

Article

Linear Trimeric Hafnium Clusters in $\text{Hf}_{0.86(1)}\text{I}_3$

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Abstract: The reduction of hafnium tetraiodide, HfI_4 , with aluminum at 600 °C or 850 °C in the presence of a NaI flux resulted in black single crystals of $\text{Hf}_{0.86(1)}\text{I}_3$. This composition corresponds well to the upper end of the non-stoichiometry range $0.89 \leq x \leq 1.00$ previously reported for Hf_xI_3 . The crystal structure ($a = 1250.3(2)$, $c = 1999.6(3)$ pm, $R-3m$, $Z = 18$) is made up of hexagonal closest packed layers of iodide ions. One third of the octahedral holes would be filled as in TiI_3 or ZrI_3 if it were $\text{Hf}_{1.00}\text{I}_3$. In $\text{Hf}_{0.86(1)}\text{I}_3$, one out of six octahedral holes along [001] are, however, only occupied by 16%. In contrast to TiI_3 -I and ZrI_3 , one striking structural feature is in the formation of linear hafnium trimers with identical Hf—Hf distances of 318.3(2) pm rather than the formation of dimers. These may be associated with Hf—Hf bonding although only 2.64 electrons are available for one $\text{Hf}_{5.16}\text{I}_{18}$ column.

Keywords: hafnium; Iodide; cluster; crystal structure

1. Introduction

The group four elements, titanium, zirconium and hafnium, are, in principle, capable of forming iodides in the +2, +3 and +4 oxidation states. The di-, tri- and tetraiodides of titanium [1–5] and zirconium [6–10] appear to be well characterized. At least, their crystal structures and the importance

of metal-metal bonding at sufficiently low temperatures are now well established. Of the hafnium iodides, only the crystal structure of HfI_4 has been determined [11].

Attention to the lower iodides of hafnium was given only rarely. Early work stated that hafnium triiodide, HfI_3 , should exist [12]. Powder X-ray diffraction established that HfI_3 , as the trichlorides, bromides and iodides of titanium and zirconium, belongs structurally to an ever growing family of trihalides with hexagonally closest packed halide layers, between which one-third of the octahedral voids are occupied by metal atoms [13].

A number of important conclusions were drawn from a closer inspection of the phase equilibria in the Hf-HfI_4 system [14]: First, no lower iodide of hafnium than hafnium triiodide, HfI_3 , exists in equilibrium. Second, beyond HfI_3 there is a non-stoichiometric phase HfI_{3+x} with x ranging from 0.2 to almost 0.5. Third, powder X-ray diffraction data show that there must be a super-structure with respect to the unit cell as established previously [13]. Fourth, the hexagonal sub-cell parameters are dependent upon the composition of HfI_{3+x} with a decreasing and c increasing with x .

New investigations into reduced hafnium iodide systems have brought about single crystals of $\text{HfI}_{3.50}$, or better: $\text{Hf}_{0.86}\text{I}_3$. The crystals have a clearly resolved superstructure although with the statistical under-occupation of one out of six hafnium sites.

2. Experimental Section

Hafnium tetraiodide, HfI_4 , was prepared from hafnium metal powder (99.6%, 2–3.5% Zr, Alfa Aesar) and iodine (resublimed p.a., Acros Organics) in stoichiometric amounts. The crude product was sublimed in high vacuum prior to use and handled only under dry box conditions (argon atmosphere, MBraun, Garching).

HfI_4 (for example 200 mg, 0.29 mmol), aluminum metal powder (99.99%, Chempur) and NaI (99.5%, Merck) were weighed in 1:4:1 molar quantities and filled in tantalum containers which were sealed by helium arc welding and jacketed in silica [15]. The sample was heated to 850 °C (or 600 °C in another reaction) and held there for 16 days. Slow cooling to room temperature (5 °C/h) yielded shiny, black, rod-shaped crystals.

Some crystals were selected under a microscope in a dry box and sealed in thin-walled glass capillaries. After their quality had been checked by Laue diffraction patterns, the best specimen was transferred to a single-crystal X-ray diffractometer (Stoe Image Plate Diffraction System, IPDS I) to collect a complete intensity data set at ambient temperature.

Structure solution and refinement was performed with the programs SHELXS-97 (direct methods) [16] and SHELXL-97 [17], scattering factors were from *International Tables for X-ray Crystallography*, Volume C [18]. Data corrections were carried out for Lorentz and polarization factors and absorption (numerical with the aid of the programs X-RED [19] and X-SHAPE [20], Stoe, Darmstadt, 1994). Further details on the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fizkarlsruhe.de), on quoting the depository number ICSD-422793, the authors and the journal citation.

Crystal data for $\text{Hf}_{0.86(1)}\text{I}_3$: Hexagonal, $R\bar{3}m$ (No. 166), $a = 1250.3(2)$, $c = 1999.6(3)$ pm, $V = 2707.3(6) \times 10^6$ pm³, $Z = 18$. Diffractometer IPDS-I, Stoe, Darmstadt; Mo- K_α (graphite

monochromator, $\lambda = 71.073$ pm); $T = 293(2)$ K; $2.77^\circ \leq \theta \leq 24.96^\circ$; 100 images, $\Delta\varphi = 2^\circ$; indices: $-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-23 \leq l \leq 23$; $\rho_{\text{calc}} = 5.891$ g cm $^{-3}$; 6403 reflection intensities measured, of which 608 were symmetrically independent, 383 with $I_0 > 2\sigma(I_0)$, $R_{\text{int}} = 0.1352$, $F(000) = 3972$, $\mu = 30.114$ mm $^{-1}$. R values on F^2 : $R_1/wR_2 [I_0 > 2\sigma(I_0)]$: 0.0435/0.0735 and for all data: 0.0737/0.0791; $\text{Goof} = 0.900$. For atomic coordinates and equivalent displacement factor coefficients see Table 1.

Table 1. Atomic coordinates and equivalent displacement factor coefficients U_{eq} (10^{-4} pm 2) for $\text{Hf}_{0.86(1)}\text{I}_3$; * Wyckoff notation, ** occupation factor.

Atom	WN*	x/a	y/b	z/c	k^{**}	U_{eq}
Hf1	3a	1/3	2/3	-1/3	0.141(14)	0.0037(11)
Hf2	3b	1/3	2/3	1/6	1	0.00196(7)
Hf3	6c	1/3	2/3	0.00750(10)	1	0.00183(5)
Hf4	6c	1/3	2/3	-0.17993(10)	1	0.00239(5)
I1	18h	0.44215(8)	0.55785(8)	0.08464(8)	1	0.00238(4)
I2	18h	0.22891(8)	0.77109(8)	-0.08132(8)	1	0.00224(4)
I3	18h	0.44210(9)	0.88420(17)	-0.24754(9)	1	0.00305(5)

3. Results and Discussion

The idealized nickel arsenide, NiAs [21], and cadmium iodide, CdI $_2$ [22], types of structure are usually described as consisting of hexagonal closest packings of spheres of As and I, respectively, with all and half of the octahedral interstices filled with Ni and Cd atoms, respectively. Thus, the hexagonal unit cell with the parameters a_0 and c_0 contains two and one formula units, respectively. For CdI $_2$, the lattice parameters are $a = 424.45(1)$ and $c = 686.42(3)$ pm [22].

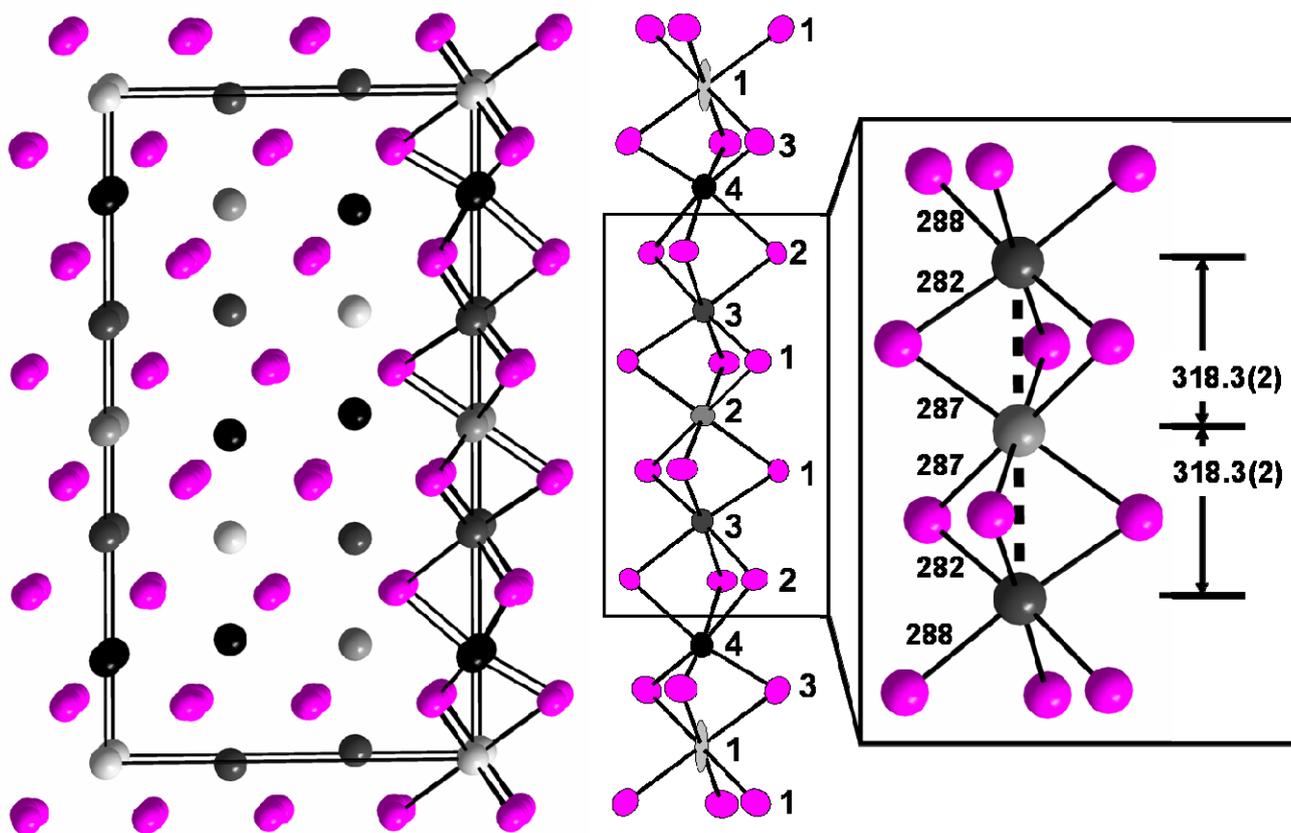
In metal triiodides MI $_3$, only one third of the octahedral interstices of a hexagonal closest packing of iodide ions need to be filled. This can be done in at least two ways: First, between every second iodide layer two thirds of the octahedral voids are occupied, the others are all empty; this is the arrangement of the BiI $_3$ type of structure [23] which has recently been refined for YI $_3$ [24]; a super-cell with $a = a_0\sqrt{3}$ and $c = 3c_0$ with $Z = 6$ results. Second, between all layers one third of the octahedral voids are filled in such a way that columns of octahedra sharing common faces are formed; this is the arrangement of the TiI $_3$ type of structure [4,5] with a super-cell with $a = a_0\sqrt{3}$ and $c = c_0$ for the hexagonal ($P6_3/mcm$, No. 193, $Z = 2$) high-temperature and $a = 3a_0$, $b = c_0$ and $c = a_0\sqrt{3}$ for the orthorhombic ($Pmnm$, No. 59, $Z = 4$) modifications, respectively.

In the low-temperature modification of titanium triiodide, TiI $_3$ -I, Ti–Ti distances in such a column are 309.6(2) and 339.6(2) pm at 293 K, attesting for single-bonded Ti–Ti dimers; in high-temperature TiI $_3$ -I, Ti–Ti distances are all equal, 326 pm at 317 K, the transition temperature for TiI $_3$ -I to TiI $_3$ -II [4]. For ZrI $_3$, this phase transition has not been observed and can probably not be observed because decomposition occurs before the bond energy for the Zr–Zr bond has been acquired. However, ZrI $_3$ is isostructural with TiI $_3$ -I, with Zr–Zr bond distances of 317.2(2) pm [9].

For “HfI $_3$ ”, a hexagonal super-structure of $a = 3a_0$ and $c = 3c_0$ with $Z = 18$ is observed, see Experimental Section and Table 1 for atomic parameters. Again, the structure is determined by a hexagonal closest packing of iodide anions, see Figure 1. The 54 iodide ions per unit cell produce 54 octahedral holes, of which 18 would be filled if it were HfI $_3$. The single crystal that we refer to has the

composition $\text{Hf}_{0.86(1)}\text{I}_3$, or $\text{HfI}_{3.50(1)}$, and marks the most oxidized end of the non-stoichiometry range. The previously reported sub-cell, $a' = 723$, $c' = 667$ pm (± 1 pm) [14], is in excellent agreement with the sub-cell lattice parameters calculated from the super-cell, $a' = a/\sqrt{3} = 721.9$, $c' = c/3 = 666.5$ pm.

Figure 1. Projection of the crystal structure of $\text{Hf}_{0.86(1)}\text{I}_3$ down [010] (left). Middle: One column of face-sharing octahedra as the repeat unit along [001] in $\text{Hf}_{0.86(1)}\text{I}_3$ (thermal ellipsoids are at a 90% probability level) and a cut-out of the trimer with relevant distances (in pm, right).



There are four crystallographically independent hafnium sites in the super-cell of $\text{Hf}_{0.86(1)}\text{I}_3$ of which three sites, Hf2 (3*b*), Hf3 (6*c*), and Hf4 (6*c*) are fully occupied. Site Hf1 (3*a*) has an occupancy factor of $k = 0.141(14)$ accounting to 0.42 hafnium atoms occupying statistically three octahedral voids, which is associated with a large displacement factor, see Table 1 and Figure 1. No solid indications for a further ordered superstructure could be found; refinement with split positions is not indicated by SHELX and does not yield a better result. The center of gravity of the electron density for Hf1 is in the special position 3*a*. If the hafnium site (3*a*) were fully occupied, this iodide would have the composition $\text{Hf}_{18}\text{I}_{54} = \text{HfI}_3$.

Within the non-stoichiometry range for Hf_xI_3 with $0.86 \leq x \leq 1.00$ [14], the empty voids are gradually filled, which is in accord with the decrease of the *c* lattice constant. More voids filled means more electrons available for metal-metal bonding interactions and thus shorter distances in the [001] direction. Complete non-occupation of the Hf1 site—which would correspond to the composition $\text{Hf}_{0.83}\text{I}_3$ or $\text{HfI}_{3.6}$ —apparently destabilizes the structure electrostatically. Full occupation, *i.e.*, HfI_3 , is obviously possible and it is—according to the phase diagram [14]—also the most reduced hafnium

iodide, in equilibrium with the metal. The crystals that we have obtained are at the most oxidized end, $\text{Hf}_{0.86}\text{I}_3$ or $\text{HfI}_{3.50}$, because we have, with an ample excess of the reductant aluminum, at temperatures of 850 °C or 600 °C first reached the most reduced end, HfI_3 , and then, by slow cooling—hence in equilibrium—the composition gradually reaches the least reduced end of the non-stoichiometry range, $\text{Hf}_{0.86}\text{I}_3$.

In $\text{Hf}_{0.86(1)}\text{I}_3$, all $[\text{HfI}_6]$ octahedra share common faces in accord with the *Niggli* formula $\text{HfI}_{6/2}^f$. Columns of face-sharing octahedra run along the hexagonal c axis and, in accord with the space group symmetry $R\text{-}3m$, also parallel $[\frac{1}{3}, \frac{2}{3}, 1]$ and $[\frac{2}{3}, \frac{1}{3}, 1]$. The octahedral holes in the remaining six columns are empty. Thus, the columns of octahedra with holes occupied are isolated from each other such that the distribution of hafnium atoms is to be considered a one-dimensional problem. Figure 1 shows one column of the length of the c axis. Hf-I distances in the $[\text{HfI}_6]$ octahedra are 285.5 pm on the average, if the Hf1-I distances are excluded. They are thereby slightly shorter than the respective mean distances Zr-I in ZrI_3 , 290.0 pm [9].

Zr–Zr dimers are observed in ZrI_3 with an internuclear distance of 317.2(2) pm. This distance is associated with a Zr–Zr σ bond (each Zr^{3+} has one 4d valence electron). In other words, the equidistant chain of Zr^{3+} ions occupying the octahedral holes of face-sharing $[\text{I}_{6/2}]$ columns distorts to alternating short (317.2(2) pm, bonding) and long separations (350.7(2) pm, not bonding). The transition to this *Peierls* distortion is actually observed for TiI_3 [4,5] and for a number of other halides as summarized in [25]. An isolated $[\text{Zr}_2\text{I}_9]^{3-}$ dimer is also known from $\text{Cs}_3\text{Zr}_2\text{I}_9$ with a bonding distance of 312.9(4) pm. This compound is topologically very closely related to $\text{Cs}_3\text{Y}_2\text{I}_9$. There are, however, no electrons available for bonding interactions as Y^{3+} has the electronic configuration $4d^0$. Therefore, the “repulsive” Y–Y distance is 405.2(9) pm [26].

Trimeric clusters Hf3–Hf2–Hf3 occur in $\text{Hf}_{0.86(1)}\text{I}_3$, Figure 1. In these clusters, the hafnium atoms are 318.3(2) pm apart, just as the zirconium atoms in the Zr–Zr dimers in ZrI_3 (above), and close to the Hf–Hf distances in octahedral hafnium clusters, for example 320.6 (av.) in $\text{Na}_{0.8}\{\text{Hf}_6\}\text{Cl}_{15}$ [27]. There appears to be a second dimer, Hf4–Hf1–Hf4, where the Hf–Hf distance is only 306.7(2) pm. This short distance, however, is obscured by the under-occupation of the Hf1 site producing a long Hf3–Hf4 distance of 374.8(3) pm. If the Hf1–Hf4 distance was equal to the Hf2–Hf3 distance, Hf3–Hf4 were 363.3 pm apart, a distance that agrees better with the non-bonding Zr–Zr separation of 350.7(2) pm in ZrI_3 . However, for the composition $\text{Hf}_{0.86(1)}\text{I}_3$, equivalent to a $\text{Hf}_{5.16}\text{I}_{18}$ repeat unit as shown in Fig. 1, there are only 2.64 electrons available for hafnium–hafnium bonding. If these were associated with two bonds in the Hf3–Hf2–Hf3 trimer, there were much fewer electrons than for a “normal” three-center—four-electron bond (two σ bonds). On the other hand, we have recently observed a linear $[\{\text{Pr}_3\}_{16}]^{9-}$ trimer in $\text{Ba}_6\text{Pr}_3\text{I}_{19}$ (three square antiprisms $[\text{PrI}_8]$ share common faces). According to $(\text{Ba}^{2+})_6(\text{Pr}^{3+})_3(\text{e}^-)_2(\text{I}^-)_{19}$, there are two electrons available for Pr–Pr bonding. Theoretical calculations show that this situation is in accord with an “open” three-center–two-electron bond [28]. The Pr–Pr distances are, however, with 356.4(2) pm much longer than the Hf–Hf distances in $\text{Hf}_{0.86(1)}\text{I}_3$ which may be attributed to some extent to the larger coordination number of Pr (eight) in $\text{Ba}_6\text{Pr}_3\text{I}_{19}$.

4. Conclusions

Crystals of $\text{Hf}_{0.86(1)}\text{I}_3$ were obtained from HfI_4 by reduction with aluminum in the presence of a NaI flux. Their composition marks the most oxidized end of the non-stoichiometry range Hf_xI_3 with $0.86 \leq x \leq 1.00$. The crystal structure—a super-structure of the high-temperature TiI_3 type—is composed of hexagonally closest-packed layers of iodide ions between which 5.16 out of 6 voids in confacial octahedra along [001] are filled such that trimeric clusters occur with Hf–Hf distances of 318.3(2) pm. For bonding interactions within these trimers, 2.64 electrons are available.

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References and Notes

1. Klemm, W.; Grimm, L. Zur Kenntnis der Dihalogenide des Titans und Vanadins. *Z. Anorg. Allg. Chem.* **1942**, *249*, 198-208 and 209-218.
2. Klemm, W.; Krose, E. Magnetochemische Untersuchungen XLIX. Das magnetische Verhalten der Titantrihalogenide. *Z. Anorg. Allg. Chem.* **1947**, *253*, 209-217.
3. Schnering, H.G. Zur Struktur des Titan(III)-jodids. *Naturwissenschaften* **1966**, *53*, 359-360.
4. Meyer, G.; Gloger, T.; Beekhuizen, J. Halides of Titanium in Lower Oxidation State. *Z. Anorg. Allg. Chem.* **2009**, *635*, 1497-1509.
5. Angelkort, J.; Schönleber, A.; van Smaalen, S. Low- and high-temperature structures of TiI_3 . *J. Solid State Chem.* **2009**, *182*, 525-531.
6. Corbett, J.D.; Daake, R.L.; Poepelmeier, K.R.; Guthrie, D.H. Metal-Metal Bonded Clusters in Transition Metal Groups 3 and 4. Synthesis and Structure of Three M_6X_{12} -Type Clusters for Scandium and Zirconium. *J. Am. Chem. Soc.* **1978**, *100*, 652-654.
7. Guthrie, D.H.; Corbett, J.D. Synthesis and Structure of an Infinite-Chain Form of ZrI_2 (α). *J. Solid State Chem.* **1981**, *37*, 256-261.
8. Corbett, J.D.; Guthrie, D.H. A Second Infinite-Chain Form of Zirconium Diiodide (β) and Its Coherent Intergrowth with α -Zirconium Diiodide. *Inorg. Chem.* **1982**, *21*, 1747-1751.
9. Lachgar, A.; Dudis, D.S.; Corbett, J.D. Revision of the Structure of Zirconium Triiodide. The Presence of Metal Dimers. *Inorg. Chem.* **1990**, *29*, 2242-2246.
10. Krebs, B.; Henkel, G.; Dartmann, M. Kristallstruktur von Zirkoniumtetrajodid ZrI_4 : Ein neuer AB_4 -Strukturtyp. *Acta Crystallogr.* **1979**, *B35*, 274-278.
11. Krebs, B.; Sinram, D. Hafniumtetrajodid HfI_4 : Struktur und Eigenschaften. Ein neuer AB_4 -Strukturtyp. *J. Less-Common Met.* **1980**, *76*, 7-16.
12. Larsen, E.M.; Leddy, J.J. The Anhydrous Reduced Halides of Zirconium and Hafnium. *J. Am. Chem. Soc.* **1956**, *78*, 5983-5996.
13. Dahl, L.F.; Chiang, T.-I.; Seabaugh, P.W.; Larsen, E.M. Structural Studies of Zirconium Trihalides and Hafnium Triiodide. *Inorg. Chem.* **1964**, *3*, 1236-1242.

14. Struss, A.W.; Corbett, J.D. The Lower Halides of Hafnium. A Nonstoichiometric Hafnium Triiodide Phase. *Inorg. Chem.* **1969**, *8*, 227-232.
15. Corbett, J.D. Tantalum as a High-Temperature Container Material for Reduced Halides. *Inorg. Synth.* **1983**, *22*, 15-22.
16. Sheldrick, G.M. *SHELXS-97, Program for Structure Analysis*; University of Göttingen: Göttingen, Germany, 1998.
17. Sheldrick, G.M. *SHELXL-93, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.
18. Wilson, A.J.C., Ed. *International Tables for Crystallography*; Kluwer Acad. Publ.: Dordrecht, The Netherlands, 1992; Volume C.
19. Stoe. *X-RED 1.22, Stoe Data Reduction Program (C)*; Stoe & Cie GmbH: Darmstadt, Germany, 2001.
20. Stoe. *X-Shape 1.06, Crystal Optimisation for Numerical Absorption Correction (C)*; Stoe & Cie GmbH: Darmstadt, Germany, 1999.
21. Thompson, J.G.; Rae, A.D.; Withers, R.L.; Welberry, T.R.; Wills, A.C. The crystal structure of nickel arsenide. *J. Phys. C Solid State Phys.* **1988**, *21*, 4007-4015; and literature cited therein.
22. Palosz, B.; Salje, E. Lattice parameters and spontaneous strain in AX₂ polytypes: CdI₂, PbI₂, SnS₂ and SnSe₂. *J. Appl. Crystallogr.* **1989**, *22*, 622-623.
23. Ruck, M. Darstellung und Kristallstruktur von fehlordnungsreichem Bismuttriiodid. *Z. Kristallogr.* **1995**, *210*, 650-655.
24. Jongen, L.; Meyer, G. Yttrium triiodide, YI₃. *Acta Cryst.* **2005**, *E61*, i151-i152.
25. Hillebrecht, H.; Ludwig, Th.; Thiele, G. About Trihalides with TiI₃ Chain Structure: Proof of Pair Forming of Cations in β-RuCl₃ and RuBr₃ by Temperature Dependent Single Crystal X-ray Analyses. *Z. Anorg. Allg. Chem.* **2004**, *630*, 2199-2204; and literature cited therein.
26. Guthrie, D.H.; Meyer, G.; Corbett, J.D. Metal-Metal Repulsion and Bonding in Confacial Bioctahedra. Crystal Structures of Cs₃Y₂I₉ and Cs₃Zr₂I₉ and Comparison with Related Phases. *Inorg. Chem.* **1981**, *20*, 1192-1196.
27. Qi, R-Y.; Corbett, J.D. Hafnium Chloride Cluster Chemistry. An Exploration. *Inorg. Chem.* **1994**, *33*, 5727-5732.
28. Gerlitzki, N.; Mudring, A.-V.; Meyer, G. Ba₆Pr₃I₁₉: Linear [Pr₃I₁₆] Trimers with Two Excess Electrons in a Three-Centre—Two-Electron Bond. *Z. Anorg. Allg. Chem.* **2005**, *631*, 381-384.