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Hexa-μ-acetato-di-μ_3-oxo-tris[aquatungsten(IV)] Trifluoromethylsulfonate

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Abstract. $[W_3(C_2H_3O_2)_6(H_2O)_3O_2](CF_3SO_3)_2$, $C_{12}H_{24}O_{17}W_3^{2+}.2CF_3O_3S^-$, trigonal, $R\bar{3}c$, $a = 11{\cdot}424\,(4)$, $c = 40{\cdot}679\,(10)$ Å, $Z = 6$, $D_x = 2{\cdot}793$ Mg m^{-3}, $M_r = 1289{\cdot}99$, $F(000) = 3600$, $\mu_{\rm Mo} = 11{\cdot}73$ mm^{-1}. The structure was solved by direct methods and difference Fourier syntheses. Refinement with 1422 independent reflexions yielded $R = 3{\cdot}0\%$. The tungsten acetate complex ion occupies a special position with site symmetry 32 approximately showing point-group symmetry $\bar{6}2m$. The W atoms form an equilateral triangle [W—W = 2·747 (1) Å]. The $CF_3SO_3^-$ ions occupy special positions on the threefold axes. They are distorted by the action of hydrogen bonds [O—O = 2·652 (9) Å].

Introduction. After the discovery of a trinuclear Mo cluster (Bino, Ardon, Maor, Kaftory & Dori, 1976) the question arose as to whether similar clusters can be obtained with tungsten. A similar work-up procedure to that used for the Mo cluster resulted in the present crystal species. Parallel to this, three further crystal species containing W_3 clusters were prepared at Texas A & M University. The common structural properties of these four clusters were described by Bino, Cotton, Dori, Koch, Küppers, Millar & Sekutowski (1978). The present paper reports the crystallographic and structural features of the title compound.

The compound was prepared by the reaction of acetic acid with $W(CO)_6$ followed by cation-exchange chromatography of the resulting product on a resin column and elution with 0·5 *M* CF_3SO_3H (Bino *et al.*, 1978). Evaporation of the resulting solution yielded well developed yellow crystals which were found to be bounded by the rhombohedron {102} (referred to hexagonal axes). The lattice parameters, as given in the *Abstract*, were obtained by a least-squares fit to diffractometrically determined Bragg angles for 18 reflexions from a single crystal. In the preliminary communication on this structure (Bino *et al.*, 1978) a monoclinic representation of the crystal symmetry was used for the data collection and structure analysis. Higher symmetry was subsequently detected and this report is in terms of the more correct crystal system. The hexagonal axes $\mathbf{a}_h$, $\mathbf{b}_h$, and $\mathbf{c}_h$ in the present study are related to the former monoclinic axes $\mathbf{a}_m$, $\mathbf{b}_m$, and $\mathbf{c}_m$ by $\mathbf{a}_h = \mathbf{b}_m$, $\mathbf{b}_h = (\mathbf{a}_m - \mathbf{b}_m)/2$, $\mathbf{c}_h = \mathbf{a}_m + 3\mathbf{c}_m$. 4339 reflexions with $2° < \theta < 30°$ were obtained with an automatic Philips PW 1100 diffractometer with Mo $K\alpha$ radiation using a crystal of approximately isometric shape and a mean diameter of 0·2 mm. Absorption was corrected for by assuming the specimen to be spherical.

Positions of the W atoms were found by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971) and those of the remaining non-hydrogen atoms by difference Fourier syntheses. H atoms could not be detected. Refinement and further calculations were performed with the *SHELX* 76 system (Sheldrick, 1976). The atomic and anisotropic thermal parameters were refined, using 1422 symmetry-independent reflexions (trigonal) with $F_o > 2\sigma$, by a full-matrix least-squares procedure to a final $R_w = 0{\cdot}030$ (unweighted $R = 0{\cdot}053$). Squared reciprocal standard deviations were used as weights. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final positional

Table 1. *Fractional atomic coordinates and isotropic thermal parameters with standard deviations in parentheses*

	x	y	z	B (Å^2)
W	0·1388 (1)	0·0000	0·2500	1·07 (2)
O(3)	0·0000	0·0000	0·2196 (2)	1·57 (24)
O*W*	0·3254 (5)	0·0000	0·2500	1·30 (19)
O(1)	0·1431 (5)	0·2597 (5)	0·2154 (1)	1·47 (13)
O(2)	0·2595 (5)	0·1500 (5)	0·2160 (1)	1·59 (14)
C(1)	0·3363 (7)	0·3429 (8)	0·1806 (2)	2·20 (23)
C(2)	0·2402 (7)	0·2445 (7)	0·2052 (2)	1·43 (18)
CS	0·0000	0·0000	0·1224 (6)	5·00 (70)
F	0·1169 (7)	0·0965 (7)	0·1358 (2)	7·74 (29)
S	0·0000	0·0000	0·0797 (1)	3·41 (13)
OS	0·0879 (7)	0·1426 (6)	0·0720 (2)	5·54 (27)

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parameters are listed in Table 1* together with the isotropic thermal parameters $B = 8\pi^2 U$, which were obtained in a separate refinement ($R_w = 0{\cdot}050$) in which the positional parameters of the anisotropic refinement were held constant.

Discussion. Figs. 1 and 2 show stereoscopic *ORTEP* plots (Johnson, 1965) of part of the unit cell and of the $[W_3(C_2H_3O_2)_6(H_2O)_3O_2]^{2+}$ group, respectively.

The W atoms form an equilateral triangle. The $[W_3(C_2H_3O_2)_6(H_2O)_3O_2]^{2+}$ unit surrounds the special position $0,0,\frac{1}{4}$, thus exhibiting point-group symmetry 32 (D_3); it also shows approximate $\bar{6}2m$ (D_{3h}) point-group symmetry. The deviations of the acetate groups (and probably the H atoms of the water molecules) from $\bar{6}2m$ are very small and are caused by the intermolecular forces discussed below. The degree of deviation may be characterized by the displacement of the terminal C(1) atom of the acetate group of only 0·066 Å from the position it would have if $\bar{6}2m$ symmetry were realized. The H atoms of the water molecule, which could not be detected in the present structure analysis, will, of course, show deviations from $\bar{6}2m$ symmetry as well. However, these deviations will presumably be small since these H atoms form hydrogen bonds to atoms OS and OS″ (Fig. 3) which lie approximately in the plane of the W triangle.

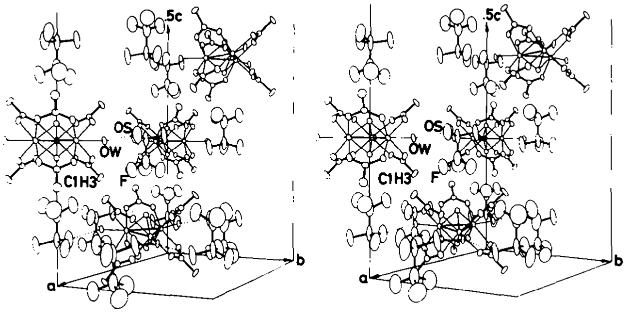

Fig. 1. Stereoscopic view of part of the unit cell.

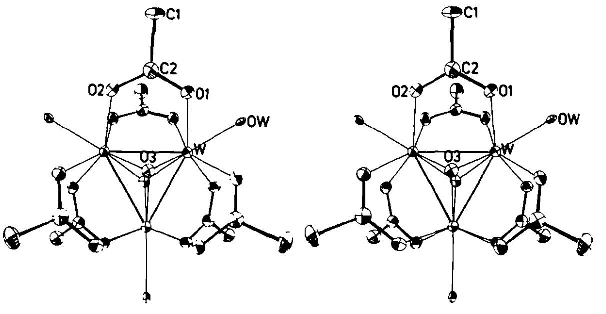

Fig. 2. Stereoscopic view of the $[W_3(C_2H_3O_2)_6(H_2O)_3O_2]^{2+}$ group.

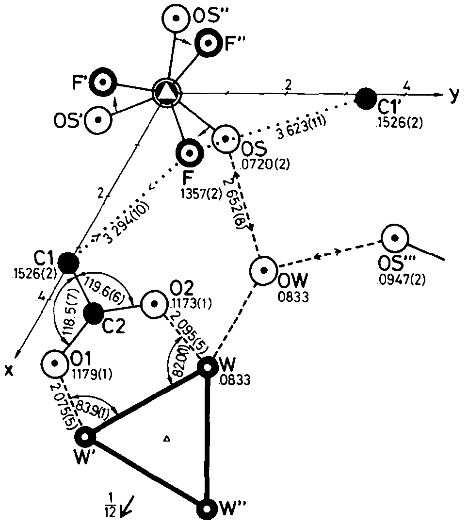

Fig. 3. Projection along the *c* axis showing the distortions of the $CF_3SO_3^-$ ion and the $[W_3(C_2H_3O_2)_6(H_2O)_3O_2]^{2+}$ group by nearest-neighbour non-bonded interactions.

Table 2. *Bond distances* (Å) *and angles* (°) *in the* $[W_3(C_2H_3O_2)_6(H_2O)_3O_2]^{2+}$ *ion*

W–W	2·746 (1) (2×)	O*W*–W–O(1)	74·2 (1)
		O*W*–W–O(2)	75·6 (1)
W–O(1)	2·075 (5) (2×)	O*W*–W–O(3)	142·1 (2)
W–O(2)	2·095 (5) (2×)	O(1)–W–O(2)	88·2 (1)
W–O(3)	2·011 (5) (2×)	O(1)–W–O(2)′	84·1 (1)
W–O*W*	2·132 (6)	O(1)–W–O(3)	78·3 (1)
		O(1)–W–O(3)′	129·2 (1)
W′–W–O(3)	46·9 (1)	O(1)–W–O(1)′	148·4 (2)
W′–W–O(1)	83·9 (1)	O(2)–W–O(3)	77·9 (1)
W′–W–O(2)	82·0 (1)	O(2)–W–O(3)′	127·0 (2)
W–O(3)–W′	86·1 (1)	O(2)–W–O(2)′	151·2 (2)
		O(3)–W–O(3)′	75·9 (1)
C(1)–C(2)	1·495 (10)	C(1)–C(2)–O(1)	118·5 (7)
C(2)–O(1)	1·276 (8)	C(1)–C(2)–O(2)	119·6 (6)
C(2)–O(2)	1·282 (8)	O(1)–C(2)–O(2)	121·9 (7)

The W atoms are surrounded by two other W atoms and seven O atoms, one of them being a water oxygen. The oxidation state of W was determined to be +3·9 (Bino *et al.*, 1978) using a $KMnO_4$ titration method. The most important distances and angles are given in Table 2.

Each $[W_3(C_3H_3O_2)_6(H_2O)_3O_2]^{2+}$ group is neighboured by two $CF_3SO_3^-$ ions lying above and below the W triangle on the threefold axis (Fig. 1) with the CF_3 groups pointing toward the cluster. Six other $CF_3SO_3^-$ ions are arranged laterally around the cluster. As a consequence of the $\bar{3}$ symmetry, the CF_3 groups of three of the ions point up and three of them down with respect to the *z* direction. The SO_3 groups of these six

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34870 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond distances* (Å) *and angles* (°) *in the* $CF_3SO_3^-$ *ion*

CS–S	1·736 (23)	S–CS–F	113·8 (1·0)
CS–F	1·349 (11)	F–CS–F′	104·9 (1·2)
S–OS	1·458 (6)	CS–S–OS	102·5 (4)
		OS–S–OS′	115·5 (3)

neighbours have approximately the same height in z as the W atoms of the central cluster. The $[W_3(C_2H_3O_2)_6(H_2O)_3O_2]^{2+}$ group in the lower part of Fig. 1 is shown surrounded by the upper and the six lateral neighbouring $CF_3SO_3^-$ ions.

The $CF_3SO_3^-$ ions are also in special positions. The C–S bonds lie on the threefold axes. Distances and angles within this ion are given in Table 3.

The thermal motion of the $CF_3SO_3^-$ ion is quite large, especially in the z direction and this, when combined the dominant scattering by the W atoms, results in lower precision in the bond distances. They deviate appreciably from those determined for the $CF_3SO_3^-$ ion in other compounds, *e.g.* $H_3O^+CF_3SO_3^-$ (Spencer & Lundgren, 1973), $H_5O_2^+CF_3SO_3^-$ (Delaplane, Lundgren & Olovsson, 1975*a*) and $H_3O^+CF_3SO_3^-.CF_3SO_3H$ (Delaplane, Lundgren & Olovsson, 1975*b*).

In the unstrained molecule, the F and O atoms should adopt a staggered conformation, *i.e.* the F–C–S–O torsional angles should be ±60 or 180°, and in all the above-cited structures containing this ion almost perfect staggered conformations are observed. In the present structure, however, the SO_3 group is rotated relative to the CF_3 group by an angle of 28·3° from the ideal staggered conformation. This is represented in Fig. 3 which shows a projection along the c axis. The deviation from the minimum-energy conformation seems to be a consequence of the attractive effect of hydrogen bonds extending from each of the three OS oxygen atoms to O*W* oxygens of the water molecules of neighbouring $[W_3(C_2H_3O_2)_6(H_2O)_3O_2]^{2+}$ groups. The O–O lengths of these hydrogen bonds are 2·652 (9) Å and the angle OS–O*W*–OS′ is 94·2°. Some of these hydrogen bonds are shown as dashed lines in Fig. 1. The tendency for the CF_3 group to rotate in order to yield the symmetric staggered conformation is inhibited by a repulsive interaction between F and the methyl group $C(1)H_3$ (dotted lines in Figs. 1 and 3). The force exerted by this repulsion results in a slight bending of the acetate groups relative to the tungsten triangle. This becomes evident (Fig. 3) by the fact that O(2)–W is larger than O(1)–W′ and that angles W–W′–O(1) and O(2)–C(2)–C(1) are larger than angles W′–W–O(2) and O(1)–C(2)–C(1). The attractive force between OS and O*W* and the repulsive force between F and C(1) are indicated in Fig. 3 by double arrows. If numerical values for non-bonded interactions were known to a higher precision, the torsional angle in the $CF_3SO_3^-$ ion would allow the estimation of the torsional force constant and the barrier to internal rotation, which cannot be determined as well from IR or Raman spectra since the corresponding mode is inactive for both techniques. Microwave measurements can, in principle, provide useful information in this context, but, because of the large moments of inertia of the CF_3 and SO_3 groups, the lines cannot be resolved at present.

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