Crystal structure of 1,3-bis(triphenylphosphonium)propane tetrakis(peroxo)tungstate tetrahydrate, $[C_3H_6\{P(C_6H_5)_3\}_2][WO_8] \cdot 4H_2O$

X.-Y. Shi and J.-F. Wei*

Shaanxi Normal University, School of Chemistry and Materials Science, Xi'an, Shaanxi 710062, P. R. China

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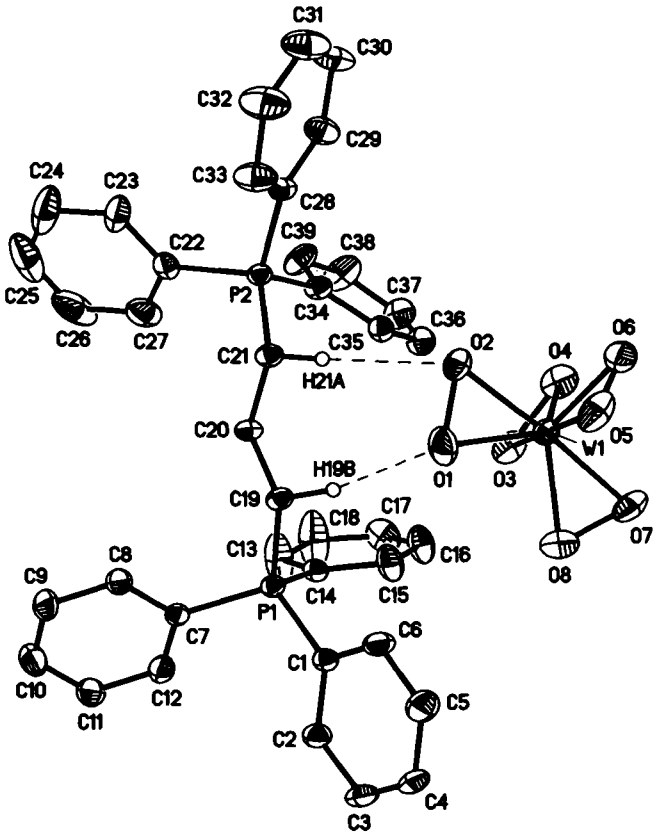

Abstract

$C_{39}H_{44}O_{12}P_2W$, monoclinic, $C12/c1$ (no. 15), $a = 31.985(1)$ Å, $b = 13.3294(5)$ Å, $c = 23.158(1)$ Å, $\beta = 123.975(2)°$, $V = 8188.1$ Å^3, $Z = 8$, $R_{gt}(F) = 0.041$, $wR_{ref}(F^2) = 0.105$, $T = 296$ K.

Source of material

0.165 g (0.5 mmol) of sodium tungstate dihydrate was dissolved in 20 ml water, then 5 ml H_2O_2 (30 %) was added with stirring at room temperature. After stirring for 15 min, a solution of 0.381 g (0.5 mmol) $Ph_3P(CH_2)_3PPh_3Br_2 \cdot 2H_2O$ in 20 ml ethanol was added to the mixture with stirring. The resulting mixture was allowed to stand at low temperature for several days, yellow crystals were precipitated, which were shown to be the title compound.

* Correspondence author (e-mail: weijf@snnu.edu.cn)

Experimental details

Water molecules (1.5 of the formula unit) were found to be disordered and refined at split positions. Hydrogen atoms attached to oxygen atoms could not be localized. The results of the DSC-TG analysis are in exact agreement with the water content obtained by the structure refinement.

Discussion

Peroxotungstates have been proved to be one kind of effective catalysts in the oxidation reaction using hydrogen peroxide as oxidant [1-4]. There is only one report about the structure of the peroxotungstate anion $[W(O_2)_4]^{2-}$ [5].

The title complex formed from $[W(O_2)_4]^{2-}$ and bis-quaternary phosphonium cation has sound stability, therefore, we obtained the crystal structure of the $[W(O_2)_4]^{2-}$ complex. The crystal structure consists of three fundamental units: a bivalent metal anion coordinated by eight oxygen atoms $[W(O_2)_4]^{2-}$, a bivalent cation of bis-quaternary phosphonium and lattice water molecules. In the anion, the peroxo bond lengths of O1—O2, O3—O4, O5—O6 and O7—O8 are 1.456(7) Å, 1.489(8) Å, 1.445(8) Å and 1.490(8) Å, respectively, the bond angles of O1–W1–O2, O4–W1–O3, O8–W1–O7, O6–W1–O5 are 44.2(2)°, 45.3(2)°, 44.9(2)° and 43.5(2)°, respectively, which indicates that the oxygen atoms assume a distorted dodecahedral arrangement around the central tungsten atom. Coordinated oxygen atoms link the anions and cations via intramolecular and intermolecular hydrogen bond including C11–H11···O2, C16–H16···O2, C17–H17···O5, C19–H19A···O4, C19–H19B···O1, C21–H21A···O2, C21–H21B···O3, C21–H21B···O7, C33–H33···O7 and C33–H33···O8. The H···O hydrogen bond distances are ranging from 2.28 Å to 2.59 Å. Except the coordinated oxygen, there are four oxygens coming from water molecules appearing in the structure. Attributing to the different occupation probability, there are four lattice waters in the crystal structure. Aromatic C–H···π stacking interactions exist between C9–H9 and Cg formed from C1 to C6, C32–H32 and Cg formed from C1 to C6. These two C–H···π stacking interactions are all strong indicated by H···Cg distances, which are 2.92 Å and 2.91 Å, respectively.

Table 1. Data collection and handling.

Crystal:	yellow, cube-shaped, size 0.21 x 0.21 x 0.26 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	29.54 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	20719, 7815
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5238
$N(param)_{refined}$:	489
Programs:	SHELXS-97 [6], SHELXL-97 [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(2)	8*f*		0.6845	–0.0110	0.4374	0.068
H(3)	8*f*		0.5970	–0.0130	0.3614	0.081
H(4)	8*f*		0.5479	0.0270	0.4005	0.080
H(5)	8*f*		0.5832	0.0636	0.5144	0.091
H(6)	8*f*		0.6694	0.0593	0.5927	0.073
H(8)	8*f*		0.8052	0.2041	0.6057	0.069
H(9)	8*f*		0.8433	0.2814	0.5574	0.093
H(10)	8*f*		0.8419	0.2109	0.4684	0.097
H(11)	8*f*		0.8017	0.0615	0.4233	0.091
H(12)	8*f*		0.7686	–0.0252	0.4742	0.075
H(13)	8*f*		0.8333	–0.1065	0.5987	0.133
H(15)	8*f*		0.7158	–0.1495	0.6118	0.092
H(16)	8*f*		0.7427	–0.3121	0.6478	0.099
H(17)	8*f*		0.8084	–0.3735	0.6510	0.101
H(18)	8*f*		0.8569	–0.2711	0.6332	0.170
H(19A)	8*f*		0.7635	0.1459	0.6555	0.054
H(19B)	8*f*		0.7491	0.0468	0.6767	0.054
H(20A)	8*f*		0.8475	0.0973	0.7139	0.058
H(20B)	8*f*		0.8347	–0.0108	0.7270	0.058
H(21A)	8*f*		0.8052	0.0724	0.7931	0.053
H(21B)	8*f*		0.8321	0.1692	0.7910	0.053
H(23)	8*f*		0.9626	0.2114	0.9344	0.095
H(24)	8*f*		1.0287	0.2708	0.9316	0.153
H(25)	8*f*		1.0520	0.1988	0.8679	0.187
H(26)	8*f*		1.0051	0.0676	0.7969	0.189
H(27)	8*f*		0.9398	–0.0044	0.8013	0.114
H(29)	8*f*		0.9237	–0.0161	1.0040	0.084
H(30)	8*f*		0.9359	0.0619	1.1035	0.114
H(31)	8*f*		0.9130	0.2248	1.0979	0.125
H(32)	8*f*		0.8815	0.3173	0.9980	0.126
H(33)	8*f*		0.8651	0.2416	0.8980	0.098
H(35)	8*f*		0.8169	–0.0977	0.8174	0.062
H(36)	8*f*		0.8166	–0.2705	0.8103	0.078
H(37)	8*f*		0.8910	–0.3557	0.8602	0.095
H(38)	8*f*		0.9662	–0.2713	0.9216	0.120
H(39)	8*f*		0.9670	–0.0956	0.9237	0.097
O(12A)	8*f*	0.51(2)	0.0404(5)	0.459(1)	0.2011(7)	0.114(6)
O(13A)	4*e*	0.51	0	0.300(2)	¼	0.23(2)
O(12B)	8*f*	0.49	0.0456(9)	0.387(3)	0.223(1)	0.23(1)
O(13B)	8*f*	0.245	0.033(1)	0.162(3)	0.253(2)	0.16(1)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	8*f*	0.182318(8)	0.58485(2)	0.24997(1)	0.0469(2)	0.0404(1)	0.0480(2)	0.0034(1)	0.0254(1)	0.0069(1)
P(1)	8*f*	0.75350(5)	0.01798(9)	0.58269(7)	0.0399(8)	0.0346(6)	0.0349(8)	0.0015(6)	0.0156(7)	0.0009(6)
P(2)	8*f*	0.89104(5)	0.0553(1)	0.86803(8)	0.0387(8)	0.0440(7)	0.0326(8)	0.0007(6)	0.0131(7)	0.0018(6)
C(1)	8*f*	0.6862(2)	0.0239(4)	0.5239(3)	0.045(3)	0.035(3)	0.036(3)	0.002(2)	0.018(3)	0.002(2)
C(2)	8*f*	0.6644(2)	0.0029(4)	0.4537(3)	0.051(4)	0.073(4)	0.043(4)	–0.003(3)	0.024(3)	–0.008(3)
C(3)	8*f*	0.6119(2)	0.0029(5)	0.4081(3)	0.049(4)	0.091(5)	0.036(4)	–0.007(4)	0.008(3)	–0.006(4)
C(4)	8*f*	0.5827(2)	0.0259(5)	0.4314(4)	0.032(3)	0.096(5)	0.046(4)	–0.006(3)	0.006(3)	–0.001(4)
C(5)	8*f*	0.6038(2)	0.0474(6)	0.4991(4)	0.044(4)	0.104(5)	0.067(5)	0.004(4)	0.024(4)	–0.002(5)
C(6)	8*f*	0.6554(2)	0.0456(5)	0.5459(3)	0.044(4)	0.086(4)	0.037(3)	0.001(3)	0.012(3)	–0.002(3)
C(7)	8*f*	0.7834(2)	0.0795(4)	0.5453(3)	0.037(3)	0.044(3)	0.039(3)	0.002(2)	0.013(3)	0.008(3)
C(8)	8*f*	0.8054(2)	0.1733(4)	0.5698(3)	0.068(4)	0.038(3)	0.052(4)	–0.007(3)	0.025(4)	0.002(3)
C(9)	8*f*	0.8275(3)	0.2198(5)	0.5401(4)	0.080(5)	0.059(4)	0.074(5)	–0.019(4)	0.030(5)	0.019(4)
C(10)	8*f*	0.8267(3)	0.1785(6)	0.4876(4)	0.079(5)	0.091(6)	0.071(5)	–0.005(4)	0.040(5)	0.024(5)
C(11)	8*f*	0.8035(3)	0.0886(6)	0.4616(4)	0.054(4)	0.122(7)	0.054(4)	–0.001(4)	0.032(4)	0.011(5)
C(12)	8*f*	0.7829(2)	0.0377(5)	0.4910(3)	0.057(4)	0.074(4)	0.056(4)	–0.011(3)	0.031(4)	–0.007(4)
C(13)	8*f*	0.8138(3)	–0.1475(5)	0.6074(5)	0.118(7)	0.061(4)	0.21(1)	0.033(5)	0.126(8)	0.041(6)
C(14)	8*f*	0.7720(2)	–0.1114(4)	0.6003(3)	0.054(4)	0.034(2)	0.040(3)	0.004(2)	0.022(3)	0.004(2)
C(15)	8*f*	0.7446(3)	–0.1733(5)	0.6155(4)	0.091(5)	0.055(4)	0.102(6)	0.016(4)	0.066(5)	0.027(4)
C(16)	8*f*	0.7604(3)	–0.2709(5)	0.6362(4)	0.104(6)	0.048(4)	0.114(7)	0.007(4)	0.073(6)	0.023(4)
C(17)	8*f*	0.7997(3)	–0.3063(5)	0.6399(4)	0.114(7)	0.048(4)	0.094(6)	0.024(4)	0.060(6)	0.018(4)
C(18)	8*f*	0.8277(4)	–0.2461(6)	0.6278(7)	0.139(8)	0.067(5)	0.28(2)	0.049(5)	0.16(1)	0.063(7)
C(19)	8*f*	0.7704(2)	0.0746(4)	0.6630(3)	0.035(3)	0.049(3)	0.039(3)	0.004(2)	0.012(3)	0.002(3)
C(20)	8*f*	0.8258(2)	0.0596(4)	0.7230(3)	0.041(3)	0.057(3)	0.036(3)	0.001(3)	0.016(3)	–0.002(3)
C(21)	8*f*	0.8331(2)	0.0964(4)	0.7913(3)	0.041(3)	0.045(3)	0.034(3)	0.007(2)	0.013(3)	0.004(3)
C(22)	8*f*	0.9437(2)	0.0996(5)	0.8679(3)	0.038(3)	0.068(4)	0.046(4)	0.013(3)	0.017(3)	0.024(3)
C(23)	8*f*	0.9709(2)	0.1796(5)	0.9063(4)	0.054(4)	0.070(4)	0.098(6)	–0.004(4)	0.033(4)	0.017(4)
C(24)	8*f*	1.0110(4)	0.2153(8)	0.9046(7)	0.074(7)	0.113(7)	0.18(1)	–0.022(5)	0.059(7)	0.039(8)
C(25)	8*f*	1.0244(5)	0.175(1)	0.8672(8)	0.066(7)	0.26(2)	0.13(1)	0.016(9)	0.050(8)	0.11(1)
C(26)	8*f*	0.9970(4)	0.095(1)	0.8263(5)	0.070(7)	0.35(2)	0.070(7)	0.057(9)	0.049(6)	0.08(1)
C(27)	8*f*	0.9567(3)	0.0525(8)	0.8271(4)	0.058(5)	0.161(8)	0.058(5)	0.014(5)	0.028(4)	0.016(5)
C(28)	8*f*	0.8949(2)	0.1069(4)	0.9413(3)	0.040(3)	0.057(3)	0.036(3)	0.000(3)	0.016(3)	–0.005(3)
C(29)	8*f*	0.9151(2)	0.0509(6)	1.0026(4)	0.067(4)	0.082(4)	0.054(4)	0.020(4)	0.029(4)	0.011(4)
C(30)	8*f*	0.9221(3)	0.0977(7)	1.0622(4)	0.092(6)	0.141(8)	0.035(4)	0.030(6)	0.025(4)	0.005(5)
C(31)	8*f*	0.9088(3)	0.1946(8)	1.0588(5)	0.097(6)	0.140(8)	0.066(6)	0.034(6)	0.040(5)	–0.022(6)
C(32)	8*f*	0.8890(4)	0.2498(7)	0.9986(5)	0.143(8)	0.085(6)	0.090(7)	0.029(6)	0.066(7)	–0.010(6)
C(33)	8*f*	0.8805(3)	0.2055(5)	0.9394(4)	0.104(6)	0.069(4)	0.050(4)	0.022(4)	0.030(4)	–0.008(4)
C(34)	8*f*	0.8919(2)	–0.0794(4)	0.8691(3)	0.046(3)	0.042(3)	0.042(3)	0.006(3)	0.013(3)	0.005(3)
C(35)	8*f*	0.8472(2)	–0.1322(4)	0.8369(3)	0.049(4)	0.050(3)	0.054(4)	0.007(3)	0.027(3)	0.009(3)
C(36)	8*f*	0.8470(3)	–0.2357(4)	0.8333(4)	0.069(5)	0.047(3)	0.070(5)	–0.003(3)	0.033(4)	0.002(3)
C(37)	8*f*	0.8912(3)	–0.2861(5)	0.8635(4)	0.086(6)	0.046(3)	0.090(6)	0.001(4)	0.040(5)	0.001(4)
C(38)	8*f*	0.9360(3)	–0.2358(5)	0.8989(5)	0.073(5)	0.062(4)	0.117(7)	0.023(4)	0.023(5)	0.010(5)
C(39)	8*f*	0.9366(3)	–0.1303(5)	0.9009(4)	0.051(4)	0.053(4)	0.096(6)	0.002(3)	0.014(4)	0.000(4)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	8*f*	0.2049(2)	0.4691(3)	0.2248(3)	0.093(4)	0.067(3)	0.099(4)	0.004(3)	0.057(4)	−0.022(3)
O(2)	8*f*	0.2381(2)	0.4901(3)	0.3002(3)	0.063(3)	0.050(2)	0.078(3)	0.012(2)	0.040(3)	0.011(2)
O(3)	8*f*	0.2227(2)	0.6774(3)	0.2354(3)	0.061(3)	0.075(3)	0.092(4)	−0.004(2)	0.042(3)	0.024(3)
O(4)	8*f*	0.2266(2)	0.6948(3)	0.3023(3)	0.086(4)	0.052(3)	0.090(4)	−0.006(2)	0.028(3)	−0.004(3)
O(5)	8*f*	0.1394(2)	0.5011(4)	0.2667(3)	0.064(3)	0.089(4)	0.124(5)	0.009(3)	0.056(3)	0.043(4)
O(6)	8*f*	0.1685(2)	0.5760(4)	0.3212(3)	0.085(4)	0.120(4)	0.076(4)	0.034(3)	0.054(3)	0.034(3)
O(7)	8*f*	0.1240(2)	0.6730(4)	0.1926(3)	0.059(3)	0.082(3)	0.081(3)	0.019(2)	0.031(3)	0.036(3)
O(8)	8*f*	0.1288(2)	0.5944(4)	0.1517(3)	0.079(3)	0.097(4)	0.057(3)	−0.003(3)	0.021(3)	0.001(3)
O(9)	4*e*	0	0.5927(9)	¼	0.113(8)	0.23(1)	0.124(9)	0	0.051(7)	0
O(10)	8*f*	0.0280(3)	0.5302(9)	0.0744(5)	0.084(5)	0.33(1)	0.182(8)	−0.046(6)	0.075(5)	−0.079(9)
O(11)	8*f*	0.0854(2)	0.7073(6)	0.2828(4)	0.108(5)	0.182(7)	0.131(6)	0.046(5)	0.067(4)	0.007(5)

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