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Hexachlorotetra-μ_3-chloro-tetra-μ_3-telluro-octohexarhenium(III)

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Abstract

The title compound, $Re_6Te_4Cl_{10}$, was obtained by reaction of $ReCl_5$ with elemental Te in an evacuated sealed fused silica tube at 773 K. The structure contains two independent Re_6 octahedral clusters, each with a crystallographic center of symmetry. The Re atoms are coordinated by four μ_3-Te atoms and four μ_3-Cl ligands that are equally distributed over the faces of the metal polyhedron. The remaining six Cl atoms are terminal ligands coordinated to the apices of the Re_6 octahedron. Distance ranges are: Re—Re 2.618 (1)–2.638 (1), Re—μ_3-*L* 2.530 (3)–2.679 (2), Re—$Cl_{terminal}$ 2.325 (6)–2.353 (5) Å (*L* is 50% Te and 50% Cl).

Comment

Octahedral Re_6 clusters are well known (Perrin & Sergent, 1988; Yaghi, Scott & Holm, 1992; Long, Williamson & Holm, 1995). The clusters $Re_6X_4Y_{10}$, with X = S, Se, Y = Cl, Br (Leduc *et al.*, 1985; Fedorov *et al.*, 1985; Gabriel, Boubekeur & Batail, 1993) and X = Te, Y = Br (Opalovskii, Fedorov, Lobkov & Erenburg, 1971) have been reported. Only the compounds with X = S, Se and Y = Cl have been characterized by single-crystal X-ray techniques. Whereas the syntheses of the single crystals used in earlier structural studies involved high temperatures (973–1073 K), synthesis of the title compound, $Re_6Te_4Cl_{10}$, required only 773 K.

The title compound is isostructural with $Re_6S_4Cl_{10}$ and $Re_6Se_4Cl_{10}$. These compounds contain an Re_6 octahedron surrounded by a cube of four Te atoms and four Cl atoms. The Te and Cl atoms are randomly distributed over the eight corners of the cube. The remaining six Cl atoms ($Cl_{terminal}$) are coordinated to the Re atoms at the apices of the octahedron. As expected (Table 2), the Re—Re and Re—$Cl_{terminal}$ distances in $Re_6Te_4Cl_{10}$ agree well with those of the S and Se analogues, and the Re—Te/Cl distances [2.530 (3)–2.679 (2) Å] are slightly longer [Re—S/Cl 2.401 (3)–2.447 (3) Å, Re—Se/Cl 2.49–2.51 Å]; bond angles are as expected.

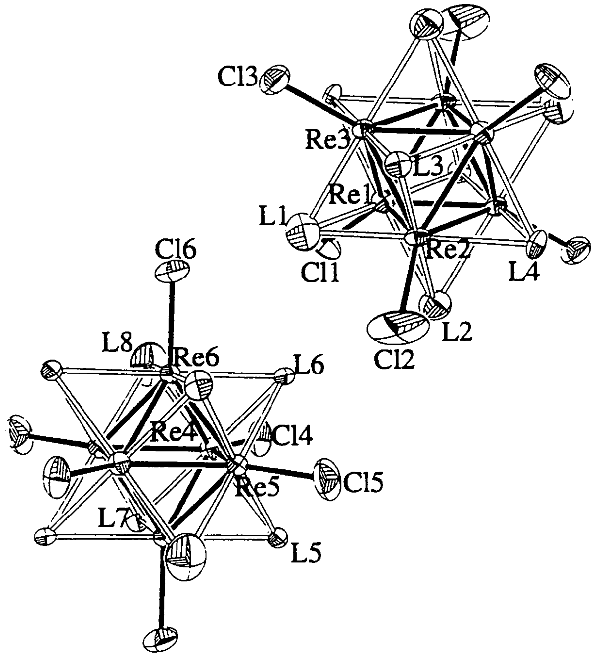

Fig. 1. Molecular structure showing 75% probability displacement ellipsoids. Unique atoms are labeled; each molecule has a crystallographic center of inversion. Atoms labeled *L* are 50% Te and 50% Cl.

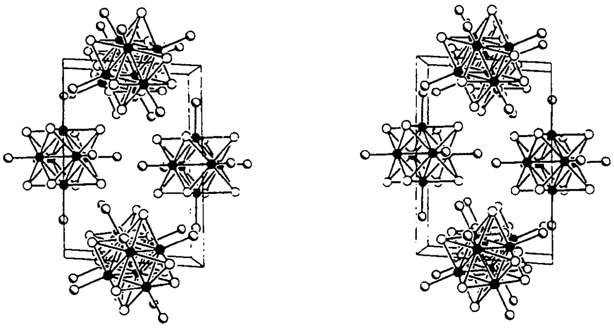

Fig. 2. Stereoview down the *b* axis of the unit cell of $Re_6Te_4Cl_{10}$. The Re atoms are drawn as filled circles, capping atoms as open circles, and $Cl_{terminal}$ atoms as shaded circles.

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Experimental

The title compound was obtained by reaction of $ReCl_5$ with elemental Te (molar ratio 1:1) in an evacuated sealed fused silica tube. The reaction tube was held at 773 K for 24 h and cooled at a rate of 2 K h^{-1}. Single crystals formed at one end of the tube.

Crystal data

$Re_6Te_4Cl_{10}$
$M_r = 1982.10$
Triclinic
$P\overline{1}$
$a = 9.004$ (1) Å
$b = 9.000$ (1) Å
$c = 12.963$ (2) Å
$\alpha = 85.25$ (1)°
$\beta = 85.55$ (1)°
$\gamma = 82.45$ (1)°
$V = 1035.5$ (2) Å^3
$Z = 2$
$D_x = 6.357$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 40$–41°
$\mu = 121.99$ mm^{-1}
$T = 113$ (2) K
Plate
0.126 × 0.046 × 0.019 mm
Black

Data collection

CAD-4 diffractometer
ω–2θ scans
Absorption correction: analytical
$T_{min} = 0.020$, $T_{max} = 0.212$
6989 measured reflections
3790 independent reflections
2936 observed reflections $[I > 2\sigma(I)]$

$R_{int} = 0.0628$
$\theta_{max} = 69.8°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -15 \rightarrow 15$
6 standard reflections frequency: 3 h X-ray exposure time intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.048$
$wR(F^2) = 0.112$
$S = 1.40$
3790 reflections
182 parameters
$w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$(\Delta/\sigma)_{max} = -0.08$
$\Delta\rho_{max} = 3.19$ e Å^{-3}
$\Delta\rho_{min} = -3.65$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00034 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Re1	−0.00159 (9)	0.51102 (11)	1.35586 (6)	0.0140 (2)
Re2	0.18515 (8)	0.38143 (11)	1.49307 (7)	0.0142 (2)
Re3	−0.09541 (8)	0.32795 (10)	1.50914 (6)	0.0125 (2)
Re4	0.46422 (9)	0.19622 (11)	0.94235 (7)	0.0145 (2)
Re5	0.58241 (9)	0.06894 (11)	1.11139 (7)	0.0136 (2)
Re6	0.31181 (9)	0.02007 (11)	1.07069 (7)	0.0149 (2)
*L*1†	0.0897 (3)	0.2226 (3)	1.3613 (2)	0.0358 (6)
*L*2	0.2821 (3)	0.5626 (3)	1.3420 (2)	0.0303 (5)
*L*3	0.0953 (2)	0.1954 (2)	1.64505 (14)	0.0150 (4)
*L*4	0.2859 (2)	0.5408 (2)	1.6256 (2)	0.0162 (4)
*L*5	0.7369 (2)	0.2468 (3)	0.9850 (2)	0.0169 (4)
*L*6	0.3594 (2)	0.2867 (2)	1.1273 (2)	0.0154 (4)
*L*7	0.5699 (2)	0.1020 (3)	0.7569 (2)	0.0214 (5)
*L*8	0.2002 (4)	0.1461 (4)	0.9076 (3)	0.0527 (9)
Cl1	0.0051 (6)	0.5175 (7)	1.1739 (4)	0.0287 (13)
Cl2	0.4166 (7)	0.2330 (10)	1.4794 (9)	0.069 (3)
Cl3	−0.2121 (5)	0.1093 (7)	1.5197 (5)	0.0274 (12)
Cl4	0.4099 (6)	0.4434 (6)	0.8687 (5)	0.0290 (12)
Cl5	0.6917 (7)	0.1461 (9)	1.2513 (5)	0.041 (2)
Cl6	0.0683 (6)	0.0515 (10)	1.1500 (6)	0.046 (2)

† *L* is 50% Te and 50% Cl.

Table 2. *Selected bond distances (Å)*

Re1—Cl1	2.351 (5)	Re4—Cl4	2.353 (5)
Re1—*L*1	2.615 (3)	Re4—*L*8	2.558 (3)
Re1—*L*4^{i}	2.651 (2)	Re4—*L*7	2.679 (2)
Re1—*L*2	2.645 (3)	Re4—Re6^{ii}	2.618 (1)
Re1—Re2^{i}	2.626 (1)	Re4—Re5	2.622 (1)
Re1—Re3^{i}	2.630 (1)	Re4—Re5^{ii}	2.635 (1)
Re1—Re3	2.634 (1)	Re4—Re6	2.635 (1)
Re1—Re2	2.638 (1)	Re4—*L*6	2.659 (2)
Re1—*L*3^{i}	2.665 (2)	Re4—*L*5	2.662 (2)
Re2—Cl2	2.326 (6)	Re5—*L*8^{ii}	2.578 (4)
Re2—*L*1	2.580 (3)	Re5—Cl5	2.325 (6)
Re2—*L*2	2.614 (3)	Re5—*L*5	2.642 (2)
Re2—*L*4	2.612 (2)	Re5—*L*6	2.624 (2)
Re2—*L*3	2.627 (2)	Re5—*L*7^{ii}	2.630 (2)
Re2—Re3	2.623 (1)	Re5—Re6^{ii}	2.624 (1)
Re2—Re3^{i}	2.633 (1)	Re5—Re6	2.632 (1)
Re3—Cl3	2.339 (6)	Re6—Cl6	2.341 (6)
Re3—*L*4^{i}	2.641 (2)	Re6—*L*8	2.530 (3)
Re3—*L*2^{i}	2.626 (3)	Re6—*L*6	2.663 (2)
Re3—*L*1	2.596 (3)	Re6—*L*7^{ii}	2.644 (2)
Re3—*L*3	2.657 (2)	Re6—*L*5^{ii}	2.664 (3)

Symmetry codes: (i) $-x, 1-y, 3-z$; (ii) $1-x, -y, 2-z$.

Initial cell parameters and symmetry information for $Re_6Te_4Cl_{10}$ were determined from Weissenberg photographs taken at 298 K. Intensity data were processed (Blessing, 1987) and corrected for absorption (de Meulenaer & Tompa, 1965) on an IBM *RS*/6000 series computer. The final refinement included anisotropic displacement parameters and an extinction parameter. The final difference electron density map showed no feature with a height greater than 1.4% that of a Re atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: peak profile analysis (Blessing, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXTL*/*PC*.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1121). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$K_2Mn(VO_3)_4$, a New Three-Dimensional Potassium Manganese(II) Polyvanadate

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Abstract

The structure of potassium manganese(II) polyvanadate, $K_2Mn(VO_3)_4$, is composed of VO_4 tetrahedra and MnO_6 octahedra. Parallel zigzag polyvanadate $(VO_3)_n^{n-}$ chains of corner-sharing VO_4 tetrahedra are cross-linked by separate MnO_6 octahedra to form a three-dimensional structure with K^+ cations situated in void space.

Comment

Two potassium manganese vanadates have already been reported: $K_{10}Mn_2V_{22}O_{64}.20H_2O$ and $K_5H_3Mn_3V_{12}O_{40}.8H_2O$ (Ichida, Nagai, Sasaki & Pope, 1989). Both are heteropolyvanadates containing Mn^{IV} cations. The potassium manganese(II) polyvanadate $K_2Mn(VO_3)_4$ has been prepared in a basic medium. Its structure is composed of VO_4 tetrahedra and MnO_6 octahedra (Fig. 1). Each VO_4 tetrahedron shares two of its vertices with two VO_4 tetrahedra to form parallel zigzag $(VO_3)_n^{n-}$ chains of alternating V(1)O_4 and V(2)O_4 tetrahedra, running along [101]. Within a chain, each V(1)O_4 tetrahedron shares its two remaining vertices with two MnO_6 octahedra, whereas each V(2)O_4 tetrahedron shares only one vertex with another MnO_6 octahedron. The fourth O atom, O(6), as yet unshared, of the V(2)O_4 tetrahedron points toward a cavity where a K^+ cation is situated. Each MnO_6 octahedron is then connected to six different tetrahedra [four V(1)O_4 tetrahedra and two V(2)O_4 tetrahedra] which belong to four different chains. Each K^+ cation is surrounded by eight O atoms with K—O distances ranging from 2.780 (4) to 3.026 (3) Å. The Mn—O and V—O bonds are unexceptional and correspond well with those typically observed in Mn^{II} and V^V oxides. The shortest V—O distance involves the terminal O atom, O(6), *i.e.* not bonded to Mn, but leading to the shortest K—O distance. Bond-valence sum calculations (Brese & O'Keeffe, 1991; Brown & Altermatt, 1985) confirm oxidation-state assignments.

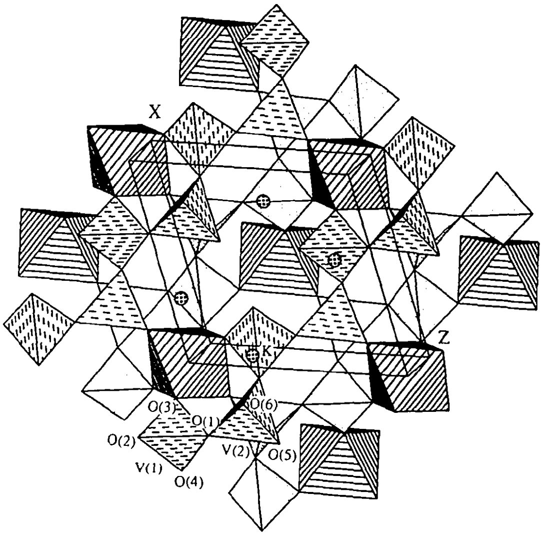

Fig. 1. Polyhedral representation of $K_2Mn(VO_3)_4$, viewed down the *b* axis.

Experimental

Single crystals of $K_2Mn(VO_3)_4$ were obtained by heating a mixture of $H_2Mn_4O_9.xH_2O$ (0.207 g, 0.5 mmol), V_2O_5 (0.364 g, 2.0 mmol), $K_2S_2O_8$ (0.135 g, 0.5 mmol), 9.5 ml of 1*M* KOH and 0.5 ml of acetone in an autoclave at 453 K (autogenous pressure) for one week.

Crystal data

$K_2Mn(VO_3)_4$
$M_r = 528.9$
Monoclinic
$P2_1/n$
$a = 8.1678\,(9)$ Å
$b = 9.226\,(1)$ Å
$c = 8.6395\,(8)$ Å
$\beta = 109.678\,(8)^\circ$
$V = 613.0\,(1)$ Å^3
$Z = 2$
$D_x = 2.865$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.3$–25.1°
$\mu = 4.668$ mm^{-1}
$T = 293$ K
Plate
0.16 × 0.11 × 0.02 mm
Red