Journal of Fluorine Chemistry, 62 (1993) 211–216

Preparation and characterization of $(NH_4)_3AlF_6$ and NH_4AlF_4 including the perdeutero salts $(ND_4)_3AlF_6$ and ND_4AlF_4

Mary Anne White*, Haiying Shi and James C. Leiper
Department of Chemistry, Dalhousie University, Halifax, N.S. B3H 4J3 (Canada)

(Received May 13, 1992; accepted September 9, 1992)

Abstract

A procedure is given for the preparation of $(NH_4)_3AlF_6$ and NH_4AlF_4 that will allow the production of the corresponding deuterated salts with good isotopic and chemical purity. The reaction proceeds from the metathesis reaction of silver fluoride and ammonium chloride, leaving ammonium fluoride in solution to be reacted with aluminium bromide to produce the hexafluoro salt which can be decomposed thermally to give the tetrafluoro salt. Characterizations of the compounds produced are presented.

Introduction

Investigations of phase transformations in ammonium salts often benefit from the availability of the corresponding perdeutero salt, particularly to probe the dynamics of orientational disorder by spectroscopic methods such as ^2H NMR. (See ref. 1, for example, for a review of methods used to observe orientational disorder in salts.) As part of our ongoing investigations of phase transitions in NH_4AlF_4 [2], we wished to probe the dynamics of ammonium ion disorder through an investigation of ND_4AlF_4.

The usual preparation of the deuterated analogue of an ammonium salt is repeated recrystallization from D_2O, thwarted in this case by the insolubility of NH_4AlF_4 in water (0.5 g l^{-1} at 25 °C from the AlF_3–NH_4F–H_2O phase diagram [3]), and the very low solubility of its precursor, $(NH_4)_3AlF_6$, *c.* 8 g l^{-1} at 25 °C [3]. The preparation of ND_4AlF_4 could proceed from the thermal decomposition of $(ND_4)_3AlF_6$ [4], which could be prepared from ND_4F and $AlBr_3$ in methanol. The stumbling block in this procedure is ND_4F which cannot be prepared from D_2O owing to its decomposition on evaporation [5]. Although ND_4F has been prepared [6] by placing NH_4F in D_2O in a desiccator next to a beaker of CH_3OD to allow ND_4F to diffuse to the CH_3OD solution from whence it was recrystallized, this method is time-consuming (several weeks) and the product always contains some traces of water. The

---

*Author to whom correspondence should be addressed.

0022-1139/93/$6.00

latter problem could lead to smearing of the solid–solid phase transition in ND_4AlF_4.

Other procedures have been described in the literature for the preparation of NH_4F. One is the passage of ammonia gas into aqueous or gaseous hydrofluoric acid; the product is isolated by filtration [7]. Another method gives NH_4F as the sublimation product from heating solid NH_4Cl and solid NaF in a platinum crucible [7]. Although ND_3, DF and ND_4F are all available, each of the above methods has disadvantages for the preparation of ND_4F in good yield, and for reasonable cost, without isotopic exchange with the environment. Of these, the ND_4F/NaF method is the most favourable for our requirements, but the quantities that can be produced are quite small (mg at a time).

Experimental

Preparative methods

We have prepared methanolic solutions of ammonium fluoride (and deuterated ammonium fluoride) for further reaction with $AlBr_3$ to give $(N(H,D)_4)_3AlF_6$, from which $N(H,D)_4AlF_4$ could be prepared as follows.

$N(H,D)_4F$ in $CH_3O(H,D)$ was prepared by the metathesis reaction of ammonium chloride (Aldrich, reagent) and silver fluoride (Aldrich, 99.9%). (ND_4Cl was prepared in *c.* 60% overall yield by the quadruplicate dissolution of *c.* 30 g of NH_4Cl in *c.* 30 ml of D_2O (Aldrich, 99.96%), followed by evaporation of the solvent and overnight drying at 78 °C in a drying tube.) Ammonium chloride and silver fluoride, in stoichiometric amounts (each 52 mmol), were dissolved in a total of 500 ml of methanol (solubilities 3.35 [8] and 1.5 g 100 ml^{-1} [9], respectively) and mixed immediately giving the relatively insoluble (6.9×10^{-5} g l^{-1} [10]) AgCl which was separated by filtration. The reaction was carried out at room temperature under red light conditions to prevent photochemical reaction of the silver salts.

Deuterated ammonium hexafluoroaluminate was prepared by the addition of 5.8 mmol of aluminum bromide (Aldrich, 98%) to the (above-described) deuterated ammonium fluoride solution in CH_3OD (Aldrich, 99.5+ at.% D), i.e. *c.* 25% excess ND_4F:

$$6ND_4F \text{ (in } CH_3OD) + AlBr_3 \text{ (in } CH_3OD) \longrightarrow (ND_4)_3AlF_6 \text{ (s)} + 3ND_3Br \text{ (in } CH_3OD)$$

The reaction was undertaken in a dry nitrogen atmosphere at 60 °C with stirring. This was the method used previously for the preparation of $(NH_4)_3AlF_6$ [11]. The solid product was isolated by suction filtration, washed with cold CH_3OD and then digested in CH_3OD in a well-sealed Nalgene® (polyallomer) bottle at 50 °C for 1 week to promote crystallization and purify the product [11]. It was then filtered and dried in a drying tube at 78 °C for 24 h. The yield of $(ND_4)_3AlF_6$ was *c.* 80%. Only Nalgene® ware was used throughout the synthesis (except for the filtering funnels) to limit fluorosilicate impurities.

Based on the following reaction [4]:

$$(ND_4)_3AlF_6\ (s) \xrightarrow{\Delta} ND_4AlF_4\ (s) + 2ND_4F\ (g)$$

c. 1 g of $(ND_4)_3AlF_6$ was placed in a ceramic boat in a stream of extra-dry nitrogen gas, and was kept at 250 °C for 1 h to give ND_4AlF_4.

Characterization of products

The $(N(H,D)_4)_3AlF_6$ and $N(H,D)_4AlF_4$ samples prepared were characterized both for their chemical and isotopic purity. However, it was not always practicable to characterize all the samples using all the methods, especially for solubility reasons, as detailed below.

As a means of quantitative analysis, the more soluble salt $(N(H,D)_4)_3AlF_6$ was analyzed for its ammonium ion content using a literature method [12]. This result showed the presence of 2.92 mol $N(H,D)_4{}^+$ per mol $(N(H,D)_4)_3AlF_6$. A similar analysis was not possible for $N(H,D)_4AlF_4$ due to its very low solubility.

The identity of $(N,(H,D)_4)_3AlF_6$ was confirmed by comparison of the X-ray powder diffraction pattern of the present products and the documented X-ray powder diffraction patterns of $(NH_4)_3AlF_6$ [13]. The agreement was very good. (However, it is worth noting that a commercial sample of $(NH_4)_3AlF_6$ (Noah Chemical Co.) had extra peaks at *d* values of 6.4, 3.6, 2.5, 2.2 and 1.8 Å. These correspond to the intense scattering peaks of NH_4AlF_4, and almost certainly show that there is substantial NH_4AlF_4 impurity present, which would explain why the thermal decomposition of these commercial samples led to apparent yields of NH_4AlF_4 greater than 100% [14].)

The X-ray powder diffraction patterns for $N(H,D)_4AlF_4$ were compatible with literature values [4] and with NH_4AlF_4 prepared from the decomposition of commercial (Noah Chemical Co.) $(NH_4)_3AlF_6$. These results are presented in Table 1.

The infrared spectra obtained for ND_4AlF_4 are summarized in Table 2, where the assignments are given according to references for the hydrogenated salt [15]. The broad, intense band near 3230 cm^{-1}, assigned to ν_3, is typical of the asymmetric stretching of ammonium ions in the solid state [4, 16]. The hydrogen bonding is indicated by the presence of a band near 1700 cm^{-1} arising from a combination of the ν_4 bending mode and the ν_6 torsional mode [17, 18]. The most important difference between the infrared spectrum of NH_4AlF_4 and that of ND_4AlF_4 is the appearance in ND_4AlF_4 of a strong single peak at 2370 cm^{-1} due to N–D stretching. (Some evidence for the 3230 cm^{-1} mode was still observed in the ND_4AlF_4 sample, probably indicating some isotopic exchange in the mull.) From the infrared results, we conclude that no water was present as the typical O–H band near 1670 cm^{-1} was absent.

The absence of $(N(H,D)_4)_3AlF_6$ in the final $N(H,D)_4AlF_4$ was confirmed from calorimetric results [19] which showed no indication of the large solid–solid phase transition occurring in $(NH_4)_3AlF_6$ at 200 K [20].

TABLE 1

X-ray powder diffraction data for $N(H,D)_4AlF_4$

hkl	NH_4AlF_4[a]		NH_4AlF_4[b]		ND_4AlF_4	
	d (Å)	Intensity (%)	*d* (Å)	Intensity (%)	*d* (Å)	Intensity (%)
001	6.38	76	6.44	83	6.38	68
100	3.59	100	3.61	95	3.59	100
002	3.28	38	–		–	
101	3.13	76	3.13	87	3.11	66
110	2.53	67	2.54	67	2.53	69
102	2.38	41	2.38	54	2.38	44
–	2.23	36	2.24	41	2.23	33
003	2.11	39	2.12	47	2.11	38
112	1.99	40	1.99	38	1.99	33
103	1.82	46	1.82	50	1.82	58
200	1.79	99	1.79	100	1.79	95
201	1.72	32	1.73	44	1.72	31
210	1.60	61	1.60	68	1.60	51
202	1.55	40	1.55	58	1.55	50
104	1.45	17	1.45	28	1.45	27
203	1.36	24	1.36	35	1.36	33
114	1.34	17	–		1.34	21
213	1.28	31	1.28	45	1.27	42

[a] From the decomposition of commercial $(NH_4)_3AlF_6$.

[b] From the decomposition of $(NH_4)_3AlF_6$, prepared as described in the text.

TABLE 2

Infrared data for $N(H,D)_4AlF_4$

	Frequency (cm^{-1})					
	ν_3	$\nu_2+\nu_4$	$2\nu_4$	$\nu_4+\nu_6$	ν_4	ν_3[a]
NH_4AlF_4[b]	3230	3120	2910	1800	1435	600
NH_4AlF_4[c]	3230	3120	2910	1800	1435	600
ND_4AlF_4	2370	3120	2900	1600	1400	600

[a] From the stretching band of the AlF_6 groups.

[b] From the decomposition of commercial $(NH_4)_3AlF_6$.

[c] From the decomposition of $(NH_4)_3AlF_6$, prepared as described in the text.

In order to determine the degree of deuteration of the salts prepared, the ^1H NMR signal of a solution of $(ND_4)_3AlF_6$ in D_2O of known concentration was integrated and compared with a series of solutions of NH_4F in D_2O. This method is similar to that used to characterize deuteration in alkali metal hydroxides [21, 22]. From the ^1H peak intensity in $(ND_4)_3AlF_6$, it was concluded that the sample was >95% deuterated (the limit of detection).

Again this analysis was carried out only for the hexafluoro salt, owing to the insolubility of ND_4AlF_4.

Conclusions

A new preparative procedure that allows the production of ND_4F in CH_3OD, ready for reaction, has allowed the preparation of the perdeutero ammonium salts, $(ND_4)_3AlF_6$ and ND_4AlF_4. These salts have been shown to have high chemical and isotopic purity. This method could allow the production of other deuteroammonium fluoride salts that are inaccessible through successive dissolution in D_2O. Although this was not the emphasis of this work, the loss of gaseous ND_4F in the thermal decomposition of $(ND_4)_3AlF_6$ to ND_4AlF_4 may lead to a useful route to ND_4F.

Acknowledgements

The authors gratefully acknowledge a useful conversion with Professor H. J. Emeléus, and additional help from D. Britten, B. Wagner, Prof. O. Knop, Dr M. Falk and Prof. T. S. Cameron. This work was supported by the Natural Sciences and Engineering Research Council of Canada through grants to M.A.W.

References

1 N. G. Parsonage and L. A. K. Staveley, *Disorder in Crystals,* Clarendon Press, Oxford, 1978.

2 M. A. White and B. D. Wagner, *J. Chem. Phys., 83* (1985) 5844.

3 W. F. Linke, *Solubilities of Inorganic and Metal-Organic Compounds,* 4th edn., Van Nostrand, Princeton, 1958, Vol. 1, p. 181.

4 D. B. Shinn, D. S. Crocket and H. M. Haendler, *Inorg. Chem., 5* (1966) 1927.

5 J. C. Bailar, H. J. Emeleús, R. Nyholm and A. F. Trotman-Dickenson (eds.), *Comprehensive Inorganic Chemistry,* Pergamon, Oxford, 1972.

6 O. Knop, personal communication (1991).

7 G. Brauer (ed.), *Handbook of Preparative Inorganic Chemistry,* 2nd edn., Academic Press, New York, 1963, Vol. 1, p. 183.

8 H. E. Armstrong and J. V. Eyre, *Proc. R. S. London, 84* (1911) 127.

9 F. A. Anderson, B. Bak and A. Hillebert, *Acta Chem. Scand., 7* (1953) 236.

10 A. N. Izmailov, I. V. Krassovskii, V. V. Aleksandrov and A. I. Vail, *Dokl. Akad. Nauk SSSR, 74* (1950) 91.

11 H. M. Haendler, F. A. Johnson and D. S. Crocket, *J. Am. Chem. Soc., 80* (1958) 2662.

12 G. D. Parkes (ed.), *Mellor's Modern Inorganic Chemistry,* John Wiley, New York, 1967.

13 H. E. Swanson and E. Tatge (eds.), *Standard X-Ray Diffraction Powder Patterns,* National Bureau of Standards, Washington, DC, 1953, Vol. 9.

14 M. A. White and B. D. Wagner, unpublished results.

15 P. Bukovec, B. Orel and J. Siftar, *Monatsh. Chem., 102* (1971) 885.

16 O. Knop, W. J. Westerhaus, M. Falk and W. Massa, *Can. J. Chem.*, *63* (1985) 3328.
17 S. D. Hamann, *Aust. J. Chem.*, *31* (1978) 11.
18 T. C. Waddington, *J. Chem. Soc.*, (1958) 4340.
19 M. A. White, H. Shi, M. MacIntosh and R. E. Wasylishen, to be published.
20 K. Kobayashi, T. Matsuo, H. Suga, S. Khairoun and A. Tressaud, *Solid State Commun.*, *53* (1985) 719.
21 M. A. White and S. A. Moore, *J. Chem. Phys.*, *85* (1986) 4629.
22 M. A. White, A. Perrott, D. Britten and M. J. M. Van Oort, *J. Chem. Phys.*, *89* (1988) 4346.