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THE OXIDATION OF MANGANESE, IRON, COBALT AND NICKEL BY THE PENTAFLUORIDES OF ARSENIC AND ANTIMONY : PREPARATION OF SOME UNSOLVATED METAL HEXAFLUOROARSENATES AND -ANTIMONATES

P.A.W. DEAN

Department of Chemistry, University of Western Ontario, London, Ontario,
N6A 3K7, Canada.

SUMMARY

Oxidation of manganese, iron, and nickel with arsenic pentafluoride in liquid sulphur dioxide is a route to $Mn(AsF_6)_2$, $FeF(AsF_6)$ and $NiF(AsF_6)$ respectively. Cobalt is also oxidised by arsenic pentafluoride but a stable cobalt hexafluoroarsenate could not be isolated. Antimony pentafluoride in liquid sulphur dioxide oxidises excess manganese, iron, cobalt and nickel giving $Mn(SbF_6)_2$, $Fe(SbF_6)_2$, $CoF(SbF_6)$ and $Ni(SbF_6)_2$, respectively. The ^{57}Fe Mössbauer Spectra of $FeF(AsF_6)$ and $Fe(SbF_6)_2$ indicate that both compounds contain six-coordinate iron(II).

INTRODUCTION

During our recent work on strong acid salts we have needed the unsolvated MF_6^- (M=As, Sb) salts of the elements from manganese to nickel in their divalent states. A literature search showed that although $Mn(AsF_6)_2$ [1] and $Co(SbF_6)_2$ [2] are known in solution, only the nickel(II) hexafluorometallates have been isolated: small amounts of $Ni(SbF_6)_2$ [3] and $Ni(AsF_6)_2$ [4] were formed when NF_3-F_2-SbF_5 and NF_3-F_2-AsF_5, respectively, were heated under pressure in monel vessels. As a general route to the desired compounds, we have investigated the oxidation of the metals with AsF_5 and SbF_5 in liquid sulphur dioxide. Ruff [5] reported that SbF_5 itself reacted with few metals, but in recent years SbF_5 and AsF_5 have been shown to be mild, versatile oxidising agents when used in liquid SO_2: the oxidation of both non-metals, e.g. chalcogens [6], and non-transition metals, e.g. mercury[7], has been reported. Very recently, Desjardin and Passmore, in an independent study, have examined the oxidation of nickel and copper with arsenic and antimony pentafluorides [8].

RESULTS AND DISCUSSION

The arsenic pentafluoride oxidation of manganese, iron, cobalt or nickel was vigorously exothermic, the solvent boiling and the metal dissolving to give a solution which was colourless (Mn), orange-yellow (Fe), purple (Co) or yellow (Ni). The final product of the manganese oxidation was always of the normal type (i.e. $Mn(AsF_6)_2$, see below) so that this oxidation occurs according to

$$Mn + 3\ AsF_5 \longrightarrow Mn^{II}(AsF_6)_2 \cdot xSO_2 + AsF_3 \qquad (1)$$

It seems likely that iron, cobalt and nickel react similarly when excess arsenic pentafluoride is used, but when the metals are in excess, iron and nickel, at least, are oxidised to what is apparently a mixture of normal*and fluorobasic salts (see Experimental). At ambient temperature, removal of solvent and arsenic trifluoride from the oxidised metal solutions yielded solvated materials.* To remove the tenaciously adherent SO_2 and so obtain the unsolvated salts of interest, these initial solvated products were heated to 50° *in vacuo*. Table 1 gives the final products. No stable normal or fluoro-basic cobalt(II) hexafluoroarsenate was isolated, only pink products which analysis showed to be mixtures of CoF_2 with $CoF(AsF_6)$ and/or $Co(AsF_6)_2$. Regardless of initial reactant ratio only fluorobasic salts could finally be obtained for iron and nickel. It seems that only for manganese was the treatment necessary for SO_2 removal not accompanied by loss of some arsenic pentafluoride. Thus while oxidation of manganese with AsF_5 in SO_2 provides a convenient synthesis of $Mn(AsF_6)_2$, the corresponding normal hexafluoroarsenates of iron(II), cobalt(II) and nickel(II) cannot be prepared in an analogous manner.

The study of the oxidation of the four metals by SbF_5 was restricted to an examination of the reaction occurring when the metal was in excess, the hope being that this limitation would reduce the chance of obtaining either mixtures of normal and fluorobasic salts or products containing polymeric antimony fluoroanions. The SbF_5 oxidations proceeded with vigour. Oxidation of manganese and cobalt gave colourless and purple solutions,

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[*] We note that Desjardins and Passmore have isolated $Ni(AsF_6)_2 \cdot 2\ SO_2$ as a product of the oxidation of excess nickel with arsenic pentafluoride in SO_2 [8].

TABLE 1

Products of the Oxidation of Manganese, Iron, Cobalt and Nickel with Arsenic and Antimony Pentafluorides.

Metal	Oxidant	Final Product	Colour	μ_{eff} (°K)
Mn	AsF_5	$Mn(AsF_6)_2$	colourless	5.87 ± 0.09 (295)
	SbF_5 (a)	$Mn(SbF_6)_2$	colourless	5.91 ± 0.09 (298)
Fe	AsF_5	$FeF(AsF_6)$	yellow	4.51 ± 0.07 (296)
	SbF_5 (a)	$Fe(SbF_6)_2$	pale yellow	5.42 ± 0.08 (295)
Co	AsF_5	(b)		
	SbF_5 (a)	$CoF(SbF_6)$ (c)	lilac	3.89 ± 0.06 (295)
Ni	AsF_5	$NiF(AsF_6)$	pale yellow	3.17 ± 0.06 (297)
	SbF_5 (a)	$Ni(SbF_6)_2$	pale yellow	3.16 ± 0.06 (294)

(a) metal in excess (b) mixture (see text) (c) together with CoF_2

respectively, as with AsF_5. During the oxidation of iron and nickel, however, a blue colour developed: this colour was not due to the major oxidised metal species which were found to give SO_2 solutions with the same colours as solutions of the corresponding hexafluoroarsenates.* Possibly a small amount of acid-catalyzed oxidation by SO_2 occurs concurrently with oxidation by SbF_5 and leads to coloured reduced sulphur species (c.f. ref.

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* In addition the ^{57}Fe Mössbauer spectrum of the solute from a "blue" iron solution showed no evidence for any Fe(I) species.

[9], where a similar reduction of sulphur(VI) by metallic antimony is demonstrated).

For manganese, iron and nickel the main reaction occurring is

$$\text{Metal} + 4\ SbF_5 \longrightarrow (\text{metal}^{II})(SbF_6)_2.y\ SO_2 + SbF_3.SbF_5 \qquad (2)$$

The oxidation of cobalt proceeds differently giving an SO_2- soluble fluoro-basic salt, $CoF(SbF_6)$, and an insoluble pink cobalt containing product, presumably CoF_2, obtained as a mixture with the excess metal and the insoluble reduced antimony species. Upon removal of adherent SO_2 from the various hexafluoroantimonates we obtained the products indicated in Table 1. Clearly antimony pentafluoride oxidation of the elements is a useful route to the normal hexafluoroantimonates of manganese(II), iron(II), and nickel (II) but not to the corresponding cobalt(II) compound.

^{57}Mössbauer spectral parameters of $FeF(AsF_6)$ and $Fe(SbF_6)_2$ are shown in Table 1, together with those of FeF_2 for comparison. The centre shifts for the two new compounds indicate that the iron(II) in these is not only high-spin (as also shown by the values obtained for μ_{eff}-see Table 2) but also six-coordinate[10a].

TABLE 2

^{57}Fe Mössbauer Parameters for FeF_2, $FeF(AsF_6)$ and $Fe(SbF_6)_2$$^{(a)}$

Compound	Centre Shift(linewidth)	Quadrupole Splitting
FeF_2	1.70$^{(b)}$(0.34)	2.91$^{(b)}$
$FeF(AsF_6)^{(c)}$	1.71(0.44)	1.86
	1.74(0.34)	2.53
$FeF(AsF_6)^{(d)}$	1.71(0.38)	1.88
	1.73(0.38)	2.57
$Fe(SbF_6)_2^{(e)}$	1.71(0.52)	2.92
	1.76(0.52)	1.78

(a) In mm s^{-1} at 80°. Errors are ± 0.03 mm s^{-1}. (b) Ref.11 gives 1.73 and 2.92 mm s^{-1} for the CS and QS, respectively, at 80°K. (c) Spectrum fitted with no constraints (see text). χ^2 is 599 with 499 degrees of freedom. (d) Spectrum fitted with all linewidths set equal (see text). χ^2 is 643 with 501 degrees of freedom (e) Spectrum fitted with all linewidths set equal (see text). χ^2 is 870 with 501 degrees of freedom.

The spectrum of $FeF(AsF_6)$ was fitted to two doublets, with and without linewidth constraints (see Table 2). The goodness of fit, as indicated by χ^2, was dependent upon the fitting method, as was the intensity ratio (lower velocity doublet)/(higher velocity doublet). The latter ratio was 1.8 when the linewidths were constrained to be equal and ~1.2 when they were not. The better spectral fit, obtained with no constraints, produces differing linewidths in the two doublets: it therefore appears that there are more than two iron sites in $FeF(AsF_6)$, but in the absence of other structural data it does not seem sensible to refine the spectral data further.

The $Fe(SbF_6)_2$ spectrum was also fitted to two doublets; the quality of the spectrum was such that it was not considered meaningful to fit it without linewidth constraints. Within the two-site equal-linewidth approximation the intensity ratio (higher velocity doublet)/(lower velocity doublet) was 1.6. However the quite high value of χ^2 indicates a rather poor fit of the spectrum, and the linewidths again show that more than two iron sites must occur in $Fe(SbF_6)_2$.

Though we have incompletely refined the data it is clear that the centre shift differences between FeF_2, $FeF(AsF_6)$ and $Fe(SbF_6)_2$ are surprisingly small by comparison with those found for the analogous tin(II) compounds [12]. Nevertheless, there is, in both new compounds, at least one iron site where, judged by the higher value of the centre shift, the iron is in a more ionic environment than that occurring in FeF_2.

The magnetic moments of the manganese and cobalt salts (Table 1) show that they too contain high-spin metal ions as expected. The colours of the cobalt and nickel salts, being very similar to those of the corresponding metal difluorides and the fluorometallate(II) species derived from these [13a], are quite consistent with their containing metal ions which are six-coordinate with respect to fluorine. In the case of the nickel salts, the relatively low effective magnetic moments also argue for six-coordination [14]. We have no evidence concerning the coordination of the manganese in $Mn(AsF_6)_2$ and $Mn(SbF_6)_2$, but by analogy with manganese difluoride and the trifluoromanganates [13b], and in view of what is known about the iron, cobalt, and nickel hexafluorometallates (vide supra), it seems safe to assume that here too the metal ion is six-coordinate. To determine the exact manner in which six-coordination is achieved in the normal and fluorobasic metal(II) hexafluoro-arsenates and -antimonates X-ray structural studies are highly desirable.

EXPERIMENTAL

Materials

Manganese powder (Fisher), iron wire (J.T. Baker), cobalt powder (Alfa) and nickel wire (Alfa) had stated purities of 99.93, > 99.9, 99.8 and 99.97%, respectively, and were used without purification as was arsenic pentafluoride (Ozark-Mahoning). Antimony pentafluoride (PCR) was purified by double distillation under an atmosphere of dry nitrogen in a well-flamed glass apparatus. Sulphur dioxide (Matheson, anhydrous grade) was dried by standing for 24 hours or more in the gas phase over 3A Molecular Sieves.

Preparations

The metal-pentafluoride reactions were carried using essentially the same apparatus and procedure as previously described for the preparation of complexes of stannous fluoride [12]. The SO_2- soluble metal salts were separated from any insoluble material by filtration through the fine glass sinter; the insoluble material was washed several times with SO_2 to ensure complete extraction of product. ^{19}F n.m.r. spectroscopy showed that the white insoluble material produced in the systems $Mn-SbF_5-SO_2$ and $Ni-SbF_5-SO_2$ was a form of $SbF_3.SbF_5$: the -90° spectra of fluorosulphuric acid solutions showed signals due to F-on-Sb(III), SbF_6^- and $SbF_5SO_3F^-$, typical of $SbF_3.SbF_5$ [15]. The system $Fe-SbF_5-SO_2$ was also found to give $SbF_3.SbF_5$ as the insoluble reduced species: 18.6 mmole of Fe react with 55.38 mmole of SbF_5 giving a total of 5.73 g of insoluble material (excess iron + reduced antimony species); equation 2 requires 5.74 g whereas oxidation to give $Fe(SbF_6)_2$ (solv) + SbF_3 requires 3.30 g.

Except in the cases of $Fe(SbF_6)_2$(solv) and $Ni(SbF_6)_2$(solv),the more or less solvated products were obtained directly on removing the solvent from the filtered solution. The iron and nickel hexafluoroantimonates were obtained free of blue-coloured impurity (see Results and Discussion) by (i) reducing the volume of the filtered salt-containing solution until crystallization of the solvated product occurred, (ii) pouring off the supernatant liquor, and (iii) washing the solvated product several times with small volumes of SO_2 prior to drying. In a glove box filled with dry nitrogen, the solvated materials were transferred to glass drying vessels. The unvolumes of SO_2 prior to drying. In a glove box filled with dry nitrogen, the solvated materials were transferred to glass drying vessels. The unsolvated products were obtained by pumping the solvating materials in vacuo ($<10^{-3}$ torr) while heating to ca. 50°; loss of volatiles was followed on a vacuum gauge. The products indicated in Table 1 were finally isolated.

The analyses are:

Calcd. for $Mn(AsF_6)_2$: As, 34.62; Mn, 12.69. Found: As, 35.43; Mn, 12.73%.

Calcd. for $Mn(SbF_6)_2$: Mn, 10.44; Sb, 46.25. Found: Mn, 10.52, 10.59; Sb, 46.17%.

Calcd. for $FeF(AsF_6)$: As, 28.40; Fe, 21.17. Found: As, 28.68; Fe, 20, 20.90%.

Calcd. for $Fe(SbF_6)_2$: F, 43.24; Fe, 10.59; Sb, 46.17. Found: F, 42.89; Fe, 10.85; Sb, 46.14%.

Calcd. for $CoF(SbF_6)$: Co, 18.78; Sb, 38.81. Found: Co, 18.66; Sb, 38.50%.

Calcd. for $NiF(AsF_6)$: As, 28.10; F, 49.88; Ni, 22.02. Found: As, 27.91; F, 50.09; Ni, 22.25%.

Calcd. for $Ni(SbF_6)_2$: Ni, 11.07; Sb, 45.93. Found: Ni, 10.92; Sb, 45.96%.

Analyses These were performed by Alfred Bernhardt Microanalytical Laboratories, West Germany.

Stoichiometry of the reactions of iron and nickel with AsF_5

An attempt was made to determine whether iron and nickel are oxidised by AsF_5 according to the stoichiometry of Eqn. 1 or the stoichiometry of Eqn.3. (Because of the extreme ease with which the oxidised cobalt product lost AsF_5, a similar experiment for Co was not considered feasible). The stoichiometry was determined by adding a known amount of AsF_5(measured

$$\text{Metal} + 2\,AsF_5 \longrightarrow (\text{Metal}^{II})F(AsF_6).\text{solv.} + AsF_3 \qquad (3)$$

by volume in a pre-calibrated greaseless vacuum line) to an excess of the metal in SO_2 in the same type of apparatus as used to prepare the salts (see above). Reaction was allowed to proceed for one week at room temperature with intermittent shaking. Following separation of the product solution and volatiles from the SO_2-washed excess metal, the weight of the latter was determined by difference, the sealed-off metal-containing section of the apparatus being weighed before and after dissolution of the metal in dilute nitric acid. The results were as follows:

Metal taken, (mmole)	AsF_5 taken (mmole)	Excess metal(mmole)		
		Found	Reqd.by Eqn.1	Reqd.by Eqn.3
Fe, 5.4	2.7	4.2	4.5	4.0
Fe, 12.8	18.0	5.2	6.8	3.8
Ni, 8.3	12.9	3.2	4.0	1.8

It is clear that oxidation of excess iron or nickel does not follow cleanly either Eqn. 1 or Eqn.3; a mixture of normal and fluorobasic salts is apparently formed in these cases.

Routine Techniques

Magnetic measurements were made at room temperature using the Gouy method. ^{19}F n.m.r. spectra were obtained using a Varian HA-100 spectrometer operating at 94.1 MHz.

Mössbauer Spectra

Mössbauer spectra were recorded with samples at liquid nitrogen temperature using a 50 mCi Co/Cu source at room temperature with equipment described earlier [16]. Finely powdered samples were made up in a nitrogen-filled glovebox and the spectra were recorded immediately after preparation. Fitting and calibration of the spectra were achieved as described previously [10b]. Centre shifts are reported relative to sodium nitroprusside at room

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