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Article

Compounds with the Electron-Rich $[W_6Cl_{18}]^{2-}$ Cluster Anion

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Cluster compounds of the general formula $A_2[W_6Cl_{18}]$ containing singly charged A cations (A = K, Rb, Ag, Tl, NH_4, $N(C_2H_5)_4$, $N(n\text{-}C_3N_7)_4$, $N(n\text{-}C_4H_9)_4$) and $[W_6Cl_{18}]^{2-}$ anions have been synthesized. Compounds were obtained by W_6Cl_{18} reduction using methanol and the corresponding metal or (alkyl-)ammonium salts. The use of $CoCp_2$ as reducing agent in inert solvents such as tetrahydrofurane also leads to the ionic compound $(Co(C_5H_5)_2)_2[W_6Cl_{18}]$. All compounds described here evidence the existence of octahedral clusters of the M_6X_{12} type with 20 cluster electrons occupying metal centered states, thus exceeding the conventional number of 16 electrons for this cluster type. Electrospray ionization (ESI) mass spectra were recorded for the neutral compound W_6Cl_{18} and for the ionic salts $K_2[W_6Cl_{18}]$, $Cs_2[W_6Cl_{18}]$, and $(Co(C_5H_5)_2)_2[W_6Cl_{18}]$, showing that the cluster W_6Cl_{18} unit in these compounds is preserved in solution. The base peak in the ESI spectra for all compounds corresponds to the $[W_6Cl_{18}]^{2-}$ anion, so that neutral W_6Cl_{18} is prone to undergo a two electron reduction process. This result is confirmed by cyclic voltametry experiments, which makes of W_6Cl_{18} a very clean mild oxidizing agent. The preparation of the complete series of ionic $A_2[W_6Cl_{18}]$ (A = K, Cs, $CoCp_2$) clusters allows to systematically investigate their structural trends as function of the distinctive cations, which is the main focus of the present work.

Introduction

Octahedral metal clusters (M_6) are abundant in metal-rich halides of the transition metals of group 5 and 6 metals such as Nb, Ta, Mo, and W. According to the arrangement of the inner halide atoms X at the M_6 cluster, two types of clusters can be distinguished, the M_6X_8 type and the M_6X_{12} type.[1] Tungsten(III) chloride, W_6Cl_{18}, is a representative of the M_6X_{12} type, that is, 12 chlorine atoms are bridging the M_6 octahedron's edges and 6 terminal chlorine ligands are located above the corners of the cluster. As summarized by Hughbanks, the electronic states of M_6X_{12} clusters can be generally represented by the molecular orbital level diagram depicted in Figure 1, with the a_{1g}, t_{1u}, t_{2g}, and a_{2u} levels representing metal−metal bonding molecular orbitals.[2] Therefore, M_6X_{12} clusters should be stable with 14−16 electrons in M−M bonding states. The only binary compounds known to date in which the "ideal" number of 16 cluster electrons is exceeded are the tungsten(III) halides W_6Cl_{18} and W_6Br_{18}

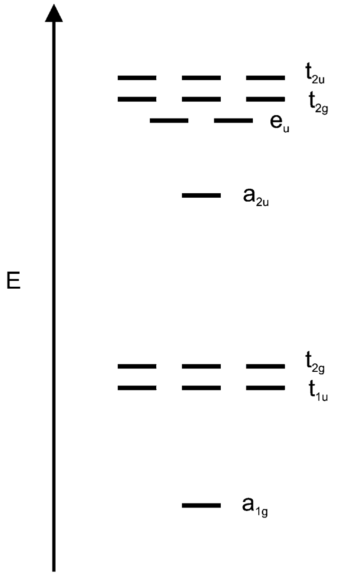

Figure 1. Molecular orbital level diagram of a M_6X_{12} type cluster.

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(18 electrons/cluster). Calculations of the electronic structure of W_6Cl_{18} using the extended Hückel method were performed by Nägele et al. in 2001 and confirmed the antibonding character of the electronic states above the a_{2u} level.[3] It was concluded that the low thermal stability and the paramagnetic behavior of W_6Cl_{18} is the result of the occupation of the antibonding states by two electrons. In consideration of the electronic properties, it seems quite likely that W_6Cl_{18} tends to undergo oxidation processes yielding the hypothetical 16 electron cluster cation $[W_6Cl_{18}]^{2+}$. But instead, W_6Cl_{18} is reduced in methanolic solution forming anionic species $[W_6Cl_{18}]^{n-}$ ($n = 1$ or 2), as previously evidenced by the crystallographic characterization of $(N(n\text{-}C_4H_9)_4)[W_6Cl_{18}]$ (19 cluster electrons)[4] and $A_2[W_6Cl_{18}]$ (20 cluster electrons, A = Cs or $N(CH_3)_4$).[5]

In this paper, the existence of the unexpected anion $[W_6Cl_{18}]^{2-}$ is substantiated by the characterization of further compounds of the composition $A_2[W_6Cl_{18}]$ with A = K, Rb, Ag, Tl, NH_4, $N(C_2H_5)_4$, $N(n\text{-}C_3N_7)_4$, $N(n\text{-}C_4H_9)_4$, and $Co(C_5H_5)_2$. Additional confirmation of the cluster's readiness to undergo reduction processes was gathered from electrospray ionization mass spectrometry and cyclic voltammetry measurements.

Experimental Section

Preparation of W_6Cl_{18}. The starting compound W_6Cl_{18} was synthesized as described previously:[3] First, WCl_6 (Strem, 99.9 %) was reduced to WCl_4 at 370 °C using aluminum (Strem, 99.999 %) as reducing agent. In a subsequent disproportionation step, WCl_4 was decomposed at 470 °C yielding WCl_5 and W_6Cl_{12}. Afterwards, W_6Cl_{12} was oxidized in a chlorine gas flow at 240 °C for 1.5 h to give W_6Cl_{18}.

Preparation of $A_2[W_6Cl_{18}]$ (A = K, Rb, Ag, Tl, NH_4). Compounds with the general formula $A_2[W_6Cl_{18}]$ were obtained as black crystalline powders or black crystals from formal W_6Cl_{18} reduction using methanol as reducing agent in the presence of the corresponding A^+ salts (A = K, Rb, Ag, Tl, NH_4) salt. In a typical raction, W_6Cl_{18} was stirred in methanol (Fisher Scientific, Analytical reagent grade) at RT for approximately 0.5 h giving dark brown solutions. After filtration, methanolic solutions of KCl (Merck, 99.5 %), RbCl (Fluka, 98 %), $AgNO_3$ (Merck, 99.7 %), Tl_2CO_3 (Merck, 99 %), or NH_4Cl (99.8 %) were added. $K_2[W_6Cl_{18}]$ was obtained to form needle-shaped crystals after complete evaporation of the solvent, whereas microcrystalline $Rb_2[W_6Cl_{18}]$ precipitated after heating the reactions mixture, leaving back a clear solution. When a solution of $AgNO_3$ in methanol was added to dissolved W_6Cl_{18}, $Ag_2[W_6Cl_{18}]$ was formed immediately as a brownish black precipitate of low crystallinity. The compounds $Tl_2[W_6Cl_{18}]$ and $(NH_4)_2[W_6Cl_{18}]$ crystallized as fine powders after evaporation of methanol from the corresponding solutions.

Preparation of $A_2[W_6Cl_{18}]$ (A = $N(C_2H_5)_4$, $N(C_3H_7)_4$, $N(n\text{-}C_4H_9)_4$). The alkyl ammonium compounds were also prepared by adding methanolic solutions of $N(C_2H_5)_4Cl$ (Schuchardt, München, 99 %), $N(n\text{-}C_3H_7)_4Br$ (Merck, 99 %), or $N(n\text{-}C_4H_9)_4Cl$ (Merck, 99 %) to W_6Cl_{18} solutions in methanol. With all three alkyl ammonium ions, the salts $A_2[W_6Cl_{18}]$ precipitated as small black crystals only a few minutes after mixing the two solutions. All reactions resulted in yields higher than 80 %.

Larger crystals were grown by the diffusion method described by Massa.[6] A small glass container ($V = 10$ mL) was filled completely with a methanolic solution of W_6Cl_{18} and then sealed by a lid with a small hole in it. The container was plunged into a beaker containing a solution of the corresponding alkyl ammonium halide in a way that the smaller glass container was completely covered by the liquid. After about 1 week, crystals suitable for single crystal diffraction measurements were formed.

Preparation of $(Co(C_5H_5)_2)_2[W_6Cl_{18}]$. To a tetrahydrofuran (THF) solution of W_6Cl_{18} was added a two-fold excess of $Co(C_5H_5)_2$ ($CoCp_2$). The mixture was stirred for 30 minutes and filtrated to give a brown solution. Slow evaporation of this solution gave prism-like single crystals of $(CoCp_2)_2[W_6Cl_{18}]$ in quantitative yields.

Physical Measurements. A hybrid QTOF I (quadrupole-hexapole-TOF) mass spectrometer with an orthogonal Z-spray-electrospray interface (Waters, Manchester, U.K.) was used. The desolvation gas, as well as nebulizing gas, was nitrogen at a flow of 800L/h and 20 L/h, respectively. The temperature of the source block was set to 120 °C, and the desolvation temperature to 200°C. A capillary voltage of 3.3 KV was used in the negative scan mode, and the cone voltage was set to 10 V to control the extent of fragmentation of the identified ions. Sample solutions (ca. 5×10^{-5} M) were infused via syringe pump directly connected to the ESI source at a flow rate of 10 μL/min. The chemical composition of each peak in the scan mode was assigned by comparison of the isotope experimental pattern with that calculated using the MassLynx 4.0 program.[7] Cyclic voltammetry experiments were performed with an Echochemie Pgstat 20 electrochemical analyzer. All measurements were carried out with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and an Ag/AgCl reference electrode containing aqueous 3 M KCl. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. $E_{1/2}$ values were determined as $1/2(E_a + E_c)$, where E_a and E_c are the anodic and cathodic peak potentials, respectively.

X-ray Diffraction. The crystal structures of $K_2[W_6Cl_{18}]$, $(N(C_2H_5)_4)_2[W_6Cl_{18}]$, $(N(n\text{-}C_3H_7)_4)_2[W_6Cl_{18}]$, $(N(n\text{-}C_4H_9)_4)_2[W_6Cl_{18}]$, and $(Co(C_5H_5)_2)_2[W_6Cl_{18}]$ were determined from single crystal diffraction data.

Intensity data of $K_2[W_6Cl_{18}]$, $(N(C_2H_5)_4)_2[W_6Cl_{18}]$, $(N(n\text{-}C_3H_7)_4)_2[W_6Cl_{18}]$, and $(N(n\text{-}C_4H_9)_4)_2[W_6Cl_{18}]$ were recorded on a Stoe IPDS diffractometer using Mo−K_α radiation ($\lambda = 0.71069$ Å, graphite monochromator). The measurements were performed at room temperature for $K_2[W_6Cl_{18}]$ and $(N(n\text{-}C_4H_9)_4)_2[W_6Cl_{18}]$, and at 210 K for $N(C_2H_5)_4)_2[W_6Cl_{18}]$ and $(N(n\text{-}C_3H_7)_4)_2[W_6Cl_{18}]$. The X-ray intensity data were corrected for absorption, polarization, and Lorentz effects by the IPDS software X-Red/X-Shape. The data collection for $(CoCp_2)_2[W_6Cl_{18}]$ was performed at room temperature on a Bruker Smart CCD diffractometer using graphite-monochromated Mo−K_α radiation. The diffraction frames were integrated using the SAINT package[8] and corrected for absorption with SADABS.[9] In all cases, structure solutions using direct methods and structure refinements were performed using the programs SHELXS and SHELXL[10] of the program package SHELX-97.[11]

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Table 1. Single Crystal Structure Data of $K_2[W_6Cl_{18}]$ (**1**), $(N(C_2H_5)_4)_2[W_6Cl_{18}]$ (**2**), $(N(n\text{-}C_3H_7)_4)_2[W_6Cl_{18}]$ (**3**), $(N(n\text{-}C_4H_9)_4)_2[W_6Cl_{18}]$ (**4**), and $(Co(C_5H_5)_2)_2[W_6Cl_{18}]$ (**5**)

	1	**2**	**3**	**4**	**5**
formula	$K_2[W_6Cl_{18}]$	$N_2C_{16}H_{40}[W_6Cl_{18}]$	$N_2C_{24}H_{56}[W_6Cl_{18}]$	$N_2C_{32}H_{72}[W_6Cl_{18}]$	$Co_2C_{20}H_{20}[W_6Cl_{18}]$
a, Å	9.3223(9)	8.6250(8)	8.7736(9)	20.501(2)	13.479(1)
b, Å	9.3223(9)	11.653(1)	12.624(1)	28.784(3)	13.479(1)
c, Å	8.4528(8)	11.912(1)	12.755(1)	20.369(3)	21.874(3)
α, deg	90	61.07(1)	64.76(1)	90	90
β, deg	90	86.53(1)	79.19(1)	90	90
γ, deg	120	84.43(1)	85.27(1)	90	90
V, $Å^3$	636.2(1)	1042.7(2)	1255(2)	12020(2)	3974.3(7)
Z	1	1	1	8	4
fw, g/mol	1819.40	2001.70	2113.91	2226.12	2119.42
space group	$P\bar{3}1m$	$P\bar{1}$	$P\bar{1}$	*Pbca*	$I4_1/amd$
T, K	293(2)	210(2)	210(2)	293(2)	293(2)
ρ_{calc}, g/cm^3	4.749	3.188	2.797	2.460	3.542
μ, cm^{-1}	292.22	176.51	146.71	122.63	193.31
R_1[a]	0.0288	0.0379	0.0296	0.1464	0.0513
wR_2[a]	0.0495	0.0793	0.0696	0.1785	0.0776

[a] all data.

Table 2. Results of the Rietveld Refinement of the Crystal Structure of $Rb_2[W_6Cl_{18}]$

formula	$Rb_2[W_6Cl_{18}]$
a, Å	9.2410(2)
c, Å	8.5197(2)
V, $Å^3$	630.07(2)
Z	1
fw, g/mol	1912.13
space group	$P\bar{3}$
T, K	293(2)
2θ range, deg	5−130
ρ_{calc}, g/cm^3	5.039
R_{Bragg}/R_{wp}	0.0807/0.1390
R_{exp}/R_p	0.1187/0.1020
χ^2	1.36

Table 3. Lattice Parameters (in Å), Unit Cell Volume (in $Å^3$), and Number of Single Indexed Reflections of Compounds

compound	*a*	*c*	*V*	single indexed reflections
$K_2[W_6Cl_{18}]$	9.228(2)	8.477(2)	625.1(3)	30
$Rb_2[W_6Cl_{18}]$	9.2410(2)	8.5197(2)	630.07(2)	*
$Cs_2[W_6Cl_{18}]$	9.3210(7)	8.53.02(6)	642.0(1)	*
$Ag_2[W_6Cl_{18}]$	9.104(4)	8.414(2)	604.0(4)	17
$Tl_2[W_6Cl_{18}]$	9.140(2)	8.435(1)	610.3(3)	29
$(NH_4)_2[W_6Cl_{18}]$	9.198(3)	8.485(1)	621.7(3)	33

* Lattice parameters were received from Rietveld refinement.

Anisotropic displacement parameters could be refined for all non-hydrogen atoms. Crystal structure data of $K_2[W_6Cl_{18}]$, $(N(C_2H_5)_4)_2[W_6Cl_{18}]$, $(N(n\text{-}C_3H_7)_4)_2[W_6Cl_{18}]$, $(N(n\text{-}C_4H_9)_4)_2[W_6Cl_{18}]$, and $(Co(C_5H_5)_2)_2[W_6Cl_{18}]$ are listed in Table 1. Additional tables and crystallographic data in CIF format are provided in the Supporting Information.

The crystal structure of $Rb_2[W_6Cl_{18}]$ was refined from powder diffraction data recorded on an Stoe STADI-P powder diffractometer (transmission geometry, Cu−$K_{\alpha 1}$ radiation (λ = 1.540598 Å), Ge monochromator). The structure refinement was performed using the program package Fullprof/WinPLOTR.[12] The atomic coordinates of $Cs_2[W_6Cl_{18}]$[5] were chosen as starting positions. Results of the Rietveld refinement of the structure of $Rb_2[W_6Cl_{18}]$ are presented in Table 2; the refined atomic positions and isotropic displacement parameters can be obtained from the Supporting Information, as well as from the crystallographic data in CIF format.

Powder XRD patterns of $K_2[W_6Cl_{18}]$, $Ag_2[W_6Cl_{18}]$, $Tl_2[W_6Cl_{18}]$, and $(NH_4)_2[W_6Cl_{18}]$ (recorded on a Stoe STADI-P powder diffractometer, Ge-monochromated Cu−$K_{\alpha 1}$ radiation) were indexed trigonally with the aid of the program system WinXPow[13] and the lattice parameters were refined therefrom. The refined unit cell parameters are listed in Table 3, alongside with the values for $Rb_2[W_6Cl_{18}]$. The lattice constants of $Cs_2[W_6Cl_{18}]$[5] are also given for comparison.

Results and Discussion

Synthesis and Electrochemistry. The synthesis of the ionic $[W_6Cl_{18}]^{2-}$ cluster is reported by simple reduction of the corresponding neutral W_6Cl_{18} homologue using methanol as reducing agent.[14] Through this approach it is possible to prepare a complete series of ionic complexes of general formula $A_2[W_6Cl_{18}]$ with various A^+ cations. These cations include inorganic K^+, Ag^+, Tl^+, NH_4^+, Rb^+, Cs^+, and tetraalkylammonium salts $(R_4)N^+$ (R = C_2H_5, C_3H_7 and C_4H_9). We have also explored the possibility to reduce the W_6Cl_{18} cluster in “inert” solvents such as THF in the presence of a mild reducing agent. Hence, the reaction of W_6Cl_{18} with a two-fold excess of $CoCp_2$ as reducing agent yields the salt-like $(CoCp_2)_2[W_6Cl_{18}]$ compound. It is remarkably that the formation of salt-like $A_2[W_6Cl_{18}]$ complexes proceeds in almost quantitative yield independently of the reducing agent used, CH_3OH or $CoCp_2$, thus indicating clean W_6Cl_{18} reduction. The structural integrity in solution of the series of salts $A_2[W_6Cl_{18}]$ (A = K, Cs, $CoCp_2$) was proved by electrospray ionization (ESI) mass spectrometry. ESI mass spectra of acetonitrile solutions of $A_2[W_6Cl_{18}]$ (A = K, Cs, $CoCp_2$) reveal the presence of a prominent signal centered at m/z = 870.6 corresponding to the $[W_6Cl_{18}]^{2-}$ anion (see Figure 2).

Remarkably, when acetonitrile solutions of the neutral W_6Cl_{18} cluster were subjected to ESI, the $[W_6Cl_{18}]^{2-}$ anion was also observed as the base peak. For the neutral W_6Cl_{18} cluster, this ionization mechanism based on the formal two

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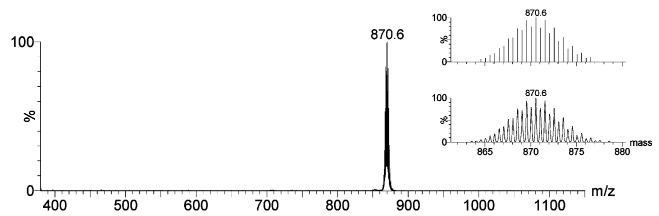

Figure 2. ESI mass spectrum of acetontrile solutions of W_6Cl_{18} at cone voltages $U_c = 10$ V. The inset shows the experimental and simulated isotopic pattern for the $[W_6Cl_{18}]^{2-}$ anion.

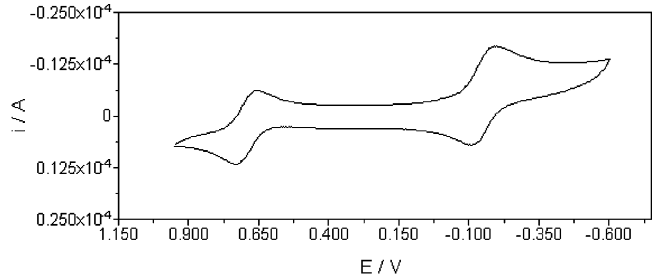

Figure 3. Cyclic voltammogram for W_6Cl_{18} in CH_3CN at a scan rate of 500 mV/s.

electron reduction is rare, as compared with other metal halide complexes. Typically metal halide cluster complexes tend to ionize through halide abstraction (formally a M−Cl cleavage) or adduct formation.[15] For example, the ESI mass spectrum of the cluster $Ta_4S_9Br_8$ reveals the presence of adducts of general formula $[Ta_4S_9Br_8{\cdot}Br]^-$.[16] In the present case, it is clear that neutral W_6Cl_{18} is very prone to undergo two electron reduction processes upon ESI conditions in excellent agreement with the cyclic voltammetry results (see below). This remarkable stability contrast with that observed for the homologous carbon centered cluster, namely $[W_6CCl_{18}]^{2-}$ which readily degrades to afford the lower nuclearity cluster species as judged by ESI-MS.[17] It is also noticeable in the present work, the soft ionization provided by ESI-MS which allows the observation of intact hexanuclear dianions upon ESI-MS of W_6Cl_{18}. Electron impact (EI) mass spectrometric investigations of W_6Cl_{18} were first reported four decades ago revealing an assortment of cations of general formula $[WCl_x]^+$ ($x = 1-3$), $[W_2Cl_y]^+$ ($y = 5, 6$) and $[W_3Cl_z]^+$ ($z = 8, 9$).[18]

Cyclic voltammetry experiments of W_6Cl_{18} were performed in acetonitrile. The cyclic voltammogram shows two quasi reversible waves between 1.0 V and −0.6 V versus Ag/AgCl, as represented in Figure 3, which correspond to one reduction process at $E_{1/2} = -0.15$ V ($\Delta E = 85$ mV) and one oxidation process at 0.71 V ($\Delta E = 67$ mV).

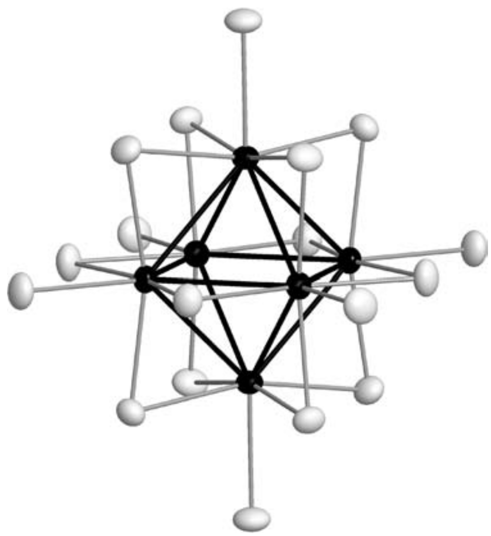

Figure 4. $[W_6Cl_{12}{}^{i}]Cl_6{}^{a}$ cluster unit in $K_2[W_6Cl_{18}]$; black: tungsten, white: chlorine. The probability factor of the thermal ellipsoids is 50%.

The first process can be tentatively assigned to a two-electron reduction based on the ESI-MS results and the isolation of $[W_6Cl_{18}]^{2-}$ species upon reduction with $CoCp_2$. As a matter of fact, the ESI mass spectrum for W_6Cl_{18} is analogous to that registered for the series of ionic $A_2[W_6Cl_{18}]$ (A = K, Cs, $CoCp_2$) complexes. A comparison between the integrated intensity for the reduction and oxidation wave represented in Figure 3 indicated that the number electrons involved in the reduction process at −0.15 V is approximately twice the number transferred in the oxidation of W_6Cl_{18} at 0.71 V. This can be schematically represented as follows:

$$[W_6Cl_{18}]^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} W_6Cl_{18} \underset{-2e^-}{\overset{+2e^-}{\rightleftharpoons}} [W_6Cl_{18}]^{2-} \qquad (1)$$

An extension of the investigated potential range shows two extra redox waves, at −0.95 V and +1.35 V, corresponding to one reduction and one oxidation process, respectively. Both waves are fully irreversible suggesting significant structural or chemical changes upon addition or removal of electrons at these potentials. The preparation of the complete series of ionic $A_2[W_6Cl_{18}]$ (A = K, Cs, $CoCp_2$) allows to systematically investigate their structural trends as function of the distinctive cations which is the main focus of the present work.

Crystal Structures of the Ternary Compounds $A_2[W_6Cl_{18}]$ with A = K, Rb, Cs, Ag, Tl and of $(NH_4)_2[W_6Cl_{18}]$. All crystal structures of the $A_2[W_6Cl_{18}]$ type are built up from monovalent A^+ cations and $[W_6Cl_{18}]^{2-}$ anions. As an example, the $[W_6Cl_{18}]^{2-}$ ion in $K_2[W_6Cl_{18}]$ is displayed in Figure 4.

The structure of $K_2[W_6Cl_{18}]$ (space group $P\bar{3}1m$) can be described as a stuffed tungsten carbide structure. The $[W_6Cl_{18}]$ cluster units form a primitive hexagonal lattice and the potassium atoms are positioned in the centers of all trigonal prismatic voids of this lattice. A similar arrangement is found for $Rb_2[W_6Cl_{18}]$ (space group $P\bar{3}$), but because of their larger radii, the Rb^+ ions are shifted out of the centers of the prismatic voids, thereby minimizing repulsive interactions between adjacent cations. Additionally, the cluster units are rotated around the threefold axis. As expected, this distortion of the $K_2[W_6Cl_{18}]$ structure is observed more

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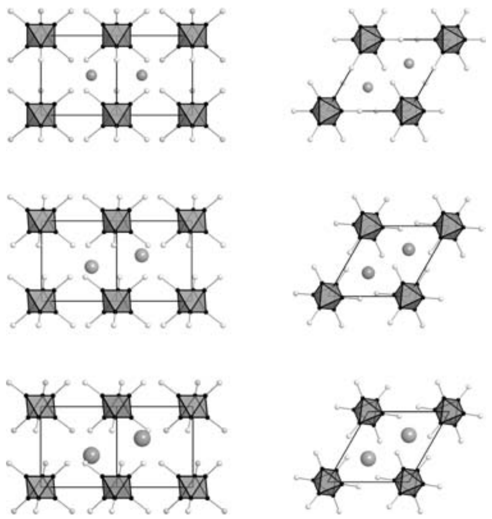

Figure 5. Comparison of the crystal structures of $K_2[W_6Cl_{18}]$ (top), $Rb_2[W_6Cl_{18}]$ (middle), and $Cs_2[W_6Cl_{18}]$ (bottom). Left column: viewing direction along [110], right column: viewing direction along [001]. For the purpose of clarity, the inner chlorine atoms are not shown.

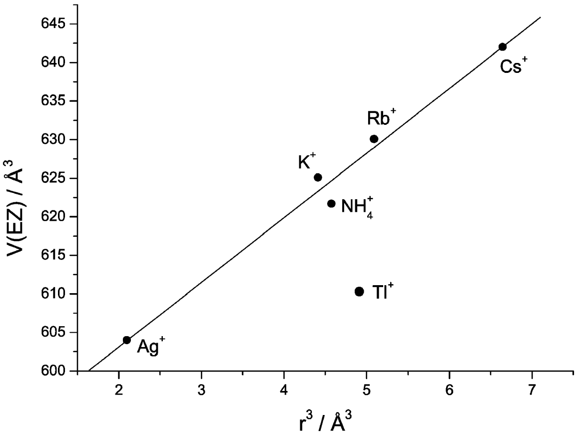

Figure 6. Plot of the unit cell volumes V(EZ) of $Ag_2[W_6Cl_{18}]$, $Tl_2[W_6Cl_{18}]$, $(NH_4)_2[W_6Cl_{18}]$, $K_2[W_6Cl_{18}]$, $Rb_2[W_6Cl_{18}]$, and $Cs_2[W_6Cl_{18}]$ versus the cubes of the ionic radii (r^3) of the cations for the C.N. 8 (Ag^+, NH_4^+) or C.N. 12 (Tl^+, K^+, Rb^+, Cs^+). The values for $Tl^+/Tl_2[W_6Cl_{18}]$ were not taken into account for the linear fit.

distinctly for $Cs_2[W_6Cl_{18}]$. The structure of $Cs_2[W_6Cl_{18}]$ can be related to the *anti*-(1T-)CdI_2 type.[5] A comparison of the crystal structures of $K_2[W_6Cl_{18}]$, $Rb_2[W_6Cl_{18}]$ and $Cs_2[W_6Cl_{18}]$ is displayed in Figure 5.

As powder patterns of $Ag_2[W_6Cl_{18}]$, $Tl_2[W_6Cl_{18}]$, and $(NH_4)_2[W_6Cl_{18}]$ were indexed trigonally with lattice parameters similar to those found for $K_2[W_6Cl_{18}]$, $Rb_2[W_6Cl_{18}]$, and $Cs_2[W_6Cl_{18}]$ (see Table 3), they can be expected to exhibit similar crystal structures. In Figure 6, the unit cell volumes of $K_2[W_6Cl_{18}]$, $Rb_2[W_6Cl_{18}]$, $Cs_2[W_6Cl_{18}]$, $Ag_2[W_6Cl_{18}]$, $Tl_2[W_6Cl_{18}]$, and $(NH_4)_2[W_6Cl_{18}]$ are plotted against the cubes of the ionic radii (r^3) of K^+, Rb^+, Cs^+, Ag^+, Tl^+, and NH_4^+.

As the alkali metal ions in $K_2[W_6Cl_{18}]$ and $Cs_2[W_6Cl_{18}]$ are coordinated by 12 chlorine atoms, the ionic radii of K^+, Rb^+, Cs^+, and Tl^+ for the coordination number (C.N.) 12 were used as they were published by Shannon.[19] In the case of the silver ions, the highest given C.N. is 8, so the ionic radius for this C.N. was used instead. For NH_4^+, the ionic radius determined by Khan and Baur for the C.N. 8 was applied.[20] As can be seen in Figure 6, an almost linear correlation is found between the cubes of the ionic radii (r^3) of A^+ and the unit cell volumes for $K_2[W_6Cl_{18}]$, $Rb_2[W_6Cl_{18}]$, $Cs_2[W_6Cl_{18}]$, $Ag_2[W_6Cl_{18}]$, and $(NH_4)_2[W_6Cl_{18}]$. However, for $Tl_2[W_6Cl_{18}]$ a significant deviation is observed. It could be suspected that Tl^+ allows for covalent interactions with the surrounding chlorine atoms, causing shorter Tl−Cl distances and a decrease of the unit cell volume. This observation is consistent with the behavior in the homologous series of binary (Li, Na, K, Rb, Cs, Ag, Tl) halides where the Shannon radius of Tl^+ leads to similar deviations for Tl^+ halides with higher polarizable anions.

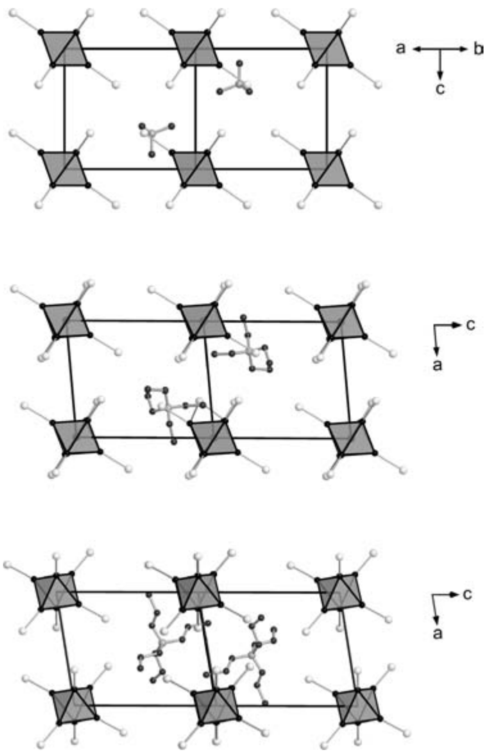

Figure 7. Comparison of the crystal structures of $(N(CH_3)_4)_2[W_6Cl_{18}]$ (top), $(N(C_2H_5)_4)_2[W_6Cl_{18}]$ (middle), $(N(n\text{-}C_3H_7)_4)_2[W_6Cl_{18}]$ (bottom). For the purpose of clarity, inner chlorine atoms and hydrogen atoms are not shown.

Crystal Structures of the Alkyl Ammonium Compounds $A_2[W_6Cl_{18}]$ with A = $N(CH_3)_4$, $N(C_2H_5)_4$, $N(C_3H_7)_4$, $N(n\text{-}C_4H_9)_4$. As described by Dill et al. in 2004,[5] $(N(CH_3)_4)_2[W_6Cl_{18}]$ crystallizes in the trigonal space group $P\bar{3}m1$. The arrangement of the $N(CH_3)_4^+$ cations and $[W_6Cl_{18}]^{2-}$ anions corresponds to the positions of iodine and cadmium, respectively in *anti*-(1T-)CdI_2. As shown in Figure 7, the atomic arrangements found for the triclinic ammonium compounds $A_2[W_6Cl_{18}]$ (A = $N(C_2H_5)_4$ and $N(C_3H_7)_4$) can be regarded as distortion variants of this structure.

For $(N(n\text{-}C_4H_9)_4)_2[W_6Cl_{18}]$, crystallizing in the space group *Pbca*, a different structure was determined: If only their centers of gravity are taken into account, the clusters form a packing arrangement of a rhombic dodecahedra, that is, each cluster is surrounded by 14 others. The $(N(n\text{-}C_4H_9)_4)^+$

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(20) Khan, A. A.; Baur, W. H. *Acta Cryst.* **1972**, *B28*, 683–693.

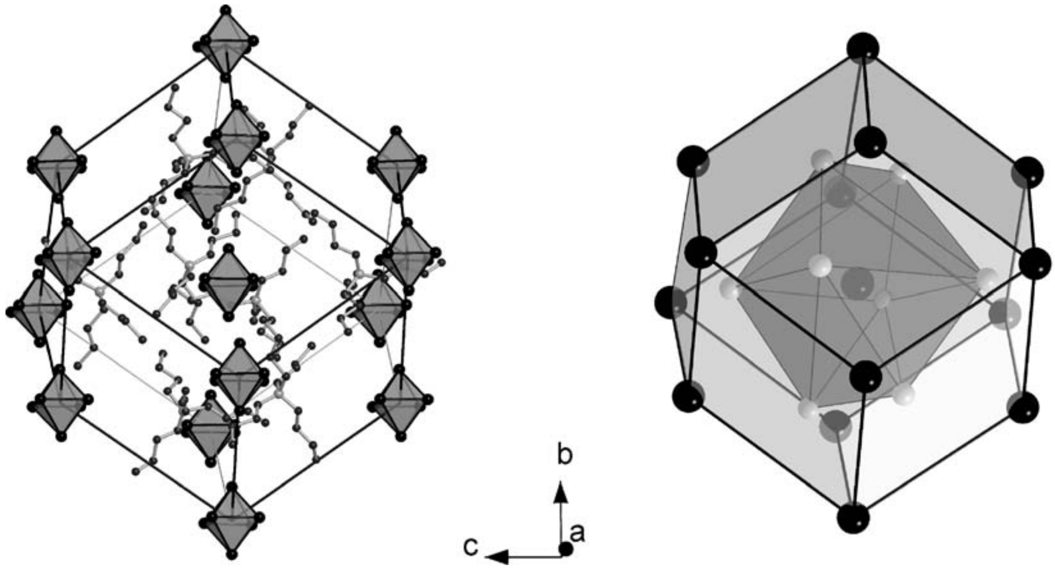

Figure 8. Arrangement of the W_6Cl_{18} cluster units and the $N(n\text{-}C_4H_9)_4^+$ ions in the crystal structure of $(N(n\text{-}C_4H_9)_4)_2[W_6Cl_{18}]$ (left hand side, chlorine and hydrogen atoms are omitted for clarity). On the right hand side, only the clusters' centers of gravity (black) and the nitrogen positions (light gray) are shown. To elucidate the structural properties, connecting lines between the clusters' centers (black) and the nitrogen atoms (white) are drawn.

ions are surrounded tetrahedrally by the cluster anions, whereas the clusters are coordinated by 8 *n*-butyl ammonium ions forming a trigonal dodecahedral arrangement (Figure 8).

Crystal Structure of $(Co(C_5H_5)_2)_2[W_6Cl_{18}]$. If only the positions of Co and of the centers of gravity of the clusters are considered, the crystal structure of $(CoCp_2)_2[W_6Cl_{18}]$ can be described as a distorted variant of the $MgCu_2$ structure:[21] The clusters are arranged in a diamond lattice like the Mg atoms in $MgCu_2$, and the Co atoms of the $CoCp_2$ units are arranged to form tetrahedra linked through all corners similar to the Cu atoms in the $MgCu_2$ structure. A comparison of the crystal structures of $MgCu_2$ and $(CoCp_2)_2[W_6Cl_{18}]$ is shown in Figure 9, where the clusters are shown by their W_6 octahedra and the cations by their Co atoms only.

Dimensions of W_6 clusters in W_6Cl_{18} and $[W_6Cl_{18}]^{n-}$. The crystal structure of W_6Cl_{18} has been determined from powder and from single crystal diffraction data.[3,5,22] The structure of the W_6Cl_{18} unit was previously elucidated from single crystals of $W_6Cl_{18}(DMSO)_4$.[23] Attention is paid to dimensional changes of the W_6 octahedra in $[W_6Cl_{18}]^{n-}$ ($n = 0-2$) structures, as the occupation of M−M antibonding orbitals should weaken the W−W bonds. A distortion of the tungsten cluster could be regarded if the antibonding e_u level is partly occupied. However, we may note, that because of the small energy separation between e_u and t_{2g} levels (in the order of 0.1 eV in $[W_6Cl_{18}]^{n-}$) the sequence of these states (Fig. 1) may change. In Table 4, a comparison of selected structural data of W_6Cl_{18} and its derivatives is given along with the number of cluster electrons and basic structure determination characteristics.

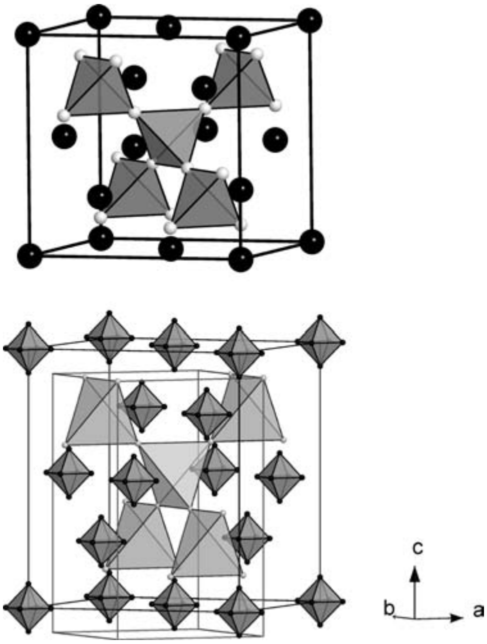

Figure 9. Comparison of the crystal structures of $MgCu_2$ (top) and $(CoCp_2)_2[W_6Cl_{18}]$ (bottom). The smaller unit cell edges of $(CoCp_2)_2[W_6Cl_{18}]$ in the bottom drawing are drawn in gray, with W atoms shown as black and Co atoms as gray spheres. For reasons of clarity, chlorine atoms and atoms of the Cp ligands are omitted.

In contrast to the feasibility outlined above, no significant increase of the W−W bond lengths is observed when the number of electrons in antibonding states rises from 2 in W_6Cl_{18} and $W_6Cl_{18}(DMSO)_4$ to 4 in compounds with the formula $A_2[W_6Cl_{18}]$: for neutral W_6Cl_{18}, the W−W bond lengths vary from 2.866(1) to 2.9021(5) Å, for anions $[W_6Cl_{18}]^{2-}$, W−W distances between 2.832(3) Å (powder, 293 K) and 2.9185(4) Å (single crystal, 210 K) are found. There is no pronounced elongation of the W−W bonds found for 20 electron clusters when compared with an 18 electron cluster. The small deviations observed in the W−W bond lengths of $[W_6Cl_{18}]^{n-}$ compounds can be explained by

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Table 4. Interatomic Distances, Space Group, Structure Determination Method, Temperature, and Number of Cluster Electrons of Compounds

compound	W−W distances min	W−W distances max	space group	method[b], *T* in K	electrons per cluster
W_6Cl_{18}[3]	2.866(1) Å	2.877(2) Å	$R\bar{3}$	p, 293	18
W_6Cl_{18}[5]	2.8915(5) Å	2.9021(5) Å	$R\bar{3}$	sc, 293	18
$W_6Cl_{18}(DMSO)_4$[23]	2.879(1) Å	2.882(1) Å	$P2_1/n$	sc, 293	18
$(N(n\text{-}C_4H_9)_4)[W_6Cl_{18}]$[4]	2.8568(6) Å	2.8934(6) Å	$C2/c$	sc, 210	19
$Cs_2[W_6Cl_{18}]$[5]	2.832(3) Å	2.873(2) Å	$P\bar{3}$	p, 293	20
$Rb_2[W_6Cl_{18}]$[a]	2.842(3) Å	2.862(2) Å	$P\bar{3}$	p, 293	20
$K_2[W_6Cl_{18}]$[a]	2.8703(6) Å	2.9054(6) Å	$P\bar{3}1m$	sc, 293	20
$(N(CH_3)_4)_2[W_6Cl_{18}]$[5]	2.8732(4) Å	2.8955(5) Å	$P\bar{3}m1$	sc, 293	20
$(N(C_2H_5)_4)_2[W_6Cl_{18}]$[a]	2.8889(5) Å	2.9185(4) Å	$P\bar{1}$	sc, 210	20
$(N(n\text{-}C_3H_7)_4)_2[W_6Cl_{18}]$[a]	2.8827(5) Å	2.9076(5) Å	$P\bar{1}$	sc, 210	20
$(N(n\text{-}C_4H_9)_4)_2[W_6Cl_{18}]$[a]	2.856(1) Å	2.888(1) Å	$Pbca$	sc, 293	20
$(Co(C_5H_5)_2)_2[W_6Cl_{18}]$[a]	2.8687(5) Å	2.8704(5) Å	$I4_1/amd$	sc, 293	20

[a] This work. [b] sc = single crystal diffraction, p = powder diffraction.

packing effects of clusters rather than by electronic destabilization effects due to the occupation of antibonding states. This assumption is supported by investigations concerning the 14 electron cluster anions $[W_6O_6Cl_{12}]^{2-}$ and $[W_6O_7Cl_{11}]^{3-}$ published by Crawford and Long.[24] These compounds also exhibit the structural characteristics of M_6X_{12} type clusters, but some of the inner, edge-bridging chlorine ligands are replaced by oxygen atoms. The W−W distances of chloro-bridged cluster edges vary from 2.869(1) to 2.914(5) Å and are in good agreement with the W−W bond lengths in W_6Cl_{18} units. In contrast, the W−W bond lengths of oxo-bridged edges are significantly shorter and amount to approximately 2.7 Å.

Conclusion

In addition to the already known compounds containing anionic $[W_6Cl_{18}]^{n-}$ species,[4,5] it could be shown in the present work, that the 20 cluster electron anion $[W_6Cl_{18}]^{2-}$ can be crystallized with a variety of monovalent cations yielding salt-like products of the composition $A_2[W_6Cl_{18}]$. The formation of these compounds is not limited to the use of methanol as reducing agent, but other chemical reducing such as $CoCp_2$ in THF solutions cleanly afford $(CoCp_2)_2[W_6Cl_{18}]$ in quantitative yield.

The mild synthetic conditions might be the reason for the stabilization of the possibly metastable $[W_6Cl_{18}]^{n-}$ ions. Although theoretical calculations on various levels of complexity always revealed antibonding characteristics of the energy levels above the a_{2u} level, experimental evidence is found for the observation of energetically stable $[W_6Cl_{18}]^{n-}$ species: cluster anions $[W_6Cl_{18}]^{n-}$ seem to be formed spontaneously when the neutral cluster is dissolved in methanol or THF, and the results of the ESI-MS and cyclic voltammetry examinations also confirmed that W_6Cl_{18} is prone to undergo reduction processes. No significant dimensional changes or distortions are obtained for the different $[W_6Cl_{18}]^{n-}$ species.

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Supporting Information Available: Additional tables and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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