

The Structure of Hexakis(tetramethylammonium) Dihydrogendodecatungstate Enneahydrate, $[(\text{CH}_3)_4\text{N}]_6[\text{H}_2\text{W}_{12}\text{O}_{40}]\cdot 9\text{H}_2\text{O}$

BY MASAHIRO ASAMI,* HIKARU ICHIDA AND YUKIYOSHI SASAKI

Department of Chemistry and Research Centre for Spectrochemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113, Japan

(Received 14 June 1983; accepted 15 August 1983)

Abstract. $M_r = 3455.2$, monoclinic, $P2_1$, $a = 13.122$ (2), $b = 21.457$ (4), $c = 13.223$ (1) Å, $\beta = 91.71$ (1)°, $V = 3721$ (1) Å³, $Z = 2$, $D_m = 3.11$, $D_x = 3.09$ Mg m⁻³, Mo K α , $\lambda = 0.71069$ Å, $\mu = 19.7$ mm⁻¹, $F(000) = 1559$, $T = 293$ K, $R = 0.085$ for 6585 independent reflexions. The metadodecatungstate anion consists of four tetrahedrally corner-shared W_3O_{13} units made by edge-sharing WO_6 , and is therefore confirmed to be the Keggin type. The molecule has T_d symmetry and its framework is regarded as a regular cubo-octahedron. The average W–W distance is 3.33 (1) Å within the same W_3O_{13} unit and 3.63 (2) Å otherwise. The W–O bond lengths, formally classified into four types, are 1.71 (4), 1.91 (5), 1.96 (9) and 2.22 (9) Å. The O atoms forming the tetrahedral cavity are 2.95 (6) Å distant from one another, suggesting that the cavity is capable of containing two non-acidic H atoms.

Introduction. Since Souchay (1943) applied various spectroscopic and spectrometric methods to the system $\text{H}^+ - \text{WO}_4^{2-}$, a number of isopolytungstate anions have been revealed. Only for a few species, however, have the structures been determined: paradodecatungstate $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ (Allmann, 1971; d'Amour & Allmann, 1972, 1973; Tsay & Silverton, 1973; Evans & Rollins, 1976; Averbuch-Pouchot, Tordjman, Durif & Guitel, 1979), decatungstate $[\text{W}_{10}\text{O}_{32}]^{4-}$ (Fuchs, Hartl, Schiller & Gerlach, 1976), and hexatungstate $[\text{W}_6\text{O}_{19}]^{2-}$ (Fuchs, Freiwald & Hartl, 1978). The structure of $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ has been reported to be the Keggin (1934) type by X-ray powder patterns (Signer & Gross, 1934) and the presence of two non-labile protons in the central cavity of the molecule has been shown by NMR spectra in D_2O (Pope & Varga, 1966). A novel isolation method for metadodecatungstate was found from aqueous solution in a previously unexpected pH region, and the structure determination of the title crystal was made.

Experimental. 100 ml aqueous solution of $\text{NaWO}_4 \cdot 2\text{H}_2\text{O}$ (10 g), 6 mol dm⁻³ HCl added to pH 4.0–6.5, mixed with solution of $R_4\text{NBr}$ ($R = \text{methyl, ethyl and tert-butyl}$) in less than stoichiometric amount; respective salts isolated in a few days, tetramethylammonium salt well crystallized from mother liquor; comparing Raman spectra of variously conditioned solutions with those reported by Tytko (1973), no dodecatungstate anion detectable even in preparative condition containing $R_4\text{N}^+$ ions; elemental analysis for $\text{C}_{24}\text{H}_{74}\text{N}_6\text{O}_{40} \cdot \text{W}_{12}\cdot 9\text{H}_2\text{O}$: found (calc.), C: 8.16 (8.34), H: 2.33 (2.63); N: 2.44 (2.43), W: 63.41 (63.85) and H_2O : 5.12 (4.69); somewhat efflorescent colourless hexagonal prismatic crystals elongated along a , preliminary lattice constants, crystal class (space group $P2_1$ from extinction rule $0k0 = 2n$) from Weissenberg photographs; D_m by flotation; crystal $0.55 \times 0.40 \times 0.36$ mm, Rigaku automated four-circle diffractometer, graphite monochromator, cell parameters by least squares on 24 independent indices; $\theta - 2\theta$ scan mode, 6959 intensities ($\pm h, +k, +l$; $h_{\text{max}} = 18, k_{\text{max}} = 30, l_{\text{max}} = 18$) measured, absorption correction made (max. 0.16, min. 0.03); three standard reflexions, intensity variation 2%; 6585 independent reflexions ($3.5 < 2\theta \leq 60.0^\circ$) with $|F_o| > 2.5\sigma(|F_o|)$ considered observed and used for structure determination; W atoms located from three-dimensional Patterson maps, remaining atoms by successive difference Fourier syntheses, structure refined by block-diagonal least squares based on F , anisotropic thermal parameters for W atoms; $R = 0.085, R_w = 0.075, w^{-1} = \sigma^2(F_o) + (0.02F_o)^2, S = 2.44$; real parts of anomalous scattering for all atoms from *International Tables for X-ray Crystallography* (1974); calculations carried out with UNICSIII (Sakurai & Kobayashi, 1979) on the HITAC M-200H computer at the Computer Centre of the University of Tokyo; final atomic parameters given in Table 1.†

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38807 (68 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Present address: Research Laboratories, Ashigara, Fuji Photo Film Co. Ltd, Minami-Ashigara, Kanagawa 250-01, Japan.

Table 1. *Positional parameters* ($\times 10^3$; for W $\times 10^4$) and *isotropic thermal parameters* (\AA^2) (B_{eq} : Hamilton, 1959)

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}/B_{\text{iso}}$
W(1)	2866 (2)	3301 (1)	1628 (2)	4.5
W(2)	4105 (2)	3741 (1)	4019 (2)	4.7
W(3)	5337 (2)	4060 (1)	1647 (2)	4.4
W(4)	3752 (2)	2117 (1)	301 (2)	4.0
W(5)	2652 (2)	1857 (1)	2511 (2)	3.9
W(6)	3943 (2)	2281 (1)	4849 (1)	3.6
W(7)	6199 (2)	2998 (1)	4806 (1)	4.0
W(8)	7403 (1)	3281 (1)	2438 (2)	3.9
W(9)	6197 (2)	2887 (1)	256 (2)	3.8
W(10)	6036 (2)	1284 (1)	1178 (2)	4.6
W(11)	4919 (2)	994 (1)	3362 (2)	4.4
W(12)	7180 (2)	1690 (1)	3363 (2)	4.8
O(1) <i>l</i>	186 (4)	378 (2)	133 (3)	7.5 (1-1)
O(2) <i>l</i>	364 (3)	439 (2)	453 (3)	6.0 (0-8)
O(3) <i>l</i>	526 (3)	487 (2)	149 (3)	5.0 (0-7)
O(4) <i>c</i>	404 (3)	374 (2)	135 (3)	5.3 (0-7)
O(5) <i>c</i>	311 (4)	352 (2)	300 (3)	7.4 (1-0)
O(6) <i>e</i>	503 (2)	407 (1)	308 (2)	2.1 (0-4)
O(7) <i>e</i>	301 (6)	293 (4)	36 (6)	5.6 (2-2)
O(8) <i>e</i>	208 (3)	260 (2)	212 (3)	5.0 (0-7)
O(9) <i>e</i>	357 (3)	317 (2)	496 (2)	4.7 (0-7)
O(10) <i>e</i>	559 (4)	380 (2)	496 (3)	7.3 (1-0)
O(11) <i>e</i>	673 (3)	407 (2)	211 (3)	6.1 (0-9)
O(12) <i>e</i>	596 (2)	379 (1)	25 (2)	3.4 (0-5)
O(13) <i>i</i>	380 (2)	235 (1)	189 (2)	3.8 (0-6)
O(14) <i>i</i>	485 (2)	281 (1)	373 (2)	3.4 (0-5)
O(15) <i>i</i>	587 (2)	303 (1)	180 (2)	3.5 (0-5)
O(16) <i>c</i>	477 (3)	272 (2)	6 (3)	4.7 (0-7)
O(17) <i>c</i>	304 (3)	205 (2)	378 (2)	4.7 (0-7)
O(18) <i>c</i>	692 (3)	333 (2)	372 (3)	5.6 (0-8)
O(19) <i>r</i>	330 (3)	190 (2)	-89 (3)	5.5 (0-8)
O(20) <i>e</i>	276 (2)	171 (1)	104 (2)	3.1 (0-5)
O(21) <i>l</i>	158 (3)	146 (2)	269 (3)	6.3 (0-9)
O(22) <i>l</i>	329 (3)	201 (2)	586 (2)	4.7 (0-7)
O(23) <i>e</i>	520 (3)	251 (2)	556 (2)	4.7 (0-7)
O(24) <i>l</i>	706 (3)	314 (2)	581 (3)	5.3 (0-7)
O(25) <i>l</i>	863 (3)	358 (2)	258 (3)	5.7 (0-8)
O(26) <i>e</i>	744 (2)	317 (1)	96 (2)	2.6 (0-4)
O(27) <i>l</i>	659 (3)	291 (2)	-100 (3)	6.3 (0-9)
O(28) <i>c</i>	464 (3)	142 (2)	54 (3)	6.4 (0-9)
O(29) <i>c</i>	361 (3)	115 (2)	272 (3)	5.2 (0-7)
O(30) <i>c</i>	453 (3)	152 (2)	447 (3)	5.4 (0-8)
O(31) <i>c</i>	689 (2)	226 (1)	449 (2)	4.1 (0-6)
O(32) <i>c</i>	765 (3)	239 (2)	259 (3)	6.8 (1-0)
O(33) <i>c</i>	645 (2)	200 (2)	48 (2)	4.3 (0-6)
O(34) <i>i</i>	573 (3)	178 (2)	257 (3)	6.0 (0-9)
O(35) <i>l</i>	635 (3)	74 (2)	29 (3)	5.5 (0-8)
O(36) <i>e</i>	535 (2)	73 (1)	201 (2)	4.2 (0-6)
O(37) <i>l</i>	470 (4)	33 (2)	383 (3)	7.5 (1-1)
O(38) <i>e</i>	639 (3)	103 (2)	386 (3)	5.5 (0-8)
O(39) <i>l</i>	832 (3)	138 (2)	384 (3)	5.7 (0-8)
O(40) <i>e</i>	731 (3)	117 (2)	215 (3)	6.0 (0-8)
O(41)	811 (4)	14 (2)	476 (3)	8.0 (1-1)
O(42)	868 (4)	37 (2)	97 (4)	8.6 (1-2)
O(43)	960 (4)	49 (2)	884 (4)	8.0 (1-1)
O(44)	-4 (4)	68 (3)	333 (4)	9.9 (1-4)
O(45)	3 (4)	148 (2)	725 (4)	8.2 (1-2)
O(46)	229 (4)	168 (2)	740 (4)	8.4 (1-2)
O(47)	763 (4)	363 (2)	754 (4)	8.0 (1-1)
O(48)	20 (4)	426 (3)	748 (4)	9.9 (1-5)
O(49)	21 (4)	435 (2)	239 (4)	8.1 (1-1)
N(1)	215 (4)	0 (2)	45 (4)	6.5 (1-1)
N(2)	223 (4)	9 (3)	526 (4)	6.5 (1-1)
N(3)	624 (4)	118 (2)	729 (3)	3.5 (1-0)
N(4)	976 (5)	222 (3)	4 (5)	8.8 (1-6)
N(5)	31 (4)	286 (2)	485 (4)	6.7 (1-2)
N(6)	384 (4)	386 (2)	768 (4)	6.4 (1-1)
C(1)	311 (5)	7 (3)	84 (4)	5.6 (1-2)
C(2)	152 (6)	21 (4)	114 (5)	7.6 (1-6)
C(3)	206 (7)	33 (4)	-62 (7)	9.4 (2-2)
C(4)	185 (5)	-61 (3)	16 (5)	6.6 (1-4)
C(5)	325 (6)	16 (4)	578 (6)	7.9 (1-7)
C(6)	135 (7)	-10 (4)	589 (7)	9.7 (2-2)
C(7)	208 (5)	71 (3)	478 (4)	5.6 (1-2)
C(8)	218 (7)	-33 (4)	457 (7)	10.2 (2-4)
C(9)	706 (6)	68 (3)	800 (5)	7.2 (1-6)
C(10)	513 (6)	116 (4)	786 (6)	8.6 (1-9)
C(11)	710 (10)	164 (6)	736 (9)	9.4 (3-6)
C(12)	571 (9)	104 (6)	628 (9)	9.1 (3-3)
C(13)	937 (7)	182 (4)	86 (7)	10.6 (2-5)
C(14)	1075 (5)	199 (3)	-40 (5)	6.8 (1-4)
C(15)	895 (7)	241 (4)	-75 (7)	10.1 (2-3)

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}/B_{\text{iso}}$
C(16)	1001 (6)	292 (4)	64 (6)	8.0 (1-8)
C(17)	-78 (6)	313 (4)	504 (6)	8.7 (1-9)
C(18)	66 (8)	319 (5)	395 (7)	9.3 (2-6)
C(19)	90 (9)	304 (5)	569 (8)	9.4 (3-1)
C(20)	33 (8)	211 (5)	467 (8)	9.1 (2-8)
C(21)	474 (5)	388 (3)	718 (5)	7.3 (1-6)
C(22)	394 (5)	421 (3)	877 (5)	6.9 (1-5)
C(23)	302 (8)	413 (5)	675 (8)	9.1 (2-7)
C(24)	351 (7)	330 (4)	807 (7)	9.3 (2-1)

Table 2. *Comparison of observed and reported interatomic distances* (\AA) and *angles* ($^\circ$) in the isopolytungstate ions

	(a)	(b)	(c)	(d)*	(e)†
W-W _{intra}	3.33 (1)	3.29 (2)	3.29 (1)	3.34 (2)	3.315 (8)
W-W _{inter}	3.63 (2)		3.792 (6)	3.75 (3)	3.677 (8)
W-O _l	1.71 (4)	1.69 (3)	1.71 (3)	1.74 (2)	1.69 (2)
W-O _c	1.91 (5)		1.90 (4)	1.91 (9)	1.91 (2)
W-O _e	1.96 (9)	1.92 (4)	1.94 (6)	1.96 (7)	1.97 (2)
W-O _i	2.22 (9)	2.325 (6)	2.31 (3)	2.29 (2)	2.33 (2)
W-O _e -W	116.3 (51)	117.5 (7)	114.3 (14)	118.3 (22)	114.3 (11)
W-O _c -W	145.3 (61)		117.4 (10)	136.5 (56)	151.0 (25)

References: (a) This work; (b) [(C₄H₉)₄N]₂[W₆O₁₉]: Fuchs, Freiwald & Hartl (1978); (c) [(C₄H₉)₃NH]₄[W₁₀O₃₂]: Fuchs, Hartl, Schiller & Gerlach (1976); (d) (NH₄)₁₀[H₂W₁₂O₄₂].10H₂O: Allmann (1971); (e) Rb₄H₈[H₂W₃^{IV}W₉^{VI}O₄₀].~18H₂O: Jeannin, Launay & Seid Sedjadi (1980).

* Averaged W₃O₁₃ moiety only.

† Exclusive of W₃^{IV}O₁₃ moiety.

Discussion. As expected, the [H₂W₁₂O₄₀]⁶⁻ anion has the Keggin structure with four tetrahedrally corner-shared W₃O₁₃ units consisting of three WO₆ octahedra by edge sharings. Fig. 1 shows the anion molecule projected along its pseudo $\bar{4}$ axis. Angles defined by the three W atoms are 60.0 (3) and 90.0 (9)°. Thus, the structure has almost T_d symmetry and its framework is probably a regular cubo-octahedron. As marked with suffixes in Table 1, O atoms are simply classified into four groups: O_l bonded to one W atom; O_c bridging two W atoms in the different units; O_e shared by two W atoms inside each unit; and O_i coordinated to three W atoms and making the tetrahedral cavity. Table 2 lists relevant averaged distances and angles compared to those of isopolytungstate anions comprising W₃O₁₃ moieties. The values agree well, except for the longer W-W distance and W-O_c-W angle which reflect the connexion modes of W₃O₁₃ in individual structures. So far as the W-O bond is concerned, the WO₆ octahedra in W₃O₁₃ may be practically described as (1+4+1) coordination. The distance between O_i atoms, 2.95 (6) Å, is the longest among those of analogous structures previously known; for example 2.66 (2) Å in [SiW₁₂O₄₀]⁴⁻ (Smith, 1971). The cavity has enough capacity to contain two delocalized non-acidic H atoms.

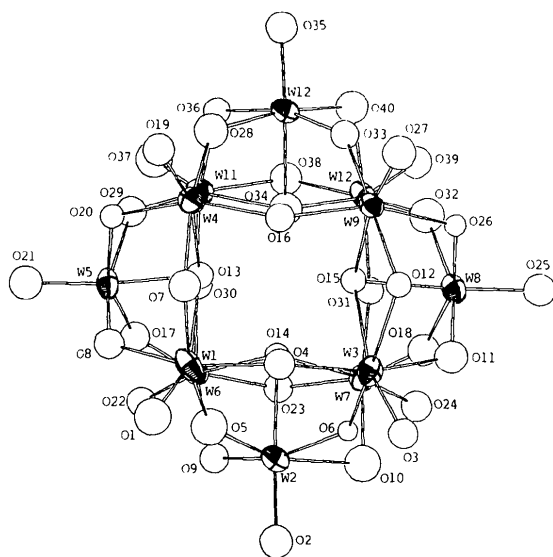


Fig. 1. The structure of the $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ anion. The thermal ellipsoids are scaled to enclose 30% probability.

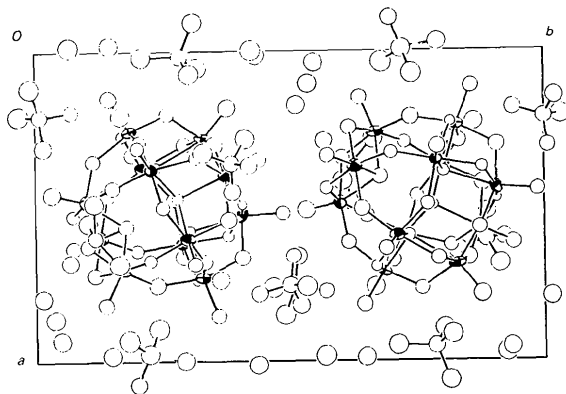


Fig. 2. The crystal structure projected along the c^* axis.

The crystal structure along the c^* axis is represented in Fig. 2. There is a three-dimensional intermolecular network. Only *Op* atoms, one of the three types of peripheral O atoms in the polyanion, are free from any strong interactions within 3.0 Å. There are no direct anion-anion interactions.

The authors thank Drs M. Boyer and J.-P. Launay for valuable discussions.

References

- ALLMANN, R. (1971). *Acta Cryst.* **B27**, 1393-1404.
 D'AMOUR, H. & ALLMANN, R. (1972). *Z. Kristallogr.* **136**, 23-47.
 D'AMOUR, H. & ALLMANN, R. (1973). *Z. Kristallogr.* **138**, 5-18.
 AVERBUCH-POUCHOT, M. T., TORDJMAN, I., DURIF, A. & GUITEL, J. C. (1979). *Acta Cryst.* **B35**, 1675-1677.
 EVANS, H. T. JR & ROLLINS, O. W. (1976). *Acta Cryst.* **B32**, 1565-1567.
 FUCHS, J., FREIHALD, W. & HARTL, H. (1978). *Acta Cryst.* **B34**, 1764-1770.
 FUCHS, J., HARTL, H., SCHILLER, W. & GERLACH, U. (1976). *Acta Cryst.* **B32**, 740-749.
 HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609-610.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 JEANNIN, Y., LAUNAY, J. P. & SEID SEDJADI, M. A. (1980). *Inorg. Chem.* **19**, 2933-2935.
 KEGGIN, J. F. (1934). *Proc. R. Soc. London Ser. A*, **144**, 75-100.
 POPE, M. T. & VARGA, G. M. (1966). *Chem. Commun.* pp. 653-654.
 SAKURAI, T. & KOBAYASHI, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69-77 (in Japanese).
 SIGNER, R. & GROSS, H. (1934). *Helv. Chim. Acta*, **17**, 1076-1080.
 SMITH, P. (1971). *X-ray and Neutron Diffraction Studies on $\text{K}_4\text{SiW}_{12}\text{O}_{40} \cdot 17\text{H}_2\text{O}$* . PhD Thesis, Georgetown Univ.
 SOUCHAY, P. (1943). *Ann. Chim. (Paris)*, **18**, 61-72.
 TSAY, Y. H. & SILVERTON, J. V. (1973). *Z. Kristallogr.* **137**, 256-279.
 TYTKO, K. H. (1973). 15th International Meeting on Solute/Solute/Solvent Interactions, Moscow.

Acta Cryst. (1984), **C40**, 37-39

Structure of *cis*-[3,4-Bis(trifluoromethyl)-2,5-dithiahexane]dichloroplatinum(II), *cis*-[Pt{CH₃SCH(CF₃)CH(CF₃)SCH₃}Cl₂]

BY WILLIAM N. HUNTER, KENNETH W. MUIR AND DAVID W. A. SHARP
 Chemistry Department, Glasgow University, Glasgow G12 8QQ, Scotland

(Received 12 August 1983; accepted 8 September 1983)

Abstract. $M_r = 524.2$, tetragonal, $P4_2/nbc$ (origin at $\bar{1}$), $a = 14.081$ (2), $c = 27.121$ (2) Å, $U = 5377$ Å³, $Z = 16$, $D_x = 2.590$ g cm⁻³; Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 112.9$ cm⁻¹, $F(000) = 3872$, $T = 293$ K; $R = 0.018$ for 1869 unique reflections with

$I \geq 3\sigma(I)$. The sulphur methyl substituents are mutually *syn* and lie on the opposite side of the chelate ring from the trifluoromethyl groups. The molecular configuration in the solid corresponds to that assigned to the predominant isomer in solution by ¹⁹F NMR.

0108-2701/84/010037-03\$01.50

© 1984 International Union of Crystallography