Hexa-iodoanions of Titanium, Zirconium, Hafnium, Palladium and Platinum: Preparation, Properties and Crystal Structures of the Caesium Salts

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In contrast to the well-known hexachloro- and hexabromo-anions, very little is known about the possible existence of hexaiodo-anions of the tetravalent group IV transition metals. Indications for a solid phase of composition K_2ZrI_6 could not be substantiated by structural data [1]; TiI_6^{2-} is reported to exist in solution [2]. A similar lack of knowledge is present in the case of Pd(IV) and Pt(IV); Cs_2PtI_6 has been described as being tetragonal [3], and recently the PtI_6^{2-} ion was isolated as the solid bis-(pyridinium) salt [4].

We wish to report the first preparations of the solid hexaiodotitanate(IV), -zirconate(IV), -hafnate-(IV) and palladate(IV) ions as the caesium salts, and to communicate the results of a reinvestigation of Cs_2PtI_6.

Cs_2PtI_6 and Cs_2PdI_6 could be prepared according to a general method used earlier [4–6] by precipitation with a large excess of CsI from acidic solutions of the corresponding hexachloro anions. The salts are obtained as microcrystalline powders. Single crystals are grown from solutions in dilute aqueous HI.

An analogous synthetic route is not possible for the corresponding group IV transition metal anions, because protolytic reactions take place in polar solvents. We succeeded, however, in the preparation of solid Cs_2TiI_6, Cs_2ZrI_6 and Cs_2HfI_6 by reaction of stoichiometric quantities of CsI and the corresponding tetraiodides in evacuated silica ampoules (length 15 cm, 1 cm diameter) at 600 °C for the Zr and Hf compounds and at 450 °C for the Ti compound. They are obtained in a crystalline form after annealing at 560–600 °C for 2–3 days. DTA measurements were used to investigate the reaction temperatures (Mettler thermoanalyzer, mixtures 2CsI + HfI_4 or ZrI_4 in evacuated, sealed silica containers of 1 cm^3, heating rate 6°/min against α-Al_2O_3 as reference). The DTA diagram for the CsI/HfI_4 mixture is shown in Fig. 1. It is typical for the systems investigated here.

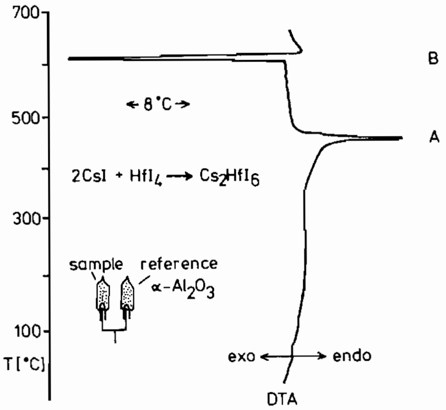

Fig. 1. DTA diagram for Cs_2HfI_6 (heating curve).

The endothermic effect A at 450 °C (max.) corresponds to the melting (under pressure) of HfI_4 in the mixture. According to our investigations the melting point (max.) of pure HfI_4 is 482 °C under these conditions (see [7]). The pronounced endothermic effect B at 605 °C (max.) indicates the formation of Cs_2HfI_6 from the components. If the reaction is followed by X-ray powder photographs, only CsI reflexions are observed after A; after B only sharp reflexions of Cs_2HfI_6 are seen. The DTA curve for CsI/ZrI_4 mixtures is very similar with a melting temperature of 475 °C for ZrI_4 in the mixture (see [7]) and exothermic formation of Cs_2ZrI_6 at 610 °C.

All compounds are coloured: Cs_2TiI_6 is orange–yellow, Cs_2ZrI_6 light orange–yellow, Cs_2HfI_6 yellow, Cs_2PdI_6 dark–red and Cs_2PtI_6 dark-red.

Thermogravimetric measurements (1 atm Ar, heating rate 4°/min) show thermal decomposition of Cs_2MI_6 (M = Ti, Zr, Hf) above 600 °C to CsI and MI_4, whereas Cs_2PtI_6 decomposes at 390 °C to CsI, Pt and iodine. Thermal decomposition of Cs_2PdI_6 proceeds in two steps with the apparent intermediate formation of Cs_2PdI_4 + I_2; the former decomposes later to CsI, Pd and iodine.

$CsPdI_6$ and Cs_2PtI_6 are stable towards air and humidity; Cs_2TiI_6, Cs_2ZrI_6 and Cs_2HfI_6 are decomposed by moisture and have to be handled in a closed system.

According to X-ray powder diagrams (CuKα, Guinier-Simon method) all five compounds are isotypic and crystallize in the K_2PtCl_6 structure type. In Table I the unit cell constants are given.

TABLE I. Unit cell Constants [Å] of K_2PtCl_6 type Caesium Hexaiodometalates.

Cs_2TiI_6	11.473(3)
Cs_2ZrI_6	11.613(3)
Cs_2HfI_6	11.609(3)
Cs_2PdI_6	11.311(3)
Cs_2PtI_6	11.361(3)

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Complete single-crystal X-ray structure determinations were done for Cs_2HfI_6 and Cs_2PtI_6. (Syntex $P2_1$ diffractometer, MoKα, 121 reflexions for Cs_2HfI_6, 480 reflexions for Cs_2PtI_6 measured, absorption corrections) which, after least-squares refinement with anisotropic temperature factors, gave R factors of 0.030 (Cs_2HfI_6) and 0.027 (Cs_2PtI_6). Coordinates and interatomic distances are given in Table II. The Pt–I bond length corresponds closely to the mean value of 2.666(2) Å found in $(C_5H_5NH)_2PtI_6$ [4]. A full report on this work, including syntheses and structure determinations of further group IV compounds in this series, will appear later.

TABLE II. x Coordinates of the Iodine Atoms and Interatomic Distances [Å] with Standard Deviations for Cs_2Mi_6 (M = Hf and Pt).

	Cs_2HfI_6	Cs_2PtI_6
x	0.2437(2)	0.2353(2)
Cs···I	4.105(1)	4.020(1)
M–I	2.829(2)	2.673(2)

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