

362. *Complex Fluorides. Part VI.* The Properties of Silver Salts of Fluoro-acids and their Interaction with Aromatic Hydrocarbons.*

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Earlier work on the interaction of silver salts and aromatic hydrocarbons is reviewed briefly. Silver fluoroborate and hexafluoro-phosphate, -arsenate, -antimonate, -niobate, and -tantarate are soluble in benzene, toluene, and *m*-xylene, and many complexes have been prepared. Infrared absorption spectra and partial structure determinations have shown that the silver salts have ionic structures. The silver ion-aromatic hydrocarbon interaction energy is discussed, and it is suggested that the bonds formed must be of the same order of strength as ordinary covalent bonds.

THE remarkable solubility of silver perchlorate in benzene was first studied by Hill,^{1,2} who showed that such substances form a complex, $\text{AgClO}_4 \cdot \text{C}_6\text{H}_6$. Silver perchlorate and toluene form an analogous compound.³ Silver perchlorate is soluble in *m*-xylene,⁴ silver trifluoroacetate⁵ and trichloroacetate⁶ in benzene, and silver fluoroborate monohydrate is readily soluble in benzene⁷ and toluene;⁸ with the preparation of anhydrous silver fluoroborate (from silver borate and bromine trifluoride) and the demonstration that it is soluble in benzene, toluene, and ether,⁹ the similarity between this substance and silver perchlorate is well established. The only other silver salts known to be soluble in aromatic hydrocarbons are the trifluoromethanesulphonate (in benzene)¹⁰ and heptafluorobutyrate.¹¹ Complexes of the trifluoroacetate and the heptafluorobutyrate with benzene, toluene, the xylenes, and mesitylene have been characterised.¹¹

Although freezing points,¹ dielectric properties,¹² and conductivities¹³ of solutions of silver perchlorate in benzene indicate that, at low concentrations, the substance is present as ion-pairs, the possibility of covalent-bond formation, especially at high concentrations, between an oxygen atom of the perchlorate ion and the silver ion cannot be eliminated. Similar considerations apply to salts of carboxylic and sulphonic acids. The study of silver salts of complex fluoro-acids, however, is unlikely to be open to the same complication: covalent-bond formation in them would involve either bivalent fluorine, or gross distortion (detectable by *X*-ray or spectroscopic methods) of the complex ion and bond formation between silver and the central atom of the anion. The instance of the fluoroborate is particularly convincing: the hypothetical compound HBF_4 cannot be formulated without the use of bivalent fluorine or quinquevalent boron, and the failure of hydrogen fluoride and boron trifluoride to combine in equimolecular proportions is thus easily understandable.¹⁴ Compounds are formed between these substances only if a donor molecule (*e.g.*, hydrogen fluoride, water, or ammonia) is available to co-ordinate with the proton. This paper describes the results of a survey of the structures and infrared spectra of silver salts of complex fluoro-acids, and their interaction with aromatic hydrocarbons. Further physicochemical studies will be described later.

Silver fluoroborate and hexafluoro-phosphate, -arsenate, -antimonate, -niobate, and -tantarate are all soluble in benzene, toluene, and *m*-xylene, the solubilities being

* Part V, *J.*, 1956, 1242.

¹ Hill, *J. Amer. Chem. Soc.*, 1921, **43**, 254.

² *Idem, ibid.*, 1922, **44**, 1163.

³ Hill and Miller, *ibid.*, 1925, **47**, 2702.

⁴ Spurgeon, Thesis, University of Michigan, 1941.

⁵ Swarts, *Bull. Soc. chim. Belg.*, 1939, **48**, 176.

⁶ Davidson and Sutton, *J.*, 1942, 565.

⁷ Haunschild, Thesis, University of Cincinnati, 1948.

⁸ Warf, *J. Amer. Chem. Soc.*, 1952, **74**, 3702.

⁹ Sharpe, *J.*, 1952, 4538.

¹⁰ Haszeldine and Kidd, *J.*, 1954, 4228.

¹¹ Tildesley and Sharpe, *Research*, 1954, **7**, S9.

¹² Hooper and Kraus, *J. Amer. Chem. Soc.*, 1934, **56**, 2265.

¹³ Luder, Kraus, Kraus, and Fuoss, *ibid.*, 1936, **58**, 255.

¹⁴ Sharpe, "Fluorine Chemistry," ed. Simons, Academic Press, New York, 1954, Vol. II.

greatest in toluene and least in benzene. The hexafluorophosphate, like silver trifluoroacetate, is also soluble in mesitylene. (For a discussion of the effect of steric hindrance by methyl groups on silver ion–aromatic hydrocarbon interaction see ref. 11.) The complexes obtained when these solutions are evaporated in a stream of dry nitrogen at room temperature are :

B =	benzene	toluene	<i>m</i> -xylene	mesitylene
	$2\text{AgBF}_4, 3\text{B}$ $\text{AgAsF}_6, 2\text{B}$ $\text{AgPF}_6, 2\text{B}$ $\text{AgSbF}_6, 2\text{B}$ $\text{AgNbF}_6, 2\text{B}$ $\text{AgTaF}_6, 2\text{B}$	$2\text{AgBF}_4, 3\text{B}$ $\text{AgAsF}_6, 2\text{B}$ $\text{AgPF}_6, 2\text{B}$ $\text{AgSbF}_6, 2\text{B}$	$\text{AgBF}_4, 2\text{B}$ $\text{AgAsF}_6, 2\text{B}$ $\text{AgPF}_6, 2\text{B}$ $\text{AgSbF}_6, 2\text{B}$	$\text{AgPF}_6, 3\text{B}$

Silver hexafluorovanadate and tetrafluoroaurate react with the solvents and no complexes can be isolated.

Silver fluoroborate crystallises at room temperature in the orthorhombic system, with $a = 7.75$, $b = 5.54$, $c = 7.16$ Å, and is isomorphous with potassium, rubidium, and ammonium fluoroborate. Silver hexafluorophosphate is isomorphous¹⁵ with α -potassium hexafluorophosphate,¹⁶ silver hexafluoroarsenate with a group of sodium salts of general formula NaXF_6 ,¹⁵ and silver hexafluoroantimonate with the corresponding potassium salt.^{17, 18} Finally, silver hexafluoronioabate and hexafluorotantalate (which have the caesium chloride structure, with $a = 9.93$ Å for both compounds) are isomorphous with the analogous potassium salts.¹⁸

Coté and Thompson found that below 1400 cm.^{-1} the infrared spectra of ammonium, potassium, and rubidium fluoroborate are identical;²¹ in this region the spectrum of the silver salt is the same as those of the other three salts. Furthermore, silver hexafluorophosphate and hexafluoroarsenate have infrared spectra almost identical with those of the corresponding rubidium and caesium compounds. The formulation of these silver salts as having purely ionic anion–cation bonding is thus further substantiated by their infrared spectra.

The interaction between the silver ion and unsaturated or aromatic hydrocarbons has been considerably discussed, the latest account being by Mulliken,²² who derived theoretically the stereochemical configuration found in the silver perchlorate–benzene complex by Rundle and Goring.²³ In this compound, each silver ion is so bonded to two benzene molecules that the angle made by the silver ion with the middle of the nearest carbon–carbon bond and the centre of the aromatic ring is 100° ; the shortest Ag–C distance is *ca.* 2.6 Å. Despite the magnitude of this distance, the silver ion–aromatic nucleus interaction energy should be fairly high in order to compensate for the work done in “diluting” the electrostatic lattice with uncharged molecules.¹¹ This argument is valid, however, only if no covalent bond is formed between silver and anion; this cannot be established for silver perchlorate, but in the fluoroborate the reasons advanced above make any such bond formation extremely improbable. Complex formation between silver salts of fluoroacids and aromatic hydrocarbons therefore indicates the need for a moderate bond energy between the silver ion and the hydrocarbon molecule.

A similar conclusion has been reached in a discussion of the closely related interaction of silver ion in aqueous solution and olefins.²⁴ From the temperature dependence of the distribution of trimethylethylene and cyclohexene between carbon tetrachloride and aqueous silver nitrate, Winstein and Lucas²⁵ found the heat of the reaction $\text{Ag}^+(\text{aq}) + \text{B} = \text{AgB}^+(\text{aq})$ (where B represents the olefin) to be about 6 kcal. As these authors pointed out, however,

¹⁵ Cox, J., 1956, 876.

¹⁶ Bode and Clausen, *Z. anorg. Chem.*, 1951, **265**, 229.

¹⁷ Bode, *ibid.*, 1951, **267**, 62.

¹⁸ Bode and Voss, *ibid.*, 1951, **264**, 144.

¹⁹ Braekken and Harang, *Z. Krist.*, 1930, **75**, 538.

²⁰ Hermann and Ilge, *ibid.*, 1931, **75**, 41.

²¹ Coté and Thompson, *Proc. Roy. Soc.*, 1951, *A*, **210**, 217.

²² Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811.

²³ Rundle and Goring, *ibid.*, 1950, **72**, 5337.

²⁴ Tildesley and Sharpe, *Research*, 1953, **6**, S51.

²⁵ Winstein and Lucas, *J. Amer. Chem. Soc.*, 1938, **60**, 836.

this value takes no account of the energy required for the partial displacement of water from the ion's neighbourhood. The silver-olefin bond energy should thus be much greater than 6 kcal.

EXPERIMENTAL

Preparations involving the use of bromine trifluoride and X-ray powder photographic investigations were carried out as described previously.³² All operations on the silver salts, which are very deliquescent, and on their complexes with aromatic hydrocarbons, which are decomposed by moisture, were conducted with "dry-box" techniques. Infrared spectra were measured on Nujol or hexachlorobutadiene mulls, a Perkin-Elmer Model 21 Spectrometer with rock-salt optics being used. Complexes were prepared by dissolving silver salts in hot hydrocarbons, cooling the solutions in a stream of dry nitrogen, and removing the solvent on a porous tile. Reproducible results were thus obtained.

Preparations.—Silver fluoroborate was made as described previously⁹ (Found: Ag, 54.8. Calc. for AgBF_4 : Ag, 55.3%). Complexes were analysed by boiling them with water to remove as much of the hydrocarbon as possible, followed by gravimetric determination of silver (Found, for the *benzene complex*: Ag, 34.7. $2\text{AgBF}_4 \cdot 3\text{C}_6\text{H}_6$ requires Ag, 34.5%. Found, for the *toluene complex*: Ag, 33.3. $2\text{AgBF}_4 \cdot 3\text{C}_7\text{H}_8$ requires Ag, 32.5%. Found, for the *m-xylene complex*: Ag, 25.5. $\text{AgBF}_4 \cdot 2\text{C}_8\text{H}_{10}$ requires Ag, 26.5%).

Silver hexafluorophosphate was obtained from silver powder, phosphoric oxide, and bromine trifluoride: this modification of Emeléus and Woolf's procedure²⁶ gave an almost white product (Found: Ag, 41.5. Calc. for AgPF_6 : Ag, 42.7%) (Found, for the *benzene complex*: Ag, 26.6. $\text{AgPF}_6 \cdot 2\text{C}_6\text{H}_6$ requires Ag, 26.4%. Found, for the *toluene complex*: Ag, 25.4. $\text{AgPF}_6 \cdot 2\text{C}_7\text{H}_8$ requires Ag, 24.7%. Found, for the *m-xylene complex*: Ag, 23.3. $\text{AgPF}_6 \cdot 2\text{C}_8\text{H}_{10}$ requires Ag, 23.2%. Found, for the *mesitylene complex*: Ag, 18.6. $\text{AgPF}_6 \cdot 3\text{C}_9\text{H}_{12}$ requires Ag, 17.6%).

Silver hexafluoroarsenate was obtained from silver, arsenious oxide, and bromine trifluoride²⁶ (Found: Ag, 35.9. Calc. for AgAsF_6 : Ag, 36.4%) (Found, for the *benzene complex*: Ag, 23.0. $\text{AgAsF}_6 \cdot 2\text{C}_6\text{H}_6$ requires Ag, 23.8%. Found, for the *toluene complex*: Ag, 21.4. $\text{AgAsF}_6 \cdot 2\text{C}_7\text{H}_8$ requires Ag, 22.4%. Found, for the *m-xylene complex*: Ag, 20.5. $\text{AgAsF}_6 \cdot 2\text{C}_8\text{H}_{10}$ requires Ag, 21.2%).

The hexafluoroantimonate was prepared according to Woolf and Emeléus's²⁶ directions (Found: Ag, 31.7. Calc. for AgSbF_6 : Ag, 31.4%) (Found, for the *benzene complex*: Ag, 20.9. $\text{AgSbF}_6 \cdot 2\text{C}_6\text{H}_6$ requires Ag, 21.6%. Found, for the *toluene complex*: Ag, 19.9. $\text{AgSbF}_6 \cdot 2\text{C}_7\text{H}_8$ requires Ag, 20.4%. Found, for the *m-xylene complex*: Ag, 19.3. $\text{AgSbF}_6 \cdot 2\text{C}_8\text{H}_{10}$ requires Ag, 19.4%).

Silver hexafluoro-niobate and -tantalate were prepared by Gutmann and Emeléus's method²⁷ (Found: Nb, 30.2. Calc. for AgNbF_6 : Nb, 29.6%. Found: Ta, 45.3. Calc. for AgTaF_6 : Ta, 45.0%). These substances were soluble in benzene, toluene, and *m-xylene*, but on warming them with toluene and *m-xylene* decomposition occurred and no complexes were isolated (Found, for the *benzene complex*: Nb, 20.2. $\text{AgNbF}_6 \cdot 2\text{C}_6\text{H}_6$ requires Nb, 19.8%. Found, for the *benzene complex*: Ta, 31.7. $\text{AgTaF}_6 \cdot 2\text{C}_6\text{H}_6$ requires Ta, 32.4%).

Silver hexafluorovanadate²⁸ and tetrafluoroaurate²⁹ were made by methods described previously; both reacted with aromatic hydrocarbons, and no complexes were isolated.

X-Ray Powder Photography.—Unit-cell dimensions have been given on p. 1856. The interpretation of the powder pattern of silver fluoroborate was made possible by its similarity to those of potassium and ammonium fluoroborates, the structures of which were known.^{30, 31}

Infrared Absorption Spectra.—Silver fluoroborate shows absorption maxima at 769, 1026, 1064, 1300, 1529, and 3509 cm^{-1} . Since no data were available for hexafluorophosphates, the rubidium and caesium salts were prepared from alkali-metal halides, phosphoric oxide, and bromine trifluoride; PF_6^- was determined as the nitron salt (Found: PF_6^- , 63.0. Calc. for RbPF_6 : PF_6^- , 62.9%. Found: PF_6^- , 50.6. Calc. for CsPF_6 : PF_6^- , 52.1%). Spectra recorded were: AgPF_6 , broad peak at 830—840 cm^{-1} , subsidiary peak at 740 cm^{-1} ; RbPF_6 , broad peaks at 845, 802 cm^{-1} , subsidiary peak at 740—720 cm^{-1} ; CsPF_6 , broad peaks at 843, 802 cm^{-1} , subsidiary peak at 740—720 cm^{-1} .

²⁶ Woolf and Emeléus, *J.*, 1949, 2865; 1950, 1050.

²⁷ Gutmann and Emeléus, *J.*, 1950, 1046.

²⁸ Emeléus and Gutmann, *J.*, 1949, 2979.

²⁹ Sharpe, *J.*, 1949, 2901.

³⁰ Hoard and Blair, *J. Amer. Chem. Soc.*, 1935, 57, 1985.

³¹ Pesce, *Gazzetta*, 1930, 60, 936.

³² Sharpe, *J.*, 1950, 3444; Cox and Sharpe, *J.*, 1954, 1798.

Analogous preparations were made, for the same reason, in the hexafluoroarsenate series (Found : As, 26.9. Calc. for RbAsF_6 : As, 27.3%. Found : As, 23.1. Calc. for CsAsF_6 : As, 23.3%). Spectra recorded were : AgAsF_6 , broad peak at 695 cm^{-1} ; RbAsF_6 , broad peak at 700 cm^{-1} , subsidiary peaks at 1295, 1064, 972, and 827 cm^{-1} ; CsAsF_6 , broad peak at 699 cm^{-1} , subsidiary peaks at 1300, 1068, 970, and 823 cm^{-1} .

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