

# Bis(N,N'-diphenylformamidine)silver(I) triflate: a three-coordinate silver formamidine compound stabilized by intramolecular hydrogen bonds

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# (Received 12 August 1996; accepted 2 October 1996)

Abstract—A formally three-coordinate silver(I) complex,  $Ag(HDPhF)_2(OSO_2CF_3)$  (1), has been prepared from the reaction of  $AgSO_3CF_3$  with HDPhF (HDPhF = N,N'-diphenylformamidine) in toluene and characterized through spectroscopic methods and single-crystal X-ray diffraction studies. The silver atom is bound through one nitrogen atom each to two neutral formamidine ligands and weakly coordinated to the triflate anion through an oxygen atom. The  $AgN_2O$  group is practically planar with an N—Ag—N angle of  $142.3(2)^{\circ}$  and O—Ag—N angles of 122.4(2) and  $92.0(1)^{\circ}$ . Hydrogen bonding possibly related to the mechanism of formamidine cleavage seen in other complexes occurs between oxygen atoms of the triflate anion and amine hydrogen atoms in 1. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: silver; three-coordinate; hydrogen bonding; crystal structure; formamidine complex.

Although formamidinates  $[RNC(H)NR]^-$  can bind in a variety of modes [1], we have been interested in them primarily as bridging ligands in dinuclear molecules which contain metal-metal bonds [2]. We have found that one of the best methods for preparing divalent compounds is to react MCl<sub>2</sub>(formamidine)<sub>2</sub> complexes [3] with methyllithium, which deprotonates the neutral ligands to afford compounds of the type  $M_2$ (formamidinate)<sub>4</sub> [4].

More recently we have observed that under suitable conditions, formamidines or formamidinate ligands undergo cleavage at a C—N bond. For example, a tantalum compound containing both the RNCH and NR fragments of a formamidinate ligand has been isolated in our laboratory [5]. In other cases, the ligand fragments react further with other ligands attached to the metal ion to produce new species as in the reaction of VO(acac)<sub>2</sub> with HDPhF shown in the scheme below [6].

We believe that in many of these reactions the formamidine probably binds to the metal center before undergoing cleavage. For this reason, it is important to study the bonding modes of formamidines in various complexes. As mentioned above, we have synthesized and studied several compounds in which the tetrahedrally coordinated central atom is bound to two halide ions and to two neutral formamidines; however, no other compounds of this type having other coordination geometries have been studied in detail.

While attempting oxidations with silver ions in the presence of formamidines, we observed that coordination can also occur between  $Ag^+$  and HDPhF. It is well known that silver can form a variety of compounds having different coordination numbers. For example, silver in its +1 oxidation state most commonly exhibits twofold linear or fourfold tetrahedral coordination [7], but there are also complexes

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known in which  $Ag^{1}$  is formally three-coordinate. Among these are  $(Me_{2}NC_{6}H_{4}PEt_{2})_{2}AgI$  [7], diphenyl bis(pyrazolyl)borate complexes [8], and mononuclear and dihalide-bridged dinuclear complexes containing tricyclohexylphosphine [9]. In this paper we report the synthesis and characterization of the three-coordinate mononuclear complex  $Ag(HDPhF)_{2}SO_{3}CF_{3}$  (1) (HDPhF = N,N'-diphenylformamidine) in which each ligand is bound to  $Ag^{1}$  through one nitrogen atom or an oxygen atom of a weakly coordinated triflate anion.

# **EXPERIMENTAL**

#### General procedures

The reaction was performed under dry nitrogen, but the solid product was handled in air; measures were taken to protect the reaction mixture and the product from light, however. Toluene and hexanes were freshly distilled under nitrogen from sodium/ potassium benzophenone ketyl. N,N'-diphenylformamidine and silver triflate were purchased from Aldrich Chemical Co.; the HDPhF was washed with warm ethanol and dried under reduced pressure prior to use. The IR spectrum of 1 was obtained on a Perkin Elmer 16 PC FT-IR spectrometer using a KBr matrix. The <sup>1</sup>H NMR spectrum was obtained on a Varian 200XL-E spectrometer in CD<sub>2</sub>Cl<sub>2</sub>. Elemental analyses were performed by Canadian Microanalytical Services, Ltd.

# Preparation

In a typical experiment 0.25 g  $(9.7 \times 10^{-4} \text{ mole})$  of AgSO<sub>3</sub>CF<sub>3</sub> and 0.39 g  $(2.0 \times 10^{-3} \text{ mole})$  of HDPhF were combined in a flask which was then evacuated for about 1 h to remove any residual moisture. About 30 cm<sup>3</sup> of toluene was added, whereupon nearly all of the solid dissolved. The reaction mixture was refluxed for 1 h to afford a clear solution with a slight beige tint. About 50 cm<sup>3</sup> of isomeric hexanes was layered

onto the cooled mixture; after a week, colorless crystals had formed and the mixture was placed in a freezer overnight. An additional 20 cm3 of hexanes was added and the mixture was stirred and replaced in the freezer. The product, a pale beige-colored semicrystalline solid, precipitated and was collected by filtration. The yield was 0.36 g (57.3% based on AgSO<sub>3</sub>CF<sub>3</sub>). IR  $(cm^{-1})$ : 2962(w), 1681(s), 1587(s), 1488(s), 1449(w), 1261(s), 1209(m), 1166(m), 1098(m), 1025(s), 987(w), 912(w), 900(w), 805(s), 754(s), 695(s), 652(m), 634(m), 601(w), 575(w), 518(m), 506(m), 431(w). <sup>1</sup>H NMR (ppm): complex multiplets of split peaks centered at 7.20 and 7.35 (phenyl C-H protons), sharp singlet at 8.25 (methine protons). Elemental analysis: Found: C, 49.6; N, 8.6; H, 3.8. Calc: C, 49.9; N, 8.6; H, 3.7%. Single crystals suitable for X-ray diffraction studies were obtained by combining about 40 mg of 1 with 10 cm<sup>3</sup> of toluene, filtering off any undissolved material, layering the solution in a Schlenk tube with 15 cm<sup>3</sup> of hexanes, and placing the tube in a freezer. Needlelike crystals formed within two weeks.

### X-ray crystallography

Data were collected on a Rigaku AFC5R diffractometer (Cu- $K_x$  radiation) equipped with a rotating anode at room temperature using procedures described elsewhere [10]. A set of 25 reflections for cell indexing were found using an automated search routine. The cell dimensions and Laue group were confirmed with axial photographs. Data were collected using  $\omega$ -2 $\theta$  scans and corrected for Lorentz and polarization effects; an absorption correction based on  $\psi$ -scans was applied. The structure was developed using SHELXS-86 and SHELXL-93 [11]. All of the non-hydrogen atoms were found in a direct methods E-map; the hydrogen atoms were placed in idealized positions. All of the atoms were refined anisotropically by full-matrix least-squares methods; the refinement on  $F^2$  converged to  $R_1 = 0.042$ , wR2 = 0.102 for  $I > 2\sigma(I)$ . Other information pertinent to the data collection and structure solution are

given in Table 1. A representation of 1 showing the atom labeling scheme is given in Fig. 1. Selected bond lengths and angles are given in Table 2. Supplementary data have been deposited with the Cambridge Crystallographic Data Centre.\*

#### **RESULTS AND DISCUSSION**

The reaction between AgSO<sub>3</sub>CF<sub>3</sub> and HDPhF in toluene produces  $Ag(HDPhF)_2SO_3CF_3$  (1), a threecoordinate complex in which two neutral formamidine ligands are each bound via one nitrogen atom to the silver ion and the triflate anion is bound through an oxygen atom as shown in Fig. 1. The Ag-N distances are 2.179(4) Å and 2.206(4) Å while the Ag-O distance is relatively long at 2.575(4) Å. The N—Ag—N angle is 142.3(2)° and the silver atom is located 0.40 Å out of the plane defined by the oxygen and nitrogen atoms coordinated to the metal atom. The Ag-N distances in 1 are comparable to those found in Ag(en)ClO<sub>4</sub> [12] (2.17(1) Å) which exhibits linear twofold coordination, but longer than those found in  $[Ag(NH_3)_2]Ag(NO_2)_2$  [13] (2.112(6) and 2.117(6) Å) which also contains linear N-Ag-N units; they are, however, shorter than those found in the planar, three-coordinate complex Ag(dmp)NO<sub>3</sub> [14] (dmp = dimethylphenanthroline) (2.283(6) and 2.300(5) Å) and in the nearly tetrahedral complex  $Ag(py)_4ClO_4$  [15] (py = pyridine) (2.322(3) Å).



Fig. 1. Thermal ellipsoid plot of  $Ag(HDPhF)_2SO_3CF_3$ . Atoms are represented by their 50% probability ellipsoids.

Threefold coordination is uncommon for Ag<sup>1</sup> complexes; consequently, there are few opportunities available for comparison of 1 with known compounds. Bruce and coworkers have reported the structure of Ag[P(p-MeC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>][BPh<sub>2</sub>(pyrazolyl)<sub>2</sub>] [8], and while this complex is not strictly analogous to 1, it displays a similar coordination geometry about the silver atom, which is bound to the pyrazolyl nitrogen atoms at 2.194(4) Å and 2.411(4) Å and to the phosphorus atom at 2.351(1) Å; the larger of the P—Ag—N angles is  $160.3(1)^\circ$ . In this case, as in that of 1, the silver atom in its +1 oxidation state is bound to two ligands and weakly coordinated to a third; this coordination is relatively weak as born out by the long bond distances, but strong enough to cause significant deviation of the P-Ag-N and N-Ag-N angles from the linearity common to two-coordinate Ag<sup>1</sup> complexes.

Our interest in 1 lies primarily in the coordination mode of and the hydrogen bonding exhibited by the neutral formamidine ligands through the N(4)—O(3) and N(2)—O(2) distances of 2.950(6) Å and 2.966(6) Å, respectively. With the hydrogen atoms placed in idealized positions, the H(4A)···O(3) distance is 2.127 Å and the O(2)···H(2A) distance is 2.167 Å; the O(3)—H(4A)—N(4) and O(2)—H(2A)—N(2) angles are 160.0 and 154.3°, respectively. These molecular dimensions are consistent with the presence of hydrogen bonds.

Cleavage of formamidines during reactions with transition metals has been observed in several instances in our laboratories, notably in the reaction between VO(acac)<sub>2</sub> and HDPhF with concomitant release of aniline [6]. We believe that hydrogen bonding similar to that exhibited in 1 by the amine hydrogen atoms of the neutral formamidine ligands may play a crucial role in the mechanism by which the ligands are cleaved in other reactions. It is possible that in the reaction between VO(acac)<sub>2</sub> and HDPhF, the formamidine initially coordinates to the metal atom at the vacant site opposite to the vanadyl oxygen atom to form a pseudooctahedral intermediate stabilized by hydrogen bonding between the amine hydrogen atom and a coordinated acac oxygen atom. The coordinated HDPhF would then attack the methyl carbon of the acac and subsequently undergo C-N bond cleavage to release aniline and form the new ligand 6-(phenylamino)-2,4-hexanedionate. The pseudooctaheral intermediate would display an O--V-N angle of approximately 90°. One of the formamidines in 1 is coordinated in just such a manner, forming an angle of  $92.0(1)^\circ$  with the silver atom and the coordinated triflate oxygen atom shown in Fig. 2. This fact and the presence of stabilizing intramolecular hydrogen bonding in 1 lends credence to our assumptions regarding the mechanism by which HDPhF is cleaved during its reaction with VO(acac)<sub>2</sub>. Further investigations into the chemistry of amidine ligands, particularly into their cleavage reactions, are currently underway in our laboratories.

<sup>\*</sup>Supplementary material available: Tables of positional parameters, full tables of displacement parameters and molecular dimensions (7 pages).

Formula	$C_{27}H_{24}AgF_3N_4O_3S$
Formula weight	649.43
Space group	$P2_{1}/c$
a (Å)	15.728(2)
b (Å)	7.406(3)
$c(\mathbf{A})$	23.855(2)
$\alpha(\circ)$	90
$\beta(^{\circ})$	98.150(9)
$\gamma(^{\circ})$	90
$V(Å^3)$	2751(1)
Ζ	4
$d_{\rm calc}({\rm g~cm^{-3}})$	1.568
Crystal size (mm <sup>3</sup> )	$0.30 \times 0.20 \times 0.20$
Absorption coefficient (mm <sup>-1</sup> )	7.084
Data collection instrument	Rigaku AFC5R
Radiation (monochromated in incident beam)	$Cu-K_{\alpha}$ ( $\lambda_{\alpha} = 1.54184$ Å)
Temperature (K)	293(2)
Data collection range, $\theta(^{\circ})$	2.84 to 60.10
Number of unique data, total with $F_0^2 > 2\sigma(F_0^2)$	4100
Number of parameters refined	352
R <sub>w</sub> <sup>a</sup>	0.042
$wR2^b$	0.102
Quality-of-fit indicator <sup>e</sup>	1.027

Table 1. Crystal data for Ag(HDPhF)<sub>2</sub>SO<sub>3</sub>CF<sub>3</sub>

 ${}^{a}R_{w} = [\Sigma w(F_{0} - F_{c})^{2}/\Sigma wF_{0}^{2}]^{1/2}.$   ${}^{b}wR2 = [\Sigma w(F_{0}^{2} - F_{c}^{2})^{2}/\Sigma w(F_{0}^{2})^{2}]^{1/2}, w = 1/[\sigma^{2}(F_{0}^{2}) + (0.0468 \times p)^{2} + 3.1016 \times p, p = [max (F_{0}^{2} \text{ or } 0) + 2(F_{c}^{2})]/3.$   ${}^{c}\text{Quality-of-fit} = [\Sigma w(|F_{0}^{2}| - |F_{c}^{2}|)^{2}/(N_{\text{obs}} - N_{\text{parameters}})]^{1/2}.$ 

Ag—N(3) 2.206(4) $C(2)$ —N(3) 1.285(6)	Ag = N(1)	2.179(4)	C(1) - N(2)	1.338(6)	
	Ag - N(3)	2.206(4)	C(2) - N(3)	1.285(6)	
Ag-O(3) $2.575(4)$ C(2)-N(4) $1.325(6)$	Ag-0(3)	2.575(4)	C(2)N(4)	1.325(6)	
C(1) - N(1) = 1.288(6)	C(1) - N(1)	1.288(6)			

Table 2. Selected bond lengths (Å) and angles (°) for Ag(HDPhF)<sub>2</sub>SO<sub>3</sub>CF<sub>3</sub>

N(1)—Ag—N(3)	142.3(2)	N(3)AgO(3)	92.0(1)
N(1)—Ag—O(3)	122.4(2)		



Fig. 2. A schematic representation of one of the hydrogen bonding interactions in  $Ag(HDPhF)_2SO_3CF_3$  and a possible interaction in a vanadyl complex requiring a similar geometry.

Acknowledgements—We are grateful to the Vicerrectoría de Investigación U.C.R. (Project 115-87-516) and the Department of Chemistry for support of work at the University of Costa Rica and to the National Science Foundation for support of work at Texas A & M University.

# REFERENCES

- 1. J. Barker and M. Kilner, Coord. Chem. Rev. 1994, 133, 219.
- 2. F. A. Cotton, L. M. Daniels and C. A. Murillo, *Inorg. Chem.* 1993, **32**, 2881 and references therein.
- (a) F. A. Cotton, L. M. Daniels, D. J. Maloney, J. H. Matonic and C. A. Murillo, *Polyhedron* 1994, 13, 815; (b) D. I. Arnold, F. A. Cotton, D. J. Maloney, J. H. Matonic and C. A. Murillo, *Polyhedron*, 1997, 16, 133.
- See for example F. A. Cotton, L. M. Daniels, X. Feng, D. J. Maloney, J. H. Matonic and C. A. Murillo, *Inorg. Chim. Acta*, in press.
- F. A. Cotton, L. M. Daniels, J. H. Matonic, C. A. Murillo and X. Wang, *Polyhedron*, 1997, 16, 1177.
- D. I. Arnold, F. A. Cotton, J. H. Matonic and C. A. Murillo, J. Chem. Soc., Chem. Commun. 1996, 2113.

- F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., pp. 940–943. Wiley, New York (1988).
- M. I. Bruce, J. D. Walsh, B. W. Skelton and A. H. White, J. Chem. Soc., Dalton Trans. 1981, 956.
- (a) G. A. Bowmaker, Effendy, P. J. Harvey, P. C. Healy, B. W. Skelton and A. H. White, J. Chem. Soc., Dalton Trans 1996, 2449; (b) G. A. Bowmaker, Effendy, P. J. Harvey, P. C. Healy, B. W. Skelton and A. H. White, J. Chem. Soc., Dalton Trans 1996, 2459.
- A. Bino, F. A. Cotton and P. E. Fanwick, *Inorg. Chem.* 1979, 18, 3558.
- (a) G. M. Sheldrick, in Crystallographic Computing 3 (Edited by G. M. Sheldrick, C. Kruger and R. Goddard), pp. 175–189. Oxford University Press, Oxford (1985); (b) G. M. Sheldrick, in Crystallographic Computing 6 (Edited by H. D. Flack, L. Parkanyi and K. Simon), pp. 111–122. Oxford University Press, Oxford (1993).
- 12. E. Bang, Acta Chem. Scand. A 1978, 32, 555.
- H. M. Maurer and A. Weiss, Z. Kristallogr. 1977, 146, 227.
- 14. G. Swarnabala and M. V. Rajasekharan, *Polyhedron* 1996, **15**, 3197.
- K. Nilsson and Å. Oskarsson, Acta Chem. Scand. A 1982, 36, 605.