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A low-temperature phase of bis(tetra-(t-butylammonium) octa-μ₃-chlorido-hexachlorido-octahedro-hexatungstate

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Received 12 February 2010
Accepted 15 September 2010
Online 24 September 2010

The title compound, (C₁₆H₃₆N)₂[W₆Cl₁₄]⁻, undergoes a reversible phase transition at 268 (1) K. The structure at 150 and 200 K has monoclinic (P2₁/c) symmetry. Both crystallographically independent tungsten chloride cluster anions sit on crystallographic inversion centers [symmetry codes: (i) x, y + 1, z; (ii) x + 1, y + 2, z]. Two previous studies at room temperature describe the structure in the space group P2₁/n with a unit-cell volume approximately half the size of the low-temperature unit cell [Zietlow, Schaefer et al. (1986). Inorg. Chem. 25, 2195–2198; Venkataraman et al. (1999). Inorg. Chem. 38, 828–830]. The unit cells of the room- and low-temperature polymorphs are closely related. The hydrocarbon chain of one of the tetrabutylammonium cations is disordered and was modeled with two sites each for three different C atoms. A packing diagram is shown in Fig. 2.

Comment

The lower halides of tungsten, including tungsten(II) chloride, have been known for over 100 years (Kepert & Vrieze, 1967; Prokopuk & Shriver, 1999) and numerous methods for their synthesis have been developed (Hogue & McCarley, 1970; Dorman & McCarley, 1974; Kolesnichenko & Messerle, 1998; Ströbele et al., 2009). The structure of the [(W₆Cl₁₃)Cl]₂⁻ anion was first determined by Zietlow, Schaefer et al. (1986) at room temperature. A subsequent structure determination of the same form was published by Venkataraman et al. (1999). The tungsten(II) halide clusters have been intensely studied because of their fascinating photochemical and electrochemical properties (Maverick et al., 1983; Nocera & Gray, 1984; Zietlow et al., 1985; Zietlow, Nocera et al., 1986; Jackson et al., 1990; Mussell & Nocera, 1990; Arratia-Pérez & Hernández-Acevedo, 1997; Gray, 2009).

At low temperature, the two independent [(W₆Cl₁₃)Cl]₂⁻ cluster units (Fig. 1) sit on crystallographic inversion centers and have bond lengths and bond angles comparable to those of previously determined structures (Zietlow, Schaefer et al., 1986; Venkataraman et al., 1999). One hydrocarbon chain of one of the tetrabutylammonium cations (Fig. 1) is disordered and was modeled with two sites each for three different C atoms. A packing diagram is shown in Fig. 2.

Figure 1
Displacement ellipsoid (50% probability level) drawing of the two individual tungsten cluster anions and the two tetrabutylammonium cations in the asymmetric unit for the 150 K structure, showing the atom-numbering scheme. [Symmetry codes: (i) −x, −y + 1, −z; (ii) −x + 1, −y + 2, −z.]
The room-temperature cell can be approximately identical to the room-temperature cell of the low-temperature form produces the following unit matrix: 

\[
\begin{pmatrix}
1 & 0 & 1/1 \\
0 & 1 & 0/2 \\
1 & 0 & 1/2
\end{pmatrix}
\]

This allows for a pseudo-orthorhombic cell shows higher metric symmetry, namely the transformation is possible because the low-temperature unit cell of the transformation matrix \[
\begin{pmatrix}
1/0 & 1/0 & 1/0 \\
1/0 & 1/2 & 1/2 \\
1/0 & 1/2 & 1/2
\end{pmatrix}
\]

The room-temperature cell can be generated from this pseudo-orthorhombic cell by dividing the unit cell along the c axis for the 150 K structure. H atoms and the atoms of the minor component of the disorder were not included in the overlay analysis and have been omitted from this figure.

90.17° and γ = 90° (Zietlow, Schaefer et al., 1986), while at 150 K the unit cell is \(a = 22.3152(2) \text{ Å}, b = 11.7220(1) \text{ Å}, c = 22.2786(1) \text{ Å}, \alpha = 90°, \beta = 112.451(1)°, \gamma = 90°\). Application of the transformation matrix \[
\begin{pmatrix}
1/0 & 1/0 & 1/0 \\
1/0 & 1/2 & 1/2 \\
1/0 & 1/2 & 1/2
\end{pmatrix}
\]

to the unit cell of the low-temperature form produces the following unit cell, which is approximately identical to the room-temperature cell: \(a = 18.534 \text{ Å}, b = 11.722 \text{ Å}, c = 12.395 \text{ Å}, \alpha = 90°, \beta = 89.90°\) and \(\gamma = 90°\). An overlay of the two unit cells is shown in Fig. 3 (r.m.s. overlay = 0.177 Å for 122 non-H atoms). This transformation was reproducible using a different crystal of the same compound.

A search of the Cambridge Structural Database (CSD; Version 5.31; Allen, 2002) revealed that the smaller \(P2_1/n\) unit cell observed for the room-temperature structure is common to a range of tetrabutylammonium salts of metal–halide and metal–chalcogenide cluster dianions. Examples include molybdenum halide clusters (Preetz et al., 1992, 1994; Kirakci et al., 2005), molybdenum chalcogenide/halide clusters (Ebihara et al., 1992), tungsten halide clusters (Zietlow, Schaefer et al., 1986; Venkataraman et al., 1999) and rhenium chalcogenide/halide clusters (Gabriel et al., 1993; Uriel et al., 1995, 1996, 2001). Only two examples were found with the same \(P2_1/c\) unit cell as the low-temperature phase of the title compound: the \([\text{Os}_2\text{Re}_2\text{Se}_8]\text{Cl}_6^{2-}\) dianion structure determined at 153 K by Tulsky & Long (2001) and the \([\text{Re}_6\text{Se}_5\text{Cl}_2\text{N}-\text{TMS}]\text{Cl}_6^{2-}\) (TMS is trimethylsilyl) anion structure determined at room temperature by Uriel et al. (1996).

Among these examples, only one structure was found that potentially undergoes a similar phase change. The \([\text{Re}_6\text{Se}_5\text{Cl}_2\text{Cl}_6]^{2-}\) dianion structure was determined in a tetragonal setting (space group \(I4/mmm\); Yaghi et al., 1992) at 198 K, while two other structure determinations of the same compound at room temperature (Uriel et al., 1995, 2001) display the \(P2_1/n\) unit cell found for the room-temperature structure of the title compound and many other structures. The analogous \([\text{Mo}_6\text{Br}_8]\text{Br}_6^{2-}\) dianion structure, however, has been determined at 100 K and room temperature (Kirakci et al., 2005) and in both cases the \(P2_1/c\) unit cell was found.
Experimental

The tungsten(II) chloride cluster was prepared via the reduction of tungsten(VI) chloride with bismuth according to published procedures (Kolesnichenko & Messerle, 1998). The hydronium salt was converted to the tetrabutylammonium salt by metathesis with tetra-butylationmonium chloride in ethanol solution. The crude product was recrystallized by slow evaporation from an acetone solution. Crystals suitable for X-ray analysis were grown by slow diffusion of diethyl ether into a solution of (I) in dichloromethane.

Compound (I) at 150 K

Crystal data

$$\begin{align*}
(C_{16}H_{36}N)_{2}[W_{6}Cl_{14}] & \\
V & = 5387.31 (7) \ \text{Å}^3 \\
Z & = 4
\end{align*}$$

Data collection

Nonius KappaCCD diffractometer

137050 measured reflections

12352 independent reflections

137050 measured reflections

12352 independent reflections

Refinement

$$\begin{align*}
R[F^2 > 2\sigma(F^2)] & = 0.031 \\
wR(F^2) & = 0.054
\end{align*}$$

Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $x + 1, -y + 2, -z$.

Table 1

| W1—W2 | 2.6048 (3) | W4—W5 | 2.6092 (3) |
| W1—W2$^a$ | 2.6212 (3) | W4—W5$^a$ | 2.6127 (3) |
| W1—W3 | 2.6163 (3) | W4—W6 | 2.6133 (3) |
| W1—W3$^a$ | 2.6091 (3) | W4—W6$^a$ | 2.6143 (3) |
| W2—W3 | 2.6102 (3) | W5—W6 | 2.6152 (3) |
| W2—W3$^a$ | 2.6073 (3) | W5—W6$^a$ | 2.6071 (3) |
| W1—C1 | 2.4181 (13) | W4—C18 | 2.4243 (14) |
| W1—C12 | 2.4192 (13) | W5—C19 | 2.4187 (13) |
| W3—C13 | 2.4310 (13) | W6—C10 | 2.4328 (13) |
| W1—C14 | 2.5037 (12) | W4—C11 | 2.4941 (13) |
| W1—C15 | 2.5028 (13) | W4—C12 | 2.4926 (13) |
| W1—C16 | 2.4968 (13) | W4—C13 | 2.5034 (12) |
| W1—C17 | 2.4953 (12) | W4—C14 | 2.4979 (13) |
| W2—C14 | 2.5044 (13) | W5—C11$^a$ | 2.4969 (14) |
| W2—C15 | 2.4927 (12) | W5—C12 | 2.5044 (14) |
| W2—C16 | 2.4919 (13) | W5—C13$^a$ | 2.4954 (13) |
| W2—C17 | 2.4987 (12) | W5—C14 | 2.4974 (13) |
| W3—C14 | 2.4977 (13) | W6—C11$^a$ | 2.4972 (13) |
| W3—C15$^a$ | 2.4856 (12) | W6—C12$^a$ | 2.4978 (13) |
| W3—C16 | 2.5090 (13) | W6—C13 | 2.5062 (14) |
| W3—C17$^a$ | 2.5055 (13) | W6—C14 | 2.4844 (13) |

Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $x + 1, -y + 2, -z$.

Table 2

| W1—W2 | 2.6056 (3) | W4—W5 | 2.6113 (3) |
| W1—W2$^a$ | 2.6228 (3) | W4—W5$^a$ | 2.6157 (3) |
| W1—W3 | 2.6191 (3) | W4—W6 | 2.6169 (3) |
| W1—W3$^a$ | 2.6101 (3) | W4—W6$^a$ | 2.6170 (3) |
| W2—W3 | 2.6131 (3) | W5—W6 | 2.6186 (3) |
| W2—W3$^a$ | 2.6239 (3) | W5—W6$^a$ | 2.6096 (3) |
| W1—C11 | 2.4177 (14) | W4—C18 | 2.4187 (16) |
| W2—C12 | 2.4289 (14) | W5—C19 | 2.4174 (13) |
| W3—C13 | 2.4285 (14) | W6—C10 | 2.4297 (15) |
| W1—C14 | 2.5012 (14) | W4—C11 | 2.4928 (14) |
| W1—C15 | 2.4961 (14) | W4—C12 | 2.4903 (14) |
| W1—C16 | 2.4980 (15) | W4—C13 | 2.5029 (14) |
| W1—C17 | 2.4962 (14) | W4—C14 | 2.4965 (14) |
| W2—C14 | 2.5067 (14) | W5—C11$^a$ | 2.5003 (16) |
| W2—C15 | 2.4905 (14) | W5—C12 | 2.5033 (15) |
| W2—C16$^a$ | 2.4864 (14) | W5—C13$^a$ | 2.4932 (14) |
| W2—C17$^a$ | 2.4967 (13) | W5—C14 | 2.4967 (14) |
| W3—C14 | 2.4965 (13) | W6—C11$^a$ | 2.4964 (15) |
| W3—C15$^a$ | 2.4888 (13) | W6—C12$^a$ | 2.4936 (13) |
| W3—C16 | 2.5088 (15) | W6—C13 | 2.5046 (14) |
| W3—C17$^a$ | 2.5020 (14) | W6—C14 | 2.4836 (13) |

Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $-x + 1, -y + 2, -z$.

Hydrocarbon chains was found to be disordered and was modeled with two sites for each of the last three C atoms of the n-butyl chain. The occupancies of the two disorder components were refined freely and converged at 0.555 (11) for the 200 K structure and at 0.616 (10) for the 150 K structure; the sum of the site-occupancy factors for each disorder was constrained to unity. The major component of the disordered chain contains atoms C14, C15 and C16, while the minor component consists of atoms C14A, C15A and C16A.

Similarity restraints on 1–2 and 1–3 distances (standard uncertainties = 0.02 and 0.04 Å, respectively) were used to geometrically relate the two components of the disordered n-butyl chain to one another and also to the remaining three butyl chains of the first tetrabutylammonium ion. In addition, similarity restraints on displacement parameters (standard uncertainty = 0.04 Å$^2$, or 0.08 Å$^2$ for terminal atoms), as well as rigid-bond restraints for anisotropic displacement parameters (standard uncertainty = 0.01 Å$^2$), were applied to all disordered atoms as well as to C13.

The asymmetric unit of (I) at both temperatures consists of two tetrabutylammonium cations and two half-octahedra of the [W$_6$Cl$_{14}$]$^-$ cluster anion, with each octahedron containing a crystallographic inversion center.

Not surprisingly, the two low-temperature structures, determined at 150 and 200 K, are essentially identical. In both cases, one of the metal-organic compounds

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metal-organic compounds

The top four peaks in the final difference electron-density map range from 1.09 to 1.20 e Å⁻³ (150 K data) and from 1.62 to 2.35 e Å⁻³ (200 K data). All of these peaks are located within 1.5 Å of a W atom and are presumably Fourier truncation artifacts due to the presence of multiple heavy atoms.

For both compounds, data collection: COLLECT (Nonius, 2000); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997), Mercury (Macrae et al., 2008) and POV-RAY (Cason, 2004); software used to prepare material for publication: WinGX (Farrugia, 1999).

This work was supported in part by the National Science Foundation through grant No. CHE-0532510. Thanks are due to Tom Concolino of Rigaku for the use of the SCXmini diffractometer and to the organizers and faculty of the 2010 ACA Summer Course on Small Molecule Crystallography.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MX3029). Services for accessing these data are described at the back of the journal.

References

