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The thermal decomposition of guanidinium hexafluorometallates under quasi-isobaric conditions

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Abstract

The guanidinium hexafluorometallates are very stable compounds because of the formation of NH···F bonds in the structure. The compounds form series with isotype structures that depend on the charge of the central atom: $[C(NH_2)_3]_3MF_6$ (cubic), $[C(NH_2)_3]_2MF_6$ (monoclinic), $[C(NH_2)_3]MF_6$ (polymorphic). The thermal decomposition of 19 guanidinium hexafluorometallates has been investigated under quasi-static conditions (DTA, TG and DTG). In this way, hydrolysis reactions were repressed and a correlation of the obtained results with thermodynamic data became possible. The solid and gaseous reaction products were characterized by X-ray analysis, IR spectroscopy and mass spectroscopy. The results are discussed with the help of oxidation state diagrams.

INTRODUCTION

Guanidinium hexafluorometallates form series of isotype compounds in which the structure is dependent on the charge of the central atom. Bukovec [1] described the isotype guanidinium hexafluorometallates $[C(NH_2)_3]_3MF_6$ where M is Al, Ga, In, and Mn, which crystallize in the cubic system, space group Pa3. $[C(NH_2)_3]_3FeF_6$ also belongs to this series, its structure having been determined by Fourquet et al. [2]. The high stability of $[C(NH_2)_3]_3MF_6$ is due to the formation of a strong network of NH···F bridges. The thermal decomposition of these compounds does not occur before these bridging bonds have been activated, as has been demonstrated by appropriate ESR investigations [3].

Sengupta and Dasgupta [4] described $[C(NH_2)_3]_2$ TiF_6, the first representative of the series of compounds $[C(NH_2)_3]_2MF_6$, crystallizing with the space group *Cm*. Further members of this series with M being Si, Ge, and Sn were prepared by Calov et al. [5] who also determined the structure of

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$[C(NH_2)_3]_2TiF_6$ which shows that this compound is built up from layers with strong NH···F connections between the MF_6 octahedrons and the cations.

The guanidinium fluorometallates with five-valent central atoms, however, form different structures at room temperature, but heating of these compounds above a given temperature always leads to a reversible phase transformation into a cubic modification [6].

The thermal decomposition of nitrogenous fluorometallates includes the formation of fluorides and the evaporation of NH_3 and other nitrogenous gases, depending on the cation. Some side reactions also take place: hydrolysis, reduction of the central atom of the fluorometallates, and nitride formation have been reported [7–9].

Thermal treatment of the guanidinium salts leads to condensation reactions of the cation via the intermediates biguanide and melamine and via the formation of NH_3. Grahek and Bukovec [10] have reported the thermal decomposition of $[C(NH_2)_3]_3FeF_6$; under dynamic conditions, FeF_2, Fe, N_2, $(CN)_2$, NH_3, HF, $C_3N_6H_6$ and other gaseous products are formed. The decomposition reaction of melamine was described by Costa and Camino [11], who showed that up to 700°C the nitrogenous products of the thermolysis remain in the system. Therefore, reduction as well as nitride formation reactions should be possible.

The intermediates and final products of the thermal decomposition of $[C(NH_2)_3]_3FeF_6$ described by Grahek and Bukovec [10] can only be formed by an interaction of the gaseous and solid decomposition products. Therefore, the partial pressure of the gaseous reaction products has an enormous influence on the structure and amounts of the products formed. Furthermore, under dynamic conditions, hydrolysis often dominates the whole process and oxides are formed as final products. Therefore, it is necessary to use standard conditions for the decomposition reactions in order to compare the results obtained from several guanidinium hexafluorometallates. We used the non-reciprocal quasi-isobaric method of thermal analysis.

Using the non-reciprocal quasi-isobaric method of thermal analysis, hydrolysis reactions are repressed and a correlation of the results with thermodynamic data is possible [12]. Moreover, using non-reciprocal quasi-isobaric conditions, it is possible to investigate the side reactions taking place during the thermal decomposition of fluorometallates with nitrogenous cations.

EXPERIMENTAL

Thermal analysis was carried out using a Q1500D Derivatograph that had been modified for analysing highly reactive substances [12], coupled with an MC80 computer. Non-reciprocal quasi-isobaric conditions were obtained using a Q-crucible in which the partial pressure of the gaseous reaction products reaches 70 kPa (self-generated atmosphere) [12]. The following parameters were used: sample mass, 200–400 mg; dynamic heating rate, 5 K min^{-1}; atmosphere, N_2; pumping rate, 8 l/h^{-1}; reference, Al_2O_3; crucible material, Pt.

Methods used for the preparation and characterization of the samples are described elsewhere [1, 2, 4, 5].

The intermediate and final products of the decomposition reactions were characterized by X-ray analysis (Guinier method, Cu Kα radiation) and by IR spectroscopy (Specord, KBr pellets) after cooling to room temperature.

Gaseous reaction products were characterized by mass spectrometry (MAT 212, Finnigan, direct inlet system, continuous heating, Au crucible).

RESULTS

The results of the thermal analyses are summarized in Table 1. The value T_{max} for the first thermogravimetric step was taken as a criterion for the stability; the temperature of the last step was taken as a measure of the

TABLE 1

Results of the thermal decomposition of guanidinium hexafluorometallates

Compound	T_{max}/(°C) of the TG steps		Crystalline products		
	First	Last	Therm. decomp.	Side reaction	Hydrolysis
$[C(NH_2)_3]_3AlF_6$	365	778	AlF_3		
$[C(NH_2)_3]_3GaF_6$	362	951	(GaF_3)	GaN	
$[C(NH_2)_3]_3InF_6$	380	856	InF_3		
$[C(NH_2)_3]_3TiF_6$	270	665	TiF_3	(TiN)	
$[C(NH_2)_3]_3VF_6$	392	658	VF_3		
$[C(NH_2)_3]_3CrF_6$	380	825	CrF_2	CrN	
$[C(NH_2)_3]_3MnF_6$	300	792	MnF_2	(Mn_5C_2)	(MnO)
$[C(NH_2)_3]_3FeF_6$	370	738	FeF_2	Fe_3C	
$[C(NH_2)_3]_3CoF_6$	140	709	CoF_2		
$[C(NH_2)_3]_2SiF_6$	288 [a]	738		No residue	
$[C(NH_2)_3]_2GeF_6$	294 [a]	500		No residue	
$[C(NH_2)_3]_2SnF_6$	252 [a]	757		Sn	(SnO_2)
$[C(NH_2)_3]_2PbF_6$	180	720	PbF_2	Pb	
$[C(NH_2)_3]_2TiF_6$	265	660		(TiN)	(TiO_2)
$[C(NH_2)_3]_2ZrF_6$	278 [a]	790	ZrF_4		(ZrO_xF_y)
$[C(NH_2)_3]PF_6$	293	729		No residue	
$[C(NH_2)_3]AsF_6$	293	700		No residue	
$[C(NH_2)_3]SbF_6$	298	727		No residue	
$[C(NH_2)_3]TaF_6$	324 [a]	704		(TaN)	TaO_2F

[a] Melting point.

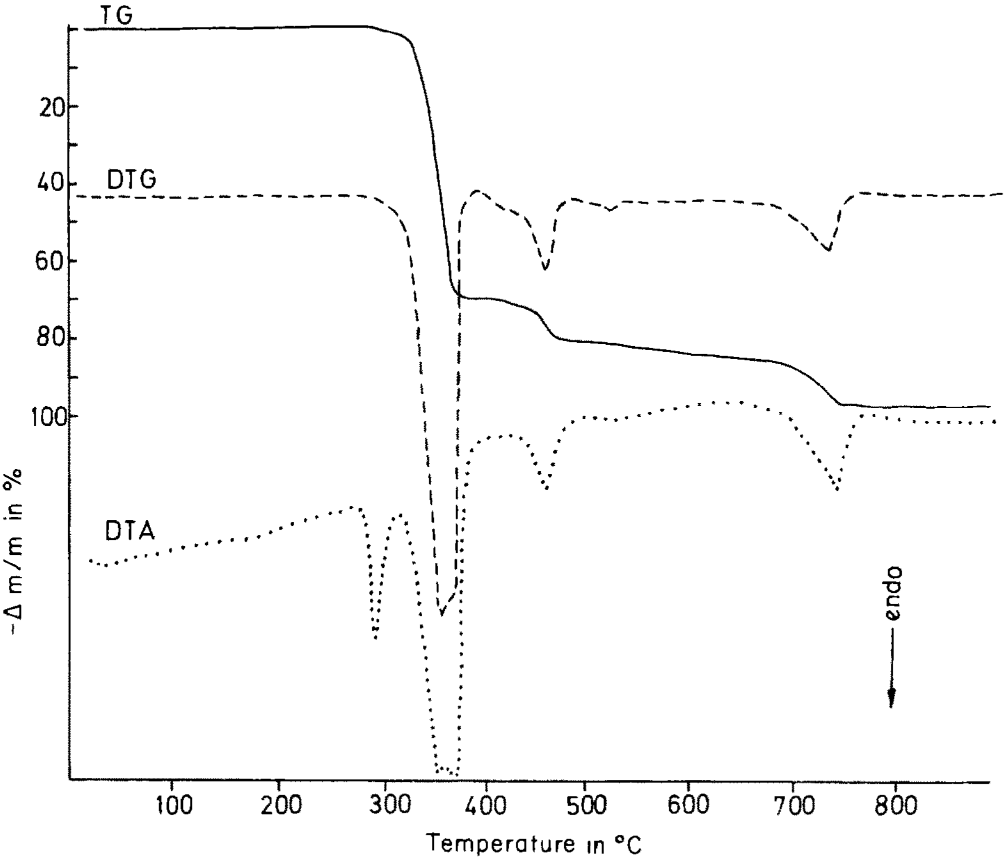

Fig. 1. Thermal analysis of $[C(NH_2)_3]_2SiF_6$ under non-reciprocal quasi-isobaric conditions.

time that volatile nitrogenous compounds remain in the system. Except for those cases in which nitrides are formed, no bands in the IR spectra of the final residues were found that can be attributed to the presence of nitrogen in the sample. The solid reaction products were studied by X-ray analysis and these results are compared with the thermoanalytical results.

The results given in Table 1 are complemented by Figs. 1–3 which show typical decomposition curves.

The thermal decomposition of $[C(NH_2)_3]_2SiF_6$ (see Fig. 1) is given as an example for decomposition reactions where volatile fluorides are formed. The DTA curve indicates that the compound melts at 288°C before it decomposes. The first thermogravimetric step [350°C] is due to generation of SiF_4, HF, and thermolysis products of guanidine. A gas mixture of NH_3, SiF_4, HF, H_2O, and guanidine (fragments $CN_3H_5^+$ and $CN_2H_3^+$) was detected by mass spectroscopy; silicon evaporates completely in the form of SiF_4. The thermogravimetric steps at 480 and 738°C are due to further condensation and decomposition reactions of thermolysis products of

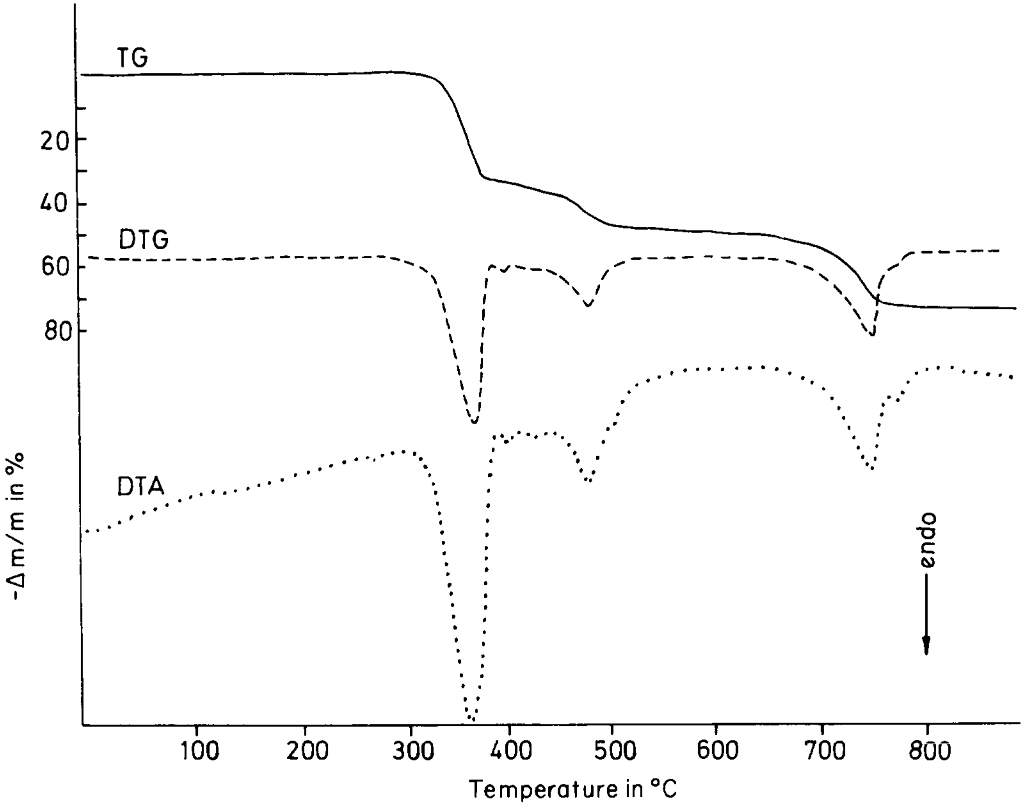

Fig. 2. Thermal analysis of $[C(NH_2)_3]_3AlF_6$ under non-reciprocal quasi-isobaric conditions.

guanidine. Outside the crucible, SiO_2 is formed by hydrolysis and deposits on the sample holder; hence, the observed total mass losses are not valid.

Figure 2 shows the thermal decomposition of $[C(NH_2)_3]_3AlF_6$ as an example of a decomposition reaction where only the solid fluoride is formed, and the decomposition products of the cation evaporate completely. In addition to NH_3, HF and guanidine, melamine ($C_3H_6N_6^+$) was also detected by mass spectroscopy as a gaseous decomposition product. The only crystalline intermediate is NH_4AlF_4 which is formed by decomposition of the starting compound at 360°C. The decomposition of NH_4AlF_4 occurs as described earlier [9] via β-AlF_3 into α-AlF_3 in the temperature range between 480 and 700°C. The subsequent thermogravimetric step is again due to thermolysis reactions of guanidine. White, pure α-AlF_3 is the final product of the decomposition.

The decomposition of $[C(NH_2)_3]_2PbF_6$ is given as an example of a decomposition where the reduction reactions dominate (see Fig. 3). Already at 180°C, a strongly exothermic reaction accompanied by a mass loss takes place and leads to the formation of β-PbF_2. The subsequent thermogravimetric steps at 290 and 720°C are again due to thermolysis

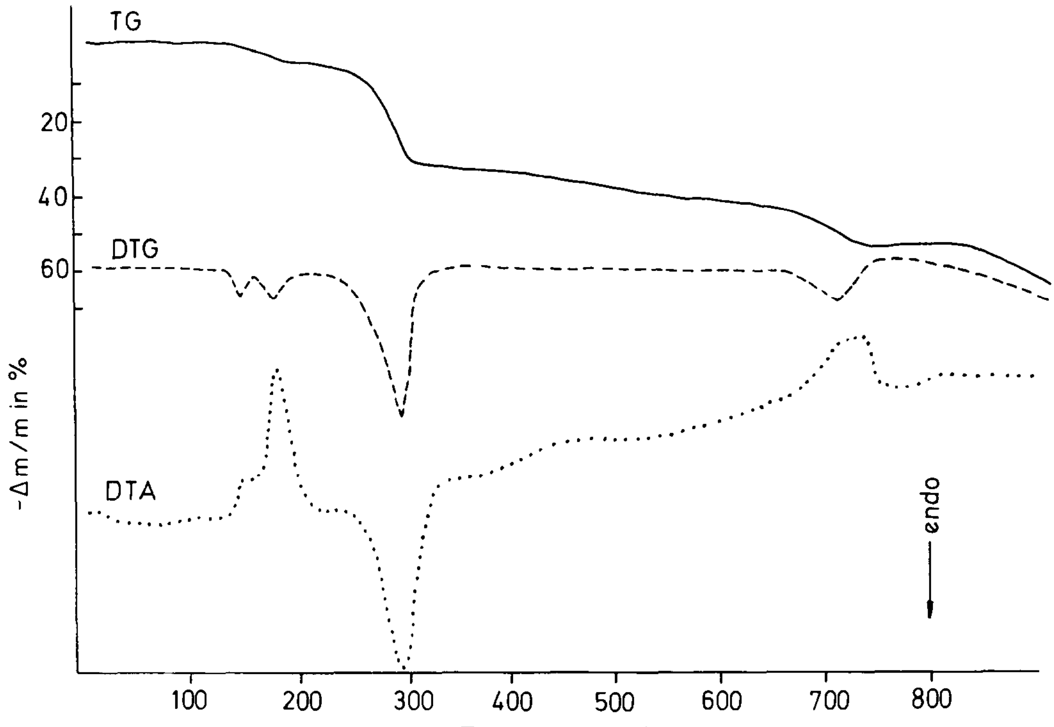

Fig. 3. Thermal analysis of $[C(NH_2)_3]_2PbF_6$ under non-reciprocal quasi-isobaric conditions.

reactions of the cation together with a phase transformation of PbF_2. At 290°C, α-PbF_2 is formed, whereas β-PbF_2 is reformed at 720°C. Further crystalline products were not detectable. Above 650°C, PbF_2 partially reacts with the thermolysis products of guanidine to form metallic lead in an exothermic reaction. The continuous mass loss above 950°C is caused by evaporation of PbF_2.

DISCUSSION

The stability of guanidinium hexafluorometallates increases, not only at room temperature but also at elevated temperatures, with an increasing number of NH···F bonds (Table 1).

The guanidinium cation and its thermolysis products condense stepwise with increasing temperature, forming very stable organic compounds (derivates of melamine and their thermolysis products), or react with the metal fluorides. Consequently, reduction reactions, and nitride and carbide formations become the dominant reactions in addition to the formation of fluorides. These side reactions occur to different extents for the different investigated fluorometallates.

Below, we attempt to explain these side reactions using oxidation state diagrams.

Oxidation state diagrams

Oxidation state diagrams [13] illustrate the course of a redox reaction. They are constructed by plotting volt equivalents ($zH^{\ominus}$) of a compound against its oxidation number z, the electrically neutral element having $z = 0$. Connecting the points of a redox pair yields a gradient the value of which is a measure of the oxidizing or reducing effect of the redox pair. The higher the absolute value, the stronger the redox effect. Positive gradients represent oxidizing systems, negative gradients reducing systems [13].

The direct correlation to the free enthalpy is given by the equation

$$\Delta G^{\ominus} = zU_{H^{\ominus}}F$$

where F is the Faraday constant.

From the thermodynamic point of view, all these reactions proceed spontaneously if the reduction product shows a lower volt equivalent than the starting compound. One can use this to estimate graphically whether a redox reaction takes place [14]. The gradients for the oxidizing and the reducing agents are drawn on the diagram in such a way that the starting points of both compounds coincide. If this point is situated above the line connecting the points of the reaction products, the reaction occurs spontaneously. In Fig. 4, examples taken from ref. 14 are shown. The

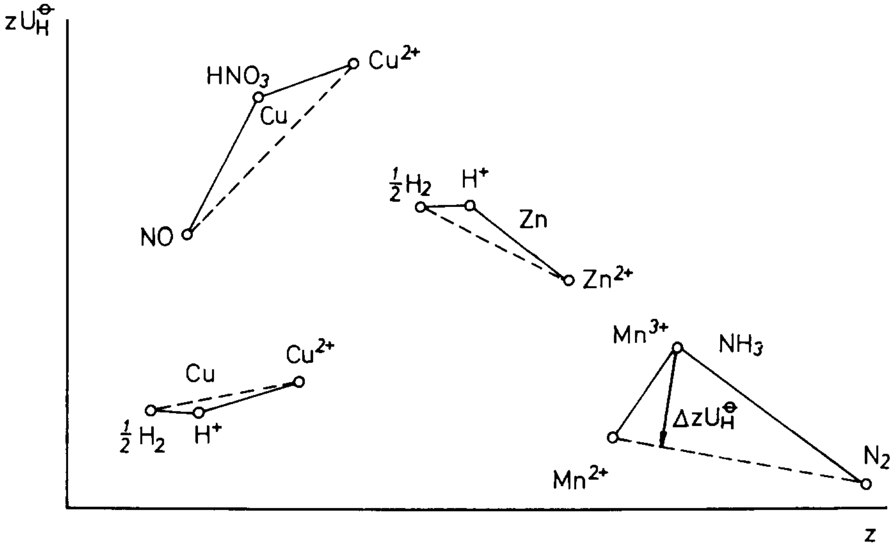

Fig. 4. Graphical estimation of the direction of redox processes, see text.

TABLE 2

Results of the graphical estimate of the redox processes in comparison to the experimental results

Central atom		$gzU^{\ominus}$/arbitrary units		Estimate	Result
Before Mn^{n+}	After $M^{(n-m)+}$	$NH_3 + M^{n+}$ "Basic"	$NH_4^+ + M^{n+}$ "Acidic"		
Cr^{3+}	Cr^{2+}	−3	+7	Cr^{2+}	Cr^{2+}
Co^{3+}	Co^{2+}	−26	−13	Co^{2+}	Co^{2+}
Fe^{3+}	Fe^{2+}	−14	−5	Fe^{2+}	$Fe^{2+}Fe_3C$ [a]
Fe^{2+}	Fe	−4	+12	Fe	
Fe^{3+}	Fe	−13	+7		
Mn^{3+}	Mn^{2+}	−22	−10	Mn^{2+}	Mn^{2+} [a]
Pb^{2+}	Pb	−9	+7	Pb	Pb^{2+}, Pb
SnF_6^{2-}	Sn	−11	+13	Sn	Sn
V^{3+}	V^{2+}	−4	+6	V^{2+}	V^{3+}
WO_3	W	−17	+10	W	WC [b]

[a] Also from NH_4 compounds. [b] Result from ref. 6.

height of the triangles is a measure of the change in the free enthalpy (shown in the same figure).

It has been shown that this estimation method (although with certain restrictions) is also applicable for reactions that do not occur in aqueous media [14].

Correlation of experimental results with theoretical estimations

Table 2 summarizes the results from the graphical estimates of the redox processes, based on the partial processes $M^{n+}/M^{(n-m)+}$ and NH_3/N_2 or NH_4^+/N_2, respectively. Although rough approximations are made (a heterogeneous solid-state reaction is assumed and the dependence of the partial processes $M^{n+}/M^{(n-m)+}$ on pH is neglected), the experimental results agree surprisingly well with the estimations. Hence, it can be concluded that thermodynamic control obviously predominates under quasi-isobaric conditions.

Trivalent fluorides are formed by dissociation of fluorometallates which are not spontaneously reduced by NH_3. In these cases, the thermogravimetric steps above 700°C are due to condensation and pyrolysis reactions of the cation only.

Bivalent fluorides are formed when guanidinium hexafluoromanganate, ferrate, cobaltate, and chromate are heat treated, whereas guanidinium hexafluoroplumbate and stannate are reduced to metals.

Metal carbides are possible decomposition products for those guanidinium hexafluorometallates which can be reduced to metals by NH_3 (Fe_3C).

This was demonstrated in the study of the thermal decomposition of another guanidinium fluorometallate, guanidinium oxofluorotungstate. The final decomposition products of this compound is WC [6]. For the analogous reaction of WO_3 and amines, Härter et al. [15] proved the existence of metallic W in the reaction mixtures before WC was formed. Therefore, the carbide formation can be attributed to a reaction of the metal formed intermediately with pyrolytically formed carbon (see also the results of Grahek and Bukovec [10]).

Only with the vanadium compound do results contradict the thermodynamic prediction, probably due to the low thermal stability of the intermediates; for the vanadium compound, the final thermogravimetric step occurs at distinctly lower temperatures than for the other compounds. The influence of reaction temperature and the stability of the intermediates on the outcome of the decomposition is described in some detail in ref. 16, with several fluorochromates as examples.

The formation of carbide, as with nitride formation, is associated with high decomposition temperatures. Therefore, the different decomposition products of the guanidium hexafluorometallates of the main group III elements (AlF_3 and InF_3, but GaN) are caused by the unusually high temperature of the final thermogravimetric step of the gallium compound. This once again emphasizes the importance of the structure and thermal stability of the intermediates.

The differences in solubility, the great resistance against hydrolysis at room temperature, and the described thermal behaviour of the guanidinium hexafluorometallates open up interesting fields of application for this class of compounds, e.g. in separation techniques, in high-temperature syntheses, and in modifications of material surfaces.

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