Tungsten Iodide

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A Facile Method for the Synthesis of Binary Tungsten Iodides

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Abstract: *The preparation of tungsten iodides in large quantities is a challenge because these compounds are not accessible using an easy synthesis method. A new, remarkably efficient route is based on a halide exchange reaction between WCl_6 and SiI_4. The reaction proceeds at moderate temperatures in a closed glass vessel. The new compounds W_3I_{12} ($W_3I_8{\cdot}2\,I_2$) and W_3I_9 ($W_3I_8{\cdot}{}^1\!/_2\,I_2$) containing the novel [$W_3I_8$] cluster are formed at 120 and 150 °C, and remain stable in air. W_3I_{12} is an excellent starting material for the synthesis of other metal-rich tungsten iodides. At increasing temperature these trinuclear clusters undergo self-reduction until an octahedral tungsten cluster is formed in W_6I_{12}. The synthesis, structure, and an analysis of the bonding of compounds containing this new trinuclear tungsten cluster are presented.*

Elemental tungsten has the highest melting point among metals ($T \approx 3414\,°C$) as well as the largest enthalpy of vaporization ($\Delta H_v = 849.4\ \mathrm{kJ\,mol^{-1}}$)[1] and could possibly be capable of developing the strongest metal–metal bonds.[2] Until now, the synthesis of tungsten iodides remained an unresolved problem because the reaction between elemental tungsten and elemental iodine is ineffective.[3–7] Several years ago another way of synthesis was introduced not only for the preparation of super-hard WC[8] but also for the development of tungsten iodide compounds. In this context the thermal decomposition of $W(CO)_6$ in presence of elemental iodine was reported in 1969.[9] This most successful method was refreshed in a comprehensive study for the preparation of tungsten iodides in 1995,[10] and also evaluated by us.[11]

As part of these studies, reactions were conducted in which $W(CO)_6$ was thermally decomposed with varying amounts of I_2 in a closed glass vessel, or in a flow of argon, at temperatures in excess of 140 °C. Despite the intrinsically low yields and the poor product homogeneities obtained from these reactions, several new tungsten iodide compounds could be characterized.

This tungsten hexacarbonyl route served for the preparation of metal-rich tungsten iodides such as the well-known compound W_6I_{12}, containing an octahedral tungsten cluster $[(W_6I_8^{i})I_2^{a}I_{4/2}^{a\text{-}a}]$ (i = "innen" or inner, a = "außen" or outer, a-a = outer–outer bridging). The crystal structure of this compound is isotypic to that of Mo_6X_{12} and W_6X_{12} (X = Cl, Br).[4,12] It is worth pointing out that there are several tungsten iodide clusters containing four or five tungsten atoms[10] and that there is evidence for the existence of WI_4.[6,7,13,14] To date, there is no evidence for the existence of the more iodine-rich tungsten iodides such as WI_5 and WI_6, although their homologous chlorides and bromides WX_5 and WX_6 (X = Cl, Br) are known.

The structure of WCl_6 is represented by two crystalline modifications. When α-WCl_6 is heated at 150 °C it undergoes an irreversible phase transition into β-WCl_6, which melts at 275 °C.[15] This compound was considered for a halide exchange reaction in which chloride would be exchanged by iodide ions. Similar exchange reactions were successfully applied for the preparation of elusive metal halides, for example $MoCl_6$, via halide exchange reaction between MoF_6 and BCl_3.[16] The synthesis of $MoCl_6$ has been described to run fast at room temperature and slow at −78 °C. At room temperature, $MoCl_6$ slowly releases Cl_2, a property that parallels what we have observed for tungsten iodides, which are reported as follows.

The preparation of new tungsten iodides was successfully accomplished by heating a powder mixture of WCl_6 and SiI_4 in a Schlenk tube with two valves at moderate temperatures. When this mixture is heated to 120 °C, a black crystalline powder of W_3I_{12} ($W_3I_8{\cdot}2\,I_2$) is obtained. Heating at 150 °C yields black plate-like crystals of W_3I_9 ($W_3I_8{\cdot}{}^1\!/_2\,I_2$). Both compounds can be treated in air without significant decomposition, while the polychlorosilane side-products evaporate and the excess of iodine can be sublimed off. Both compounds are structurally characterized on basis of a powder sample of $W_3I_8{\cdot}2\,I_2$ and a single-crystal of $W_3I_8{\cdot}{}^1\!/_2\,I_2$ by means of X-ray diffraction techniques.[17]

Crystal structures of both compounds contain the same [W_3I_8] cluster, which can be envisioned from the motif of a triangular prism formed by iodine atoms, whose rectangular faces are centered by tungsten atoms, rather situated slightly outside the prism face, thereby constituting the trigonal cluster. Two out of three apical iodine atoms of the cluster have a bridging functionality with adjacent clusters in accordance with the notation $[(W_3I_6^{i})I^{a}I_{2/2}^{a\text{-}a}]$, as can be seen in Figure 1.[18]

Noteworthy is the arrangement of iodine atoms around individual tungsten atoms because they resemble a square pyramid, as has been obtained in many cluster compounds. This arrangement may be seen as a result of the condensation of octahedrally coordinated tungsten atoms found in WCl_6.

The $[(W_3I_6^{i})I^{a}I_{2/2}^{a\text{-}a}]$ cluster displayed in Figure 1 is interconnected to form a chain, which is the representative pattern in both crystal structures. Adjacent chains in the structure of $W_3I_8{\cdot}2\,I_2$ are arranged to form layers with the I_2 molecules

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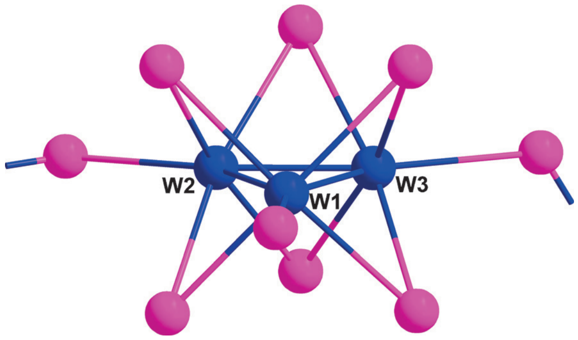

Figure 1. The $[(W_3I_6^i)I^aI_{2/2}^{a\text{-}a}]$ cluster from the structure of $W_3I_8{\cdot}2\,I_2$ and $W_3I_8{\cdot}{}^1\!/_2\,I_2$ (W blue, I violet). The W–W distances in $W_3I_8{\cdot}2\,I_2$ (W1–W2 245.5(6) pm, W1–W3 246.3(5) pm, W2–W3 250.0(5) pm) are only slightly different from those in $W_3I_8{\cdot}{}^1\!/_2\,I_2$ (W1–W2 245.0(1) pm, W1–W3 246.4(1) pm, W2–W3 248.0(1) pm). The longest W–W distance is that of the tungsten atoms bound to the bridging iodine atoms.

packed in between layers. Cluster chains in the crystal structure of $W_3I_8{\cdot}{}^1\!/_2\,I_2$ form waved layers with the I_2 molecules packed inside the layers.

The embedded I_2 molecules in the structure of $W_3I_8{\cdot}2\,I_2$ are successively released on heating until the clusters undergo a self-reduction with the formation of larger cluster aggregates under release of more I_2. According to our thermoanalytical study (DSC), the thermolysis of $W_3I_8{\cdot}2\,I_2$ involves a series of compounds following the sequence $W_3I_8{\cdot}{}^1\!/_2\,I_2 \rightarrow W_4I_{13} \rightarrow W_5I_{16}$ shown in Figure 2, which has been verified by combined DSC-XRD studies described elsewhere.[19]

The formation of $W_3I_8{\cdot}{}^1\!/_2\,I_2$ is an endothermic process that is accompanied by the release of iodine. The following cluster compounds are formed exothermically and comprise reconstructive transformations into tetrahedral and square-pyramidal tungsten clusters.

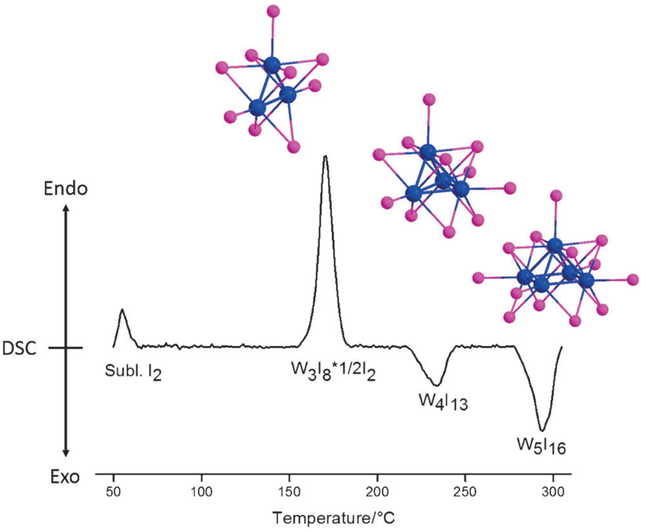

Figure 2. Differential scanning calorimetry analysis (DSC) of the thermal conversion of $W_3I_8{\cdot}2\,I_2$ into $W_3I_8{\cdot}{}^1\!/_2\,I_2$, W_4I_{13}, and W_5I_{16} in a gold-lined steel sample holder (100 μL, BFT 94, Bächler Feintech AG) using a heating rate of 2 °C min^{-1} (DSC 204 F1 Phoenix, Netzsch) after background correction. Representative structural motifs of $W_3I_8{\cdot}{}^1\!/_2\,I_2$, W_4I_{13}, and W_5I_{16} are included.

The final step in this series of conversions is the formation of W_6I_{12}, which is not shown in Figure 2 because the excess iodine would react with the gold lining of the calorimeter. In practice W_6I_{12} is formed from W_5I_{16} (or W_3I_{12}) in a sealed silica tube at temperatures in excess of 450 °C.

The currently known trinuclear metal halide clusters are essentially related to two basic structure motifs: The $[Nb_3Cl_{13}]^{5-}$ unit in the structure of Nb_3X_8 (X = Cl, Br, I)[20,21] is isostructural to the $[W_3Cl_{13}]^{3-}$ ion in $Na_3[W_3Cl_{13}]$,[22] and the structure of binary rhenium halides Re_3X_9 (X = Cl, Br, I).[23,24] These two structure types are shown along with the structure of a $(W_3I_9)^-$ cluster in Figure 3. The bonding in these known trinuclear metal halide clusters has already been described.

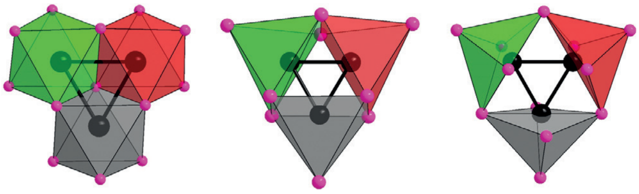

Figure 3. Comparison of the trinuclear clusters derived from edge-sharing $[WCl_6]$ octahedra in $(W_3Cl_{13})^{3-}$ (left), edge-sharing $[WI_5]$ square pyramids in $(W_3I_9)^-$ (center), and edge-sharing $[ReCl_5]$ square pyramids in the structure of Re_3Cl_9 (right).

The $[W_3I_8]$ cluster, an example of a new cluster type, can be considered as a fragment of the W_6I_{12} structure, which is also apparent in the structures of W_4I_{13} und W_5I_{16}, shown in Figure 2.

In terms of their formal charge, $(W_3Cl_{13})^{3-}$ has 8 e$^-$/cluster, the $[W_3I_8]$ cluster in W_3I_9 and in W_3I_{12} has 10 e$^-$/cluster, and Re_3Cl_9 has 12 e$^-$/cluster. These are the number of electrons available for metal-metal bonds.

The bonding in Re_3I_9 has been interpreted in terms of three Re=Re double bonds.[25] In comparison, the bonding situation in $[W_3I_8]$ can be interpreted in terms of three W–W d-σ-type single bonds, one d-π-type and one d-δ-type three-center two-electron bonds (Figure 4).[26] The interactions between the 5d orbitals of the three tungsten atoms is described for a $(W_3I_9)^-$ ion, which has been previously isolated and characterized as a $(Bu_4N)^+$ salt by solvent extraction.[10] As can be seen in Figure 4, the three lowest-lying tungsten 5d orbitals with $1a_1'$ and $1e'$ symmetry are equivalent to three d-σ-type two-center two-electron bonds. The $2e'$ LUMO is W–W antibonding and allows the formation of $(W_3I_9)^{2-}$ ions which are formed when $(W_3I_9)^-$ undergoes a reversible reduction, causing a Jahn–Teller distortion.[10]

Based on the method described for the preparation of W_3I_{12}, it is possible to synthesize octahedral tungsten clusters with the $[(W_6I_8^i)I_6^a]^{2-}$ ion in a single step. The six outer I^- may then be exchanged by any other ligand, as has been demonstrated for the equally difficult to synthesize $[Mo_6I_{14}]^{2-}$ ions in order to obtain $[(Mo_6I_8)L_6]^{2-}$ ions, which have shown fascinating photophysical properties. For example, with the antenna ligand L = CF_3COO^-, high photoluminescence quantum yields (up to 100%) have been reported. This luminescence is quenched in the presence of O_2 in favor of the generation of singlet oxygen.[27]

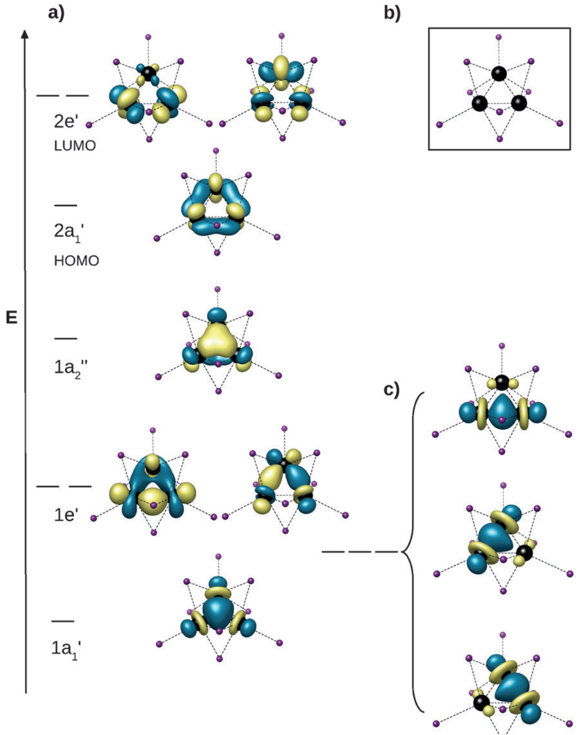

Figure 4. MO diagram of $(W_3I_9)^-$ with idealized D_{3h} symmetry (a) and the projected structure of $(W_3I_9)^-$ (b). The HOMO ($2a_1'$) and the molecular orbital right below it ($1a_2''$) can be interpreted as d-δ- and d-π-type three-center–two-electron bonds, while the 1e′ and the $1a_1'$ molecular orbitals are equivalent to the three two-center two-electron bonding shown in (c).

In conclusion, the preparative method exemplified herein for tungsten iodides can be also applied for the preparation of other binary metal halides. Initial attempts for the preparation of molybdenum iodides departing from $MoCl_5$ and SiI_4 have been successfully accomplished.

Experimental Section

W_3I_{12} ($W_3I_8{\cdot}2\,I_2$):[28] WCl_6 (2 g, 504 mmol) and SiI_4 (4.0525 g, 7.565 mmol) were carefully ground in a glove box under argon atmosphere and placed into a Schlenk flask with two PTFE valves. The Schlenk flask was then heated to 120 °C for 16 h in a drying oven. The side products, polychlorsilanes and I_2, were removed under an argon flow and by heating the product in a water bath (95 °C). Yield: 3.4 g (98 % of the theoretical yield).

W_3I_9 ($W_3I_8{\cdot}{}^1/_2\,I_2$):[29] WCl_6 (100 mg, 0.25 mmol) and SiI_4 (203 mg, 0.38 mmol) were carefully ground in a glove box under argon atmosphere and placed in a quartz ampoule that was then sealed under vacuum and heated in a Simon Müller oven for 12 h at 150 °C. The side product, I_2, was sublimed off, and black single crystals of $W_3I_8{\cdot}{}^1/_2\,I_2$ were obtained and used for X-ray studies.

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[26] The molecular orbitals of $(W_3I_9)^-$ have been calculated at a B3LYP/def2-TZVP level of theory with relativistic large-core pseudopotentials. Owing to the very similar electronegativites of tungsten and iodine, there is a strong mixture of tungsten 5d and iodine 5p orbitals. The tungsten 5d orbitals presented in Figure 4 are the occupied orbitals of the quantum chemical calculation that result after a symmetry conserving projection (see the Supporting Information). The three localized d-σ-type orbitals are obtained by a further localization of the 1a′ and the 1e′ orbitals.
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[28] $W_3I_8{\cdot}2I_2$: $M_r = 2074.404$ gmol^{-1}; *Pbcn* (No. 60), $a = 1466.21(2)$, $b = 2197.17(3)$, $c = 1504.99(2)$ pm, $V = 4848.4(1) \times 10^6$ pm^3; $Z = 8$; $\rho_{calcd} = 5857$ g cm^{-3}; $\mu(Cu_{K\alpha}) = 145\,584$ mm^{-1}; CuK$_{\alpha 1}$ radiation; $\lambda = 154.060$ pm; $T = 298(2)$ K; $2\theta_{max} = 110°$; 3218 measured refections; 77 parameters; data collection: STOE STADIP diffractometer; structure solution with EXPO2014; direct methods; refinement with FullProf.

[29] $W_3I_8{\cdot}{}^1\!/_2\,I_2$: $M_r = 1693.65$ g mol^{-1}; $P4_12_12$ (No. 92), $a = b = 1192.47(9)$, $c = 2538.0(2)$ pm, $V = 3609.0(6) \times 10^6$ pm^3; $Z = 8$; $\rho_{calcd} = 6.234$ g cm^{-3}; $\mu(MoK_\alpha) = 34.441$ mm^{-1}; Mo K$_\alpha$ radiation; $\lambda = 71.073$ pm; $T = 293(2)$ K; $2\theta_{max} = 50.054°$; 20832 measured reflexes; 3189 symmetry independent reflexes; Rint = 0.056, $R_\sigma = 0.028$; 111 parameters; extinction coefficient $1.57(7) \times 10^{-3}$; $R_1(F_o > 2\sigma(F_o)) = 0.0362$, wR_2(all F_o^2) = 0.0817, GooF = 1.021; Flack parameter 0.50(2); min./max. remaining electron density $-1.315/1.369$e $\times 10^{-6}$ pm^{-3}; data collection STOE IPDSII,T, structure solution/refinement SHELX2015. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-429823 ($W_3I_8{\cdot}2\,I_2$) and 429822 ($W_3I_8{\cdot}{}^1\!/_2\,I_2$).

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