

[PtIn₆] octahedra in low valent indiumfluorides and indiumoxides – a new class of highly ionic compounds containing main group element clusters

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The search for new compounds containing low valent metal atoms seems especially worthwhile since unusual chemical and physical properties are mostly connected to the *non-closed* shell configurations of individual elements. This applies especially to fluorides or oxides, as the highly ionic character of these compounds in combination with the kind of chemical bonding of the excess valence electrons (delocalized, lone pairs, metal clusters ...) leads to interesting properties. However, low valent oxides and fluorides are often difficult to obtain because of their tendency to disproportionate.

The chemistry of In serves as a good example. Any efforts to prepare InO or In₂O have failed so far. With the exception of InBF₄, which has been synthesized at low temperature in liquid HF, fluorides containing In in an oxidation state less than +3 are also up to now unknown, in spite of some efforts for its syntheses which date back into the thirties.

The two new mixed valent fluorides PtIn₇F₁₃ = [PtIn₆]¹⁰⁺In³⁺F₇⁻ and Pt₃In₂₂F₄₀ = ([PtIn₆]¹⁰⁺)₃In₃³⁺In⁺F₄₀⁻ have been obtained by the reduction of InF₃ by In in the presence of Pt. Characteristic building units in both structures are [PtIn₆]¹⁰⁺ octahedra, which are surrounded by 24 F to form a [PtIn₆]F₂₄ cluster, see Fig. 1 a. The Pt-In distances are very short ($d_{\text{Pt-In}} = 254\text{--}256$ pm) compared to the corresponding distances in intermetallic phases like Pt₃In₇, in which Pt is square antiprismatically coordinated by 8 In ($d_{\text{Pt-In}} = 273\text{--}277$ pm).

The [PtIn₆]F₂₄ clusters are connected through [InF₆]³⁻ octahedra to a three-dimensional network. Besides [PtIn₆]¹⁰⁺ and [InF₆]³⁻ octahedra Pt₃In₂₂F₄₀ contains additional In⁺ embedded into a cage of 15 F with In-F distances of 280–360 pm, see Fig. 1 b. Such a high coordination number is normally only found in intermetallic phases and has never been observed in an ionic compound. Obviously In⁺ is an extremely large ion because of the extension of the lone pair of electrons. According to

extended Hückel calculations this lone pair has nearly pure 4s character and exhibits no stereochemical activity despite the rather asymmetric surrounding.

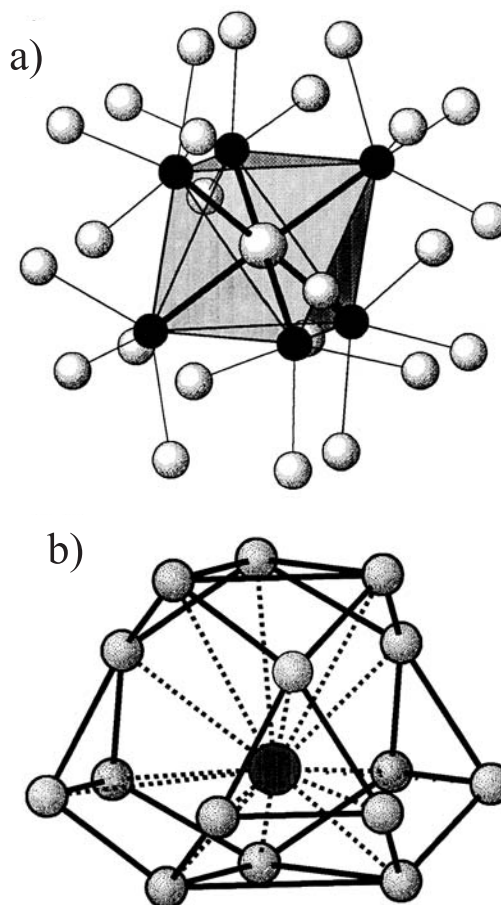
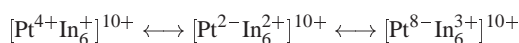


Figure 1: a) [PtIn₆]¹⁰⁺ octahedron together with the 24 surrounding F, and b) [InF₁₅]¹⁴⁻ polyhedron in Pt₃In₂₂F₄₀.

There are three possibilities for the charge distribution within the [PtIn₆]¹⁰⁺ octahedra resulting in integer oxidation states for the In and Pt atoms, which are all in agreement with an octahedral surrounding for Pt with respect to the approach of the ligand field theory. In all three cases Pt achieves a stable 18 electron configuration assuming that In⁺ is a 2-electron σ -donor and In²⁺ is a 1-electron σ -donor, respectively.



According to bond order summations, calculations of the Madelung part of lattice energy and also Mulliken population analysis the most reasonable oxidation states seem to be +2 for the In atoms and -2 for the Pt atoms, which are then isoelectronic to the well-known Au^- , as it is found in CsAu . However, semi-empirical quantum mechanical calculations show, that considerations in terms of an ionic limit are too simplified and that within the PtIn_6 octahedra both Pt-In interactions and In-In interactions are present, see Fig 2.

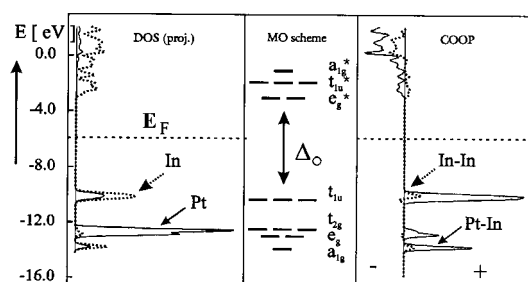


Figure 2: Projected density of states (DOS, left), energy level diagram (middle) and crystal orbital overlap population (COOP, right) for the metal centered orbitals of a $[\text{PtIn}_6]\text{F}_{24}$ -cluster.

In contrast to the well-known complexes $[\text{Pt}(\text{NH}_3)_6]^{4+}$, $\text{W}(\text{CO})_6$ or $[\text{PtCl}_6]^{2-}$, the HOMO of a $[\text{PtIn}_6]^{10+}$ cluster is a t_{1u} state and the calculated band gap Δ_0 is determined by the difference in energy between this state and e_g^* (LUMO). This band gap Δ_0 is, as expected, slightly larger than the optical gap determined by UV absorption spectroscopy of approximately 3.3 eV, which corresponds to the pale yellow color of the crystals of $\text{PtIn}_7\text{F}_{13}$ and $\text{Pt}_3\text{In}_{22}\text{F}_{40}$.

Besides Nb_6F_{15} which is known for a long time $\text{PtIn}_7\text{F}_{13}$ and $\text{Pt}_3\text{In}_{22}\text{F}_{40}$ are the first fluorides containing clusters with metal-metal bonds. The structure solutions of other compounds in the system Pt-In-F is difficult because of the bad quality of the obtained crystals. The replacement of In by Ga and F by

O has recently led to the discovery of the new mixed valent compounds $\text{Pt}_2\text{In}_{14}\text{Ga}_3\text{O}_8\text{F}_{15}$ and $\text{PtIn}_6(\text{GaO}_4)_2$, which also contain PtIn_6 octahedra. Both, the oxidfluoride and the oxid, are stable in air, against water and *non-oxidizing* acids. $\text{PtIn}_6(\text{GaO}_4)_2$ is isotypic to Co_9S_8 (or the mineral Pentlandit $(\text{Fe},\text{Ni})_9\text{S}_8$) which according to $[\text{CoS}_6](\text{SCO}_4)_2$ consists of CoS_6 octahedra and SCO_4 tetrahedra, see Fig. 3.

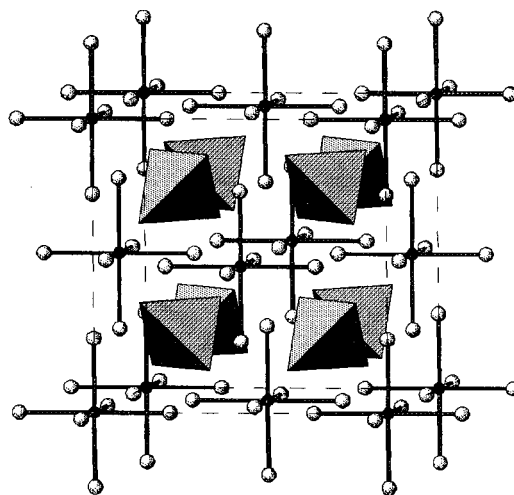


Figure 3: Projection of the crystal structure of $\text{PtIn}_6(\text{GaO}_4)_2$. Dashed lines represent the cubic unit cell. PtIn_6 octahedra and GaO_4 tetrahedra are graphically emphasized.

The remarkably simple cubic structure derives from the CaF_2 type structure by replacing Ca by PtIn_6 octahedra and F by GaO_4 tetrahedra. The Pt-In distances ($d_{\text{Pt-In}} = 254$ pm) are comparable to the corresponding distances in the fluorides discussed above. Powder samples of $\text{PtIn}_6(\text{GaO}_4)_2$ are black, indicating a semiconducting or metallic conductivity, which might result from short *inter-cluster* and short *intra-cluster* distances leading to an extended three-dimensional network of PtIn_6 and empty $\square\text{In}_6$ octahedra. This arrangement of octahedra corresponds to the three-dimensionally net of corner-sharing Nb_6 octahedra in NbO . It seems promising to look for further representatives of this new class of highly ionic compounds with main group element clusters centered by a transition metal atom and their chemical bonding and properties.