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TG AND DTA INVESTIGATIONS ON HEXAIODOMETALLATES

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ABSTRACT

K_2ThI_6, Rb_2ThI_6, Cs_2ThI_6 and Cs_2TiI_6 could be prepared from the reactions of alkali metal iodides with ThI_4 and TiI_4. By precipitation with an excess of alkali metal iodide, Rb_2OsI_6, Cs_2OsI_6, K_2PtI_6 and Rb_2PtI_6 were obtained from acid solutions of the hexaiodometallate(IV) anions, Rb_2OsBr_6 was synthesized in a similar way from the corresponding bromine compounds.

The formation of the 4th group hexaiodometallates was investigated by DTA. The thermal stability of the complex salts was determined.

INTRODUCTION

Complex halides with the general composition A_2MX_6 with A = K, Rb, Cs and X = Cl, Br, I are well known for the majority of the 3d, 4d and 5d transition metals as well as for several main group elements [1-3]. However, it is remarkable that the number of hexaiodometallates within this series is comparatively small. The iodo compounds which are known are in most cases only poorly characterized.

Recently we have reported the preparation, properties and structures of some hexaiodometallates [4]. Additional results will be decribed in the following.

EXPERIMENTAL

The investigations were done with a Mettler recording thermoanalyzer. For the thermal degradation experiments Pt crucibles (contents 1 cm^3, with cover) were used within a stream of argon (6 $l \cdot h^{-1}$) or in vacuum ($1.3 \cdot 10^{-7}$ bar) with heating rates of 4 $K \cdot min^{-1}$. For the DTA investigations on the formation of the hexaiodometallates from alkali metal iodides and metal tetraiodides quartz glass crucibles with a contents of 1 cm^3 were chosen (Fig.1). α-Al_2O_3 was used as a reference, the heating rate being 6 $K \cdot min^{-1}$. Because of the high sensitivity of ThI_4 and TiI_4 towards protolysis, the stoichiometric mixtures of the starting compounds ($2AI + MI_4$) had to be transferred to the quartz glass containers excluding all traces of moisture. After evacuating the quartz glass crucibles for measurement to 10^{-7} bar they were sealed.

The magnetic susceptibilities were determined using the cylinder method (Gouy method) at variable field strengths (H_{max} = 1.4, 2.8, 4.1, 5.4 kG) and temperatures (90, 195, 295 K). The temperature dependence was also determined at elevated temperatures up to 800 K.

The unit cell dimensions of the compounds were obtained from X-ray powder diagrams using a Nonius Simon-Guinier camera (114.7 mm; CuKα radiation) and a special variable temperature Guinier-Simon camera (Nonius).

RESULTS AND DISCUSSION

K_2ThI_6, Rb_2ThI_6, Cs_2ThI_6, Cs_2TiI_6

The DTA diagrams for the mixtures of the binary iodides under the conditions given are quite similar to each other. In Fig. 2 a typical curve is given.

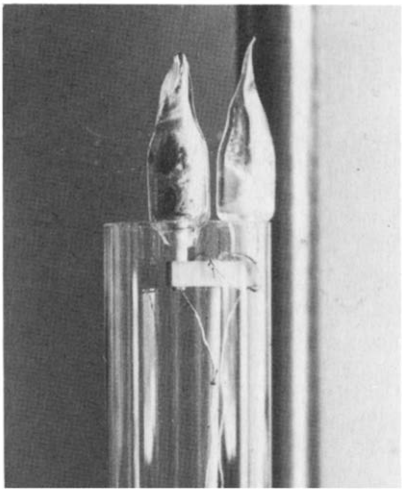

Fig. 1. Sample holder with the quartz glass crucibles.

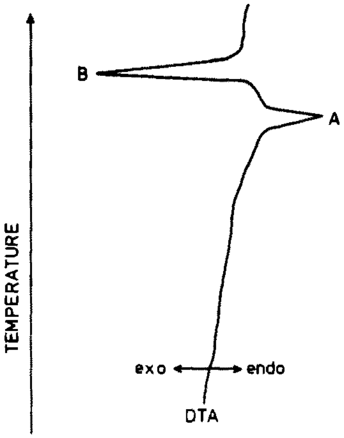

Fig. 2. DTA curve indicating formation of A_2MI_6 compound.

On heating, at first an endotherm A is observed which has to be assigned to the eutectic melting point of the mixture ThI_4/2AI. On further heating an exotherm B is registered, indicating formation of the ternary compound. This interpretation is confirmed by X-ray diagrams collected in the course of the reaction. If the heating is interrupted after A, no X-ray reflexions of the expected compounds are observed. Only after B a characteristic X-ray diagram of the compound A_2MI_6 appears. The observed temperatures at the peak maxima of the eutectic melting and of the formation of the compounds are : Rb_2ThI_6 A 783 K, B 803 K; Cs_2ThI_6 A 728 K, B 803 K. Under the conditions given similar DTA diagrams are obtained on the formation of Cs_2HfI_6 and Cs_2ZrI_6 [4].

Deviations from the DTA curve type described are observed during the formation of K_2ThI_6 and Cs_2TiI_6. In the system $2KI/ThI_4$ no melting of the starting mixture is observed before compound formation. K_2ThI_6 is formed with an exothermic effect above 715 K. On further heating an endotherm is obtained at 895 K, identified to be the melting point of K_2ThI_6. On cooling, a further exotherm at 663 K is registered besides the exotherm due to solidification at 883 K. This effect has to be attributed to a phase transformation which is confirmed by high temperature X-ray diffaction data. The phase transformation is reversible.

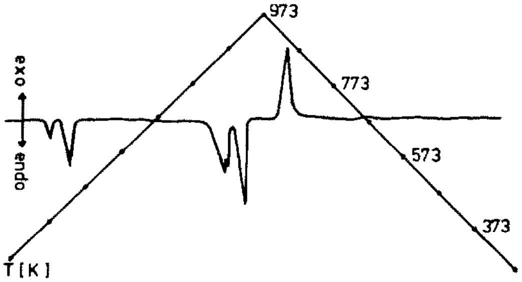

Fig. 3. DTA curve of Cs_2TiI_6.

The DTA curve observed with the system $2CsI/TiI_4$ is shown in Fig. 3. The endothermic phase transition from T-TiI_4 to H-TiI_4 at 378 K is followed by melting of TiI_4 (peak maximum 418 K). On further heating, a broad split DTA signal (endotherm) is observed in the region from 823 to 933 K. On subsequent cooling only one exotherm is found at 908 K which is to be assigned to the solidification of the Cs_2TiI_6 formed.

TABLE 1

Unit cell constants (293 K, for K_2ThI_6: 673 K) as determined from X-ray powder data and colours of the compounds

	H-K_2ThI_6	Rb_2ThI_6	Cs_2ThI_6	Cs_2TiI_6
a [pm]	1228.0	1180.0	1199.2	1147.3
Colour	yellow	yellow	yellow-orange	red-orange

	Rb_2OsBr_6	Rb_2OsI_6	Cs_2OsI_6	Rb_2PtI_6
a [pm]	1043.3	1121.1	1135.9	1121.6
Colour	black-red	black-red	black-red	black-red

The by far largest number of known compounds of composition A_2MX_6 with A = K, Rb, Cs and X = Cl, Br, I belong to the K_2PtCl_6 type. If the smaller cations in the series of the heavy alkali metals (K, Rb) are combined with the larger ligands (I, Br) the K_2PtCl_6 type tends to become unstable resulting in distorted variants of the K_2PtCl_6 structure [5]. For these cases, the variants with lower symmetry should occur at lower temperatures and transform to the K_2PtCl_6 type at higher temperatures [2,5]. So, the K_2PtCl_6 structure type is also found in the compounds Rb_2ThI_6, Cs_2ThI_6 and Cs_2TiI_6 described here; for K_2ThI_6 it is observed only above the phase transformation temperature (see Table 1).

Rb_2OsBr_6, Rb_2OsI_6, Cs_2OsI_6, Rb_2PtI_6, K_2PtI_6

Hexahalogeno-osmates(IV) can be prepared by precipitation of the salts from solutions containing the OsX_6^{2-} ions. Hexaiodoplatinates(IV) were formed by halogen transfer [6] from the corresponding hexachloroplatinate(IV) ion using hydrogen iodide and subsequent precipitation by the corresponding alkali metal iodide.

In contrast to the hexaiodothorates and -titanates which are cleaved into the alkali metal halides and thorium (titanium) tetrahalides at temperatures above 870 K (1 bar Ar) or above 670 K (in vacuum), the hexahalogeno-osmates(IV) and -platinates(IV) are decomposed on heating according to :

$$A_2MX_6 \longrightarrow 2MX + M + 2X_2. \qquad (1)$$

Experimental TG data are given in Table 2.

TABLE 2

Experimental data for the decomposition according to eq. (1) (1 bar Ar; heating rate 4 K·min^{-1}

	Sample weight [mg]	Temperature [K] for % decomposition 5	50	95	Weight loss [%] calc.	obs.
Rb_2OsBr_6	79.00	798	891	933	38.03	38.4
Rb_2OsI_6	44.10	653	713	733	45.22	45.5
Rb_2PtI_6	50.88	668	728	753	45.0	44.8
K_2PtI_6	62.36	633	703	721	49.06	49.07

The X-ray diffraction data show that K_2PtI_6 crystallizes in a tetragonal distortional variant of the K_2PtCl_6 type. This is in accordance with recent single crystal structure data [3]. The TG/DTA investigation of K_2PtI_6 (Fig.4) reveals two endotherms in the DTA. The thermal effect B corresponds to the decomposition of K_2PtI_6, the endotherm A at 398 K has to be assigned to a phase transition which is reversible. By comparison with the DTA effect measured for the NH_4Cl transformation (457.5 K: ΔH 3.9·kJ mole^{-1}), the transformation enthalpy for K_2PtI_6 is estimated to be 5 kJ·mole^{-1}. X-ray powder data show the phase transformation to be a transition from the tetragonal distortional variant to the K_2PtCl_6 type structure of K_2PtI_6. In Fig. 5 a line diagram obtained from a variable temperature Guinier camera is shown. The cell constant for H-K_2PtI_6 obtained from the Guinier diagram is a(473 K) = 1114.5 pm.

The measurement of the magnetic susceptibilities of the halogeno-osmates(IV) showed a temperature- and field strength-independent paramagnetism. After correction for the diamagnetic values, the molar susceptibilities and effective magnetic moments given in Table 3 were obtained. These results are in accordance with magnetic moments for osmium(IV) complexes known from the literature which are in the range 1.2 - 1.7 B.M. at room temperature [7,8].

TABLE 3
Molar susceptibilities [10^{-6}· cm^3·mole^{-1}] and effective magnetic moments [B.M.].

T [K]	Rb_2OsBr_6 χ_{mole}	μ_{eff}	Cs_2OsI_6 χ_{mole}	μ_{eff}
295	705	1.3	705	1.3
195	743	1.1	707	1.1
90	722	0.7	732	0.7

The reason for the anomalous magnetic behaviour of osmium(IV) complexes is the high degree of spin-orbit coupling in osmium. At high temperatures the osmium(IV) complexes should be magnetically normal.

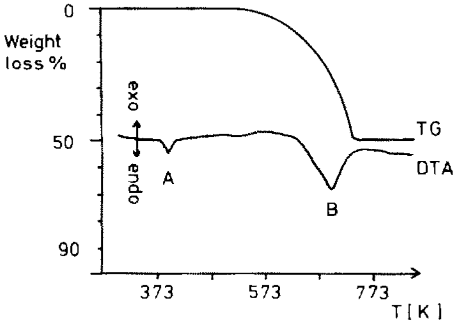

Fig. 4. TG/DTA curves of K_2PtI_6.

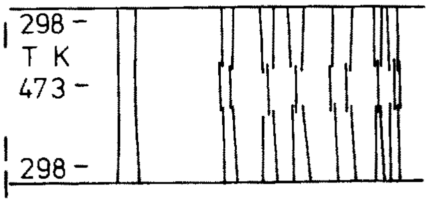

Fig. 5. Line diagram of K_2PtI_6 obtained with a variable temperature Guinier camera.

The magnetic susceptibility of Rb_2OsBr_6 (this compound has the highest thermal stability of those investigated here) was measured up to 733 K. No change of the magnetic behaviour could be observed. The dependence of the magnetic moment on the temperature is shown in Fig. 6.

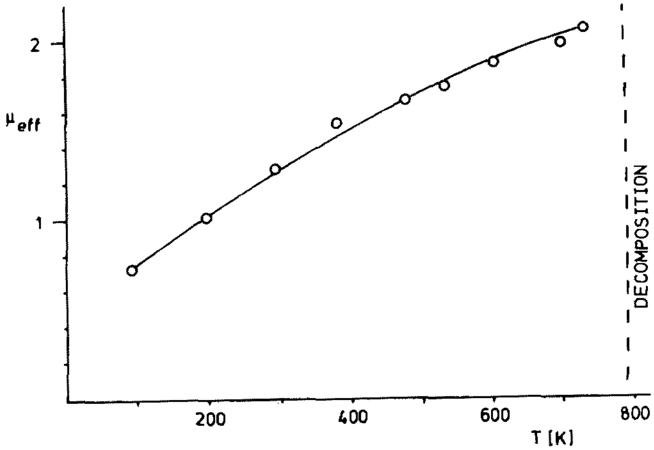

Fig. 6. Temperature dependence of the magnetic moment of Rb_2OsBr_6.

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