363. *Complex Fluorides. Part VII.* The Interaction of Cuprous Salts of Fluoro-acids and Aromatic Hydrocarbons.*

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Copper displaces silver from solutions of silver fluoroborate, fluorosulphonate, and hexafluoro-phosphate, -arsenate, -niobate, and -tantalate in toluene, forming the corresponding cuprous compounds. The implications of these observations are discussed.

THE formation of complexes between cuprous salts and olefins is well established. Cuprous chloride forms addition products with ethylene, propene, and *iso*butene under pressure, but the products are unstable at ordinary temperature and pressure.[1, 2] Water-soluble complexes of cuprous ion and unsaturated alcohols or carboxylic acids have also been reported.[3-5] It is only recently, however, that a cuprous salt has been shown to form a complex with an aromatic hydrocarbon.

Warf [6] obtained a solution containing cuprous fluoroborate in toluene by decomposition of a solution of an aryldiazonium fluoroborate in boiling toluene in the presence of copper powder, and also by the action of boron trifluoride on a mixture of equivalent quantities of copper powder and cupric fluoride suspended in toluene. Recent investigations [8] of the interaction of silver salts of complex fluoro-acids and aromatic hydrocarbons suggested that solutions of the analogous cuprous complexes might be obtained by displacement of silver by copper, a method used to prepare a solution of cuprous nitrate in acetonitrile.[7]

This method was applied to the preparation of solutions of cuprous fluoroborate, fluorosulphonate, and hexafluoro-phosphate, -arsenate, -niobate, and -tantalate in toluene. The solutions are colourless, and the oxidation state of the copper in the fluoroborate has been established by the determination of the equivalent weight of the copper which goes into solution, and by the diamagnetism of the solution (all cupric compounds are paramagnetic). Dry solutions of all the cuprous compounds are stable indefinitely, but on addition of water disproportionation takes place, with the formation of metallic copper, toluene, and a hydrated cupric salt. Solid cuprous salts have not been obtained by evaporation of toluene solutions; when attempts were made to remove the solvent in a stream of dry nitrogen at room temperature or *in vacuo*, colourless solids were deposited, but these rapidly turned brown as disproportionation occurred. These observations are similar to Morgan's [7] on the impossibility of isolating cuprous nitrate from solution in acetonitrile.

* Part VI, preceding paper.

[1] Tropsch and Mattox, *J. Amer. Chem. Soc.*, 1935, **57**, 1102.
[2] Gilliland, Seebold, Fitz-Hugh, and Morgan, *ibid.*, 1939, **61**, 1960.
[3] Andrews and Keefer, *ibid.*, 1948, **70**, 3261; 1949, **71**, 2379.
[4] Keefer, Andrews, and Kepner, *ibid.*, 1949, **71**, 2381.
[5] Kepner and Andrews, *J. Org. Chem.*, 1948, **13**, 208.
[6] Warf, *J. Amer. Chem. Soc.*, 1952, **74**, 3702.
[7] Morgan, *J.*, 1923, 2901.
[8] Sharp and Sharpe, preceding paper.

It has been argued [8] that for a salt such as silver fluoroborate, covalent-bond formation between anion and cation is exceedingly unlikely, and a similar argument should apply to cuprous salts of complex fluoro-acids. The formation of a solvated silver or cuprous ion in toluene may be regarded as taking place in the following stages (M = Ag or Cu):

$$M_{(s)} \longrightarrow M_{(g)} \longrightarrow M^{+}{}_{(g)} \longrightarrow M^{+}{}_{(\text{solv.})}$$

The first stage involves the absorption of the latent heat of sublimation of the metal, the second stage the absorption of energy equivalent to the first ionisation potential. Both quantities for copper (81·5 and 260·8 kcal., respectively) exceed those [9] for silver (69·1 and 245·3 kcal.). Owing to experimental difficulties, the heat of the displacement reaction has not been measured, but if we make the reasonable assumption that the reaction is thermoneutral or exothermic, and that the structures (and hence the entropies) of the solvated cations are not very different, the heat of solvation of the cuprous ion should be greater than that of the silver ion by at least 20 kcal./g.-ion.

This argument suggests a method of obtaining information about the nature of the aromatic hydrocarbon–metal ion interaction. If the bonding electrons are provided exclusively by the hydrocarbon, complex formation by cuprous salts should result in a much larger decrease in the aromatic C–C vibration frequency than complex formation by silver salts. If, on the other hand, the *d*-electrons of the metal ion are used, such a decrease might, but would not necessarily, occur. This should be shown by comparison of the Raman spectra of concentrated solutions of cuprous and silver fluoroborates in toluene.

EXPERIMENTAL

Silver salts were prepared as described in Part VI.[8] Silver fluorosulphonate was obtained by Woolf's method [10] (Found: Ag, 52·2. Calc. for $AgSO_3F$: Ag, 52·1%); it was soluble in benzene, toluene, *m*-xylene, and mesitylene. The use of bromine trifluoride in the preparation ensured the dryness of the silver salts; toluene was dried over sodium; copper powder was dried at 130° and preserved over phosphoric oxide. All additions of reagents and filtrations were carried out in a "dry-box"; sintered-glass filters were used since filter papers contain sufficient moisture to effect partial disproportionation of cuprous compounds in toluene.

In a typical experiment, excess of copper powder, followed by toluene, was added to a known weight of silver fluoroborate in a glass tube. The whole was shaken for 2 days, after which no silver remained in the solution. The excess of copper was filtered off, and copper in the filtrate (found by the Gouy method to be diamagnetic) was determined iodometrically after oxidation to the cupric state [Found: equiv. of dissolved Cu (Ag ≡ 108), 58·8. Calc. for Cu^+: 63·5]. No solid cuprous salts were obtained.

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[9] Nat. Bur. Stand. Tables, Circular 500.

[10] Woolf, *J.*, 1950, 1053.