Journal of Fluorine Chemistry, 61 (1993) 111–116

Adducts of manganese-(III) and -(IV) fluorides with antimony pentafluoride

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(Received March 2, 1992; accepted June 2, 1992)

Abstract

With the starting materials Mn, MnF_2 or MnF_3 with Sb, SbF_3 and SbF_5, the following amorphous adducts are formed by fluorination at elevated temperature and under pressure: $MnF_3 \cdot SbF_5$ (75–100 °C, 30–60 bar F_2); $4MnF_4 \cdot SbF_5$ (110–350 °C, 60–1000 bar F_2); $MnF_4 \cdot SbF_5$ (250–330 °C, 230–350 bar F_2, deposited in part of vessel cooled to 30–60 °C). With traces of oxygen present, $8MnF_4 \cdot SbF_5$ was found instead of $4MnF_4 \cdot SbF_5$. Conductivity measurements and infrared spectra indicate that the compounds are not ionic, but contain covalent fluorine bridges. No trace of a pentavalent $[MnF_4]^+[SbF_6]^-$ was found.

Introduction

Whereas the ionic compound $Mn(SbF_6)_2$ is known with the hexahydrate cation [1] as well as in dehydrated form [2], Mn^{III} and Mn^{IV} fluorides form mostly complexes $[MnF_4]^-$, $[MnF_5]^{2-}$, $[MnF_6]^{3-}$, $[MnF_5]^-$ and $[MnF_6]^{2-}$ [3–11]. For MnF_4, adducts with XeF_2 and XeF_6 have been synthesized [12–14], and the salts $[O_2]_2{}^+[MnF_6]^{2-}$ and $[O_2]^+[Mn_2F_9]^-$ obtained [15, 16], but no reactions with Lewis acids have been reported for MnF_3 and MnF_4 so far. As there might be the possibility of the formation of an $[MnF_4]^+[SbF_6]^-$ compound – by analogy to the well-known $[NF_4]^+[SbF_6]^-$ [17–19] – with a pentavalent d^2 Mn^V ion in a tetrahedral environment, an investigation of the fluorination of a mixture of MnF_4 and SbF_5 under various conditions seemed worthwhile.

Experimental

Different autoclaves made from Monel 400, partly with a Cu coating, or from CuBe 2 with volumes of 3 ml (for pressures between 300 and 1000 bar; for the high-pressure experiments this was manufactured by Nova Swiss) up to 27 ml (for pressures below 300 bar) were used, with Ni fittings and 10 V 610 and 10 VA 6082 valves (Autoclave Engineers, Inc.) respectively;

0022-1139/93/$6.00

one of the autoclaves was fitted with a cooling system of Cu tubes around its upper part. All vessels having contacts with elementary fluorine were carefully cleaned, evacuated and conditioned with diluted fluorine, being heated slowly up to the working temperature. The solid and liquid compounds (Mn, MnF_2, MnF_3; Sb, SbF_3 or SbF_5) were filled into the autoclaves under strictly anhydrous conditions. The autoclaves were closed and evacuated, under cooling, if necessary. The proper amount of fluorine (determined by volume, pressure and temperature data) was condensed slowly into the autoclave after cooling down to −200 °C by liquid nitrogen containing some helium. After closing the valve, the autoclaves were placed into the oven and first warmed up to room temperature, then heated slowly up to the reaction temperature. In the case where elemental Mn and Sb were used, this has to be done very slowly to avoid too vigorous fluorination. After reaction, the autoclave was cooled down to −196 °C, connected to the vacuum line and the excess fluorine condensed into a vessel at −200 °C or reacted with Al_2O_3. The autoclave was then warmed up to −90 °C and the free SbF_5 pumped off. After reaching room temperature, the vessels were filled with absolutely dry nitrogen and opened in a dry box. The samples were stored in sealed Teflon vessels in a dry box or at liquid nitrogen temperature.

The fluoride content was determined by the method of Allenstein and Kampmann [20]. For analysis of manganese and antimony, the samples were hydrolyzed in a closed apparatus (as volatile Mn^{VII} compounds may be formed by disproportionation and must be kept in the reaction mixture). Manganese was either precipitated as $MnO(OH)_2$ and heated to form Mn_3O_4, or determined colorimetrically after oxidation to permanganate by KIO_4. Antimony was precipitated as Sb_2S_3. It was shown that the samples contained no nickel from the material of the autoclaves. The analytical results are reported in Table 1.

Except for $MnF_3 \cdot SbF_5$, which was not formed using MnF_3 or SbF_5 even as one component of the reaction mixture, the products were always identical under the given temperature and pressure conditions regardless of the starting materials used. The various experimental conditions (F_2 pressure and temperature) and products obtained are summarized in Fig. 1.

TABLE 1

Elemental analyses (%) of adducts formed

	$MnF_3 \cdot SbF_5$		$MnF_4 \cdot SbF_5$		$4MnF_4 \cdot SbF_5$		$8MnF_4 \cdot SbF_5$	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
Mn	16.71	16.9 ± 0.7	15.80	16.1 ± 0.7	29.88	29.6 ± 1.3	34.77	34.4 ± 0.7
Sb	37.04	36.7 ± 1.2	35.02	34.8 ± 1.0	16.44	16.9 ± 0.6	9.63	10.0 ± 0.5
F	46.24	46.4 ± 0.4	49.18	49.2 ± 0.5	53.88	53.1 ± 1.0	55.60	55.4 ± 1.0

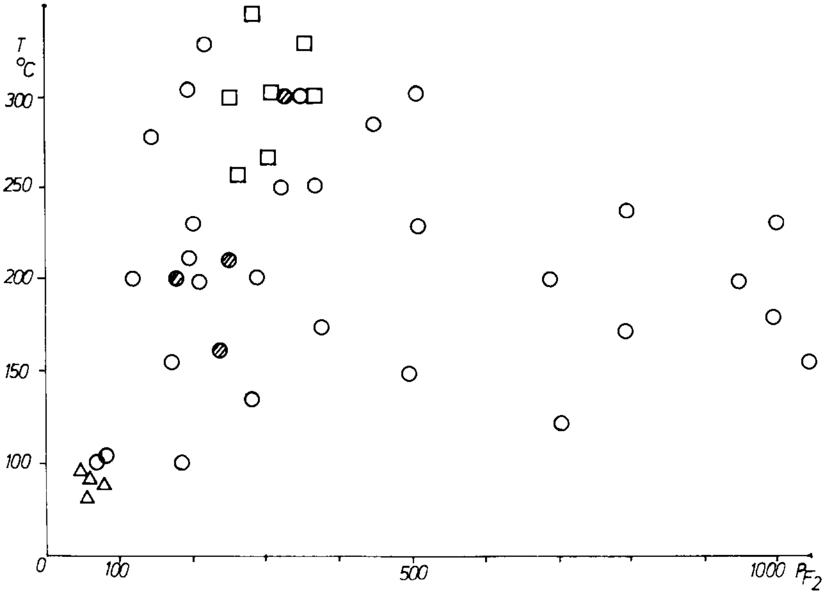

Fig. 1. Conditions for the fluorination of Mn/Sb mixtures and results obtained. △, $MnF_3 \cdot SbF_5$; □, $MnF_4 \cdot SbF_5$; ○, $4MnF_4 \cdot SbF_5$; and ●, $8MnF_4 \cdot SbF_5$.

Results and discussion

At temperatures between 75 °C and 110 °C and F_2 pressures between 30 bar and 60 bar, only $MnF_3 \cdot SbF_5$ was formed in 100% yield from Mn or MnF_2 and Sb or SbF_3. The adduct is a grey porous substance, stable in dry air at room temperature, which turns brown as a result of the formation of $MnO(OH)_2$ if moisture is present. The magnetic moment of 5.02 ± 0.02 BM is indicative of the high-spin d^4 configuration of Mn^{III}.

At elevated temperatures (110–350 °C) and F_2 pressures (60–1000 bar), the blue–violet adduct $4MnF_4 \cdot SbF_5$ was obtained in 100% yield. It is stable in dry air at room temperature, turning brown in the presence of moisture (formation of $MnO(OH)_2$). With water, violet vapours were evolved which are probably due to a volatile Mn^{VII} compound indicating disproportionation; an ozone-like smell was also perceptible. At 220 °C, the adduct decomposed. If traces of O_2 were present (as indicated by some white crystals of $[O_2]^+[Sb_nF_{n+1}]^-$ deposited in the colder regions (valve) of the autoclave and characterized by their Raman line at 1860 cm^{-1}), $8MnF_4 \cdot SbF_5$ was formed instead of the 4:1 adduct; however, the other properties remained essentially the same. The magnetic moments found were 3.75 ± 0.03 BM for $4MnF_4 \cdot SbF_5$ and 3.76 ± 0.04 BM for $8MnF_4 \cdot SbF_5$, showing the value for high-spin d^3 Mn^{IV}.

With a temperature of 300–350 °C (at least 250 °C) and an F_2 pressure of 300–350 bar (at least 230 bar), cooling the upper part of the vessel to 0–100 °C (best yield at 30–50 °C) led to the deposition of green $MnF_4 \cdot SbF_5$

in the cold region with a maximum yield of 65% (on the bottom of the vessel, an inhomogeneous grey, partly violet product remained). At room temperature, the samples decomposed slowly but they were stable at -196 °C. Glass vessels were etched and a deposit of brownish–black MnO_2 with some dark violet particles (permanganate with cations from the glass phase) formed. With water, violet vapours of a volatile Mn^{VII} compound were evolved and an ozone-like smell was perceptible. The magnetic moment was found to be 3.78 ± 0.08 BM indicative for Mn^{IV}.

No lines could be observed in the X-ray powder diffractograms of the compounds. Thus, all the adducts, even $MnF_4 \cdot SbF_5$, obtained by a transport mechanism, seem to be amorphous. Conductivity measurements with SbF_5 and IF_5 as solvents showed no solubility and no increase in conductivity.

No Raman spectra could be obtained, even with the use of a variety of laser exciting lines. Infrared spectra in the 400–1000 cm^{-1} region were measured using the powder between sealed AgCl windows (other usual window materials such as KBr, CsI, etc. could not be used because of the high oxidizing power of the samples). The infrared spectra are summarized in Table 2 and compared with the spectra of MnF_3, MnF_4, SbF_5, $[SbF_6]^-$ and $[Sb_2F_{11}]^-$ in the same spectral region. Spectra of higher condensed anionic species ($[Sb_3F_{11}]^-$; $[Sb_4F_{16}]^-$) are not known to date, but should show only additional splitting of those bands observed for the binuclear anion.

For $MnF_3 \cdot SbF_5$, no bands of SbF_5 or its anions were observed. However, two bands at 714 and 696 cm^{-1}, with an additional shoulder at 686 cm^{-1}, were found. These may belong to terminal MnF and SbF stretchings, although they are not observed in the spectra of the separate components (a Raman line at 655 cm^{-1} is found for MnF_3 corresponding to such a vibration [21]). The bands at 619 and 530 cm^{-1} can be assigned to stretchings of F bridges, mainly between Mn atoms [21]. The spectrum of $MnF_4 \cdot SbF_5$ is clearly dominated by the bands of SbF_5, with an additional MnF bridging vibration at 530 cm^{-1} (a terminal MnF stretching may coincide with the SbF stretching at 742 cm^{-1}). The band at 666 cm^{-1} may be interpreted as the stretching vibration of $[SbF_6]^-$, but it is much more probable that it belongs to the SbF_5 pattern. The infrared spectrum of $4MnF_4 \cdot SbF_5$ is essentially a superposition of the spectra of the components with a predominance of the MnF_4 bands.

The structures of solid SbF_5 and MnF_4 are very similar. Four molecules are connected by fluorine bridges in *cis* positions to form a tetrameric ring, which is isolated in the case of SbF_5 [25], but connected to bands which are interlinked in MnF_4 [26]. The stoichiometry and the infrared spectra of $4MnF_4 \cdot SbF_5$ and $8MnF_4 \cdot SbF_5$ suggest that the tetrameric rings of MnF_4 remain intact, but that their linkage is partly opened and replaced by the addition of SbF_5 on to one of the external fluorine atoms of MnF_4. The data obtained do not allow firm conclusions about the structures of the mono-adducts of MnF_3 and MnF_4, although for $MnF_4 \cdot SbF_5$ oligomeric SbF_5 species may be present from the spectroscopic features. No bands of fluoroantimonate anions were present in the reaction products of Mn^{III} and Mn^{IV} fluorides with

TABLE 2

Infrared spectra (400–750 cm^{-1}) of $MnF_3 \cdot SbF_5$ and $nMnF_4 \cdot SbF_5$ compared with the components of these adducts

MnF_3 [21]	MnF_4 [21]	SbF_5 [22]	$[SbF_6]^-$ [23]	$[Sb_2F_{11}]^-$ [24]	$MnF_3 \cdot SbF_5$ (this work)	$MnF_4 \cdot SbF_5$ (this work)	$4MnF_4 \cdot SbF_5$ $8MnF_4 \cdot SbF_5$ (this work)
	742 (s)	742 (s)				742 (s)	746 (vs)
720 (vw)	730 (ms)						729 (s)
		705 (s)			714 (s)	704 (vs)	710 (sh)
					696 (s)		
					686 (sh)		685 (sh)
		669 (s)	672			666 (m)	
			– (vs)				
			655	655 (vs)			
				645 (sh)			
611 (vs)	603 (vs)				619 (m)		606 (s)
556 (sh)				568 (m)			
				540 (wm)			
	530 (vs)				530 (m)	530 (m) (b)	532 (s)
	515 (sh)						500 (sh)
		450 (w) (b)		488 (ms)		464 (sh)	
421 (w)							

SbF_5, but they exhibited infrared bands in the 450–600 cm^{-1} region which must be attributed to fluorine bridges. Thus, all these adducts seem to be F-bridged as has also been found for $MOF_4 \cdot SbF_5$ (M = Mo, W, Re) [27], and not ionic species with $[MnF_2]^+$ or $[MnF_3]^+$ cations. In particular, no $[MnF_4]^+$ cation was formed, as also demonstrated by the magnetic measurements.

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