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Preparation and Properties of Ammonium Hexachlorozirconate(IV) and Its Reaction with Gaseous Ammonia

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Ammonium hexachlorozirconate $(NH_4)_2ZrCl_6$ was prepared by the direct reaction of $ZrCl_4$ with NH_4Cl. The X-ray powder diffraction and the density measurements showed that it has a face-centered cubic lattice with a=10.127(2) Å and is isostructural with K_2PtCl_6. The hexachlorozirconate undergoes ammonolysis in gaseous ammonia at room temperature, forming $ZrCl_3(NH_2)\cdot xNH_3$ and NH_4Cl. The ammonolysis product reverts to the initial $(NH_4)_2ZrCl_6$ on heating to 250 °C in the ammonia atmosphere. The hexachlorozirconate vaporizes at about 450 °C. The reaction of $ZrCl_4$ with gaseous ammonia was also studied in comparison with that of the hexachlorozirconate.

Most fine powders used for production of nitride ceramics are prepared by the reactions of metal chlorides with ammonia at elevated temperatures. Therefore, it is essentially important to understand these reaction mechanisms to obtain more refined powders for the production of improved nitride ceramics. In the reaction system of $ZrCl_4$–NH_3, a layer structured compound β-ZrNCl is formed in the intermediate temperature range prior to the formation of zirconium nitride at higher temperatures.[1)] In previous papers,[2,3)] we showed that this layer compound forms lithium intercalates Li_xZrNCl and could be a promising candidate for electrochromic electrode material.

Usually β-ZrNCl is prepared according to the method reported by Juza and Heners:[4)] the solid sample of anhydrous $ZrCl_4$ is heated stepwise to 600 °C in dry ammonia. However, this method suffers the disadvantage of low yield. Yajima et al.[1)] reported that in the reaction of $ZrCl_4$ vapor with ammonia, an adduct $ZrCl_4\cdot 2NH_3$ was formed in the temperature range below 400° C. The same ammonia adduct seems to be formed during the above preparation procedure for β-ZrNCl. It is very likely that the formation of this adduct is responsible for the low yield, because the adduct vaporizes easily at above 400 °C and is transported to the cooler part without decomposing to β-ZrNCl.

In the course of the present study for a better understanding of the properties of the adduct, we have found that the true composition of the adduct is $(NH_4)_2ZrCl_6$ rather than $ZrCl_4\cdot 2NH_3$. The same compound has been prepared by the direct reaction of $ZrCl_4$ with NH_4Cl and its thermal behavior in ammonia has been investigated.

Experimental

Preparation of $(NH_4)_2ZrCl_6$. Ammonium hexachlorozirconate(IV) $(NH_4)_2ZrCl_6$ was prepared by the dry method similar to that reported by Lister and Flengas[5)] for K_2ZrCl_6 in the following procedure: Zirconium tetrachloride was purified by sublimation and mixed with ammonium chloride dried at 180 °C under vacuum in the molar ratio of 1:2 in a dry box. The mixture was placed in a Pyrex boat and heated to 400 °C in a stream of dry nitrogen. After the mixture was kept at the temperature for 5 h, the resulting residue in the Pyrex boat was taken out and vacuum sealed in a Pyrex tube, which was then placed in a two-zone furnace. The temperature of the residue was regulated at 400 °C, the other end of the sealed tube being at 100 °C. After standing for 5 h, white crystals of $(NH_4)_2ZrCl_6$ were transported to the lower temperature zone. Found: Zr, 27.4; N, 8.23; Cl, 62.6%. Calcd for $(NH_4)_2ZrCl_6$: Zr, 26.8; N, 8.24; Cl, 62.6%.

Analyses. Since most of the products treated in this study are sensitive to the humidity in air, those were manipulated in a dry box unless otherwise noted. X-Ray powder diffraction (XRD) patterns were measured under a dry argon atmosphere by using a cylindrical cover having thin polyethylene windows; nickel filtered Cu $K\alpha$ radiation was used.

Elemental analyses for zirconium, chlorine and nitrogen were carried out after the sample was dissolved in 2 mol dm^{-3} sulfuric acid. The nitrogen content was determined by Kjeldahl method; zirconium and chlorine were determined gravimetrically as ZrO_2 and AgCl, respectively. The density of $(NH_4)_2ZrCl_6$ was measured pycnometrically with toluene at 25 °C.

Thermogravimetric Study in Ammonia. The amount of ammonia taken up by $(NH_4)_2ZrCl_6$ was measured gravimetrically by using a quartz spring balance as a function of pressure of ammonia at 25 °C. The sample was heated in an ammonia stream (flow rate of 50 ml min^{-1}) to 650 °C for a heating rate of 3 °C min^{-1}. For comparison similar experiment was performed on $ZrCl_4$.

Results

X-Ray Diffraction Study. The XRD data of $(NH_4)_2ZrCl_6$ is shown in Table 1. The XRD pattern is very similar to that of K_2ZrCl_6 reported by Lister and Flengas[5)] and all the diffraction peaks can be indexed on the basis of a cubic lattice with a=10.127(2) Å. Moreover, the lattice type of $(NH_4)_2ZrCl_6$ is face-centered cubic because the diffraction peaks are only present when h,k,l are all even or all odd. Engel[6)] showed that a series of hexachloro complexes with the general formula A_2MCl_6 (A=K, NH_4, Rb, Cs, Tl; M=Ti, Se, Zr, Sn, Te, Pt, Pb) has the K_2PtCl_6 structure and that for the complexes with an A ion in common, the lattice constants can be related with those of the corresponding Rb- salts by a linear relation as shown in Fig. 1. Although $(NH_4)_2ZrCl_6$ is not included in his plot, the value obtained above fits well on the line for the ammonium series. This fact indicates that $(NH_4)_2ZrCl_6$ has the K_2PtCl_6 structure. The density determined for the $(NH_4)_2ZrCl_6$ prepared by the direct method in this study is 2.14 g cm^{-3}, which is in good agreement with the value of 2.17 g cm^{-3} calculated on the basis of the K_2PtCl_6 structure with a=10.127 Å.

Ammonium hexachlorozirconate can be also prepared by the wet method from hot aqueous solutions of zirconium dichloride oxide and ammonium chloride.[7,8] If the solution is saturated with hydrogen chloride and gradually cooled, the crystals of $(NH_4)_2ZrCl_6$ precipitate. It is found that the crystals thus prepared exhibit the XRD pattern identical to that of the crystals obtained by the direct method. Toptygina and Barskaya[7] prepared $(NH_4)_2ZrCl_6$ by the wet method and reported its XRD data, which however, do not coincide with ours. Since their chemical analysis data are in agreement with ours for $(NH_4)_2ZrCl_6$, they probably used the sample hydrolyzed in air for the measurement of the XRD pattern. Yajima et al.[1] investigated the reaction of gaseous $ZrCl_4$ with ammonia at elevated temperatures, and reported that in the temperature range 300—400 °C, white crystals with composition $ZrCl_4 \cdot 2NH_3$ were formed. Strangely, the XRD pattern reported by them for the crystal is identical to that of $(NH_4)_2ZrCl_6$. Although the detailed procedures are not reported, it is likely that Yajima et al. analyzed the as-deposited sample without purification: the sample was probably a mixture of $(NH_4)_2ZrCl_6$ and noncrystalline zirconium amide trichloride $ZrCl_3(NH_2) \cdot xNH_3$ and the overall ratio of Zr:N:Cl of the mixture is 1:2:4. The formation of the zirconium amide trichloride will be discussed later in more details.

Table 1. X-Ray Diffraction Data of $(NH_4)_2ZrCl_6$

d_{obsd}/Å	d_{calcd}/Å	hkl	I/I_0
5.844	5.847	111	100
5.068	5.064	200	65
3.577	3.580	220	15
3.050	3.053	311	50
2.923	2.923	222	60
2.534	2.532	400	100
2.320	2.323	331	20
2.263	2.264	420	50
2.070	2.067	422	5
1.947	1.949	333	25
1.791	1.790	440	60
1.712	1.712	531	20
1.687	1.688	600, 442	25
1.462	1.462	444	10

Uptake of Ammonia by $(NH_4)_2ZrCl_6$. Figure 2 shows the amounts of ammonia taken up by $(NH_4)_2ZrCl_6$ at 25 °C as a function of increasing-decreasing pressure of ammonia. The amount was recorded after standing for 2 d at each pressure although the rate of uptake or release of ammonia is so slow that it takes more than 2 d to attain complete equilibrium. As seen in the figure, the amount of uptake gradually increases with the pressure and approaches 9 mol per mole of $(NH_4)_2ZrCl_6$ at the pressure of about 1 atm. On reducing the pressure to 1.4×10^3 Pa, only 2 mol of ammonia are removed. By prolonged evacuation at the pressure of 10^{-1} Pa for 4 d, additional 5 mol of ammonia are removed, but 2 mol of ammonia are tenaciously retained.

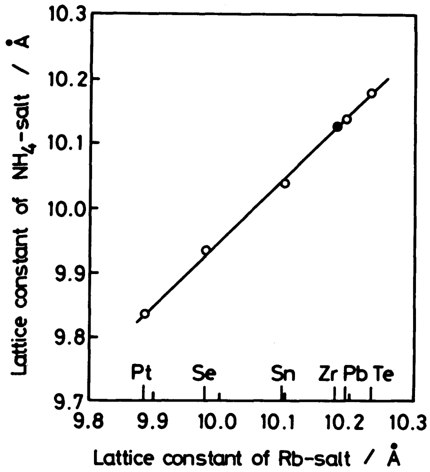

Fig. 1. Linear relationship between the lattice constants of NH_4-salts and those of Rb-salts. (●): This work, (○): results done by Engel.[6]

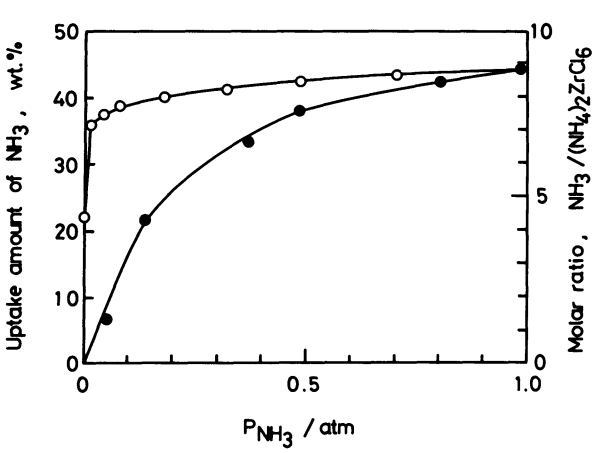

Fig. 2. Amount of ammonia taken up by $(NH_4)_2ZrCl_6$ at 25 °C as a function of the pressure of ammonia. (●), increasing pressure; (○), decreasing pressure.

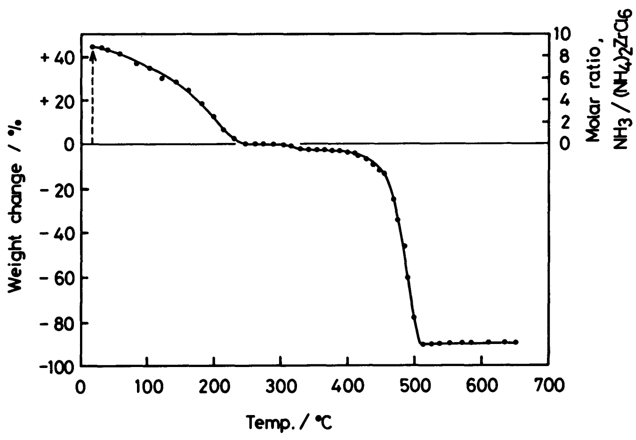

Fig. 3. Thermogravimetric curve for $(NH_4)_2ZrCl_6$ in an ammonia stream.

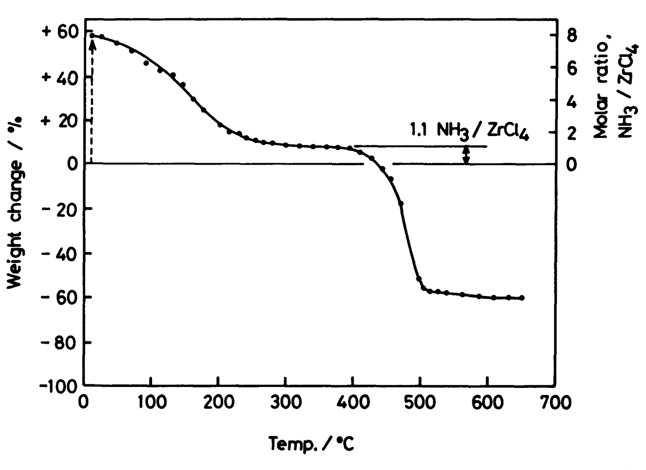

Fig. 4. Thermogravimetric curve for $ZrCl_4$ in an ammonia stream.

Separate samples of $(NH_4)_2ZrCl_6$ were also treated similarly and taken out to see the crystalline phases present at the different stages of uptake of ammonia. The XRD pattern of the sample equilibrated with 1 atm of ammonia exhibited the intense diffraction peaks due to NH_4Cl with the disappearance of the peaks due to $(NH_4)_2ZrCl_6$. The sample evacuated after the uptake of ammonia still exhibited only the peaks due to NH_4Cl.

The thermogravimetric analysis of $(NH_4)_2ZrCl_6$ was carried out in a stream of ammonia after about 9 mol of ammonia were taken up. As shown in Fig. 3, the ammonia is gradually removed with an increase in the temperature, and at 250 °C the sample reverts to the initial state in weight. The XRD pattern of the sample measured at this state indicated that the diffraction peaks of NH_4Cl extremely decreased in the intensity and, on the contrary, those of $(NH_4)_2ZrCl_6$ were almost completely recovered. The sample vaporized at about 450 °C and only 15% of the initial weight was left in the thermogravimetric analysis cell. The residue was found to be a mixture of α- and β-ZrNCl.

For comparison similar analysis was performed on $ZrCl_4$ in a stream of ammonia. During standing in ammonia of the pressure of 1 atm for 8 h, one mole of $ZrCl_4$ took up ammonia as much as 8 mol. Then, the temperature of the sample was raised in the manner similar to that of the analysis of $(NH_4)_2ZrCl_6$. Figure 4 shows the thermogravimetric curve observed. The curve is very similar to that observed for $(NH_4)_2ZrCl_6$ except that the weight does not revert to the initial state; as seen from the figure, about 1 mol of ammonia is retained up to 400 °C at which the vaporization of the sample begins. On heating to 650 °C, about 60% of the initial weight was lost and the residue was β-ZrNCl.

Discussion

Drake and Fowles[8] studied the ammonolysis of $(NH_4)_2ZrCl_6$ with liquid ammonia. They showed that $(NH_4)_2ZrCl_6$ behaves essentially like $ZrCl_4$. $ZrCl_4$ is subjected to ammonolysis to only one Zr–Cl bond in liquid ammonia, giving the zirconium amide chloride:[9]

$$ZrCl_4 \xrightarrow{NH_3} ZrCl_3(NH_2)\cdot xNH_3 + NH_4Cl. \qquad (1)$$

Similarly $(NH_4)_2ZrCl_6$ undergoes ammonolysis to one Zr–Cl bond

$$(NH_4)_2ZrCl_6 \xrightarrow{NH_3} (NH_4)_2[ZrCl_5(NH_2)]\cdot xNH_3 + NH_4Cl. \qquad (2)$$

On washing with liquid ammonia, the complex decomposes into ammonium chloride and zirconium amide trichloride:

$$(NH_4)_2[ZrCl_5(NH_2)]\cdot xNH_3 \longrightarrow 2NH_4Cl + ZrCl_3(NH_2)\cdot xNH_3. \qquad (3)$$

The tensimetric study by Fowles and Pollard,[10] and our previous study[11] on the decomposition of the zirconium amide trichloride showed that x is about 6—7 in the above equations.

The results of thermogravimetric analyses seem to suggest that $(NH_4)_2ZrCl_6$ and $ZrCl_4$ are subjected to ammonolysis with gaseous ammonia in a similar manner:

$$(NH_4)_2ZrCl_6 + 9NH_3 \longrightarrow 3NH_4Cl + ZrCl_3(NH_2)\cdot 7NH_3, \qquad (4)$$

$$ZrCl_4 + 8NH_3 \longrightarrow NH_4Cl + ZrCl_3(NH_2)\cdot 6NH_3. \qquad (5)$$

In the reaction with gaseous ammonia, however the resulting NH_4Cl is not washed out, but remains in the product. The XRD pattern of the product indicates the formation of NH_4Cl with the disappearance of $(NH_4)_2ZrCl_6$. The zirconium amide trichloride $ZrCl_3(NH_2)\cdot xNH_3$ is likely a noncrystalline polymeric solid as suggested by Allbutt and Fowles.[12] The XRD results tell us that on heating, the reaction of Eq. 4 is reversed, and NH_4Cl reacts with $ZrCl_3(NH_2)$ and reforms $(NH_4)_2ZrCl_6$. A very small drop in weight is observed at 330 °C in the thermogravimetric curve of Fig. 3. This drop can be attributed to the sublimation of NH_4Cl remaining unreacted in the system.

In the case of $ZrCl_4$, one mole of ammonia remains in the system above 250 °C until the vaporization of the sample begins at 400 °C. This difference in the behavior of the ammonolysis products of $(NH_4)_2ZrCl_6$ and $ZrCl_4$ can be interpreted in terms of the insufficient NH_4Cl in the latter ammonolysis product. Since only one mole of NH_4Cl is present in the product (Eq. 5), only one third of $ZrCl_3(NH_2)$ is converted into $(NH_4)_2ZrCl_6$ according to the following reaction:

$$\begin{aligned} &ZrCl_3(NH_2)\cdot 6NH_3 + NH_4Cl \longrightarrow \\ &\quad \frac{1}{3}(NH_4)_2ZrCl_6 + \frac{2}{3}ZrCl_3(NH_2) + 6\frac{2}{3}NH_3. \end{aligned} \tag{6}$$

It is interesting to note that the abrupt decreases in weight occur at the same temperature irrespective of the kinds of starting samples. It is apparent that the temperature of 450 °C corresponds to the vaporization of $(NH_4)_2ZrCl_6$, although the decomposition of $ZrCl_3(NH_2)$ to β-ZrNCl is also accompanied around this temperature.[11]

In summary, ammonium hexachlorozirconate $(NH_4)_2ZrCl_6$ can be prepared by the direct reaction of $ZrCl_4$ with NH_4Cl. $ZrCl_4$ and $(NH_4)_2ZrCl_6$ are subjected to ammonolysis with gaseous as well as liquidous ammonia and form the amide $ZrCl_3(NH_2)\cdot nNH_3$. The amide reverts to $(NH_4)_2ZrCl_6$ in the presence of NH_4Cl at elevated temperature. In the preparation procedure of β-ZrNCl from $ZrCl_4$ and NH_3, the formation of $(NH_4)_2ZrCl_6$ as a by-product is unavoidable, which is removed from the reaction system by vaporization above 400 °C. This should be responsible for the low yield of β-ZrNCl.

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