5986 Inorg. Chem. 2010, 49, 5986–5991
DOI: 10.1021/ic100516t

Inorganic Chemistry
Article

The Trigonal Prismatic Cluster Compound W_6CCl_{15} and a Carambolage of Tungsten Clusters in the Structure of the Heteroleptic Cluster Compound $W_{30}C_2(Cl,Br)_{68}$

Markus Ströbele and H.-Jürgen Meyer*

Abteilung für Festkörperchemie und Theoretische Anorganische Chemie, Institut für Anorganische Chemie,
Universität Tübingen, Ob dem Himmelreich 7, D-72074 Tübingen, Germany

Received March 21, 2010

Reactions between W_6Cl_{12} and carbon halides can initiate a cascade of reactions and reaction products, yielding W_6Cl_{18}, W_6CCl_{18}, and W_6CCl_{15} with increasing temperature, before decomposition into tungsten carbide is obtained. The new compound W_6CCl_{15} and the new heteroleptic compound $W_{30}C_2(Cl,Br)_{68}$ obtained from these reactions were structurally characterized. The structure of $W_{30}C_2X_{68}$ combines a carambolage of two distinct octahedral and one centered trigonal prismatic cluster in one structure as refined by X-ray single-crystal diffraction ($P\bar{1}$, $Z = 1$; $a = 12.003(2)$ Å, $b = 14.862(3)$ Å, $c = 15.792(3)$ Å, $\alpha = 88.75(2)°$, $\beta = 68.85(2)°$, $\gamma = 71.19(2)°$). The unit cell content $W_{30}C_2X_{68}$ accommodates five hexanuclear tungsten clusters, similar by a total of three octahedral $[W_6X_8]$ type clusters and two carbon-centered trigonal prismatic $[W_6CX_{12}]$ type clusters, sharing terminal halogen atoms to form a network structure. The trigonal prismatic cluster compound W_6CCl_{15} ($P2_1/c$, $Z = 4$; $a = 9.8830(4)$ Å, $b = 11.8945(4)$ Å, $c = 17.8670(7)$ Å, $\beta = 107.883(2)°$) is related to the already known compound W_6CCl_{16}. According to X-ray powder structure refinement, the structure is showing a special connectivity pattern with short intercluster W−W contacts between trigonal prismatic cluster units.

Introduction

Various shapes of tungsten halide clusters have been described in the literature. Among them are the binary compounds W_6X_{12}[1,2] ($X = Cl, Br, I$) and W_6X_{18}[3] (Cl, Br), containing octahedral tungsten cluster cores with eight face-capping halide ligands in $(W_6X_8^{i})X_2^{a}X_{4/4}^{a\text{-}a}$ and 12 edge-capping halide ligands in $(W_6X_{12}^{i})X_6^{a}$, respectively, plus bridging and terminal ligands (Figure 1). A few more binary cluster compounds have been found in the field of tungsten iodides,[4] recently extended by the newly discovered compound $W_{15}I_{47}$ containing square pyramidal cluster cores.[5]

Compared with less reduced tungsten halides (WX_4, WX_5), most of the parent cluster compounds show a remarkable stability in the air and against water.[6] As a result of their exceptional electronic situation, these compounds and their derivatives have been explored with respect to their potential in the fields of photoluminescence,[7,8] oxygen sensing,[9] in organic catalysis,[10] as cathode materials in lithium batteries,[11] and as X-ray contrast agent.[12]

In the past, syntheses of W_6X_{12} ($X = Cl, Br, I$) compounds were established by oxidation of tungsten metal with halogen (Br_2, I_2),[2,4,13] or by reduction of higher tungsten halides, such as WX_6 ($X = Cl, Br$), with electropositive metals like aluminum.[14] Recently, a very convenient synthesis has been described for W_6X_{12} ($X = Cl, Br$) compounds based on the reduction of WX_6 with bismuth metal.[7,15,16]

W_6Cl_{18} has been obtained by oxidation of W_6Cl_{12} with chlorine, however, in intrinsically low yields, due to the loss of

---

*To whom correspondence should be addressed. E-mail: juergen.meyer@uni-tuebingen.de.

(1) Schäfer, H.; Schnering, H. G.; Tillack, J.; Kuhnen, F.; Wöhrle, H.; Baumann, H. *Z. Anorg. Allg. Chem.* **1967**, *353*, 281–310.

(2) Zheng, Y.-Q.; Peters, K.; Hönle, W.; Grin, Y.; von Schnering, H. G. *Z. Kristallogr.* **1997**, *212*, 453–457.

(3) (a) Siepmann, R.; Schnering, H. G.; Schäfer, H. *Angew. Chem., Int. Ed.* **1967**, *6*, 637. (b) Nägele, A.; Glaser, J.; Meyer, H.-J. *Z. Anorg. Allg. Chem.* **2001**, *627*, 244–249.

(4) Franolic, J. D.; Long, J. R.; Holm, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 8139–8153.

(5) Ströbele, M.; Meyer, H.-J. *Z. Anorg. Allg. Chem.* **2010**, *636*, 62–66.

(6) Schäfer, H.; Plautz, H. *Z. Anorg. Allg. Chem.* **1972**, *389*, 57–67.

(7) Ströbele, M.; Jüstel, T.; Bettentrup, H.; Meyer, H.-J. *Z. Anorg. Allg. Chem.* **2009**, *635*, 822–827.

(8) Gray, T. G. *Chem.—Eur. J.* **2009**, *15*, 2581–2593.

(9) Ghosh, R. N.; Baker, G. L.; Ruud, C.; Nocera, D. G. *Appl. Phys. Lett.* **1999**, *75*, 2885–2887.

(10) (a) Kamiguchi, S.; Nagashima, S.; Komori, K.; Kodomari, M.; Chihara, T. *J. Cluster Sci.* **2007**, *18*, 414–430. (b) Kamiguchi, S.; Noda, M.; Miyagishi, Y.; Nishida, S.; Kodomari, M.; Chihara, T. *J. Mol. Catal.* **2003**, *A 195*, 159–171.

(11) (a) Gocke, E.; Schöllhorn, R.; Aselmann, G.; Müller-Warmuth, W. *Inorg. Chem.* **1987**, *26*, 1805–1812. (b) Kuhn, A.; Dill, S.; Meyer, H.-J. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1565–1567.

(12) Franolic, J.; Long, J.; Holm, R.; Droege, M.; Downey, S. PCT Int. Appl., WO 9640287, 1996.

(13) Siepmann, R.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1968**, *357*, 269–298.

(14) McCarley, R. E.; Brown, T. M. *Inorg. Chem.* **1964**, *3*, 1232–1236.

(15) Kolesnichenko, V.; Messerle, L. *Inorg. Chem.* **1998**, *37*, 3660–3663.

(16) Ströbele, M.; Meyer, H.-J. *Z. Anorg. Allg. Chem.* **2010**, *636*, 1517–1519.

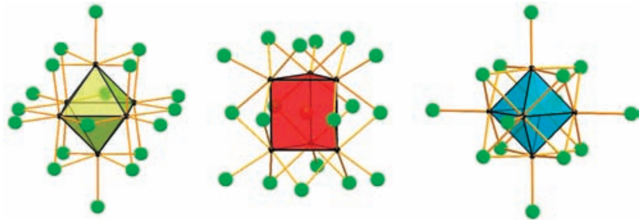

Figure 1. Structures of molecular W_6Cl_{18} and W_6CCl_{18} clusters, and a section of the W_6Cl_{12} ($(W_6Cl_8{}^{i})Cl_2{}^{a}Cl_{4/2}{}^{a\text{-}a}$) structure (from left to right).

higher chlorides (e.g., WCl_6), when being performed by heating W_6Cl_{12} (at 80 − 240 °C) under flowing chlorine gas.[3]

A few years ago, the discovery of compounds W_6CCl_{18} (Figure 1) and W_6CCl_{16} was a novelty in the field of tungsten cluster chemistry, synthesized from powdered tungsten metal, WCl_4, and graphite under a temperature gradient (700/690 °C, 1 week, in a fused silica tube).[17] Clusters in these structures are made up from trigonal prismatic arrangements of tungsten atoms centered by a carbon (or nitrogen) atom following the motif of the sulfur-centered niobium cluster in $A_3[(Nb_6SBr_{12}{}^{i})Br_4{}^{a}Br_{2/2}{}^{a\text{-}a}]$ in which A is a monovalent cation.[18] Trigonal prismatic tungsten chloride clusters were structurally characterized to contain molecular $(W_6CCl_{12}{}^{i})Cl_6{}^{a}$ clusters in W_6CCl_{18} and two-dimensionally bridged $(W_6CCl_{12}{}^{i})Cl_2{}^{a}Cl_{4/2}{}^{a\text{-}a}$ clusters in W_6CCl_{16}.

After discovery of these compounds, a rapid development took place in the synthesis of complex compounds with carbon- or nitrogen-centered $[(W_6ZCl_{12}{}^{i})Cl_6{}^{a}]^{n-}$ anions (Z = C, N; n = 1−4).[19,20] In addition, chemical transformation reactions between tungsten clusters were described following directions $W_6Cl_{12} \leftrightarrow W_6Cl_{18} \rightarrow [W_6CCl_{18}]^{n-} \leftarrow [W_3Cl_{13}]^{u-}$.[21]

After the original and fortuitous discovery of W_6CCl_{18} and W_6CCl_{16} by the reduction of carbon-contaminated WCl_4 with tungsten metal, and the subsequent development of a rational preparation from W, WCl_4, and graphite under a temperature gradient, a convenient route for the synthesis of quasi-binary cluster compounds W_6CCl_{18} and W_6CCl_{16} is still desirable. Therefore, a new preparative approach was investigated by us, departing from W_6Cl_{12} and intrinsically reactive carbon-halide sources at various reaction temperatures. As a result, from these experiments, a cascade of reduced tungsten halide compounds was obtained, and new crystal structures were determined for the intriguing cluster compounds $W_{30}C_2(Cl,Br)_{68}$ and W_6CCl_{15}.

Experimental Section

Syntheses. W_6Cl_{12} was synthesized following the reduction of WCl_6 (ABCR, 99%) with bismuth metal (Riedel-de Haen, 99%) as described previously.[7] A bright yellow powder of W_6Cl_{12} was obtained by vacuum thermolysis of $(H_3O)_2[W_6Cl_{14}]\cdot 7H_2O$ at 325 °C. Solid carbon−halide compounds C_2Cl_6, C_6Cl_6 (Aldrich, 99%), and C_6Br_6 (Aldrich, 98%) were used as purchased. The handling of reaction partners was performed under an Ar inert gas atmosphere in a drybox. Mixtures of W_6Cl_{12} and C_2Cl_6 or C_6X_6 (X = Cl or Br) were loaded (total amounts ca. 150 mg) into evacuated silica tubes and sealed therein. Afterward, the silica tubes were heated (10 K/min) in Simon-Müller furnaces to final temperatures between 175 and 750 °C for 1−2 days. The solid products obtained at various reaction temperatures were inspected by powder X-ray diffraction (PXRD).

W_6Cl_{18}. A mixture of 100 mg of W_6Cl_{12} (0.0655 mmol) and 15.5 mg of C_2Cl_6 (0.0655 mmol) was mixed in a glovebox under argon, charged into a silica tube, and sealed under vacuum. The mixture was heated in a Simon-Müller furnace at 175 °C for 24 h, using a heating rate of 1°/min and a cooling rate of 0.5°/min. Estimated yield (PXRD): 95% W_6Cl_{18}.

W_6CCl_{15}. A mixture of 100 mg of W_6Cl_{12} (0.0655 mmol) and 31 mg of C_6Cl_6 (0.131 mmol) was mixed in a glovebox under argon, charged into a silica tube, and sealed under vacuum. The mixture was heated in a Simon-Müller furnace at 700 °C for 48 h, using a heating rate of 1° min and a cooling rate of 0.5°/min. Estimated yield (PXRD): 95% W_6CCl_{15}.

W_6CCl_{16}. A mixture of 100 mg of W_6Cl_{12} (0.0655 mmol) and 12.45 mg of C_6Cl_6 (0.0437 mmol) was mixed in a glovebox under argon, charged into a silica tube, and sealed under vacuum. The mixture was heated in a Simon-Müller furnace at 650 °C for 24 h, using a heating rate of 1°/min and a cooling rate of 0.5°/min. Estimated yield (PXRD): >60% W_6CCl_{16}.

W_6CCl_{18}. A mixture of 100 mg of W_6Cl_{12} (0.0655 mmol) and 31 mg of C_6Cl_6 (0.131 mmol) was mixed in a glovebox under argon, charged into a silica tube, and sealed under vacuum. The mixture was heated in a Simon-Müller furnace at 550 °C for 24 h, using a heating rate of 1°/min and a cooling rate of 0.5°/min. Estimated yield (PXRD): 90% W_6CCl_{18}.

$W_{30}C_2(Cl,Br)_{68}$. A mixture of 100 mg of W_6Cl_{12} (0.0655 mmol) and 36.1 mg of C_6Br_6 (0.0655 mmol) was mixed in a glovebox under argon, charged into a silica tube, and sealed under vacuum. The mixture was heated in a Simon-Müller furnace at 650 °C for 48 h, using a heating rate of 1°/min and a cooling rate of 1°/min. Estimated yield (PXRD): 95% $W_{30}C_2(Cl,Br)_{68}$.

Powder X-ray Diffraction (PXRD). Diffraction data were collected on a Stoe StadiP X-ray powder diffractometer using Ge-monochromated Cu $K_{\alpha 1}$ radiation. Powder patterns were employed to inspect the purity of W_6Cl_{12} and the identity of reaction products such as W_6Cl_{18}, W_6CCl_{18}, and W_6CCl_{16}. The powder patterns corresponding to $W_{30}C_2(Cl,Br)_{68}$ and W_6CCl_{15} were assigned after solving the crystal structures. The structure of W_6CCl_{15} was solved using the EXPO[22] program, and the solution refinement was performed with the WinPlotr (FullProf) program[23] package. Crystallographic data and results of the structure refinement are shown in Table 1.

Single-Crystal X-ray Diffraction. Black single crystals of $W_{30}C_2(Cl,Br)_{68}$ were fixed on the tips of glass fibers for single-crystal XRD measurements (Stoe IPDS I diffractometer, graphite-monochromated Mo K_α radiation) at room temperature. Intensities were corrected for Lorentz factors, polarization, and absorption effects. $W_{30}C_2(Cl,Br)_{68}$ was found to crystallize in the triclinic space group $P\bar{1}$. Structure and anisotropic refinements were performed with the SHELXL[24] program. Crystallographic data are given in Table 1, and interatomic distances are provided in Table 2.

---

(17) Zheng, Y.-Q.; von Schnering, H. G.; Chang, J.-H.; Grin, Y.; Engelhardt, G.; Heckmann, G. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1256–1264.

(18) (a) Womelsdorf, H.; Meyer, H.-J. *Angew. Chem., Int. Ed.* **1994**, *33*, 1943–1944. (b) Womelsdorf, H.; Meyer, H.-J. *Z. Anorg. Allg. Chem.* **1996**, *622*, 2083–2088.

(19) (a) Welch, E. J; Yu, C. L.; Crawford, N. R. M.; Long, J. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 2549–1553. (b) Welch, E. J.; Crawford, N. R. M.; Bergman, R. G.; Long, J. R. *J. Am. Chem. Soc.* **2003**, *125*, 11464–11465.

(20) Weisser, M.; Burgert, R.; Schnöckel, H.; Meyer, H.-J. *Z. Anorg. Allg. Chem.* **2008**, *634*, 633–640.

(21) Weisser, M.; Tragl, S.; Meyer, H.-J. *J. Cluster Sci.* **2009**, *20*, 249–258.

(22) Altomare, A.; Camalli, M.; Cuocci, C.; Giacovazzo, C.; Moliterni, A.; Rizzi, R. *J. Appl. Crystallogr.* **2009**, *42*, 1197−1202.

(23) Roisnel, T.; Rodriguez-Carvajal, J.; WinPLOTR: A Windows tool for powder diffraction patterns analysis. *Proceedings of the Seventh European Powder Diffraction Conference*; Delhez, R.; Mittenmeijer, E. J., Eds.; 2000; pp 118−123.

(24) Sheldrick, G. M. SHELX-97: program package for the solution and refinement of crystal structures; University of Göttingen: Göttingen, Germany, 1997.

Table 1. Crystallographic Data for W_6CCl_{15} and $W_{30}C_2(Cl,Br)_{68}$

formula	W_6CCl_{15}	$W_{30}C_2(Cl,Br)_{68}$
unit cell dimensions	a = 9.8830(4) Å	a = 12.003(2) Å
	b = 11.8945(4) Å	b = 14.862(3) Å
	c = 17.8670(7) Å	c = 15.792(3) Å
		α = 88.75(2)°
	β = 107.883(2) Å	β = 68.85(2)°
		γ = 71.19(2)°
volume	1998.9(3) Å^3	2472.9(8) A^3
space group	$P\,2_1/c$ (No. 14)	$P\bar{1}$
Z	4	1
fw	6587.61 g/mol	9337.27 g/mol
T	293 K	293 K
λ	1.5406 Å	0.71073 Å
d_{calc}	5.472 g·cm^{-3}	6.270 g·cm^{-3}
R_1, wR_2 (all data)		0.0415, 0.0755
R_p, R_{wp}	0.0987, 0.152	
R_{Bragg}	0.0736	
range, step width	7° < 2Θ < 109.98°, 0.02°	4.24° < 2Θ < 49.8°
total number of reflns	2616	28335
effective number of reflns	516	8077
refined params	86	485
refined structural params	68	

Magnetic Studies. The magnetic susceptibility of $W_{30}C_2(Cl,Br)_{68}$ was measured with a SQUID magnetometer (Quantum Design, MPMS) in the temperature region from 300 to 5 K. The sample was placed into a gelatin capsule and cooled down to 5 K in a magnetic field of 50 000 Oe. The measurement revealed temperature-independent paramagnetic (TIP) behavior.

Results and Discussion

Syntheses. Reactions of W_6Cl_{12} with solid carbon–halide sources were performed at certain temperatures in the temperature regime between 175 and 750 °C. Initial reactions at 175 °C were performed considering the low melting or decomposition temperatures of carbon halides used (C_2Cl_6: decomp. at 183–185 °C; C_6Cl_6: m.p. = 227–229 °C; and C_6Br_6: m.p. > 300 °C). The thermal decomposition behavior of carbon–halides of this type has been studied previously to open up a hazardous waste disposal option related to the combustion problem of these compounds and of chlorinated hydrocarbons.[25] According to these studies, a versatile change of gas phase equilibrations can be regarded under various temperature conditions.

In our experiments, W_6Cl_{12} was heated with these carbon–halide sources in sealed silica vessels to yield several solid products, with a few of them still remaining unknown. The most reactive solid carbon–halide source used in our experiments was hexachloroethane. The reaction of a 1:1 molar ratio of W_6Cl_{12} and C_2Cl_6 involves the chlorination of the cluster to yield a dark brown crystalline powder of W_6Cl_{18} at 175 °C (1 day), described in reaction 1. According to our experience, this reaction performs much better than the direct chlorination of W_6Cl_{12} with Cl_2 gas, with respect to easier handling of reaction partners and of the reaction itself, revealing higher yields of W_6Cl_{18} (estimated 95% from PXRD).

$$W_6Cl_{12} + C_2Cl_6 \rightarrow W_6Cl_{18} + 2C \qquad (1)$$

The oxidation of W_6Cl_{12} (WCl_2) to W_6Cl_{18} (WCl_3) yielded small amounts of WCl_4[26] as a side phase in the reaction product, and the presence of traces of a liquid phase in the ampule, being considered CCl_4, which has been reported as a pyrolysis product of hexachloroethane.[27] The formation of finely divided elemental carbon in the reaction product must be assumed but could expectedly not be verified by PXRD.

Mixtures of W_6Cl_{12} and C_2Cl_6 behave differently when they are heated at higher temperatures. After W_6Cl_{18} is formed in the low temperature region around 175 °C, the influence of more elevated temperatures no longer involves an oxidation but a reduction of the cluster, which may be due to the presence of highly reactive carbon as a reductive source in the reaction mixture. A 1:2 molar composition of W_6Cl_{12} and C_2Cl_6 results in the formation of W_6CCl_{18} at 550 °C. A treatment of the same mixture at 700 °C leads to the formation of W_6CCl_{15}. When we consider the loss of C_2Cl_6 at this temperature, this reaction may be simply expressed by eq 2.

$$2W_6Cl_{12} + C_2Cl_6 \rightarrow 2W_6CCl_{15} \qquad (2)$$

This remarkable reaction involves a transformation from an octahedral cluster into a carbon-centered trigonal prismatic cluster, which has been described previously, when heating reaction mixtures of W_6Cl_{18} with Na_2C_2 or NaN_3, respectively, yielding $Na[W_6ZCl_{18}]$ with Z = C or N at 500 °C.[21] However, it is clear that the mechanism of this kind of reaction must involve a breakdown of the octahedral cluster in order to allow the interstitial atom Z to enter the cluster core.

The thermally more stable hexachlorobenzene (C_6Cl_6) appeared to also be useful for the synthesis of tungsten clusters. W_6CCl_{18} was obtained in high yield (estimated 90%) from a 1:2 molar ratio of W_6Cl_{12} and C_6Cl_6 reacted at 550 °C for 1 day. When the same reaction mixture was heated at 700 °C (for 2 day), W_6CCl_{15} was obtained (estimated yield 95%). At even higher temperatures (> 750 °C), cluster decomposition was obtained to yield WC, W_2C, W, and WCl_4 according to the results of PXRD measurements. Using a 3:2 molar ratio at 650 °C for 1 day yielded W_6CCl_{16} (> 60%).

Reactions of W_6Cl_{12} with hexabromoethane did not parallel the reactions of the corresponding hexachloroethane. The surprising result of a reaction of W_6Cl_{12} and C_6Br_6 in a 1:1 ratio at 650 °C (2 day) was the new heteroleptic compound $W_{30}C_2(Cl,Br)_{68}$ (estimated yield 95%) identified by single-crystal XRD.

Structure of $W_{30}C_2(Cl,Br)_{68}$. Black, plate-like crystals of $W_{30}C_2(Cl,Br)_{68}$ appeared insoluble in common solvents and in soft acids. The crystal structure of this remarkable compound contains three distinct clusters like in a carambolage, namely, a (carbon-centered) trigonal prismatic and two distinct octahedral tungsten clusters. One formula unit, $W_{30}C_2(Cl,Br)_{68}$, contains two carbon-centered trigonal prismatic $[W_6C]$ tungsten clusters and two plus one distinct octahedral $[W_6X_8]$ clusters, which is consistent with the unit cell content displayed in Figure 2. Trigonal prismatic clusters $[(W_6CX_{12}^{\,i})X_2^{\,a}X_{4/2}^{\,a-a}]$ are interconnected by

---

(25) El Mejdoub, N.; Souizi, A.; Delfosse, L. *J. Analyt. Appl. Pyrolysis* **1998**, *47*, 77–94 and literature cited therein.

(26) Kolesnichenko, V.; Swenson, D. C.; Messerle, L. *Inorg. Chem.* **1998**, *37*, 3257–3262.

(27) White, M. L.; Kuntz, R. R. *Int. J. Chem. Kin.* **1973**, *5*, 187–195.

Table 2. Interatomic Distances (in Å) of the Individual $[(W_6CX_{12}{}^{i})X_2{}^{a}X_{4/2}{}^{a\text{-}a}]$, $[(W_6X_8{}^{i})X_3{}^{a}X_{3/2}{}^{a\text{-}a}]$, and $[(W_6X_8{}^{i})X_{6/2}{}^{a\text{-}a}]$ Clusters in the Structure of $W_{30}C_2(Cl,Br)_{68}$ and the $(W_6CCl_{11}{}^{i})Cl_2{}^{a}Cl_{4/2}{}^{a\text{-}a}$ Cluster of W_6CCl_{15}[a]

	W−W Δ	W−W □	W-X^i Δ[b]	W-X^i □[c]	W-X^a and W-X$^{a\text{-}a}$
$[(W_6CX_{12}{}^{i})X_2{}^{a}X_{4/2}{}^{a\text{-}a}]$	2.6356(8)−2.697(1)	3.006(1)−3.040(1)	2.441(3)−2.486(2)	2.452(3)−2.525(3)	2.473(2)−2.650(2)
$[(W_6X_8{}^{i})X_{6/2}{}^{a\text{-}a}]$	2.6252(9)−2.6384(9)			2.583(1)−2.620(2)	2.542(2)−2.566(2)
$[(W_6X_8{}^{i})X_3{}^{a}X_{3/2}{}^{a\text{-}a}]$	2.6114(8)−2.640(1)			2.552(2)−2.635(2)	2.479(2)−2.593(2)
$(W_6CCl_{11}{}^{i})Cl_2{}^{a}Cl_{4/2}{}^{a\text{-}a}$	2.514(7)−2.753(7)	2.897(7)−3.064(7)	2.36(3)−2.40(2)	2.43(1)−2.47(2)	2.41(3)−2.77(3)
W_6CCl_{16}[17]	2.6325(7)−2.6703(9)	3.0068(7)−3.045(1)	2.379(4)−2.396(4)	2.448(3)−2.479(3)	2.385(5)−2.556(4)
W_6CCl_{18}[17]	2.743(1)	2.930(1)	2.355(5)−2.366(4)	2.431(6)−2.435(6)	2.377(6)
W_6Br_{12}[2]	2.632(2)−2.634(2)			2.612(4)−2.636(4)	2.550(3)−2.656(5)
AgW_6Br_{14}[31]	2.647(2)−2.649(2)			2.592(4)−2.640(4)	2.575(6)
$Ag_2W_6Br_{14}$[31]	2.6284(8)−2.6370(8)			2.615(2)−2.630(2)	2.604(2)−2.624(2)
$(BiCl)W_6Cl_{14}$[7]	2.6000(7) −2.6262(7)			2.465(3) −2.502(3)	2.422(3) −2.486(3)
$(BiCl_2)W_6Cl_{13}$[16]	2.5987(7)−2.6218(8)			2.450(3)−2.508(3)	2.415(4)−2.521(3)
$Cu_2W_6Cl_{14}$[32]	2.605(2) −2.613(2)			2.48(1)−2.519(9)	2.47(1)

[a] A comparison with distance values in other tungsten cluster compounds is also given. [b] Over triangular edges. [c] Over rectangular edges.

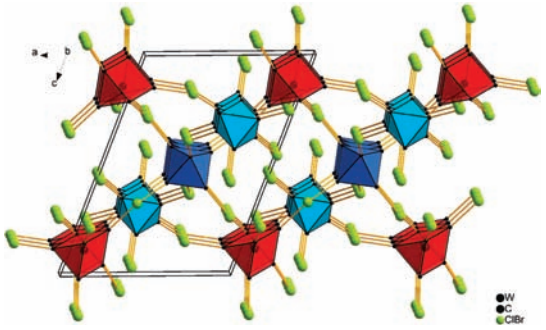

Figure 2. Projected crystal structure of $W_{30}C_2X_{68}$ (X^i atoms are omitted from the drawing).

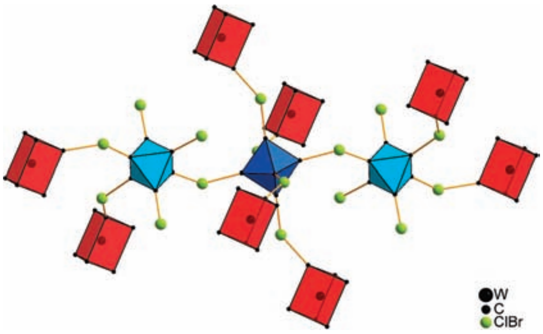

Figure 3. Connectivity patterns of three octahedral $(W_6X_8{}^{i})$ clusters following the sequence $[(W_6X_8{}^{i})X_3{}^{a}X_{3/2}{}^{a\text{-}a}]-[(W_6X_8{}^{i})X_{6/2}{}^{a\text{-}a}]-[(W_6X_8{}^{i})X_3{}^{a}X_{3/2}{}^{a\text{-}a}]$ with X^i atoms of octahedral clusters and all X atoms of trigonal prismatic (W_6C) clusters being omitted from the drawing.

four terminal X atoms with adjacent (octahedral) clusters. The octahedral $[W_6X_8{}^{i}]$ type clusters in the structure are represented by two distinct clusters with their connectivity patterns following $[(W_6X_8{}^{i})X_3{}^{a}X_{3/2}{}^{a\text{-}a}]$ (2×) and $[(W_6X_8{}^{i})X_{6/2}{}^{a\text{-}a}]$ (1×). A section of a sequence of halide bridged octahedral clusters $[(W_6X_8)X_3{}^{a}X_{3/2}{}^{a\text{-}a}]-[(W_6X_8)X_{6/2}{}^{a\text{-}a}]-[(W_6X_8)X_3{}^{a}X_{3/2}{}^{a\text{-}a}]$ surrounded by trigonal prismatic clusters is shown in Figure 3, with the central $[(W_6X_8)X_{6/2}{}^{a\text{-}a}]$ cluster being situated in the center of the inversion. The connectivity behavior of the central $[(W_6X_8)X_{6/2}{}^{a\text{-}a}]$ cluster via six outer X atoms being shared between two clusters has been observed in a similar manner, e.g., in the structure of $(Ta_6Cl_{12})Cl_{6/2}{}^{a\text{-}a}$.[28] The connectivity patterns obtained for the two remaining symmetry equivalent $[(W_6X_8)X_3{}^{a}X_{3/2}{}^{a\text{-}a}]$ clusters can be considered as unusual in cluster chemistry, because the subdivision in 3/2 shared X atoms yields an odd number of constituents, in contrast to the example of the (4/2) connectivity pattern $(W_6Cl_8{}^{i})Cl_2{}^{a}Cl_{4/2}{}^{a\text{-}a}$ obtained in the structure of W_6Cl_{12}. In other words, when bridging ligands are equally divided up among adjacent octahedral clusters in the structure of $W_{30}C_2(Cl,Br)_{68}$, the compositional sequence $[W_6X_{12.5}]-[W_6X_{11}]-[W_6X_{12.5}]$ is obtained. Thus, when we consider symmetrical $W-X^{(a\text{-}a)}-W$ bridges of 2.559(3) Å between the two types of octahedral clusters, an unequal electron distribution may be regarded for the individual clusters. According to the structural results, no pronounced differences are detected in W−W core dimensions of these distinctly bridged octahedral clusters, which both have average W−W distances of 2.63 Å (Table 2). However, W−W distances in octahedral tungsten cluster compounds have been shown not to be a reliable indicator for the oxidation state of tungsten clusters.[29]

The coincidence of two or more distinct clusters occurring in one structure[30] has been rare until now, and examples of linkages between distinct octahedral clusters, or distinct trigonal prismatic and octahedral clusters via shared halide atoms, are rare or unknown. This creates a new temptation to understand the electronic situation of $[(W_6CX_{12}{}^{i})X_2{}^{a}X_{4/2}{}^{a\text{-}a}]_2[(W_6X_8{}^{i})X_3{}^{a}X_{3/2}{}^{a\text{-}a}]_2[(W_6X_8{}^{i})X_{6/2}{}^{a\text{-}a}]$. The enclosed trigonal prismatic cluster species ($[W_6CX_{16}]$) is known to be susceptible in electron count, as can be regarded from the known examples W_6CCl_{18} and W_6CCl_{16}. The W−W distances within the $[W_6C]$ core of the $[(W_6CX_{12}{}^{i})X_2{}^{a}X_{4/2}{}^{a\text{-}a}]$ unit in the present structure average at 2.67 Å within cluster triangles and at 3.02 Å for the prism edges of the cluster, which both compare well with corresponding values of 2.66 Å and 3.02 Å in W_6CCl_{16}. Octahedral $(W_6X_8{}^{i})$ type tungsten clusters derived from binary W_6X_{12} (X = Cl, Br, I) usually have 24 electrons occupying W−W bonding states per cluster, but there are some examples reported with only 23 electrons, too[31] (Table 2). Average W−W distances of $[(W_6X_8)X_3{}^{a}X_{3/2}{}^{a\text{-}a}]$ and $[(W_6X_8)X_{6/2}{}^{a\text{-}a}]$ units in the structure of $W_{30}C_2X_{68}$ amount to 2.63 Å in both cases, which compare well with values obtained for other cluster compounds of this type (Table 2).

---

(28) Bauer, D.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1968**, *361*, 259–276.

(29) Tragl, S.; Ströbele, M.; Glaser, J.; Vicent, C.; Llusar, R.; Meyer, H.-J. *Inorg. Chem.* **2009**, *48*, 3825–3831.

(30) Basic, I.; Brnicevic, N.; Beck, U.; Simon, A.; McCarley, R. E. *Z. Anorg. Allg. Chem.* **1998**, *624*, 725–732.

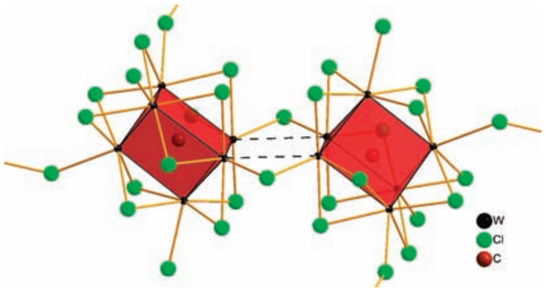

Figure 4. Connectivity pattern of two $[(W_6CCl_{11}{}^{i})Cl_2{}^{a}Cl_{4/2}{}^{a\text{-}a}]$ clusters in the structure of W_6CCl_{15} with short intercluster W−W contacts (3.261(6) Å).

In spite of the distinct connectivity pattern of the octahedral clusters $[(W_6X_8)X_3{}^{a}X_{3/2}{}^{a\text{-}a}]-[(W_6X_8)X_{6/2}{}^{a\text{-}a}]-[(W_6X_8)X_3{}^{a}X_{3/2}{}^{a\text{-}a}]$, we expect the three clusters to resume a 24−24−24 electron situation. This would be plausible because it is known that the bond valence does not necessarily coincide with the oxidation state, as known from examples, of which the O_3 molecule may be one. The concept of octahedral 24-electron clusters is also consistent with the obtained magnetic temperature independent paramagnetic (TIP) behavior and thus with the absence of a paramagnetic moment, which could result from an odd number of cluster electrons. In addition, the occupation of energy states above the 24 electron HOMO ("$[W_6X_{11}]$") would require a significant drawback in total energy due to a quite large HOMO−LUMO band gap on the order of 3 eV.[8] This overall description of the electronic situation may be altered or superimposed by the presence of electronic mobility. However, efforts in studying electronic conductivity properties of single crystals of $W_{30}C_2(Cl,Br)_{68}$ have suggested only semiconducting behavior.

Structure refinements performed on three different crystals of $W_{30}C_2(Cl,Br)_{68}$ yielded a phase width in $W_{30}C_2(Cl_xBr_{68-x})$ within the compositional range $30 \leq x \leq 35$, which may be in fact extendable when employing W_6Br_{12} in the reaction. A pure chloride or a pure bromide compound having the overall composition $W_{30}C_2X_{68}$ (X = Cl or Br) has not yet been successfully synthesized.

Structure of W_6CCl_{15}. W_6CCl_{18} and W_6CCl_{16} have been structurally characterized as carbon-centered trigonal prismatic clusters, forming a molecular structure and a structure with chloride bridged $(W_6CX_{12}{}^{i})X_2{}^{a}X_{4/2}{}^{a\text{-}a}$ clusters, respectively. After the discovery of these two compounds, the existence of the intermediate member W_6CCl_{17} remains still unknown. A feasible structure of W_6CCl_{17} may be regarded as chainlike, according to notation $(W_6CCl_{12}{}^{i})Cl_4{}^{a}Cl_{2/2}{}^{a\text{-}a}$, which is consistent with the connectivity pattern obtained for the $[Nb_6SBr_{17}]^{3-}$ anion.[18]

The structure of the new compound W_6CCl_{15} could be regarded to have a three-dimensional connectivity pattern following the notation $(W_6CCl_{12}{}^{i})Cl_{6/2}{}^{a\text{-}a}$, which would parallel the connectivity pattern of the layered arrangement of octahedral $(Ta_6Cl_{12}{}^{i})Cl_{6/2}{}^{a\text{-}a}$ clusters in Ta_6Cl_{15}. However, when comparing the patterns of a trigonal prismatic and an octahedral cluster, it is obvious that the six terminal halide ligands span up the motif of their respective clusters. Therefore, these two distinct cluster moieties will have to constitute different structural arrangements.

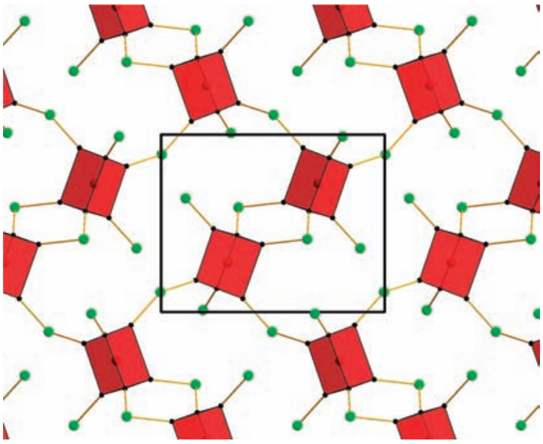

Figure 5. Projection of one layer of the crystal structure of W_6CCl_{15} (Cl^{i} atoms are omitted from the drawing).

The crystal structure of W_6CCl_{15} is characterized by a novel feature in cluster chemistry, which is one missing chloride atom over one trigonal edge, out of the 12 inner chloride ligands, being expressed by the notation $(W_6CCl_{11}{}^{i})Cl_2{}^{a}Cl_{4/2}{}^{a\text{-}a}$. The absence of an inner chloride ligand is clearly related with the formation of cluster pairs, having short W−W intercluster distances of 3.261(6) Å (Figure 4). Short metal−metal distances between adjacent clusters (in three-dimensional space) have accounted for the remarkable (superconducting) properties of Chevrel phases. The connectivity of $(W_6CCl_{11}{}^{i})Cl_2{}^{a}Cl_{4/2}{}^{a\text{-}a}$ clusters via four outer chloride atoms makes up a two-dimensional layer structure of W_6CCl_{15} (Figure 5), with the clusters being bridged to form six-membered rings.

A comparison of W−W distances within the (W_6C) cluster cores of the series W_6CCl_x (x = 15, 16, 18) shows related average W−W distance values within triangles and between adjacent triangles for W_6CCl_{15} (2.68 Å, 3.00 Å), W_6CCl_{16} (2.66 Å, 3.02 Å), and W_6CCl_{18} (2.74 Å, 2.93 Å). However, due to W−W interactions between trigonal edges of adjacent clusters in W_6CCl_{15} (at 3.261(6) Å), there is a significant distortion of the cluster body, with a short trigonal edge (2.514(7) Å) being the bridging edge, which also results in relatively long W−Cl distances of bridging $Cl^{a\text{-}a}$ ligands interconnecting the cluster pairs (Figure 4, Table 2).

Conclusion

Reactions between W_6Cl_{12} and C_2Cl_6 can initiate a cascade of reactions and reaction products, yielding W_6Cl_{18}, W_6CCl_{18}, and W_6CCl_{15} with increasing temperature, before decomposition into tungsten carbides is obtained. A mixed halide attempt by using W_6Cl_{12} and C_6Br_6 yielded the heteroleptic cluster compound $W_{30}C_2(Cl,Br)_{68}$. The structure of this compound is revealing an unusual (3/2) connectivity pattern, pointing out once more the exceptional electronic preferences in the field of tungsten halide cluster compounds.

The structure of W_6CCl_{15} reveals a missing chloride ligand within the inner chloride shell of the $[W_6CCl_{11}]$ cluster moiety, allowing for interactions between adjacent cluster

---

(31) Zheng, Y.-Q.; Borrmann, H.; Grin, Y.; Peters, K.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1999**, *625*, 2115–2119.

(32) Zheng, Y.-Q.; Nuss, J.; von Schnering, H. G. *Z. Kristallogr.* **1998**, *213*, 680–680.

edges via short W–W contacts. Thus, this new cluster compound can be viewed to contain dimeric $(W_6CCl_{15})_2$ cluster units. W_6CCl_{15} is a new member of carbon-centered trigonal prismatic cluster compounds, among the already known compounds W_6CCl_{16} and W_6CCl_{18}. With respect to electronic criteria known from the already discovered $[(W_6CCl_{12})Cl_6]^{n-}$ anions with $n = 0-4$, compositions like W_6CCl_{14} and W_6CCl_{17} may be also regarded to exist.

These unusual structures of tungsten halides show the remarkable diversity of tungsten halide clusters in architecture and in oxidation states, awaiting still more compounds to be discovered.

Supporting Information Available: Crystallographic data of $W_{30}C_2(Cl,Br)_{68}$ and W_6CCl_{15} in CIF format. This material is available free of charge via Internet at http://pubs.acs.org.