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THE PREPARATION OF COPPER(II) AND COPPER(I) SALTS IN ACETONITRILE USING GROUP VA AND VB PENTAFLUORIDES

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SUMMARY

Copper(II) fluoride reacts with the pentafluorides, TaF_5, PF_5, and AsF_5, in acetonitrile to give solvated Cu^{II}, hexafluoroanion salts. These react with copper metal to give the corresponding Cu^{I} compounds. Similar reactions occur between AsF_5 and silver(I) or thallium(I) fluorides, but silver(II) fluoride reacts with MeCN, and Ag^{I} hexafluoroarsenate is formed. PF_5 oxidises Cu slowly in MeCN to give Cu^{I} hexafluorophosphate, but AsF_5 has no oxidising ability towards metals in MeCN. Spectroscopic data for $Cu(MF_6)_2 \cdot 5MeCN$ and $Cu(MF_6) \cdot 4MeCN$ (M = Ta or P) are discussed.

INTRODUCTION

The reactions of ionic metal chlorides with Lewis acid covalent chlorides in acetonitrile to give solvated metal salts are well documented [1], and copper(II) and thallium(I) heptafluorotungstates(VI) have been prepared by analogous

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reactions [2]. Fluoroacid salts of transition and post-transition metals have also been prepared by oxidation of metals, for example using $NO^+BF_4^-$ in MeCN [3], transition metal hexafluorides in MeCN [4], or arsenic and antimony pentafluorides in SO_2 [5]. A requirement for Cu^{II} and Cu^{I} salts, soluble in MeCN and containing non-coordinating anions which are kinetically stable to hydrolysis, has led us to investigate reactions of CuF_2 and Cu metal with Group V pentafluorides. The preparation and properties of Cu^{II} and Cu^{I}, MF_6^- salts are described, together with related reactions of silver(I) and (II) and thallium(I) fluorides. We find that fluoride ion transfer reactions occur readily in MeCN, but the pentafluorides have negligible oxidising ability towards metals.

EXPERIMENTAL

All operations were carried out in a Pyrex vacuum system or a Lintott inert atmosphere box. Solid fluorides (Fluorochem Ltd. or Ozark Mahoning), of stated purities AgF (98%), AgF_2 (99%), CuF_2 (99·5%), TaF_5 (99%), TlF (97%), were stored in the dry box and degassed before use. Cu and Ag foils were cleaned with HNO_3, abraided, and degassed before use. AsF_5 and PF_5 (Ozark Mahoning and Fluorochem Ltd.) were purified by several low temperature trap to trap distillations over NaF, and were stored over NaF. MeCN (Hopkin and Williams reagent grade) was dried with CaH_2, then by three 24h. periods of reflux over P_2O_5, then by treatment with activated 4A molecular sieves *in vacuo*.

Reaction vessels comprised two limbs enabling solutions to be decanted *in vacuo*, and were fitted with P.T.F.E. stopcocks (Rotaflo). Similar vessels, in which one limb was replaced by a Pyrex capillary, an n.m.r. tube, or a 10mm Spectrosil cell, were used to prepare solutions for Raman, n.m.r. or electronic spectra. Both reaction mixtures and redissolved solid products were studied with identical results. Solution i.r. samples were prepared in predried AgCl cells (Beckman R.I.I.C.). Solid Raman and i.r. samples were contained in capillaries or mulled between AgCl, Si, or polythene windows.

Laser Raman spectra were recorded using a Spex Ramalog instrument, i.r. spectra using a P.E. 557 spectrometer and Beckman R.I.I.C. interferometer, electronic spectra using Pye Unicam SP700C and SP800 spectrometers, and n.m.r. spectra using a Jeol C60HL spectrometer, ^{1}H at 60 MHz, ^{19}F at 56•4 Hz, and ^{75}As and ^{31}P INDOR spectra with the addition of a Schomandl frequency synthesiser, Racal 9022 frequency meter and XY recorder. Spectra were referred to Me_4Si and CCl_3F externally, as internal referencing caused precipitation. Chemical shifts (δ p.p.m.) are positive to low field.

Microanalyses were by A. Bernhardt, Elbach, W. Germany.

Preparation of salts

These were performed on a 1-5 mmol scale as follows. A flamed out reaction vessel was loaded with CuF_2 and TaF_5 (ca. 3:2 mole ratio) in the dry box. The flask was re-evacuated, MeCN (5 ml) added by distillation, and the mixture mechanically shaken at room temperature for 24h. The blue liquid phase was decanted into the empty limb, and the solvent removed to leave blue copper(II) hexafluorotantalate, pentakis(acetonitrile) (nc). A solution of $Cu(TaF_6)_2$•5MeCN in MeCN reacted with Cu metal under similar conditions to give a pale yellow solution, from which white copper(I) hexafluorotantalate, tetrakis(acetonitrile) (nc) was isolated. Analogous Cu^{II} and Cu^{I} hexafluorophosphate, acetonitrile solvates were similarly prepared, except that PF_5 was added in vacuo via a calibrated bulb. Analytical data are given in Table 1.

PF_5 reacted with Cu metal in MeCN over 3 weeks to give PF_3, identified by its i.r. spectrum [6], and Cu^{I} hexafluorophosphate. Similar reactions between AsF_5 and Cu or Ag metals in MeCN yielded only the 1:1 adduct AsF_5•NCMe, identified by its Raman and i.r. [7] and its ^{19}F n.m.r. spectra [8].

A mixture of AgF_2 (9•3 mmol) and AsF_5 (4•6 mmol) in MeCN (5 ml), allowed to warm to ambient temperature, gave a

TABLE 1

Analytical data

	Found (required)					
	C	H	Cu or Ag	F	N	P or As
$Cu(TaF_6)_2 \cdot 5MeCN$	13·8 (14·0)	1·9 (1·8)	7·4 (7·4)	26·7 (26·6)	7·9 (8·2)	
$Cu(PF_6)_2 \cdot 5MeCN$	21·1 (21·5)	2·6 (2·7)	11·5 (11·4)	40·6 (40·8)	12·2 (12·5)	11·3 (11·1)
$Cu(TaF_6) \cdot 4MeCN$	18·5 (18·4)	2·4 (2·3)	12·3 (12·15)	21·75 (21·8)	10·55 (10·7)	
$Cu(PF_6) \cdot 4MeCN$	26·0 (25·8)	3·35 (3·3)	17·0 (17·0)	30·5 (30·6)	15·1 (15·0)	8·1 (8·3)
$Ag(AsF_6) \cdot 2MeCN$[a]	12·8 (12·7)	1·7 (1·6)	28·6 (28·5)	30·3 (30·1)	7·2 (7·4)	19·6 (19·8)
$Ag(AsF_6) \cdot 3MeCN$[b]	17·3 (17·1)	1·9 (2·1)	25·7 (25·7)	27·0 (27·1)	9·9 (10·0)	17·7 (17·85)

[a] From $AgF + AsF_5$

[b] From $AgF_2 + AsF_5$

white solid, presumed to be $AsF_5 \cdot NCMe$. This dissolved, and an exothermic reaction occurred which was moderated by cooling the vessel. After 0·5h the liquid phase was decanted and, from this, an off-white solid was isolated which was identified as silver(I) hexafluoroarsenate, tris(acetonitrile) (Table 1). If the reaction was not moderated local boiling occurred, and a dark red solution was formed. Continued reaction led to a reduction in solvent volume and an insoluble brown solid. A smooth reaction occurred when a large excess of AsF_5 was used, but the product contained both AsF_6^- and AsF_5NCMe.

A mixture of AgF (8·0 mmol) and AsF_5 (5·0 mmol) in MeCN (5 ml), shaken for 2h at room temperature, gave a pale green solution from which silver(I) hexafluoroarsenate, bis(acetonitrile) (Table 1) was isolated.

Properties and spectra

All salts were stable at room temperature in the absence of moisture. Solubilities of the copper salts in MeCN at ambient temperature depended on the oxidation state and the anion. Both Cu^{I} salts were very soluble ($\geqslant 1{\cdot}0$ mol l^{-1}); Cu^{II} hexafluorophosphate was more soluble (ca. $0{\cdot}1$ mol l^{-1}) than Cu^{II} hexafluorotantalate (ca. $0{\cdot}01$ mol l^{-1}).

Bands in the salts' vibrational spectra were assigned to co-ordinated MeCN and MF_6^- anions by comparison with analogous compounds [9, 10]. In addition to the data in Table 2, bands assigned to ν_1, ν_5, ν_6, ν_3, ν_7, ν_8 and $2\nu_8$ of co-ordinated MeCN were observed. A shoulder on the ν_3 band of PF_6^-, at 870-880 cm^{-1} observed in the i.r. spectrum of the Cu^{I} salt and in the solution spectrum of the Cu^{II} salt, was tentatively assigned to $(\nu_2 + \nu_6)$ by analogy with KPF_6 [10b]. Raman spectra of Cu^{II} hexafluorophosphate and Ag^{I} hexafluoroarsenate solvates could not be obtained as decomposition occurred in the laser beam.

The ^{19}F n.m.r. spectra of the salts in MeCN showed small variations with concentration, but in each case sharp signals were obtained characteristic of the MF_6^- anion present. Average values were, for Cu^{II} and Cu^{I} hexafluorotantalates, δ 37; Cu^{II} hexafluorophosphate, δ -78, $^{1}J(FP)$ 729; Cu^{I} hexafluorophosphate, δ -77, $^{1}J(FP)$ 735; Ag^{I} hexafluoroarsenate, δ -72 p.p.m., $^{1}J(AsF)$ 948 Hz. ^{75}As and ^{31}P INDOR spectra confirmed the presence of AsF_6^- and PF_6^-. ^{1}H n.m.r. spectra of Cu^{I} and Ag^{I} consisted of unshifted solvent resonances, but in the Cu^{II} salts the solvent resonance was broad and shifted to high field. Separate signals due to bulk and co-ordinated solvent were not resolved at -40°C.

The electronic spectra of Cu^{II} hexafluorotantalate and hexafluorophosphate in MeCN contained a broad band at 13,200 cm^{-1} (ε = 15) with a pronounced shoulder at 9,500 cm^{-1}, characteristic of Cu^{II} in a distorted octahedral environment due to MeCN, $Cu(NCMe)_6^{2+}$, ν_{max} 13,300 cm^{-1} (ε = 21) [1,3], rather than F^- ligands [11]. Strong bands ca. 40,000 cm^{-1},

TABLE 2

Vibrational spectra of solid salts

Compound	Band positions (cm^{-1})[a]						
	Co-ordinated MeCN			MF_6^-			
	$\nu_3+\nu_4$ a_1	ν_2 a_1	ν_4 a_1	ν_1 a_{1g}	ν_3 t_{1u}	ν_4 t_{1u}	ν_5 t_{2g}
$Cu(PF_6)_2 \cdot 5MeCN$[b] (i.r. only)	2330m 2300m 2280m		965m 955m	740m (i.r.)	850s 810s	560m	
$Cu(PF_6) \cdot 4MeCN$	2300m	2270m	946m	748s[c]	840s[c]	560m[c]	
$Cu(TaF_6)_2 \cdot 5MeCN$	2320m 2300m 2280m		945m	699s[c]	590m		286w
$Cu(TaF_6) \cdot 4MeCN$	2315m	2280m	925m	697m[c]	580s		288w
$Ag(AsF_6) \cdot 2MeCN$[d] (i.r. only)	2315m 2300w	2285m 2275w	940w 925, 930w		700s,br	390m	

[a] Bands have the expected activities except where noted.

[b] In MeCN solution 2320sh, 2300m, 2270sh, 940m br, 840s, 560m cm^{-1}.

[c] Also observed in MeCN solution

[d] For $Ag(NCMe)_3^{2+}$ MeCN bands are 2300m, 2275m, 925,930m cm^{-1}

present also in the Cu^I salts, were assigned to charge transfer. The band in Cu^{II} hexafluorophosphate had a pronounced tail into the visible region, and concentrated solutions were green rather than blue.

The soluble white solid isolated from the reaction between TlF (8·5 mmol) and AsF_5 (5·0 mmol) in MeCN was identified as thallium(I) hexafluoroarsenate from its vibrational and ^{19}F n.m.r. spectra. Raman: ν_1 682 s, ν_2 566 m, ν_5 367 m; i.r.: ν_3 700 s br, ν_4 390 m cm^{-1}. ^{19}F n.m.r.: δ -72 p.p.m.,

^1J(AsF) 950 Hz. Solvated Cu^{II} hexafluoroarsenate was identified from its electronic spectrum, ν_{max} 13,200, 9,400 sh cm^{-1} and its i.r. spectrum, ν_{max} 2325 m, 2305 m, 2285 m, 955 947 m due to co-ordinated MeCN, and 678 w, 700 s br, 395 m cm^{-1} due to AsF_6^-.

RESULTS AND DISCUSSION

Anhydrous CuF_2 reacts with the pentafluorides, MF_5 (M = Ta, P, As) in MeCN at ambient temperature according to equation (1).

$$CuF_2(s) + 2MF_5(solv) \rightarrow Cu^{II}(solv) + 2MF_6^-(solv). \qquad (1)$$

The reactions are a consequence of the good solvating properties of MeCN and the pentafluorides' fluoride ion acceptor properties. TaF_5 and AsF_5 are generally regarded as stronger Lewis acids than PF_5, and in MeCN exist as monomeric $MF_5{\cdot}NCMe$ complexes [12,7,8]. The ^{19}F [8] and ^{31}P n.m.r. [13] spectra of PF_5 in MeCN, which were confirmed in the present work, are consistent with a rapid exchange between complexed and free PF_5. No adduct is isolable at room temperature.

Providing an excess of CuF_2 is used in the reactions, pure MF_6^- salts are obtained. There is no evidence for the formation of TaF_7^{2-}, which exists in solution only when the F^- ion activity is high [10c,14].

Neither cobalt(II) nor nickel(II) fluorides react with the pentafluorides in MeCN to any extent. As their lattice energies are comparable to that of CuF_2 [15], and the solvated cations $M(NCMe)_6^{2+}$ (M = Co or Ni) are well known [1,16], it is considered that kinetic factors are responsible for the different behaviour. As expected from thermodynamic considerations [17], both silver(I) and thallium(I) fluorides react with AsF_5 to give soluble AsF_6^- salts. Attempts to prepare Ag^{II} hexafluoroarsenate from AgF_2 and AsF_5 were unsuccessful, as reduction to Ag^I with concomitant solvent attack occur. The latter is envisaged as being initiated by AgF_2 rather than $Ag(AsF_6)_2$, as Ag^{II} hexafluoromolybdate(V) is stable in MeCN, the reaction mechanism being similar to that proposed for the reaction of MeCN with CoF_3 or $KCoF_4$ [18].

Copper metal reacts rapidly with $Cu^{II}TaF_6^-$ or PF_6^- in MeCN at room temperature to give the corresponding Cu^I salts, due to the favourable solvation of Cu^I [17]. Cu^I hexafluorophosphate is formed also from the reaction of Cu metal with PF_5 in MeCN according to equation (2).

$$2Cu + 3PF_5(solv) \rightarrow 2Cu^I(solv) + 2PF_6^-(solv) + PF_3 \qquad (2)$$

However the reaction is slow, and is not an attractive synthetic route. AsF_5 shows no redox behaviour towards Cu or Ag metals in MeCN, although it is normally regarded as a stronger oxidant than PF_5, and it oxidises Cu to Cu^{II} or $Cu(AsF_6)$ in SO_2 [5b]. Either the reduction of $AsF_5 \cdot NCMe$ is thermodynamically unfavourable or, more likely, the adduct is kinetically stable to reduction. In MeCN therefore, the interplay of thermodynamic and kinetic factors results in PF_5 and AsF_5 having less oxidising ability than the hexafluorides MF_6 (M = U, Mo, W, and Re) [4]. In IF_5 however, AsF_5 and PF_5 have greater oxidising ability towards I_2 than WF_6 and MoF_6 [4,19].

With the exception of $Tl(AsF_6)$, all the solid salts isolated contain MeCN, and their vibrational spectra (Table 2) are consistent with the presence of ionic species in which MeCN is co-ordinated to the metal ion. Two types of MeCN are present in $Ag(NCMe)_2(AsF_6)$ and the Cu^{II} salts. This indicates, either different site symmetries for the cations or, in the case of the Cu^{II} salts, the presence of square pyramidal $Cu(NCMe)_5^{2+}$ cations; the latter would be in contrast to the distorted octahedral $Cu(NCMe)_6^{2+}$ or $[Cu(NCMe)_4(MX_n)_2]$ groups found in hexa- or tetra-chlorometallates and in the tetrafluoroborate [1,3]. Weak co-ordination of anions to Cu^{II} in the solid state is well known [20], for example of PF_6^- to Cu^{II} in $Cu(py)_4(PF_6)_2$ [21]. Although the i.r. spectrum of $Cu(PF_6)_2 \cdot 5MeCN$ indicates a reduction in symmetry of PF_6^-, which is not observed for TaF_6^-, this by itself is not sufficient evidence for co-ordination, *cf.* [22].

The spectra of the salts in MeCN are consistent with O_h symmetry for the anions in all cases. Significantly the ^{19}F n.m.r. spectra of the Cu^{II} salts are sharp and unshifted from the Cu^{I} analogues although the values of $^{1}J(FP)$ are somewhat greater than normally found. In contrast the ^{1}H signals due to MeCN in the Cu^{II} solutions are broad and concentration dependent. Cu^{I} tetrafluoroborate and hexafluorophosphate are known to be associated to some extent in MeCN from conductivity studies [23], and a similar situation will obtain for the Cu^{II} salts. However in all cases solvent separated ion pairs are more likely than direct interaction between cation and anion.

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REFERENCES

1 A.P. Zuur and W.L. Groeneveld, Rec. Trav. chim. Pays-Bas, 86, (1967) 1089; J. Reedijk and W.L. Groeneveld, ibid., 86, (1967) 1103; 87, (1968) 513.

2 A. Prescott, D.W.A. Sharp, and J.M. Winfield, J.C.S. Dalton Trans., (1975) 934.

3 B.J. Hathaway, D.G. Holah, and A.E. Underhill, J.Chem.Soc., (1962) 2444.

4 A. Prescott, D.W.A. Sharp, and J.M. Winfield, J.C.S. Dalton Trans., (1975) 936; J.A. Berry, R.T. Poole, A. Prescott, D.W.A. Sharp, and J.M. Winfield, ibid., (1976) 272; J.A. Berry, A. Prescott, D.W.A. Sharp, and J.M. Winfield, J. Fluorine Chem., in press.

5 (a) P.A.W. Dean, J. Fluorine Chem., 5 (1975), 499; (b) C.D. Desjardins and J. Passmore, ibid., 6 (1975), 379.

6 M.K. Wilson and S.R. Polo, J. Chem. Phys., 20, (1952) 1716.

7 D.M. Byler and D.F. Shriver, Inorg. Chem., 13, (1974) 2697.

8 F.N. Tebbe and E.L. Muetterties, Inorg. Chem., 6, (1967) 129.

9 J. Reedijk, A.P. Zuur, and W.L. Groeneveld, Rec. Trav. chim. Pays-Bas, 86, (1967) 1127.

10 (a) G.M. Begun and A.C. Rutenberg, Inorg. Chem., 6, (1967) 2212; (b) A.M. Heyns and C.W.F.T. Pistorius, Spectrochim Acta , 30A, (1974) 99; ibid., 31A, (1975) 1293; (c) O.L. Keller, jun., and A. Chetham-Strode, jun., Inorg. Chem., 5, (1966), 367; (d) R.D. Peacock and D.W.A. Sharp, J. Chem. Soc., (1959) 2762.

11 D. Oelkrug, Structure and Bonding, 9, (1971) 1.

12 J.A.S. Howell and K.C. Moss, J. Chem. Soc. (A), (1971) 2483; J.C. Fuggle, D.W.A. Sharp and J.M. Winfield, J. Fluorine Chem., 1, (1971/72) 427.

13 W. Wieker, A.-R. Grimmer, and L. Kolditz, Z. Chemie, 7, (1967) 434.

14 W.P. Griffith and T.D. Wickins, J. Chem. Soc. (A), (1967) 675; N.A. Matwiyoff, L.B. Asprey, and W.E. Wageman, Inorg. Chem., 9, (1970) 2014.

15 M.F.C. Ladd and W.H. Lee, Prog. Solid State Chem., 1, (1964) 37; 2, (1965) 378

16 A.E. Wickenden and R.A. Krause, Inorg. Chem., 4, (1965) 404; N.A. Matwiyoff and S.V. Hooker, ibid., 6, (1967) 1127.

17 R. Alexander, D.A. Owensby, A.J. Parker, and W.E. Waghorne, Austral. J. Chem., 27, (1974) 933; B.G. Cox, A.J. Parker, and W.E. Waghorne, J. Phys. Chem., 78, (1974), 1731.

18 J. Burdon, J.R. Knights, I.W. Parsons, and J.C. Tatlow, J. Chem. Soc., Perkin Trans. I, (1976) 1930.

19 R.D.W. Kemmitt, M. Murray, V.M. McRae, R.D. Peacock, M.C.R. Symons, and T.A. O'Donnell, J. Chem. Soc. (A), (1968) 862

20 B.J. Hathaway, Structure and Bonding, 14, (1973) 49

21 H.G. Mayfield, jun., and W.E. Bull, J. Chem. Soc. (A), (1971) 2279; S.A. Bell, J.C. Lancaster, and W.R.McWhinnie, Inorg. Nuclear Chem. Letters, 7, (1971) 405

22 R.M. Morrison and R.C. Thompson, Inorg. Nuclear Chem. Letters, 12, (1976) 937

23 B. Kratochvil and H.L. Yeager, Topics in Current Chemistry, 27, (1972) 1.