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A synthesis route for carbon-centered triprismo-hexatungsten cluster compounds and the crystal structure of $\text{Cs}[\text{W}_6\text{CCl}_{18}]\cdot\text{CH}_3\text{OH}$

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Abstract

$\text{Li}_x[\text{W}_6\text{CCl}_{18}]$ was synthesized by the reaction of WCl_4 with Li_2CN_2 , and used as source material for the synthesis of a new carbon-centered triprismo-hexatungsten cluster compound. Black crystals of $\text{Cs}[\text{W}_6\text{CCl}_{18}]\cdot\text{CH}_3\text{OH}$ were obtained by cation-exchange reaction of $\text{Li}_x[\text{W}_6\text{CCl}_{18}]$ with CsCl in methanol. The air-stable compound crystallizes orthorhombic with unit-cell parameters $a = 9.6957(5)$ Å, $b = 14.046(1)$ Å, and $c = 20.238(1)$ Å in the space group $P2_12_12_1$ (No. 19). The crystal structure of $\text{Cs}[\text{W}_6\text{CCl}_{18}]\cdot\text{CH}_3\text{OH}$ contains isolated $[\text{W}_6\text{CCl}_{18}]^-$ ions. If these ions are considered as spheres, their arrangement in the structure follows the principle of hexagonal closest packing, with cesium ions and methanol molecules filling voids in the hexagonal cluster layers. **To cite this article:** *M. Weisser et al., C. R. Chimie 8 (2005).*

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Résumé

$\text{Li}_x[\text{W}_6\text{CCl}_{18}]$ a été préparé par la réaction de WCl_4 avec du Li_2CN_2 et utilisé comme source pour la synthèse du nouveau cluster carbo-centré triprismo-hexatungstène. Des cristaux noirs de $\text{Cs}[\text{W}_6\text{CCl}_{18}]\cdot\text{CH}_3\text{OH}$ ont été obtenus par réaction d'échange de cations entre du $\text{Li}_x[\text{W}_6\text{CCl}_{18}]$ et du CsCl dans du méthanol. Le composé est stable à l'air et cristallise dans le groupe spatial orthorhombique $P2_12_12_1$ (No. 19), avec les paramètres cellulaires suivants : $a = 9.6957(5)$ Å, $b = 14.046(1)$ Å et $c = 20.238(1)$ Å. La structure cristalline contient des ions de $[\text{W}_6\text{CCl}_{18}]^-$ isolés. Si l'on considère ces ions comme des sphères, leur arrangement dans la structure suit le principe d'un empilement compacte hexagonal, avec des ions de césium et des molécules de méthanol occupant des cavités dans les couches hexagonales des clusters. **Pour citer cet article :** *M. Weisser et al., C. R. Chimie 8 (2005).*

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1. Introduction

Octahedral metal clusters with six metal (M) atoms represented by the $[M_6X_8]$ and $[M_6X_{12}]$ type are well known and their structural and electronic properties have been investigated in detail [1,2]. The well-established compound W_6Cl_{18} with an octahedral tungsten cluster of $[W_6Cl_{12}]Cl_6$ is, however, considered as an exception of an $[M_6X_{12}]$ type cluster because it hosts 18 electrons per cluster instead of the conventionally accepted maximum number of 16 electrons per cluster [3]. This number is even exceeded with the discovery of $A_n[W_6Cl_{18}]$ compounds with $A = (n-Bu)_4N$ for $n = 1$ [4] and $A = Li, K, Rb, Cs, Tl, Ag$ and Me_4N, Et_4N, NH_4 for $n = 2$ [5,6].

Closely related with the composition of the binary W_6Cl_{18} is the compound W_6CCl_{18} that was recently discovered [7]. The crystal structure of W_6CCl_{18} contains carbon-centered trigonal prismatic tungsten clusters. The structure of an individual W_6CCl_{18} molecule is similar to a sulfur-centered triprismo-hexaniobium bromide fragment in $A_3[Nb_6SBr_{17}]$ compounds with $A = K, Rb, Cs, Tl$ [8,9]. One striking difference of both crystal structures is that the $[Nb_6SBr_{16}Br_{2/2}]^{3-}$ clusters are linked into chains by two shared Br atoms, and W_6CCl_{18} forms a molecular structure. $A_3[Nb_6SBr_{17}]$ compounds have 14 electrons for Nb–Nb bonding, and according to electronic structure calculations there are only weak Nb–Nb interactions between adjacent cluster triangles in the prism.

The electrochemistry of W_6CCl_{18} is remarkably rich. According to the cyclic voltammogram of $(Bu_4N)_2[W_6CCl_{18}]$ five oxidation states should exist for $[W_6CCl_{18}]^{n-}$ with $n = 0, 1, 2, 3, 4$ [10]. Until now three $[W_6CCl_{18}]^{n-}$ containing compounds ($n = 1, 2, 3$) have been mentioned with Bu_4N^+ as counter cations. In addition, the gas phase dissociation of $[W_6CCl_{17}]^-$ anions was studied by mass spectroscopy as to investigate the formation mechanism of this unusual cluster compound [11].

Syntheses of W_6CCl_{18} and the related W_6CCl_{16} were performed by solid state reactions of WCl_6 with carbon sources such as graphite, or CCl_6 [7]. Other reactions of WCl_6 with CCl_4 have produced an X-ray amorphous precursor that can be extracted with $HCl/(Bu_4N)Cl$ to yield $(Bu_4N)_2[W_6CCl_{18}]$ after recrystallization in CH_3CN [10].

Recently we found a simple and efficient high yield synthesis for $Li_x[W_6CCl_{18}]$ that can open perspectives

for the solution chemistry of carbon-centered triprismo-hexatungsten chlorides. With the synthesis and structure of the methanol solvated compound $CsW_6CCl_{18} \cdot CH_3OH$ we here present the first example of this chemistry.

2. Syntheses

$Cs[W_6CCl_{18}] \cdot CH_3OH$ was crystallized from a solution of $Li_x[W_6CCl_{18}]$ and $CsCl$ in methanol. The $Li_x[W_6CCl_{18}]$ used in the reaction was synthesized by the solid state reaction of WCl_4 with Li_2CN_2 in 2 to 1 molar ratio. The syntheses of WCl_4 , Li_2CN_2 , and $Li_x[W_6CCl_{18}]$ are described as follows.

2.1. WCl_4 [12]

WCl_4 was synthesized by metallo-thermic reduction of WCl_6 (Strem, 99.9%) with aluminium (shot, Strem, 99.999%). An evacuated silica tube charged with 9 mmol (3.569 g) WCl_6 and 6.3 mmol (170 mg) Al was placed upright in a Simon–Müller furnace and heated at 370 °C for 48 h. After cooling to room temperature the WCl_4 was found in the bottom part of the ampoule. To purify the product, one side of the ampoule was heated up to 270 °C, while the opposite side of the tube remained at room temperature so that volatile components such as the $AlCl_3$ were sublimed to the colder part of the ampoule.

2.2. Li_2CN_2 [13]

Li_2CN_2 was prepared by reacting Li_2CO_3 (Merck, p. a.) with ammonia. In our reaction 12 mmol (0.9 g) of Li_2CO_3 were heated up to 610 °C in a continuous flow of ammonia. This temperature was held for 14 h. Afterwards the obtained reaction mixture was ground in an argon atmosphere and once more heated at 610 °C for 10 h in the ammonia flow. According to the X-ray powder diffraction pattern, the product contained only Li_2CN_2 .

2.3. $Li_x[W_6CCl_{18}]$

For the synthesis of $Li_x[W_6CCl_{18}]$, a mixture of WCl_4 (0.5 mmol, 162.8 mg) and Li_2CN_2 (0.25 mmol, 13.5 mg) was ground in an argon atmosphere, sealed in

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