THERMOGRAVIMETRIC INVESTIGATIONS ON $A(H_2O)_6BX_6$ COMPLEXES AND THE FORMATION OF ABX_6 AND ABO_3 STRUCTURES

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ABSTRACT

Thermogravimetry (TG) of $A(H_2O)_6BX_6$ complexes are presented, with $A = Cd^{2+}$, Co^{2+}, Cu^{2+}, Fe^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, $B = Si^{4+}$, Sn^{4+}, Ti^{4+}, Zr^{4+}, and $X = Cl^-$, F^-. On a selected number of complexes, differential thermal analyses (DTA) and differential scanning calorimetric measurements (DSC) have been performed. It was found possible to synthesize most complexes including $Cd(H_2O)_6TiF_6$ as single crystals. The hexafluoride and the titanate compounds are formed from the corresponding cadmium hexaquo–hexafluoride complex. The cadmium titanate could be made either in the ilmenite or in the perovskite structure. The decomposition programs for the preparation of $NiTiO_3$ and $CdTiO_3$ are presented.

The hexaquo–hexahalide complexes, in general, show one of two decomposition types. The intermediate product in one type is the metal(II) fluoride AX_2 and in the other the mixed hexahalide compounds ABX_6. Which type of decomposition occurs depends on the anion BX_6^{2-}.

INTRODUCTION

A well-known class of complexes $A(H_2O)_6BX_6$[1,2] has been studied in more detail in this laboratory (A is a bivalent metal ion such as Mg^{2+}, Fe^{2+}, Ni^{2+}, Pb^{2+}, B is a quadrivalent ion such as Si^{4+}, Ti^{4+}, and X is a halide ion). These complexes can be used to synthesize homogeneous and stoechiometric compounds ABO_3 with perovskite or ilmenite type structures[3–5]. In this method, the ABO_3 compounds are formed by the thermal decomposition of the corresponding $A(H_2O)_6BX_6$ complex. In order to obtain more information about this synthesis further investigations have been performed. This part of the study presents the thermal decomposition of the various $A(H_2O)_6BX_6$ complexes. In future papers we will report on single crystal X-ray diffraction results of a few complexes and on the electron paramagnetic resonance measurements (EPR) of the Ni^{2+} complexes.

Few studies have been published concerning the thermal analysis of these complexes. Folek and Kowol[6] have recently reported the thermal decomposition of $Zn(H_2O)_6SiF_6$ and $Cd(H_2O)_6SiF_6$. Odenthal and Hoppe[7] have reported the synthesis of some ABX_6 compounds by thermal decomposition of the corresponding hexaquo complexes. Odenthal and Hoppe were not able to prepare the $Cd(H_2O)_6TiF_6$ complex and as a consequence the $CdTiF_6$ compound in this simple way. Only $CdTiO_3$ and $CdSnO_3$ occur both in the ilmenite structure (at low temperature and pressure) and in the perovskite structure (at high temperature and pressure)[8-10]. The question is which structure would be formed upon decomposition of the corresponding hexaquo–hexahalide complexes. The temperature range at which the transition of $CdTiO_3$ from ilmenite to perovskite takes place is between 1150 and 1300 K, whereas the reverse transition occurs at about 1000 K. The temperature at which ilmenite $CdTiO_3$ is prepared by a solid state reaction is about 1100 K, whereas the temperature for perovskite $CdTiO_3$ lies at about 1350 K[10].

EXPERIMENTAL METHODS

Synthesis of the complexes

The method of synthesis of the complexes has been described elsewhere[2,3]. The twenty-eight complexes mentioned in Table 1 have been synthesized. There are eight SiF_6^{2-}, eight $SnCl_6^{2-}$, two SnF_6^{2-}, nine TiF_6^{2-} and one ZrF_6^{2-} complexes. Special care is necessary in the synthesis of those complexes where the AX_2 compound is very insoluble (e.g., PbF_2 and CdF_2). In these cases the reaction

$$BO_2(s)+6HX(aq) \rightarrow H_2BX_6(aq)+2H_2O$$

requires two or three days to remove all traces of HX and also an excess of BO_2, which is filtered off before the next step in the process. The best method for the addition of the metal is in the form of the reactive metal carbonate with the H_2BX_6 in excess, to prevent precipitation of insoluble simple fluorides.

It is necessary to take some precautions in order to obtain single crystals. Some complexes are very soluble and dilution should be avoided. Some other complexes are relatively insoluble and the H_2BX_6 solution has to be diluted with H_2O to get single crystals. Sometimes the only method of obtaining single crystals is by slow cooling of a supersaturated solution. For all eight complexes, in which single crystal preparation was attempted, it was successful (Table 1). However, all attempts to prepare $TiCl_6^{2-}$ and $SiCl_6^{2-}$ complexes either as a powder or as single crystals were unsuccessful.

Decomposition of the complexes

The method used to obtain the ABO_3 compound, begins with the careful powdering of the hexaquo–hexafluoride complex. The powder is put into a quartz vessel, the bottom of which is covered with platinum foil to prevent silicon contamination and heated in a stream of air or a special atmosphere. Heating should take place very carefully with the heating program taking into account the decomposition

properties. In general, the complex is heated slowly for 2 h increasing from ambient to between 450 and 550 K. Then it is kept at a constant temperature between 500 and 800 K, the duration of time depending on the type of complex concerned. For lack of a better term this period is called the "delay time". Subsequently, the substance is gradually heated for 2 or 3 h to a temperature of 1100 K. This temperature is maintained for 15 min to 1 h. Heating programs for $FeTiO_3$ and $PbTiO_3$ have been published in other papers[3,4].

For $NiTiO_3$ very slow heating in air with a delay time of about 60 h gave the best results. This long delay time can be shortened by performing the decomposition in an atmosphere consisting of a mixture of air and water vapour.

As was found after repeated experiments, pure $CdTiO_3$ can only be obtained by applying the following procedure. The complex is heated slowly for $2\frac{1}{2}$ h to a temperature of 620 K in an atmosphere of air and water vapour, undergoes a delay time of 16 h at 620 K, and is then gradually heated for 2 h to 1100 K. This temperature is maintained for 1 h, still in the same atmosphere.

Similar principles can be applied to all SnF_6^{2-}, TiF_6^{2-} and ZrF_6^{2-} complexes. Also from these same complexes, ABX_6 type compounds can be prepared by ending the decomposition in the temperature range between 500 and 600 K and introducing atmospheres of dry air, or, as in the method published by Odenthal and Hoppe[7] a mixture of air and hydrogen fluoride. Starting with these ABX_6 compounds, the $A(H_2O)_6BX_6$ complex can be restored within a few days by keeping it over a saturated NH_4Cl solution.

Thermal analysis

TG and DTA measurements have been carried out on DuPont instruments Models 950 and 900 and DSC measurements on a Perkin-Elmer Model 1B. In TG, the temperature range is from ambient to 1300 K, whereas in DTA the temperature range is from ambient to 850 K. DSC measurements have been carried out on the complexes prepared as single crystals in order to see if phase transition occurs between 170 and 320 K.

EPR measurements

Electron paramagnetic resonance measurements have been performed during the decomposition of the $Ni(H_2O)_5TiF_6$ complex. Measurements have been carried out with a Varian V-4502/10 spectrometer, equipped with a 12-in. fielddial-regulated magnet. High temperatures have been obtained with the Varian accessories V-4557 and V-4546.

X-ray measurements

At the intermediate and final stages of decomposition of the complexes, powder Guinier X-ray diffraction photographs were taken with a Philips diffraction spectrometer PW 1320/1310 using $CuK\alpha$-radiation.

Chemical analysis

The metal content of the complexes and decomposition products was determined titrimetrically or gravimetrically. Water analyses of the complexes and of intermediate products were in agreement with the TG results. Fluorine analyses showed, within the detection limit (0.1%), no fluorine present in the ABO_3 compounds.

RESULTS

A summary of the results has been collected in Table 1. The number of water molecules present in the complex in general is six, but at room temperature this number is sometimes smaller, indicating that the decomposition step for the first molecules of crystal water lies below room temperature. When the synthesis is carried out carefully, the Cu-complexes were also found, in contrast to the literature[1,11] to contain six H_2O if kept above a saturated NH_4Cl solution. The only exceptions are the Pb^{2+}-complexes as they never have a higher hydration number than three. From the DSC results, it is seen (Table 1), that for the investigated complexes, no low temperature phase transitions were found which were not already known in the literature. Until now low temperature phase transitions have been found only for some SiF_6^{2-} complexes.

From thermogravimetry, the qualitative analysis of gasses and the chemical analysis of intermediate products, it is seen that the decompositions can be divided into two types designated as I and II. The type I decomposition in air with little moisture, takes place according to the reaction scheme:
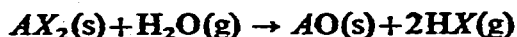
$$A(H_2O)_6BX_6(s) \rightarrow AX_2(s) + BX_4(g) + 6H_2O(g)$$

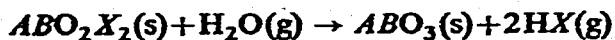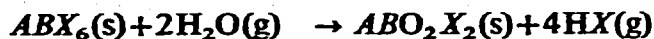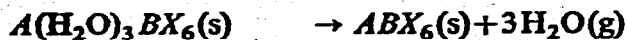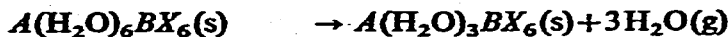$$AX_2(s) + H_2O(g) \rightarrow AO(s) + 2HX(g)$$

Table 1 gives the two decomposition temperatures for the complexes which show decomposition type I. Because the addition of water vapour has not been regulated in these series of experiments, the second temperature does not indicate the real stability. Decomposition type I is found for all $SnCl_6^{2-}$ and SiF_6^{2-} complexes.

Decomposition type II takes place as follows:

$$A(H_2O)_6BX_6(s) \rightarrow A(H_2O)_3BX_6(s) + 3H_2O(g)$$

$$A(H_2O)_3BX_6(s) \rightarrow ABX_6(s) + 3H_2O(g)$$

$$ABX_6(s) + 2H_2O(g) \rightarrow ABO_2X_2(s) + 4HX(g)$$

$$ABO_2X_2(s) + H_2O(g) \rightarrow ABO_3(s) + 2HX(g)$$

In several cases, the water is given off in three steps of two molecules each instead of in two steps of three molecules as indicated above. This depends strongly on the cation A^{2+} concerned. Table 1 gives the four or five decomposition temperatures found for type II. Because the TG measurements were carried out in air, there is a

TABLE 1

SURVEY OF PREPARED COMPOUNDS $A(H_2O)_xBX_6$ AND RESULTS

Compound A	B	X	No. of H_2O molecules x at 300 K	Transition temp. from DSC (K)	Decomposition type	Decomposition temp. from TG (K)	Decomposition temp. from DTA (K)	Preparation and/or X-ray results previously described in ref.
Cd	Si	F	6		I	380 / ~1000		11
	Sn	Cl	6		I	380 / ~1000		
	Tl	F*	6/4	none	II	300/340/370 / 550/700	405/420/440/465 / ~600/>850	
Co	Si	F	6	240/250¹⁴	I	430 / 750		12, 13, 14
	Sn	Cl	6		I	350 / 750		15
	Tl	F	6		II	390/440/500 / 700/900		11
Cu	Si	F	6		I	400 / 700		11
	Sn	Cl	6		I	340 / 700		
		F	6		II	440 / 600/800		13
	Tl	F	6		II	450 / 650/850		1, 11
Fe	Si	F*	6	215/225	I	400 / 600	450 / 690	12, 16
	Sn	Cl	6		I	420 / 600		
	Tl	F	6		II	380/430/470 / 750/1000		3, 11

TABLE 1 (continued)

Compound A B X	No. of H_2O molecules x at 300 K	Transition temp. from DSC (K)	Decomposition type	Decomposition temp. from TG (K)	Decomposition temp. from DTA (K)	Preparation and/or X-ray results previously described in ref.
Mg Si F[a]	6	295/305	I	400 ~1200		12, 17
Sn Cl	6		I	430 650		15
Ti F	6		II	360/410/470 750		12, 15
Mn Si F	6	220/230[16]	I	400 ~1200		12, 18
Sn Cl	6		I	520 750		15
Ti F	6		II	380/420 700/800		15
Ni Si F	6	none	I	450 750	470 >850	12, 13
Sn Cl[b]	6	none	I	420 850	440 >850	15
F[b]	6	none	II	460/500 600/750	465/500 640/>850	2
Ti F	6	none	II	440/500 600/1000	460/475 605/>850	
Pb Ti F	3		II	350/430 ~1000		4
Zr F	3		II	400 ~1000		
Zn Si F	6		I	380 750		12, 13
Sn Cl	6		I	360 700		
Ti F	6		II	380/480 700/800		12, 15

[a] Also prepared as single crystals.

strong correlation between the presence of water vapour and the temperature at which the last two steps take place. It has been noticed that an increase in the heating rate increases the first two or three decomposition temperatures only some tenths of degrees, whereas the last two decomposition temperatures increase sometimes more than two hundred degrees. The values of Table 1 have been taken at a rate of temperature increase of 15 K min^{-1}. To investigate these decompositions in more detail, a rate of temperature increase of less than 1 K min^{-1} is necessary and has been used and special atmospheres have also been applied. Chemical and X-ray analyses of the intermediate products showed the real existence of the ABX_6 compounds. Decomposition type II is found for all SnF_6^{2-}, TiF_6^{2-} and ZrF_6^{2-} complexes.

The DTA measurements are consistent concerning number, intensity and broadening of the bands with the decomposition types as found from TG. In the case of the $Cd(H_2O)TiF_6$ complex the water is given off in four steps of respectively one, one, two and two molecules according to DTA, whereas, according to TG, it is given off in three steps of two molecules. This means that TG, which has a low resolving power, is not able to discern the two separate first steps. The decomposition temperatures of the DTA as opposed to the TG sometimes differ. This is due to different experimental circumstances between these techniques since the decompositions depend strongly on the partial water pressure. In Table 1 the DTA decomposition temperatures, taken with a rate of temperature increase of 15 K min^{-1}, are presented. All DTA bands are endothermic.

The ABX_6 and ABO_3 structures can be prepared from all complexes which show decomposition type II, i.e., $ATiF_6$, $AZrF_6$, $ASnF_6$, $ATiO_3$, $AZrO_3$ and $ASnO_3$. The $CdTiO_3$ prepared at 1100 K shows an ilmenite structure. It has also been possible to obtain the perovskite structure by applying a final heat treatment for about $\frac{1}{2}$ h at 1300 K instead of 1 h at 1100 K. EPR measurements taken at the beginning of the decomposition of the $Ni(H_2O)_6TiF_6$ complex, show a spectrum with a high zero-field parameter D and with a zero-field parameter E equal to zero. This EPR spectrum will be described in a forthcoming paper. In the temperature range where the water leaves the complex this spectrum disappears. $Ni(H_2O)_3TiF_6$ does not give a powder EPR spectrum. The zero-field splitting may be too large or the structure may be too strongly distorted. Subsequently a spectrum is observed with $g = 2.2$ and $D = 0$ at the point where all water molecules have left the complex. This spectrum is consistent with octahedrally coordinated Ni^{2+} in the $NiTiF_6$ structure. This spectrum remains unchanged, with $g = 2.2$ and $D = 0$, even after $NiTiO_3$ has been formed. This is in agreement with the fact that the Ni^{2+} in this structure is also octahedrally coordinated.

DISCUSSION

The relationship between decomposition type I or II and the type of anion can be explained as a direct result of the boiling or sublimation points of the BX_4 compounds. For SiF_4 and $SnCl_4$ these are 187 and 387 K, respectively, while the

SiF_6^{2-} and $SnCl_6^{2-}$ complexes all show decomposition type I. The complexes corresponding with TiF_4, ZrF_4 and SnF_4, with sublimation points of 557, 873 and 978 K, respectively, all show decomposition type II. The last water molecules are given off at temperatures ranging from 350 to 500 K. The type of cation is not important with respect to the decomposition type. From the above, it is clear, that ABX_6 can be made when $X = F$ and $B = Ti$, Sn, Zr, whereas A may be any bivalent metal. When this bivalent metal can exist in several oxidation states a special decomposition atmosphere has to be applied, e.g., for Fe.

It is now clear that the role of the H_2O in the synthesis of $FeTiO_3^?$ is three-fold: (a) It performs the exchange of F^- against O^{2-}; (b) it provides the correct oxidation potential in the H_2/N_2 mixture to preserve the bivalent state of iron; (c) it prevents the reaction

$$Fe(H_2O)_3TiF_6(s) \rightarrow FeF_2(s) + TiF_4(g) + 3H_2O(g)$$
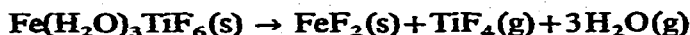
before $FeTiF_6$ has been formed. Also, the equilibrium of the reaction

$$TiF_4(g) + 2H_2O(g) \rightarrow TiO_2(s) + 4HF(g)$$

lies to the extreme right, which prevents loss of Ti relative to Fe.

Mixed chlorides are impossible to prepare in this simple way because, in general, BCl_4 compounds have low boiling points. To prepare ABO_3 compounds the hexaquo–hexafluorides have to be used as the initial product. It may also be possible to prepare a compound still starting with a chloride by preventing the following reaction from reaching completion

$$A(H_2O)_6SnCl_6(s) \rightarrow ACl_2(s) + SnCl_4(g) + 6H_2O(g)$$

by applying a very high water and/or HCl partial pressure during the decomposition of $A(H_2O)_6SnCl_6$. Possibly this may lead to the formation of an $ASnCl_6$ compound, from which an $ASnO_3$ compound can be prepared by heating in wet air. This possibility is not investigated in this paper as the hexafluoride method makes it unnecessary for stannates. To prevent a similar reaction in the case of the synthesis of the silicates, $ASiF_6$ and $ASiO_3$ was found to be, after numerous attempts, impossible because SiF_4 has such a low boiling point. As a consequence, it is not possible to prepare $ASiF_6$ compounds starting with the hexaquo complexes.

The preparation of ABO_3 structures starting with the hexaquo-complexes makes it possible to obtain these in homogeneous and stoechiometric form. Only relatively low reaction temperatures from 900 to 1100 K are necessary. The delay time in the decomposition during the exchange of F^- against O^{2-} appears as a negative point. However, this delay time may be shortened by using a high H_2O partial pressure. In this procedure only fluorides but not chlorides can be used. This may make it difficult to remove all traces of fluorine from the final products. For some practical applications this may be critical. The low reaction temperatures make it possible to obtain products with very small particle size which can be very useful in special circumstances, for example, sintering.

There are two reasons for the necessity of a delay time: (a) The exchange of F^- against O^{2-} is performed by solid state diffusion, which is a slow process; (b) before the F^- exchange can take place at the higher temperature, the ABF_6 compound has to be formed, otherwise BF_4 will leave the solid phase.

The $Cd(H_2O)_6TiF_6$ complexes gives $CdTiO_3$ in the ilmenite structure when the final temperature of 1000–1100 K is maintained for 1 h. This agrees with the result of the solid state reaction, where ilmenite is prepared at 1100 K for 24 h. The Guinier photographs of intermediate decomposition stages never showed perovskite lines. This means that the temperature of 1000 K for the transition perovskite to ilmenite is determined kinetically and not thermodynamically. Already a short heat treatment at 1350 K changes the $CdTiO_3$ to the perovskite structure showing that the product is still very reactive.

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REFERENCES

1 C. de Marignac, *Ann. Mines*, 5, 15 (1859) 221, 90, 262.
2 B. Gossner, *Z. Kristallogr.*, 44 (1908) 417, 476.
3 P. J. Gellings, K. A. de Jonge and G. M. H. v.d. Velde, *Chem. Ind.*, (1971) 1433.
4 G. M. H. v.d. Velde, U. Spitsbergen and P. J. Gellings, *J. Inorg. Nucl. Chem.*, 35 (1973) 675.
5 P. J. Gellings and G. M. H. v.d. Velde, *Z. Naturforsch.*, 28b (1973) 405.
6 S. Folck and K. Kowol, *J. Therm. Anal.*, 7 (1975) 199.
7 R.-H. Odenthal and R. Hoppe, *Z. Anorg. Allg. Chem.*, 384 (1971) 104.
8 E. Posnjak and T. F. W. Barth, *Z. Kristallogr.*, 88 (1934) 271.
9 J. Liebertz and C. J. M. Rooymans, *Z. Phys. Chem. (Frankfurt am Main)*, 44 (1965) 242.
10 J. M. Neil, A. Navrotsky and O. J. Kleppa, *Inorg. Chem.*, 10 (1971) 2076.
11 *Gmelins Handbuch der anorganischen Chemie*, Springer-Verlag, Berlin, 8th ed.
12 O. Hassel and J. Richter Salvesen, *Z. Phys. Chem.*, 128 (1927) 345.
13 S. Ray, A. Zalkin and D. H. Templeton, *Acta Crystallogr.*, B29 (1973) 2741.
14 H. Lynton and P.-Y. Siew, *Can. J. Chem.*, 51 (1973) 227.
15 L. Pauling, *Z. Kristallogr.*, 72 (1930) 482.
16 W. C. Hamilton, *Acta Crystallogr.*, 15 (1962) 353.
17 S. Syoyama and K. Osaki, *Acta Crystallogr.*, B28 (1972) 2626.
18 I. Tsujikawa and L. Couture, *J. Phys. Radium*, 16 (1955) 430.