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COMPLEXES OF MANGANESE TRIFLUORIDE WITH PYRIDINE

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SUMMARY

The complex MnF_3.3 pyridine and its deutero-derivative were synthesized, characterized by analytical, spectroscopic and X-ray data and its thermal decomposition to MnF_3 . 2 pyridine, MnF_2 .2 pyridine and MnF_2 was studied.

INTRODUCTION

Contrary to the many known addition compounds of the other trihalides of transition metals with organic nitrogen bases [1,2], only one complex, CrF_3.3 pyridine, has been reported so far for trifluorides [3,4] . For MnF_3, only salts with protonated organic bases as cations of $[MnF_4]^-$ and $[MnF_5]^{2-}$ complexes seem to exist [5].

RESULTS AND DISCUSSION

A stable 1:3 adduct is formed from MnF_3 and pyridine. The brown crystals are monoclinic (space group $P2_{1/C}\text{-}C_{2h}$) with lattice constants a = 1600.5 (0.9) pm, b = 815.7 (0.4) pm, c = 1255.5 (0.5) pm, α and γ = 90 , β = 102.8 (0.4) . The volume of the unit cell is 1639.09 $10^6 pm^3$, with 4 molecules in general position ($1\text{-}C_1$), the density is 1.41 g/cm^3. A more exact determination of the structure was not possible because of permanent twinning.

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The infrared spectra of MnF_3.2 pyridine, MnF_3 .3 pyridine and MnF_3·3 pyridine(d5) are reported in Table 1. Besides the many pyridine bands, which can be easily located by comparison with pyridine and pyridine-d5 itself [6,7], but show frequent splitting due to the presence of three such ligands, the bands at 613, 562 and 482 cm^{-1} can be attributed to MnF stretching vibrations, others below 300 cm^{-1} may either be MnN stretchings or MnF deformations. Though the precise position of the ligands cannot be derived exactly from these data, a local C_{3v} symmetry of the MnF_3 group seems very improbable due to the observed number of MnF stretchings.

The complex MnF_3· 3 pyridine is thermally stable up to 60° C. Thermogravimetric measurements give the results depicted in Figure 1. Between 65° and 90° C, one mole of pyridine is released, giving MnF_3· 2 pyridine which could be isolated as a light brown powder. The slow loss of weight between 90 and 160° C corresponds to one fluorine atom, thus, MnF_2· 2 pyridine should have been formed, which loses the two pyridine ligands between 160° and 220° C, leaving MnF_2 behind, as proved by chemical analysis.

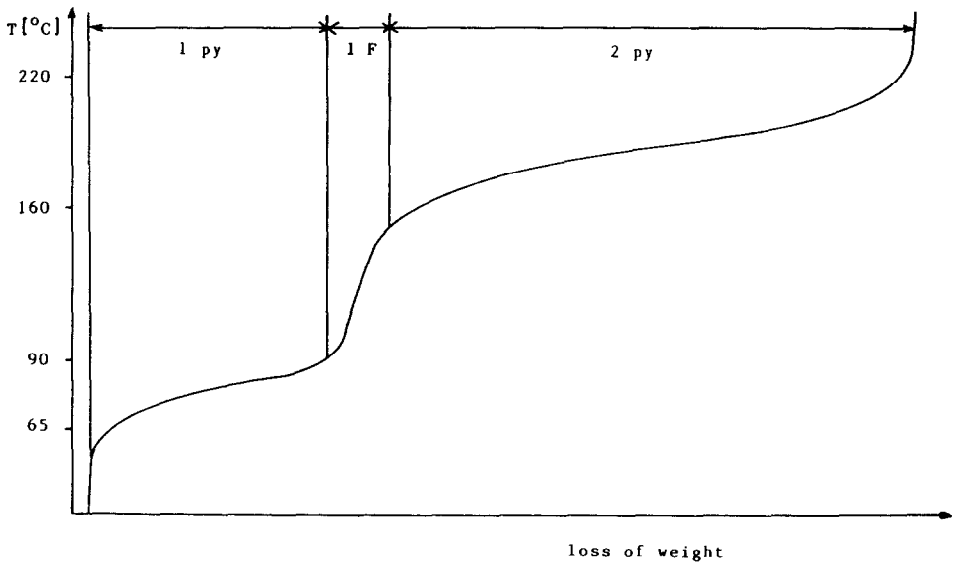

Fig. 1. Thermal decomposition of MnF_3·3 pyridine.

TABLE 1

Infrared spectra of MnF_3.2 pyridine, MnF_3.3 pyridine and MnF_3.3 pyridine - d5 (region 1650-2000 cm^{-1} omitted)

MnF_3.2 py	MnF_3.3 py	MnF_3.3 py-d5	assignment
3180 w			
3150 w			
3117 m			
3105 m	3104 vs		
3084 m	3082 s		$\nu_2, \nu_{7b}, \nu_{13},$
3076 m			
3062 m	3062 s		ν_{20a}, ν_{20b}(py)
3051 m	3049 s		
	3033 m		
	3020 sh		
3008 w	3000 m		
		2383 w	
		2336 w	
		2300 sh	$\nu_2, \nu_{7b}, \nu_{13},$
		2289 s	ν_{20a}, ν_{20b}(py-d5)
		2268 m	
		2260 m	
		2227 w	
1633 w	1632 wm		
1606 vs, 1598 s	1606 s, 1598 m	1601 m	ν_{8a}(py)
1588 sh			
1573 m, 1568 m	1573 m	1573 sh	ν_{8b}(py)
		1563 s, 1553 s	ν_{8a}(py-d5)
		1534 s	ν_{8b}(py-d5)
1485 s	1487 sh, 1482 s		ν_{19a}(py)
1453 s, 1447 s, 1442 s	1449 vs, 1445 vs		ν_{19b}(py)
		1412 vw	
1358 w	1359 w		ν_{14}(py)
		1344 w	ν_{19a}(py-d5)
		1319 s, 1311 s, 1300 sh	ν_{19b}(py-d5)
	1306 vw		
1244 wm	1248 w	1255 wm	
		1242 w, 1231 sh	ν_{14}(py-d5)
1219 s, 1216 s	1213 s		ν_{9a}(py)
1162 s, 1147 s	1162 sh, 1154 s		ν_{15}(py) ?
		1092 m	
1077 sh, 1068 vs	1071 sh, 1066 vs		ν_{18a}, ν_{18b}(py)
1046 s, 1038 s	1045 s, 1034 vs		ν_{12}(py)
		1041 m, 1028 sh	ν_3(py-d5)

(Continued)

TABLE 1 (cont.)

1016 s	1017 s, 1012 m		ν_5(py)
1006 s	1007 m		ν_1(py)
		1018 m, 1007 m	ν_{12}(py-d5)
		982 s, 973 s	ν_1(py-d5)
975 w, 966 w	971 vw, 958 w		ν_{17a}(py)
892 vw, 883 w	883 w	889 s	ν_{9a}(py-d5), ν_{10a}(py)
870 w		855 sh	ν_{15}(py-d5)
		845 sh, 839 s	ν_{18b}(py-d5)
		828 s, 823 sh	ν_5,ν_{18a}(py-d5)
		801 m	ν_{17a}(py-d5)
775 vs, 770 vs, 761 vs	788 s, 770 w, 757 s		ν_{11}(py)
704 vs, 693 vs	720 sh, 704 vs	688 w	ν_4(py), ν_{10a}(py-d5)
655 vs	652 m		ν_{6b}(py)
644 sh, 633 vs	645 ms, 623 ms		ν_{6a}(py)
		633 sh,w	ν_{11}(py-d5)
		624 s	ν_{6b}(py-d5)
633 vs	613 s	612 s	MnF stretching
		600 s	ν_{6a}(py-d5)
548 vw	562 s	563 sh	MnF stretching
		555 s, 539 s	ν_4(py-d5)
474 m	482 s	481 s	MnF stretching
	438 m		ν_{16b}(py)
430 m	428 sh		
425 m	423 m, 416 m		ν_{16a}(py)
		401 s	ν_{16b}(py-d5)
393 m			MnF ?
		384 s, 378 s	ν_{16a}(py-d5)
327 vs			
300 sh			
	279 sh	280 sh	
	267 s	268 vs	N_3MnF_3 skeleto
258 s	250 sh	255 sh	vibrations
233 sh		232 sh	
		228 sh	

EXPERIMENTAL

A Schlenk tube of 100 mm length and 15 mm diameter, containing a magnetic stirrer, is filled with 50 - 100 mg MnF_3. Pyridine (pyridine-d5) is added at a rate of 1 ml per 25 mg MnF_3. After cooling down with liquid nitrogen, the Schlenk tube is evacuated and sealed. Then the tube is warmed up to room temperature, and the content is stirred slowly and constantly. After 4 to 5 days, brown crystals begin to deposit on the glass wall above the surface of the liquid, which grow slowly in a several weeks' period. These crystals are isolated and dried in a fast stream of argon. They are stable in dry air, but decompose quickly with moisture. Thus, its strict exclusion during handling all products is mandatory.

Infrared spectra were obtained with a Perkin-Elmer spectrometer 883 for the nujol and hostaflon mulls of the substances, with CsJ as window material.

Thermogravimetric measurements were made using a Netzsch apparatus TG 409 E. The rate of heating was 2 ^{0}C per min. in air.

Magnetic moments were measured by the Faraday-Curie method with a magnetic balance by Bruker, giving 5.1 B.M. for MnF_3.3 pyridine and 4.85 B.M. for MnF_3.2 pyridine, which is indicative of the trivalent state of manganese.

Analytical data (theoretical values in brackets):

MnF_3 .3 pyridine: 15.9±0.5 (15.73)%Mn, 16.5±0.5 (16.32)%F, 51.0±0.5 (51.59)%C, 4.2±0.2 (4.33)%H, 11.9±0.3 (12.03)%N.

MnF_3 .3 pyridine-d5: 14.9±0.5 (15.08)%Mn, 19.9±0.5 (15.64)%F, 48,9±0.5 (49.45)%C, 8.1±0.4 (8.30)%D, 11.4±0.7 (11.53)%N.

$MnF_3 \cdot 2$ pyridine: 20.1±0.5 (20.34)%Mn, 21.2±0.5 (21.10)%F, 44.2±0.3 (4.46)%C, 3.7±0.1 (3.73)%H, 10.3±0.1 (10.37)%N.

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