6(5)°] is very large and strikingly different from the value of 98.8° observed for the Co–F–Co angle in the centrosymmetrical binuclear complex $[(C_5H_8N_2)_3Co(\mu_2\text{-}F)_2Co(C_5H_8N_2)_3]^{++}$, having two fluoro-bridges, in which one of the two Co–F bonds (1.924 and 2.146 Å) has high covalent character [16, 17]. It is also far from the values of the Ag–X–Ag ($X = Cl^-$, Br^-, I^-) angles, which in many cases do not differ much from 90°, observed in several complexes containing X-bridges and Ag–X bonds with high covalent character [11–14].

The P–Ag–P angles are very similar and average 144.2(1)°, a value slightly higher than that observed in Ag(*1*)Cl [140.74(3)°] [9].

The four Ag–P bonds have lengths which agree with the sum of the single bond covalent radii (2.439 Å) [15] and fall in the range (2.38–2.52 Å) normally found for silver–phosphine complexes. Three of them are almost equivalent and average 2.418(5) Å, while the fourth [Ag(2)–P(4), 2.477(7) Å] is slightly but significantly longer (by ~8.50 σ). No explanation is evident for this difference.

The geometry of the BF_4^- anion fits well with that determined elsewhere [18]. B–F distances range from 1.21(6) to 1.42(4) Å and F–B–F angles from 100(2) to 118(3)°.

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References

1 N. J. De Stefano, D. K. Johnson, R. M. Lane and L. M. Venanzi, *Helv. Chim. Acta, 59*, 2674 (1976).
2 D. K. Johnson, P. S. Pregosin and L. M. Venanzi, *Helv. Chim. Acta, 59*, 2691 (1976).
3 R. W. M. Ten Hoedt and J. Reedijk, *Inorg. Chim. Acta, 51*, 23 (1981).
4 F. Bachechi, L. Zambonelli and G. Marcotrigiano, *J. Cryst. Mol. Structure, 7*, 11 (1977).
5 *International Tables for X-ray Crystallography*, vol. IV, Kynoch Press, Birmingham, England, 1974.
6 J. R. Carruthers and R. Spagna, *Ital. Crystallogr. Assoc., 7th Meet.*, Abstract, 1975, 65.
7 S. Cerrini and R. Spagna, *4th Europ. Crystallogr. Meet.*, Abstracts, 1977, 7.
8 G. Bracher, D. M. Grove, L. M. Venanzi, F. Bachechi, P. Mura and L. Zambonelli, *Helv. Chim. Acta, 63*, 2519 (1980).
9 M. Barrow, H. B. Burgi, D. K. Johnson and L. M. Venanzi, *J. Amer. Chem. Soc., 98*, 2356 (1976).
10 M. Camalli, F. Caruso and L. Zambonelli, submitted to *Inorg. Chem.*
11 A. Cassel, *Acta Crystallogr., B32*, 2521 (1976).
12 A. Cassel, *Acta Crystallogr., B35*, 174 (1979).
13 B. K. Teo and J. C. Calabrese, *J.C.S. Chem. Comm.*, 1976, 185.
14 B. K. Teo and J. C. Calabrese, *Inorg. Chem., 15*, 2474 (1976).
15 L. Pauling, 'The Nature of the Chemical Bond', Third Edition, Cornell University Press, Ithaca, 1960.
16 C. G. Van Kralingen and J. Reedijk, *J.C.S. Chem. Comm.*, 1976, 533.
17 J. C. Jansen and H. Van Koningsveld, *Cryst. Struct. Comm., 5*, 441 (1976).
18 D. S. Milbrath, J. P. Springer, J. C. Clardy and J. G. Verkade, *Inorg. Chem., 14*, 2665 (1975).