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Room-Temperature Synthesis of the Highly Polar Cluster Compound Sn[SnCl][W_3Cl_{13}]

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A new synthetic strategy is employed to synthesize a tungsten trinuclear cluster compound with an ionic liquid (IL) as the reaction medium. Dark brown block-shaped crystals of Sn[SnCl][W_3Cl_{13}] were obtained at room temperature by reacting tin and WCl_6 in Lewis acidic ionic liquid [BMIM]Cl/$AlCl_3$ ($[BMIM]^+$ = 1-butyl-3-methylimidazolium). Compound Sn[SnCl][W_3Cl_{13}] crystallizes in the polar hexagonal space group $P6_3$ with cell parameters a = 959.8(1) and c = 1190.3(2) pm. The crystallographic point group of the $[W_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3Cl_9]^{3-}$ cluster anions is C_3, but C_{3v} pseudosymmetry is observed within twice the standard deviation of the bond lengths. The W–W bond length is 272.18(6) pm. The tin(II) cations, which are in trigonal pyramidal and in distorted trigonal-antiprismatic coordination spheres that comprise chloride ions, connect the clusters into layers that are stacked according to the 6_3 screw axis. One of the chloride ions is bound only to a single tin cation resulting in a $[Sn^{II}Cl]^+$ group with a Sn–Cl bond length of 236.1(5) pm. The pronounced polarity of the crystal structure means that its diffraction pattern exhibits huge deviations from Friedel's law. Most remarkable is that the intensity (F_c^2) of reflection 004 is 175 % of the intensity of the $00\bar{4}$ reflection.

Introduction

Heteroleptic trinuclear tungsten cluster compounds in which triply-bridging chalcogenides are present are well known.[1,2] Tritungsten clusters with triply-bridging halogenides are rare.[3,4] Messerle et al. synthesized the first trinuclear $W_3(\mu_3\text{-}L)(\mu\text{-}L)_3L_9$ cluster containing identical ligands (L = Cl).[5] These authors used a two-step reaction to prepare this compound, first they synthesized, in situ, $A_3[W_3Cl_{13}]$ (A = Li, Na, K) cluster compounds and then carried out metathesis reactions in organic solvents to obtain the tetraalkylammonium derivatives $(NR_4)_3W_3Cl_{13}$ [R_4 = $(CH_2Ph)Et_3$, $(CH_2Ph)Bu_3$, and Bu_4]. However, pure inorganic cluster compounds, $A_3[W_3Cl_{13}]$, were not isolated, and structural information was lacking from the author's paper. Meyer et al. were successful in isolating single crystals of $Na_3[W_3Cl_{13}]$ via a solid-state reaction route performed at 500 °C.[6] The symmetry of the cluster was found to be C_s, but idealized C_{3v} symmetry was applied to the structure in molecular orbital calculations.

As part of our research is to explore new and convenient routes for the synthesis of metal clusters, we have employed ionic liquids as reaction media. In a comproportionation reaction of a halide and a metal, low-valent main group clusters were obtained.[7] Considering the significantly milder conditions of such a synthesis method compared to others reported in the literature, and the opportunities to use reducing agents of various strengths, this synthetic route has the potential to produce transition metal cluster compounds as well.

Performing a synthesis in ionic liquid media offers an opportunity of conducting a one-pot synthesis involving a redox process at room temperature. This low temperature synthesis route eliminates the risk of product decomposition. Moreover modifying the controllable parameters, such as solvent acidity, oxidizing/reducing agent, or halide acceptor, allows the synthesis to be tailored to produce different products. The application of this approach in the synthesis of tungsten cluster compounds at room temperature resulted in the isolation of the highly polar cluster compound $Sn_2W_3Cl_{14}$, which is formulated as Sn[SnCl]-[W_3Cl_{13}].

Results and Discussions

Synthesis and Structure of Sn[SnCl][W_3Cl_{13}]

Reacting elemental tin with WCl_6 in Lewis acidic ionic liquid [BMIM]Cl/$AlCl_3$ at room temperature gives a dark brown solution within minutes. After overnight stirring, the reaction solution was allowed to stand and single crystals of Sn[SnCl][W_3Cl_{13}] were obtained in good yield (43%) after only two days. Contrary to the solid-state syntheses (240–500 °C, 6–7 d) of $A_3[W_3Cl_{13}]$ (A = Li, Na, K) cluster compounds that were performed by Messerle et al. and Meyer et al., we have established a gentle and convenient room-temperature synthesis route. In this synthetic scheme we have utilized, for the first time, tin as a reducing agent

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to convert WCl_6 to a trinuclear $[W_3Cl_{13}]^{3-}$ cluster and performed the reaction in ionic liquid media. The resulting Sn^{2+} cations are included in the product.

The symmetry of the diffraction pattern of $Sn[SnCl][W_3Cl_{13}]$ is hexagonal. Wilson plot and $(E^2 - 1)$ statistics clearly support an acentric structure for this crystalline material. The only systematic absence condition that is met by the data is $00l$ with $l = 2n$. Structure solution was successful in the polar space group $P6_3$, and the results confirmed the absence of any further symmetry elements in the crystal structure. Although the coordinates seemed to be reasonable, nonpositive definite atomic displacement parameters were obtained, the refinement statistics were $wR_2 = 28\%$, $R_1[F_o > 4\sigma(F_o)] = 12\%$, and the residual electron densities were +8.4 to –4.8 e/(10^6 pm^3), all of which were clear indicators of a crystallographic problem. Refinement in the monoclinic space group $P2_1$ with the application of a twinning law for a threefold twin about [001] did not solve the issue. The correct solution was found based on the observation that the dataset merges quite well in the higher Laue class 6/*mmm*. Refinement in space group $P6_3$ with the application of a merohedral twin law for a mirror plane $(\bar{1}10)$ twinning element [volume fraction of the second twin component = 44.7(1)%] gave $wR_2 = 3.6\%$, $R_1[F_o > 4\sigma(F_o)] = 1.9\%$, and residual electron densities of +0.58 to –0.72 e/(10^6 pm^3). Remarkably, the alternative twin law, for a twofold axis along [110], led to refinement statistics $wR_2 = 6.4\%$ and $R_1[F_o > 4\sigma(F_o)] = 2.9\%$. Such sensitivity to the preservation or the reversal of the polar axis [Flack parameter $x = -0.01(1)$] must be a result of large differences between the Bijvoet pairs.[8] In fact, huge deviations from Friedel's law were found for the intensities of the $00l$ reflections (Table 1). Most striking is that the intensity of the 004 reflection is 175% of the intensity of the $00\bar{4}$ reflection. Since the $00l$ reflections are the Fourier transform components arising from the projection of the structure onto the *c* axis, the enormous polarity that is visible in the X-ray diffraction data can be rationalized by analyzing the distribution of the atoms according to their *z* parameters. The relative scattering powers (atomic form factor *f* at $\theta = 0$, i.e. atomic number *Z*) from the layers of atoms as a function of the *z* parameter are shown in Figure 1. The tungsten atoms are a dominating factor in the scattering power. Relative to them, the scattering powers of the other atoms are unequally distributed. This clearly noncentrosymmetric scattering power sequence along *z*, in combination with the anomalous dispersion of the heavy atom tungsten ($\Delta f' = -0.849$, $\Delta f'' = +6.8722$), gives rise to the observed Bijvoet differences for the $00l$ reflections.

With respect to the sum formula $Sn[SnCl][W_3Cl_{13}]$, the structure can be subdivided into a $[W_3Cl_{13}]^{3-}$ cluster, a Sn^{2+} cation, and a $[SnCl]^+$ cation. The crystallographic point group of the $[W_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3Cl_9]^{3-}$ cluster anion is C_3, but C_{3v} pseudosymmetry is observed within twice the standard deviation of the bond lengths. The bonding W–W distance of 272.18(6) pm is in excellent agreement with that observed in $Na_3[W_3Cl_{13}]$ [273.7(1) pm].[6] The W atoms are additionally connected to one μ_3-Cl$^-$ and three μ-Cl$^-$ ligands. Each W atom is further coordinated to three terminal Cl$^-$ ions. Irrespective of the connectivity, the W–Cl distances are very similar and are within the range 238.4(3) to 247.6(3) pm. Consequently, the W atoms are in slightly distorted octahedral environments (Figure 2). Comparable isolated $[Bi_3Br_{13}]^{4-}$ groups (without metal–metal bonds)[9] as well as interconnected clusters $[Nb_3Cl_{13}]^{n-}$[10] have been described previously.

Table 1. Bijvoet differences $\Delta = 2[F_c^2(hkl) - F_c^2(\bar{h}\bar{k}\bar{l})]/[F_c^2(hkl) + F_c^2(\bar{h}\bar{k}\bar{l})]$ observed in the XRD data for $Sn[SnCl][W_3Cl_{13}]$.

h k l	$F_c^2(hkl)$	$F_c^2(\bar{h}\bar{k}\bar{l})$	Δ (%)	$F_o^2(hkl)$	$F_o^2(\bar{h}\bar{k}\bar{l})$
0 0 4	613	350	54.6	621(8)	336(7)
0 0 6	520	463	11.6	547(7)	451(6)
0 0 8	1296	1269	2.2	1317(8)	1345(11)
0 0 10	662	614	7.5	663(6)	630(6)
0 0 12	220	181	19.4	220(5)	181(3)

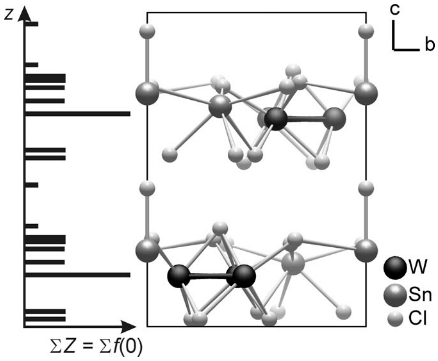

Figure 1. Projection of the unit cell of $Sn[SnCl][W_3Cl_{13}]$ along [100] demonstrating the layer motif as well as the polarity of the structure. The histogram indicates the relative X-ray scattering power of the atomic layers along *z*.

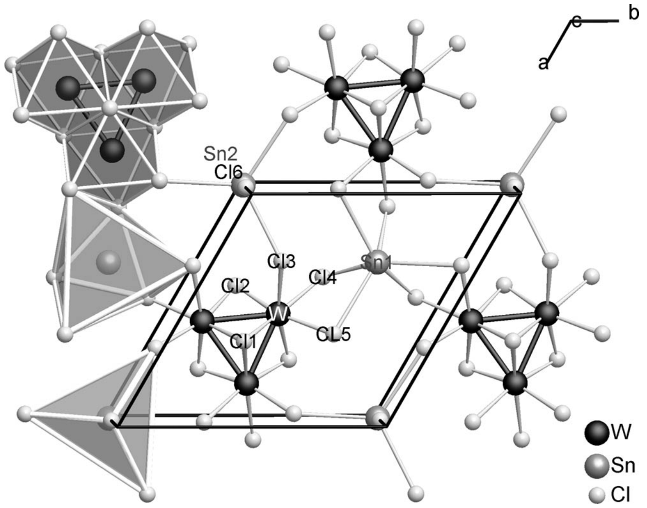

Figure 2. One layer in the crystal structure of $Sn[SnCl][W_3Cl_{13}]$. The second layer is obtained by application of a 6_3 screw rotation along the *c* axis.

The trinuclear $[W_3Cl_{13}]^{3-}$ cluster anions are encircled by Sn^{2+} cations, which link them into a two-dimensional network that lies parallel to the *ab* plane. The Sn1 cation is in a distorted trigonal-antiprismatic environment and is coordinated to six Cl^- anions with three short [269.0(3) pm] and three long Sn–Cl bond distances [307.7(4) pm]. The lone-pair of the Sn^{2+} cation might be directed towards the center of the wide triangular face that is formed by Cl5 atoms (Cl···Cl, 517 pm).

Cation Sn2 is in a trigonal pyramidal coordination environment, which is fairly common for Sn^{2+} complexes.[11] If the virtual position of the lone-pair is taken into account a ψ-bipyramid arrangement results. Remarkably, the Cl6 anion is only bonded to this cation (Figure 1), which is highlighted in its formulation as a $[Sn^{II}Cl]^+$ group. Furthermore, the distance of 236.1(5) pm could be regarded as the length of a Sn^{II}–Cl single bond, in accordance with Brese and O'Keeffe who have listed a $R(Sn^{II}$–Cl) bond valence parameter of 236 pm.[12] However, when considering bond lengths, it must be emphasized that the Sn2 and Cl6 atoms are displaced from the 6_3 axis by about 34 and 23 pm, respectively. In the presented structural model the disorder is approximated by enlarged atomic displacement parameters U_{11} and U_{12}. Alternatively, splitting the atomic positions with secondary sites Sn2' at $x = 0.0000(8)$, $y = 0.0355(5)$ and Cl6' at $x = 0.025(3)$, $y = 0.021(4)$ can be done. The longest distance between these split positions is 242.4(6) pm. Bond valence sums calculated with this standard length give $\Sigma v = 2.00$ for Sn1 and $\Sigma v = 1.83$ for Sn2.

Conclusions

We have successfully developed an ionic liquid based approach to synthesize a trinuclear tungsten cluster compound at room temperature. The impact of the present study is significant. Tin is a very effective reductant for the convenient direct preparation at ambient temperature and in high overall yield of $Sn[SnCl][W_3Cl_{13}]$ from WCl_6. Performing redox reactions in ionic liquids provides an efficient one-step route to the inorganic clusters, which does not require particularly stringent temperature control or gradients, or the use of highly purified WCl_6. The additional advantages of this synthetic route over other methodologies include:

(i) Inclusion of the organic cation in the final structure has not been observed.

(ii) Ionic liquids aid the stability of the ionic reaction intermediates.

(iii) Unlike for solid-state methods, reactions in ionic liquids are fast; crystal growth requires only few days rather than weeks, and the overall product yields can be high.

(iv) Ionic liquids are regarded as economical and environmentally friendly solvents.[13]

These features make ionic liquid based synthetic methods convenient chemical procedures that are versatile and general routes for the development of tritungsten complexes and clusters of high nuclearity.

Experimental Section

Chemicals: Starting materials were commercially purchased, 1-methylimidazole (Merck, 99%), 1-chlorobutane (Merck, 98.5%), $AlCl_3$ (Fluka, anhydrous, 98%), Sn (Aldrich, 99.999%), and WCl_6 (ABCR, 99.9%). $AlCl_3$ was sublimated three times prior to use. Organic reagents were distilled before use. Due of the high moisture sensitivity of the anhydrous metal halides, all manipulations were performed under dry argon (99.999%) in standard Schlenk tubes.

Synthesis of $Sn[SnCl][W_3Cl_{13}]$: The ionic liquid $[BMIM]Cl/AlCl_3$ ($[BMIM]^+$ = 1-butyl-3-methylimidazolium) was prepared according to a literature procedure.[14] Stoichiometric amounts of Sn and WCl_6 (total mass: 285 mg) were added to the Lewis-acidic ionic liquid $[BMIM]Cl/AlCl_3$ (molar ratio = 1:1.3, volume: 1.5 mL). The reaction mixture was stirred overnight at room temperature. After two days, dark brown block-shaped crystals were obtained; yield 43%.

X-ray Crystallography: Since $Sn[SnCl][W_3Cl_{13}]$ is prone to hydrolysis when exposed to moist air, crystals for XRD analysis were selected in a glove box [$c(O_2) < 0.1$ ppm, $c(H_2O) < 0.1$ ppm] and sealed in glass capillaries 0.2 mm in diameter. Intensity data for a single crystal were recorded at 293(2) K with an imaging-plate diffraction system IPDS-I (Stoe) with graphite-monochromated Mo-K_α radiation. The raw data were corrected for background, polarization, and Lorentz effects. The microscopic description of the crystal shape, which was implemented in the numerical absorption correction,[15] was optimized by consideration of a sets of reflections that are equivalent in the hexagonal crystal class 6.[16] The structure was solved by direct methods and refined with SHELXL-97.[17] Graphics for the structure were created with the program Diamond 3.2e.[18] The results of the structure determination are summarized in Tables 2, 3 and 4.

Table 2. Crystallographic data and details of the structure determination of $Sn[SnCl][W_3Cl_{13}]$.

Empirical formula	$Sn_2W_3Cl_{14}$
Crystal system	hexagonal
Space group	$P6_3$
Temperature (K)	293(2)
a, c (pm)	959.8(1), 1190.3(2)
V (10^6 pm^3)	949.6(2)
Z	2
Calculated density (g cm^{-3})	4.50
Measurement device	imaging plate diffractometer (IPDS-I, Stoe)
Radiation (graphite-monochromated)	$\lambda = 71.073$ pm (Mo-K_α)
Measurement range	$-10 \le h, k \le 10$; $-13 \le l \le 13$
μ(Mo-K_α) (mm^{-1})	22.64
Measured reflections	7694
Unique reflections [$F_o > 4\sigma(F_o)$]	928 [909]
R(int), $R(\sigma)$	0.060, 0.024
R_1 [$F_o > 4\sigma(F_o)$]	0.019
R_1 (all F_o)	0.020
wR_2 (all F_o^2)	0.036
Twin fraction	0.447(1)
Flack parameter	–0.01(1)
Extinction parameter	0.0006(1)
Number of parameters, restraints	60, 1
Goodness of fit	1.18
$\Delta\rho$(max., min.) (e·10^{-6} pm^{-3})	+0.58, –0.72

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), by quoting depository number CSD-421915.

Table 3. Wyckoff positions, coordinates, and equivalent thermal displacement parameters for the atoms in $Sn[SnCl][W_3Cl_{13}]$. U_{eq} (pm^2) is defined as one third of the trace of the orthogonalized tensor U_{ij}.

Atom	Wyckoff position	*x*	*y*	*z*	U_{eq}
W	6*c*	0.55686(5)	0.41171(5)	0.16074(4)	143(1)
Sn1	2*b*	1/3	2/3	0.2012(1)	279(4)
Sn2	2*a*	0	0	0.2419(1)	784(7)
Cl1	2*b*	2/3	1/3	0.3128(3)	139(9)
Cl2	6*c*	0.4411(4)	0.2014(4)	0.0237(2)	242(7)
Cl3	6*c*	0.3240(4)	0.3036(5)	0.2775(3)	292(8)
Cl4	6*c*	0.4040(4)	0.5062(4)	0.0473(2)	262(8)
Cl5	6*c*	0.6380(4)	0.6541(5)	0.2637(3)	280(8)
Cl6	2*a*	0	0	0.4402(4)	469(15)

Table 4. Selected interatomic distances (pm) in $Sn[SnCl][W_3Cl_{13}]$.

Atoms		Distances	Atoms		Distances
W–	W	272.18(6)	Sn1–	Cl4	269.0(3)
	Cl1	239.7(3)		Cl5	307.7(4)
	Cl2	239.4(3)	Sn2–	Cl3	304.6(3)
	Cl3	238.4(3)		Cl6	236.1(5)
	Cl4	247.6(3)			
	Cl5	238.9(4)			

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