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On the Synthesis of Ammonium Xenon(VI) Hexafluoromanganate(IV)

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SUMMARY

The reaction between NH_4MnF_3 and xenon hexafluoride yields ammonium xenon(VI) hexafluoromanganate(IV). The persistance of the NH_4^+ in the environment of the XeF_6, during the synthesis of the salt, can be attributed to the positive charge because XeF_6 is electrophylic and will oxidize neutral or negatively charged species but not cations. Ammonium xenon(VI) hexafluoromanganate(IV) was characterized by chemical analysis, magnetic susceptibility measurements, thermogravimetric studies and vibrational spectroscopy. The spectroscopic evidence supports the formulation $NH_4^+XeF_5^+MnF_6^{2-}$.

INTRODUCTION

Hydrazinium fluorometalates proved to be very convenient starting materials in comparison with the corresponding binary fluorides for the syntheses of new xenon(VI) fluorometalates [1–3]. Recently this study was also extended to reactions with ammonium fluorometalates [4]. The advantages of this system are similar to those with hydrazinium fluorometalates, with the difference that ammonium fluorometalates are usually less reactive and therefore they also offer the possibility of synthesis of mixed ammonium xenon(VI) fluorometalates.

RESULTS

The reaction between NH_4MnF_3 and xenon hexafluoride yields ammonium xenon(VI) hexafluoromanganate(IV). The reaction was carried out very slowly, first at 0°C for several days so that the oxidation of manganese from 2+ to 4+ valency state would be not too vigorous, because in that case only impure products are obtained. At the end the reaction vessel was warmed up to 60°C for several hours. During the isolation of the product neither nitrogen nor nitrogen fluorides were detected, but only xenon and lower xenon fluorides, as shown by mass spectrometry and infrared spectroscopy. Also, approximately 1 mmol of xenon hexafluoride is bound to 1 mmol of ammonium fluoromanganate as was shown by mass balance. The chemical analyses of the products obtained in different runs always show that the mole ratio $NH_3:Xe:Mn:F$ is 1:1:1:11.

Therefore the overall equation could be written as follows:

NH_4MnF_3 + $nXeF_6$ $\rightarrow$ $(NH_4^+)(XeF_5^+)MnF_6^{2-}$ + XeF_x + some Xe + excess XeF_6
$n \geqslant 15$
$x = 2; 4$

This is, as far as we know, the first compound of this type. At room temperature it has negligible vapour pressure and is stable in throughly dried nickel, teflon or glass vessels. The compound is yellow, like the corresponding alkali and alkaline earth hexafluoromanganates(IV).

The persistence of the NH_4^+ in the environment of the XeF_6, during the synthesis of the salt, can be attributed to the positive charge. XeF_6 is electrophilic and will oxidize neutral or negatively charged species but not cations.

The magnetic susceptibility was measured in a screw capped Kel–F container using the Faraday method on a modified Newport Instrument magnetic balance. The magnetic susceptibility measurements confirm that manganese is in the 4+ valency state, which is in accordance with other known xenon(II) or xenon(VI) fluoromanganates. The compound follows the Curie–Weiss law with a magnetic moment of 3.94 B.M. and a Weiss constant $\theta = 10°C$.

A Mettler Thermoanalyzer TA–1 was used for the determination of the thermal properties of the sample under the following experimental conditions: an argon atmosphere with a flow rate of 5 l/h, heating rate 1°C/min and an alumina crucible with α–Al_2O_3 as the reference substance. Thermogravimetric studies are complex, and the only thing we are sure of at present is that the end product is MnF_3, as shown by the X–ray powder diffraction pattern.

Raman spectra were obtained using a Spex 1401 double monochromator with Ar^+ and Kr^+ lasers. Powdered samples were loaded in the rotating cell or into 2 mm o.d. quartz tubes in the dry box. The Raman spectrum of $(NH_4^+)(XeF_5^+)MnF_6^{2-}$ was recorded by different exciting lines (514.5 nm, 568.2 nm and 647.1 nm) in the rotating cell because the compound decomposes in the capillary in all three beams. The spectrum in the range from 100 cm^{-1} to 800 cm^{-1} is practically identical with the spectrum of $(XeF_5^+)_2MnF_6^{2-}$ (Fig. 1), with the exception of the band around 490 cm^{-1} which is split in the case of $NH_4^+XeF_5^+MnF_6^{2-}$. It looks as though the NH_4^+ ion does not have any significant effect on the XeF_5^+ and MnF_6^{2-} vibrations.

There is an other interesting feature. The intensity of Raman bands observed in the region between 1000 and 3300 cm^{-1} is some orders of magnitude higher than in the region up to 1000 cm^{-1} if the spectra were recorded with the green Ar^+ ion laser (514.5 nm) or yellow–green Kr^+ ion laser (568.2 nm) (Fig. 2). When the red line (647.1 nm) of Kr^+ ion laser was used as exciting light this effect was not observed. This is the most probably a resonance Raman effect. The same effect was also observed with the compound NH_4MnF_4 [5]. The electronic spectra of six coordinated manganese(III) and manganese(IV) derivatives exhibit strong absorption bands in the region 16000 to 21000 cm^{-1} and absorption in this region must be responsible for the Raman intensity enhancement.

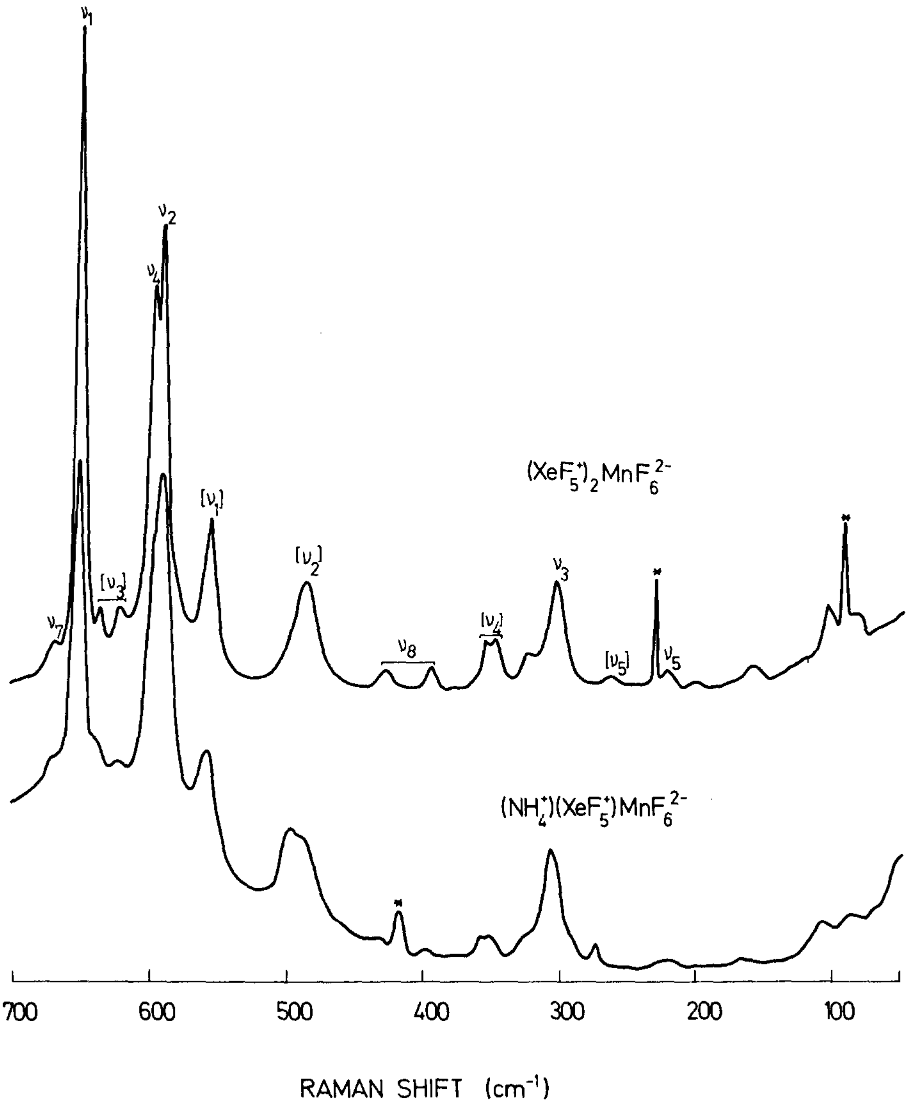

Fig. 1. Raman spectra of $(XeF_5^+)_2MnF_6^{2-}$ and $(NH_4^+)(XeF_5^+)MnF_6^{2-}$. The band at 417 cm^{-1} is due to the sapphire window of the rotating cell, while the bands at 95 cm^{-1} and 234 cm^{-1} are due to the plasma lines of the Kr^+ exciting line (647,1 mm). The frequencies in brackets belong to MnF_6^{2-} vibrations

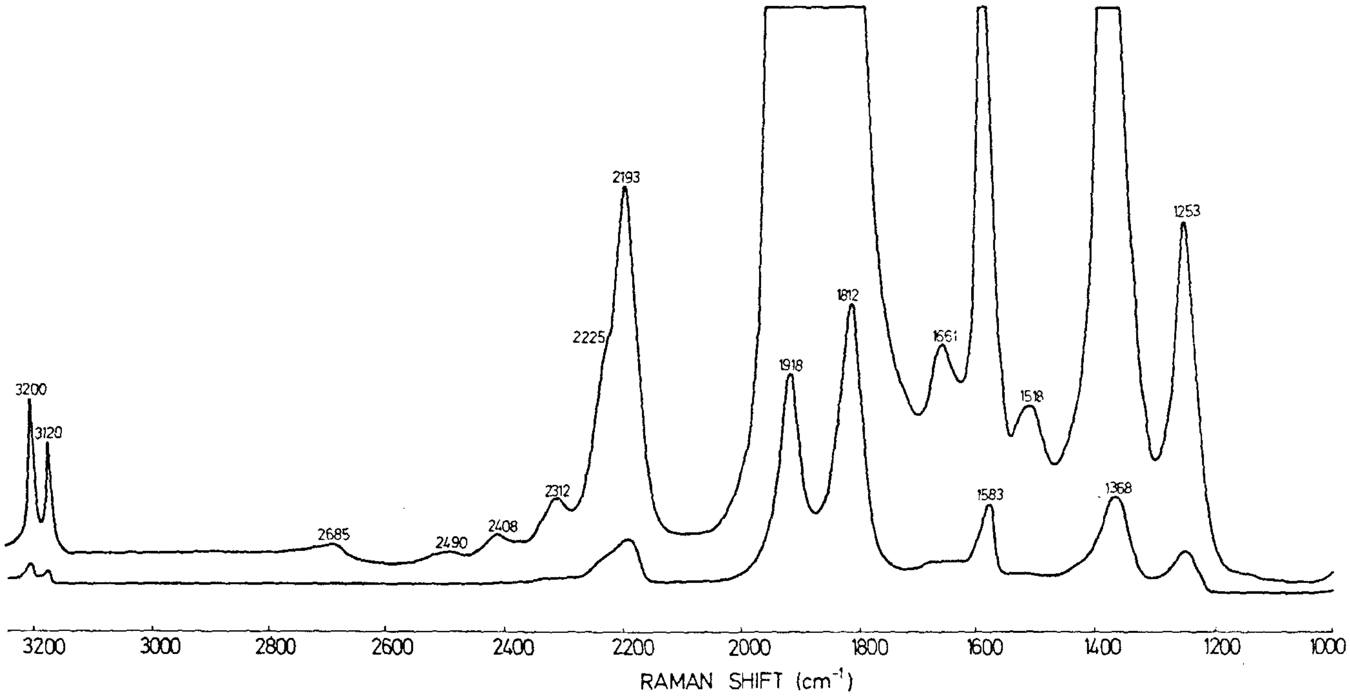

Fig. 2. Raman spectrum of $(NH_4^+)(XeF_5^+)MnF_6^{2-}$

TABLE 1

Infrared spectra of $NH_4^+XeF_5^+MnF_6^{2-}$ and $(XeF_5^+)_2MnF_6^{2-}$

$NH_4^+XeF_5^+MnF_6^{2-}$	$(XeF_5^+)_2MnF_6^{2-}$
420 (m)	415 (m)
430 (m)	425 (m)
453 (w)	455 (sh)
470 (w)	480 (m)
485 (m)	487 (sh)
575 (m)	567 (s)
618 (s)	615 (s)
640 (s)	635 (vs)
1425 (s)	
3270 (s,br)	

(s) – strong, (m) – medium, (w) – weak, (v) – very, (br) – broad, (sh) – shoulder

Infrared spectra were recorded using Perkin–Elmer 521 and Zeiss UR–20 spectrometers. Spectra of the solids were obtained by dusting samples onto silver chloride plates which were later sandwiched in a leak tight brass holder. Infrared spectra of the compounds $NH_4^+XeF_5^+MnF_6^{2-}$ and $(XeF_5^+)_2MnF_6^{2-}$ are also similar in the region from 400 to 700 cm^{-1} (Table 1), while the presence of NH_4^+ is determined by the bands at 1425 cm^{-1} and 3270 cm^{-1}. The spectroscopic evidence supports the formulation $NH_4^+XeF_5^+MnF_6^{2-}$.

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