

Copper(II) Salts of Very Strong Acids

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SILVER salts of very strong acids are soluble in organic solvents such as diethyl ether, benzene, and nitromethane but salts containing other metals are not generally known to be soluble in this type of solvent. Reaction between anhydrous cupric chloride and solutions of silver perchlorate, trifluoroacetate, tetrafluoroborate, and hexafluoroantimonate in these solvents gives rise to two series of compounds. When a large excess of halide is used the solutions contain copper(II) salts of the type CuClX ($\text{X} = \text{ClO}_4, \text{CF}_3\text{CO}_2, \text{BF}_4,$ or SbF_6). These are discrete species, as cupric chloride is virtually insoluble in the organic solvents used: on addition of ligands, complexes [*e.g.* $(\text{Ph}_3\text{As})_2\text{CuClBF}_4$] containing both halide and the residue of the strong acid are precipitated.

When the solutions containing the copper salts CuClX are titrated with a further solution of the appropriate silver salt dissolved in the same solvent the colour of the solution changes and the calculated weight of silver chloride is precipitated. With copper(II) perchlorate and trifluoroacetate the copper salt remains in solution and the spectrum of the solution does not change on addition of excess of silver salt. Thus, complex anionic species do not appear to be formed. On addition of further silver salt to the solution of copper(II) chloride fluoroborate and copper(II) chloride hexafluoroantimonate in solution in ether or benzene, the green copper salt CuX_2 is precipitated

as a 1:1 mixture with silver chloride. Copper(II) fluoroborate and hexafluoroantimonate are soluble in nitromethane.

The visible and near infrared spectra of the solutions containing CuX_2 species are completely distinct from the spectra of the solutions containing CuClX species, showing that the halide groups are bonded to the copper. The visible and near infrared spectra of the solutions show strong dependence upon the anion, X, present [*e.g.* $\text{CuCl}(\text{ClO}_4)$, 12.6; $\text{Cu}(\text{ClO}_4)_2$, 13.2; $\text{CuCl}(\text{BF}_4)$, 11.6, 10.6; $\text{CuCl}(\text{SbF}_6)$, 12.3, 11.0. Figures in cm^{-1} ; spectra measured in diethyl ether], again suggesting strong anion-cation interaction. The infrared spectra of solid copper(II) fluoroborate and hexafluoroantimonate show very marked splittings in the peaks originating from the fluoroborate and hexafluoroantimonate groupings. Cupric fluoroborate shows two distinct bands at 1080 and 1030 cm^{-1} compared with what is effectively a single peak at 1100 cm^{-1} in the spectrum of potassium fluoroborate.¹ Cupric hexafluoroantimonate shows bands at 666, 656, and 624 cm^{-1} compared with a single peak at 660 cm^{-1} in the spectrum of potassium hexafluoroantimonate.² These infrared results favour strong interaction between the anion and the cation and are very similar to the spectra observed for trimethyltin fluoroborate³ and hexafluoroantimonate.⁴ Anhydrous copper(II) perchlorate has been previously

¹ N. N. Greenwood, *J.*, 1959, 3811.

² R. D. Peacock and D. W. A. Sharp, *J.*, 1959, 2762.

³ B. J. Hathaway and D. E. Webster, *Proc. Chem. Soc.*, 1963, 14.

⁴ H. C. Clark, private communication.

reported to be volatile and covalent in nature⁵ and the present work suggests that all copper(II) salts are, when unsolvated, largely covalent. In addition to anion-cation interaction it is almost certain that there must be solvation of the transition-metal atom in solution. This is not surprising

⁵ B. J. Hathaway and A. E. Underhill, *J.*, 1961, 3091.

for diethyl ether and nitromethane but the present results suggest that interaction between a metal and the π -electron system of benzene is not confined to silver(I) and copper(I) but must be extended to copper(II).

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