Table 2

Ion	c_0/a_0 (25°C)	Ref.
ClO_4^-	0·725	[8]
IO_4^-	0·724	This work
CrO_3^-	0·723	[9]
MnO_4^-	0·713	[8]
ReO_4^-	0·714	[6]

been shown to be isostructural with the corresponding salt of perchlorate, ClO_4^- ion.

Previous to this investigation the fact that perchlorates are not, in general, isostructural with the corresponding metaperiodate was justified theoretically on the basis of their sizes.

The c/a values for a few isostructural (tetragonal) tetramethyl ammonium salts are given in Table 2.

The DTA study of $N(CH_3)_4IO_4$ was undertaken. But no phase changes were observed up to 220°C when the compound violently exploded.

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Reactions of zirconium, hafnium and cerium tetrafluoride with hydrazine

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IN OUR previous work we had examined the reactions of thorium and uranium tetrafluorides with hydrazine[1–3]. The formation of addition compounds $MF_4{\cdot}nN_2H_4$ was observed with anhydrous hydrazine and hydrolysis of the tetrafluorides took place with hydrazine hydrate. In our further study on hydrazine reactions with metal fluorides we have included two transition metal tetrafluorides (ZrF_4 and ThF_4) and one lanthanide tetrafluoride (CeF_4).

$ZrSO_4{\cdot}N_2H_4$[4] is the only zirconium addition compound with hydrazine know so far, while several hydrazinium(1+) and hydrazinium(2+) fluorozirconates have been isolated[5, 6]. As far as we know reactions of zirconium(IV) halides with hydrazine have not been investigated, but with ammonia the $5\,ZrF_4{\cdot}2NH_3$ adduct was described[7]. With hafnium tetrafluoride no compounds either with hydrazine or with ammonia have been reported to our knowledge. In the case of hafnium only two hydrazinium(2+) fluoride complexes are known[8].

Cerium(3+) compounds with hydrazine, known so far are the oxalates[9]. Cerium(4+) sulphate was described to form hydrazine adducts $Ce(SO_4)_2{\cdot}2N_2H_4$ and $2Ce(SO_4)_2{\cdot}3N_2H_4$[10] with tetravalent cerium. On the other side cerium(4+) sulphate was reduced to Ce(3+) with hydrazine[11] and with hydrazinium(2+) sulphate in aqueous sulphuric acid solutions[12]. Cerium tetrafluoride does not react with ammonia[13].

We found this study interesting because of the lack of data, mentioned above, because of the chemical relationship between the tetrafluorides examined and those described in our former articles and because of the doubt whether Ce(4+) is reduced by hydrazine in the investigated system or not.

EXPERIMENTAL

Zirconium tetrafluoride was prepared either by thermal decomposition of $N_2H_6ZrF_6$ in vacuum at 300°C [5] or by hydrofluorination of $ZrOCl_2{\cdot}8H_2O$, followed by a subsequent fluorination with elemental fluorine at 400°C (Found: Zr, 54·2; F, 44·7. Calcd.: Zr, 54·55; F, 45·45%).

Cerium and hafnium tetrafluorides were prepared by hydrofluorination of the oxides at 100°C, followed by subsequent fluorination of the product at 450 and 500°C respectively. The fluorination was repeated after the crushing and mixing of the product was done. (Anal. HfF_4: Found: Hf, 71·3; F, 29·5. Calcd.: Hf, 70·14; F, 29·86%. CeF_4: Found: Ce, 64·1; F, 36·2. Calcd: Ce, 64·84; F, 35·16%).

The preparation of anhydrous hydrazine, the experimental technique and the methods of analysis were described elsewhere[1–3]. Zirconium and hafnium were determined gravimetrically[14], cerium was determined by EDTA titration[15].

Table 1. Thermal analysis of $ZrF_4{\cdot}2N_2H_4$

Compound formed	DTA peak (°C)	End temp. of decomposition	% wt. loss Found	% wt. loss Calcd.
$ZrF_4{\cdot}2N_2H_4$				
	endo 230	245°C	14·1	13·9
$ZrF_4{\cdot}N_2H_4$				
	exo 283			
	endo 310	340°C	22·4	
	endo 378			
ZrF_4		400°C	27·1	27·7

endo—endothermic perk; *exo*—exothermic peak.

RESULTS AND DISCUSSION

ZrF_4-N_2H_4 *system*

With excessive anhydrous hydrazine zirconium tetrafluoride yields an addition compound of the formula $ZrF_4{\cdot}2N_2H_4$ after drying in vacuum (Found: N_2H_4, 27·8; Zr, 39·9; F, 32·8. Calcd.: N_2H_4, 27·7; Zr, 39·4; F, 32·8%). Drying at different temperatures (0, 20 and 60°C) gives always the same product. It has to be pointed out that traces of water cause hydrolysis of zirconium tetrafluoride. The reaction of zirconium tetrafluomide with hydrazine hydrate supports this observation. Hydrazinium(1+) oxyfluorozirconate is formed in this case as shown by chemical analysis and i.r. spectroscopy (Found: N_2H_4, 25·6; Zr, 39·3; F, 15·6%). The product was not investigated in detail.

Because zirconium tetrafluoride tends to hydrolize, it was very difficult to carry out the tensimetric titration. From the pressure measurements we concluded that $ZrF_4{\cdot}2N_2H_4$ was the compound with the highest hydrazine content and that $ZrF_4{\cdot}N_2H_4$ might exist. The last mentioned supposition was confirmed by the thermal analysis, shown in Table 1. The presence of $ZrF_4{\cdot}N_2H_4$ was confirmed by i.r. spectroscopy and the final product, zirconium tetrafluoride, by the chemical analysis.

The i.r. spectra of $ZrF_4{\cdot}2N_2H_4$ and $ZrF_4{\cdot}N_2H_4$ are presented in Table 2. The spectra are consistent with the spectra of the hydrazine addition compounds. The lattice vibrations were assigned in accordance with the known Zr-F vibrations[16].

ZrF_4-N_2H_5F-H_2O *system*

Because of the close similarity of the above mentioned tetrafluorides of zirconium, thorium[3] and uranium[1, 2], we tried to carry out the reactions of zirconium tetrafluoride with aqueous solutions of hydrazinium(1+) fluoride. Zirconium tetrafluoride was partly hydrolysed in neutral hydrazinium(1+) fluoride solutions and the products were extremely soluble in the mother liquor: 8·2 g of zirconium tetrafluoride and 2·8 g of hydrazinium(1+) fluoride had to be added to 2·8 g of water in order to get a solid residue. The solid in equilibrium with this solution was filtered off and washed with methanol. The compound was identified as $(N_2H_5)_3Zr_4F_{19}{\cdot}3H_2O$ on the basis of its chemical

Table 2. I.R. spectra of zirconium tetrafluoride and hafnium tetrafluoride-hydrazines

$ZrF_4{\cdot}2N_2H_4$	$ZrF_4{\cdot}N_2H_4$	Assignment
3330 s	3371 s	$(NH_2)_s$
3296 m	3324 m	
3225 vs	3100 s, vb	
2713 w	2743 w	comb. bends
2486 w	2702 vw	
1649 w	1609 s	$(NH_2)_d$
1631 w		
1609 vs	1544 s	$(NH_2)_d$
1356 vs	1222 w	$(NH_2)_w$
1221 vs	1117 vs	$(NH_2)_t$
1190 s		
1166 vs		
999 vs	978 vs	$(N–N)_s$
681 s		$(NH_2)_r$
652 m		
583 w		$(Zr–N)_s$
518		$(Zr–F)_s$
484 vs, b		
410		

Abbreviations: s—strong; w—weak; m—medium; v—very; b—broad.

The spectrum of $ZrF_4{\cdot}N_2H_4$ was taken only to 700 cm^{-1}.

Table 3 I.R. spectra of $(N_2H_5)_3Zr_4F_{19}{\cdot}3H_2O$, $N_2H_5CeF_4$ and some other products

A*	$(N_2H_5)_3Zr_4F_{19}{\cdot}3H_2O$	B†	$N_2H_5CeF_4$	Assignment
3480 vs, vb	3556 vs	3458 w, sh		$(OH)_s$
3362 s	3388 vs	3361 vs	3336 vs	
3332 w	3350 s	3314 w	3283 w	$(NH_2)_s$
3227 w	3315 m	3380 w	3201 w	
			3060 s, b	
3166 w, b	3150 s, vb	3171 m	2982 s, b	
2740 w	2740 m, s	3136 w	2904 w	$(NH_3^+)_s$
2640 w	2657 m	2934 m	2746 w, b	
		2643 w	2624 m	
1648 w, sh	1638 w, sh	1644 w, sh		$(OH_2)_d$
	1606 s			
1620		1617 vs	1629 vs	$(NH_2)_d$
1572 m				
1541 w, sh	1552 w	1556 s	1540 vs	$(NH_3^+)_d$
1315 vw	1320 vw	1313 vw	1302 vw	$(NH_2)_b$
1255 vw	1271 w	1208 m	1243 w	$(NH_2)_b$
			1123 vs	
1120 vs	1128 vs	1120 s	1100 s	$(NH_3^+)_b$
1078 m, sh	1112 w, sh	1078 m, sh	1047 m	
974 s	999 m, sh	952 vs	942 vs	$(N–N)_s$
952 vs	983 vs			
	902 s	868 vs	730 s	
836 vs	668 w	803 m		
			503 w, sh	$(N_2H_5^+)_{tor}$

*A—the product in the ZrF_4–N_2H_4–H_2O system (taken only to 700 cm^{-1}).

†B—the product in the HfF_4–N_2H_4–H_2O system (taken only to 700 cm^{-1}).

Abbreviations: s—strong; m—medium; w—weak; v—very; b—broad; sh—shoulder.

analysis (Found: N_2H_4, 11·0; Zr, 41·4; F, 41·2. Calcd.: N_2H_4, 10·9; Zr, 41·4; F, 41·1%) and of its i.r. spectrum (Table 3). In similar systems $Li_3Zr_4F_{19}$ and $Na_3Zr_4F_{19}$ as well as $M_4Zr_4F_{20}\cdot 4H_2O$ ($M = NH_4$, Na, K, Rb, Cs, Tl) are known[17]. The results are therefore very interesting, but because of the experimental difficulties, mentioned above, no further experimental work has been carried out so far.

HfF_4–N_2H_4 *system*

Similar to zirconium tetrafluoride, hafnium tetrafluoride was also found to be extremely susceptible to traces of moisture. The tendency to react with water was much stronger as in the case of thorium tetrafluoride or uranium tetrafluoride. Although hydrazine was dried with hafnium tetrafluoride itself, it was not possible to exclude the influence of water.

With hydrazine hydrate hafnium tetrafluoride forms a hydrolysed product with the mole ratios of $N_2H_5^+$:Hf:F equal to 1:1:3 (Found: N_2H_4, 10·0; Hf, 55·7; F, 17·6%). The presence of the $N_2H_5^+$ ion was confirmed with the i.r. spectrum of the product obtained (Table 3). The product is diamagnetic, containing tetravalent hafnium with the $[Xe]f^{14}$ structure.

With anhydrous hydrazine eleven experiments were made in order to get the reproducible results. The mole ratio of hydrazine to hafnium tetrafluoride was varied from 0·5 to 25 and some characteristic results are shown in Table 4. In spite of all the care with the preparation work and with the chemical analysis, a partial hydrolysis took place. I.R. spectra are consistent with the unpure compounds obtained; hydrolysis is accompanied by the appearance of the $(NH_3^+)_n$ vibrations of the $N_2H_5^+$ ions. The same effect is evident from the chemical analysis. The compounds were found to be diamagnetic with tetravalent hafnium.

Table 4. Reaction conditions and results in the HfF_4–N_2H_4 system

Mole ratio N_2H_4:HfF_4	Chemical analysis %N_2H_4	%Hf	%F	Sum
2:1	19·0	55·1	19·9	93·0
3:1	20·5	51·4	18·4	90·3
4:1	23·4	50·6	18·2	92·0
25:1	17·5	56·3	20·2	94·0
Theoretical composition:				
$HfF_4\cdot 2N_2H_4$	20·1	56·0	23·9	100·0
$Hf(OH)F_3\cdot 2N_2H_4$	20·2	56·4	18·0	94·6

CeF_4–N_2H_4 *system*

Gas evolution was observed by reacting cerium tetrafluoride with the hydrazine hydrate, giving simple cerium(III) fluoride (Found: Ce, 72·1; F, 28·1; Calcd.: Ce, 71·3; F, 28·9%). The reduction of Ce^{4+} to Ce^{3+} was confirmed by the magnetic susceptibility measurements. The magnetic moment 2·33 ± 0·01 B.M. ($\theta = 60·1$°K) is consistent with the literature data for trivalent cerium with the $^2F_{5/2}$ configuration[18].

Reduction takes place also in anhydrous hydrazine, the product being $N_2H_5CeF_4$ (Found: N_2H_4, 12·7; Ce, 56·9; F, 30·5. Calcd.: N_2H_4, 13·8; Ce, 56·2; F, 30·5%). The magnetic moment 2·99 ± 0·01 B.M. ($\theta = 114·2$°K) is higher than normally: Jonassen and Weissberger[18] found the values between 2·25 and 2·45 B.M., while with $Ce_2(C_2O_4)_3\cdot mN_2H_4\cdot nH_2O$ magnetic moments are reported to lie between 2·37 and 2·61 B.M.[19]. But still the $4f^1$ configuration, resulting from the L–S coupling, is the most probable. The i.r. spectrum of $N_2H_5CeF_4$ excludes the presence of hydrazinium(1+) fluoride in the reaction product[19]. The spectrum is shown in Table 3 and has all the vibration modes, characteristic for the $N_2H_5^+$ ion.

Thermal decomposition of $N_2H_5CeF_4$ at 250°C in vacuum proceeds to cerium(III) fluoride (Calcd.: Ce, 71·1; F, 28·9. Found: Ce, 72·1; F, 28·6%).

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