$[PtIn_6]^{10+}$ Octahedra in $PtIn_7F_{13}$: The First Compound of a New Class of Metal-Cluster Fluorides

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Fluoride compunds containing low valent indium are largely unknown and all experiments to reduce InF_3 with H_2 or metallic In, which date back to the 1930s,[1] have failed. Our own experiments for the reduction of InF_3 with elemental In in Pt ampoules often resulted in a pale yellow products whose X-ray powder patterns could not be assigned to any known phase. Since the hypothetical "InF" is isoelectronic with SnO and the recently discovered $Ru_3Sn_{15}O_{14}$,[2] which can formally be considered as "$Ru_3Sn \cdot 14\,SnO$", it seemed likely that the corresponding low valent indium fluorides exist. Through addition of Pt powder to the well known In – InF_3 system, we succeeded in the synthesis of the new fluoride $PtIn_7F_{13}$ as pure powder samples and single crystals (see Experimental Section), from which the crystal structure was solved and the structural parameters refined.[3, 4]

The crystal structure of $PtIn_7F_{13}$ is shown in Figure 1. Characteristic building units are the $[PtIn_6]$ octahedra, which are observed for the first time. These units are stacked in an alternating fashion together with $[InF_6]$ octahedra along [001]. Platinum centers are octahedrally coordinated by six In atoms with Pt–In bond lengths ranging from 253.0 to 254.7 pm (Figure 2). These distances are significantly smaller than in intermetallic phases with six-fold coordinated Pt atoms, for example, $LaPtIn_3$[5] with $d_{Pt-In} = 269$ pm or $Sr_2Pt_3In_4$[6] with $d_{Pt-In} = 265$ pm. The In–In distances within the $[PtIn_6]$ cluster of $PtIn_7F_{13}$ are, at 344 pm to 378 pm, only slightly longer than in elemental In ($d_{In-In} = 325$ pm ($\times 4$) or in molecular In clusters (338 pm ($\times 8$)) such as $In_8(2,6\text{-}Mes_2C_6H_3)_4$ (Mes = 2,4,6-$Me_3C_6H_2$).[7] For a further comparison, $[In(2)In(1)_4]^{7+}$ tetrahedra in $Na_{23}In_5O_{15}$[8] are present with short In(1)–In(2) distances of 275 pm, whereas the In(1)–In(1) edges are relatively long (445 pm).

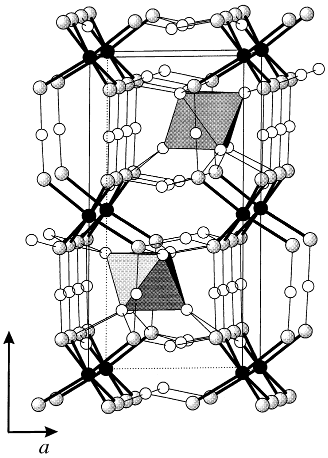

Figure 1. Projection of the crystal structure of $PtIn_7F_{13}$ with the unit cell. Small black circles represent Pt, grey circles In, and open circles F. Short Pt–In distances (< 260 pm) within the $[PtIn_6]$ octahedra are represented by thick lines and the $[In(1)F_6]$ octahedra are represented as polyhedra.

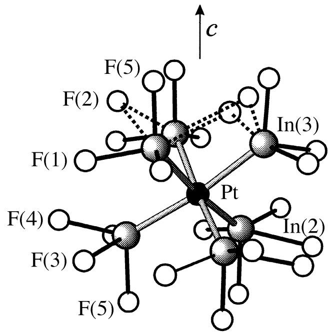

Figure 2. Projection of a $[PtIn_6F_{24}]$ cluster with threefold symmetry in $PtIn_7F_{13}$ together with the numbering of the atoms. Selected distances [pm]: Pt-In(2) 254.7(1), Pt-In(3) 253.0(1), In(2)-In(2) 378.0(1), In(2)-In(3) 360.5(1), In(3)-In(3) 344.2(1), In(2)-F(5) 207.9(12), In(2)-F(4) 209.4(2), In(2)-F(3) 237.5(6), In(3)-F(5) 198.0(12), In(3)-F(1) 206.5(3), In(3)-F(2) 254.6(10).

The $[PtIn_6]$ octahedra are surrounded by a total of 24 F ligands, which lie from 198 to 255 pm distant. Such a $[PtIn_6F_{24}]$ cluster is unique as no fluorides are known which contain comparable units. Only within the higher homologues of the halides are there compounds with discrete octahedral clusters which are centered by transition metals, for example, $Cs_4Pr_6OsI_{13}$[9] and $Bi_{34}Ir_3Br_{37}$.[10] The In(2) atoms are terminally coordinated by four F atoms, whereas the In(3) atoms have three nearest terminal F atoms and, in addition, two further F(2) atoms coordinate and these lie above the In(3) – In(3) edges. The In(3)–F(2) distances are, at 255 pm, relatively long and it is remarkable that μ_2-bridging F ligands in corresponding molecular metal clusters are unknown. Analogous to the highly ionic transition metal compounds containing $M_6X^i_{12}X^a_6$ clusters (i = inner (German: innere), a = outer (äußere))[11] with only 18 surrounding anions and significantly shorter M – M distances (for example, low valent oxoniobates[12, 13] or oxomolybdates[14]) the F(2) atoms can be denoted as inner F ligands (F^i). However, in Nb_6F_{15} [15] or $Na_2Nb_7F_{21-y}Cl_y$ ($y \cong 8$),[16] the hitherto example of a metal cluster fluoride complex ($Nb_6F^i_{12}F^a_6$), the Nb–F^i distances are shorter than those of the Nb–F^a. The different coordination spheres of the In(3) and In(2) atoms in $PtIn_7F_{13}$ are reflected in different distances from the $[In(1)F_6]$ octahedra to the three In(3) and three In(2) of neighboring $[PtIn_6]$ octahedra (Figure 1) and, as a result, the space group is acentric (*P*6$_3$*mc* instead of *P*6$_3$/*mmc*).

The In–F distances within the $[In(1)F_6]$ octahedra are between 207 and 217 pm as found in complex fluoroindates(III), for example, K_2NaInF_6,[17] and it seems reasonable to assume a +3 oxidation state for the In(1) atom. For a deeper analysis of the bonding situation in $PtIn_7F_{13}$, we have calculated bond-order sums according to $\Sigma s_i = \Sigma \exp[(r_0 - r_i)/B]$ (B = 37 pm) with $r_0 = 180$ pm for the In – F distances.[18] As expected, one obtains $\Sigma s_i \approx 1$ for the single F ligands and $\Sigma s_i =$

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2.55 for the octahedrally coordinated In(1) center. For the In(2) and In(3) atoms one obtains significantly smaller values, $\Sigma s_i \approx 1.35$ and $\Sigma s_i \approx 1.85$, respectively, and therefore their oxidation states should lie between +1 and +2. According to the representation of the ionic limit, $PtIn_7F_{13}$ is therefore $[PtIn_6]^{10+}(F^-)_7[In^{3+}F_6]^{3-}$, a mixed-valent Pt–In fluoride–fluoroindate(III).

There are two possibilities for the charge distribution within the $[PtIn_6]^{10+}$ octahedra resulting in integer oxidation states for the In(2), In(3), and Pt atoms and which are all in agreement with an octahedral coordination sphere for Pt with respect to the approach of the ligand field theory [Eq. (1)].

$$[Pt^{4+}(In^{+})_6]^{10+} \leftrightarrow [Pt^{2-}(In^{2+})_6]^{10+} \qquad (1)$$

In both cases, platinum achieves a stable 18 electron configuration on assuming that In^+ is a two-electron and In^{2+} is a one-electron σ-donor, respectively. This is in agreement with the diamagnetism of $PtIn_7F_{13}$ (see Experimental Section) and it therefore has to be considered as a valence compound with only paired electrons.

Band-structure calculations, on the basis of the Extended-Hückel method,[19, 20] indicate that $PtIn_7F_{13}$ is an insulator and both Pt–In as well as In–In interactions dominate below the Fermi level (Figure 3). It is clear from the COOP diagram (Figure 3c) that these interactions have bonding character and are, as expected, antibonding with respect to In–F interactions. The interstitial Pt atom provides electrons and orbitals to the strong bonding with the s orbitals of the surrounding In atoms. In contrast to "classical" complexes such as $[PtCl_6]^{2-}$, the highest occupied orbital (HOMO) of the $[PtIn_6]^{10+}$ cluster is not a t_{2g} state but rather a t_{1u} state because of the energetically high In 4s orbitals. The calculated band gap, Δ_0, is defined by the energy difference between this state and the lowest unoccupied orbital (LUMO), e_g^*. Band gaps obtained from Extended-Hückel calculations are normally too large and, therefore, it is not unusual that the calculated value of $\Delta_0 = 3.3$ eV for $PtIn_7F_{13}$ lies slightly above the value obtained by UV absorption spectroscopy. This value corresponds to the pale yellow color of $PtIn_7F_{13}$ crystals.

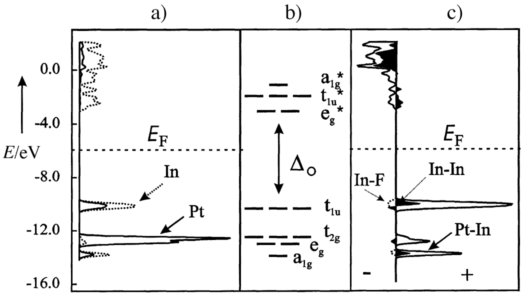

Figure 3. a) Projected density of states (DOS) for In and Pt, b) MO scheme for the metal-centered orbitals, and c) overlap population (COOP curve) for the highest occupied bands in $PtIn_7F_{13}$.

The question arises as to which oxidation states could be assigned to the atoms of the $[PtIn_6]^{10+}$ octahedra. For such a discussion, the bonding situation of the $[PtIn_6]$ octahedra in $PtIn_7F_{13}$ is compared with the $[RuSn_6]$ octahedra in $Ru_3Sn_{15}O_{14}$, in which the octahedra are connected through common corners to triple chains (Figure 4). In this oxide, it seems reasonable to assign the +1 oxidation state to the four connected Sn atoms and the +2 oxidation state to the two peripheral Sn atoms. This assignment allows 18 valence electrons for each of the single Ru atoms and additionally clarifies the condensation of the $[RuSn_6]$ octahedra.[2] As the discrete $[PtIn_6]$ octahedra contain only peripheral In atoms, In should correspondingly have the +1 oxidation state and the Pt atoms the +4 oxidation state. Then however, one would oxidize metallic Pt with InF_3 during the synthesis of $PtIn_7F_{13}$, a situation which seems less plausible. However, by band structure calculations, $Ru_3Sn_{15}O_{14}$ cannot directly be compared with $PtIn_7F_{13}$ as there is non-negligible In–In bonding within the $PtIn_6$ octahedra, whereas no Sn–Sn bonding has been observed in $Ru_3Sn_{15}O_{14}$. Alternatively, one could assume the 0 oxidation state for Pt and distribute the remaining valence electrons to In(2) and In(3).

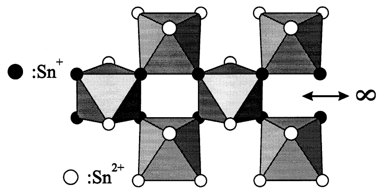

Figure 4. Projection of a fragment of the chain of corner-sharing $[RuSn_6]$ octahedra in $Ru_3Sn_{15}O_{14}$.

It seems, at first, daring to assign the −2 oxidation state to the Pt atoms within the $[PtIn_6]^{10+}$ octahedra. However, Pt is more electronegative than In and, moreover, the electron affinity of Pt (205 kJ mol^{-1}) is larger than that of S (200 kJ mol^{-1}).[21] Of course, the second electron affinity of Pt might be positive but this holds also for O in the rich chemistry of oxides. A Pt^{2-} ion would be isoelectronic with the well known Au^- ion in Cs_3AuO,[23] and therefore does not appear too unusual.[22] Furthermore, there are some hints from band structure calculations for a negatively charged Pt as shown for $CaPtIn_2$.[24] Investigation of the valence of Pt centers is necessary, yet they cannot be obtained easily as ^{196}Pt Mössbauer spectroscopy is, unfortunately, not a routine method and X-ray adsorbtion near-edge structure (XANES) measurements are relatively complex.

We have now succeeded in the preparation of further fluorides and oxides with main group element clusters with interstitial transition metal atoms, especially with $[IrIn_6]^{9+}$ octahedra. By such structures, the question of oxidation states will be easier to answer with studies of the corresponding Mössbauer spectra.

Experimental Section

Carefully dried InF_3 (Merck, p.a.) was mixed with Pt powder (Merck, p.a.) and In powder (Alfa, 99.99 %, 325 mesh) in the ratio 13:3:8, then ground in an achate mortar to a grey powder under an Ar atmosphere. The powder was pressed to a pellet, sealed under Ar in a Pt tube, and maintained at 750 °C for 14 d. On cooling to room temperature, pale yellow transparent crystals of $PtIn_7F_{13}$ with a platelike trigonal habit formed within one day. The crystals are stable in air and soluble in dilute HCl. The elemental analysis of a powder sample of $PtIn_7F_{13}$ with ICP[25] resulted in 4.5 mol% Pt and 30.9 mol% In (calculated: 4.8 mol% Pt and 33.3 mol% In).

The magnetic susceptibility of $PtIn_7F_{13}$ was measured using a Superconducting Quantum Interference Device (SQUID)-V.T.S.-Susceptometer (S.H. Corp., San Diego (USA) and Quantum Design (MPMS: Magnetic Property Measurement System)) at a constant external magnetic field as a function of temperature. The diamagnetic contribution for $PtIn_7F_{13}$ of 3.6×10^{-4} emu mol^{-1} is in approximate agreement with the value calculated from atomic increments[26] (F^-: 1.1×10^{-5}; In^{3+}: 1.9×10^{-5}; Pt^{2+} 2.0×10^{-5} emu mol^{-1}).

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[1] O. Hannebohn, W. Klemm, *Z. Anorg. Allg. Chem.* **1936**, *269*, 2.

[2] W. Reichelt, T. Söhnel, O. Rademacher, H. Oppermann, A. Simon, J. Köhler, *Angew. Chem.* **1995**, *107*, 2307; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2113.

[3] Crystallographic data and crystal structure determination of $PtIn_7F_{13}$: $M = 1245.8$ g mol^{-1}, pale yellow platelets, $0.05 \times 0.05 \times 0.01$ mm, hexagonal, space group $P6_3mc$ (No. 186); $a = 734.2(1)$, $c = 1384.4(2)$ pm, $Z = 2$, $Ag_{K\alpha}$ radiation ($\lambda = 56.086$ pm), graphite monochromator, CAD4 diffractometer, $T = 293$ K, structure solution with direct methods (SHELX86), least-squares refinement on F_0^2 values, complete matrix (SHELX93), 3132 reflections, 943 independent, 47 parameters, $R1 = 0.025$ ($896 F_0 > 4\sigma F_0$), $wR2 = 0.057$, GOF = 1.27, max./min. residual electron density $+1.2/-1.3$ e 10^{-6} pm^3. The acentric space group results from the refinement and an inversion twin (twin factor of 0.45(2)) is present.[4] Atomic positions [isotropic displacement parameters]: Pt: 0, 0, 0 [0.0080(1)]; In(1): 1/3, 2/3, 0.2770(1) [0.0188(3)]; In(2): 0.1706(1), 0.3411(1), 0.9036(1) [0.0254(2)]; In(3): 0.3096(1), 0.1548(1), 0.1149(8) [0.0277(2)]; F(1): 0.5367(9), 0.4633(9), 0.0887(8) [0.043(2)]; F(2): 0.1947(12), 0.8053(12), 0.1987(12) [0.091(5)]; F(3): 0.4669(7), 0.5331(7), 0.3744(6) [0.030(2)]; F(4): 1/3, 2/3, 0.9263(8) [0.015(2)]; F(5): 0.3595(28) 0.2151(29) 0.2548(8) [0.077(7)]. The position of F(5) is only half occupied. Refinements in a less symmetrical space group did not lead to a better result. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-41113.

[4] H. D. Flack, G. Bernardinelli, *Acta Crystallogr. Sect. A* **1985**, *41*, 500.

[5] Y. V. Galadzhun, R. Pöttgen, *Z. Anorg. Allg. Chem.* **1998**, *625*, 481.

[6] R.-D. Hoffmann, R. Pöttgen, *Z. Anorg. Allg. Chem.* **1998**, *625*, 994.

[7] B. E. Eichler, N. J. Hardman, P. P. Power, *Angew. Chem.* **2000**, *112*, 391; *Angew. Chem.* **2000**, *39*, 383.

[8] H. J. Deiseroth, H. Kerber , R. Hoppe, *Z. Anorg. Allg. Chem.* **1998**, *624*, 541.

[9] M. Lulei, J. D. Corbett, *Inorg. Chem.* **1996**, *35*, 4084.

[10] M. Ruck, *Z. Anorg. Allg. Chem.* **1998**, *624*, 521.

[11] H.Schäfer, H. G. Schnering, *Angew. Chem.* **1964**, *76*, 833.

[12] J. Köhler, G. Svensson, A. Simon: *Angew. Chem.* **1992**, *104*, 1463; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1437.

[13] G. Svensson, J. Köhler, A. Simon in *Metal Clusters in Chemistry, Vol. 3* (Eds: P. Braunstein, L. A. Oro, P. R. Raithby), Wiley-VCH, **1999**, p. 1509.

[14] R. E. McCarley, K.-H. Lii, P. A. Edwards, L. F. Brough, *J. Solid State Chem.* **1985**, *57*, 17.

[15] H. Schäfer, H. G. v. Schnering, K. J. Niehues, H. G. Nieder-Vahrenholz, *J. Less-Common Met.* **1965**, *9*, 95.

[16] S. Cordier, A. Simon, *Solid State Sci.* **1999**, *1*, 209.

[17] S. Schneider, R. Hoppe, *Z. Anorg. Allg. Chem.* **1970**, *376*, 268.

[18] I. D. Brown, D. Altermatt, *Acta Crystallogr. Sect. B* **1985**, *41*, 244.

[19] R. Hoffmann, *J. Chem. Phys.* **1963**, *39*, 1397; J. H. Ammeter, H. B. Bürgi, J. C. Thibeault, R. Hoffmann, *J. Am. Chem. Soc.* **1978**, *100*, 3686; R. H. Summerville, R. Hoffmann, *J. Am. Chem. Soc.* **1976**, *98*, 7240; M. H. Whangbo, R. Hoffmann, *J. Am. Chem. Soc.* **1978**, *100*, 6093; R. Ramirez, M. C. Böhm, *Int. J. Quantum Chem.* **1986**, *30*, 391.

[20] J. Köhler, P. Wunsch, PC version of the program EHMACC (Extended-Hückel program, written by M. H. Whangbo, R. Hoffmann, modified by M. Evain, J. Mitchel) Stuttgart, **1991**. Parameters used in the EH calculations: Orbital energies H_{ij} [eV] (coefficient $\zeta 1$): F: 2s -40.185 (2.425), 2p: -18.5 (2.425); In: 5s -12.6 (1.903), 5p -6.19 (1.677); Pt: 6s -9.08 (2.554), 6p -5.47 (2.554), 5d -12.59 (6.013). Double ζ functions have been used for Pt: 0.6334, 2.696, 0.5513.

[21] http:www/webelements.com

[22] C. Feldmann, M. Jansen, *Angew. Chem.* **1993**, *105*, 1107; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1049; C. Feldmann, M. Jansen, *Z. Anorg. Allg. Chem.* **1995**, *621*, 201.

[23] This stimulates for the search of compounds in which one can clearly assign the oxidation state -2 to Pt, for example, in hypothetical "Cs_3PtF" or "$CsBa_2PtN$".

[24] R.-D. Hoffmann, R. Pöttgen, G. A. Landrum, R. Dronskowski, B. Künnen, G. Kotzyba, *Z. Anorg. Allg. Chem.* **1999**, *625*, 789.

[25] O. Buresch, H. G. von Schnering, *Fresenius Z. Anal. Chem.* **1984**, *319*, 418.

[26] P. W. Selwood, *Magnetochemistry*, 2nd ed., Interscience, New York, **1956**.

A Novel Bovine β-1,4-Galactosyltransferase Reaction To Yield β-D-Galactopyranosyl-(1-3)-Linked Disaccharides from L-Sugars**

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Among mammalian glycosyltransferases, bovine β-1,4-galactosyltransferase (β-1,4-GalTase) has been the most extensively studied regarding substrate specificity.[1] In nature this enzyme catalyzes galactosyl transfer from UDP-galactose to the 4-OH position of *N*-acetyl D-glucosamine (D-GlcNAc) and also of D-glucose in the presence of α-lactalbumin (α-LA). The enzyme is known to catalyze other reactions, for example, the transfer of *N*-acetyl-D-galactosamine to D-GlcNAc at high concentrations of α-LA.[2] Although the β-1,4-GalTase reaction had long been thought to be regiospecific at the 4-OH position of acceptor sugars, we previously found a new type of reactions that catalyze galactosyl transfer to the β-anomeric position of *N*-acetyl kannosamine (3-acetamido-3-deoxy-D-glucose),[3] *N*-acetyl gentosamines (3-acetamido-3-deoxy-D-xylose),[4] and D-xylose.[5] In this paper, we describe the first β-1,4-GalTase reaction that utilizes L-series sugars as the acceptor substrates. Moreover, the novel

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