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Crystal Structure of Tetrabutylammonium μ-Oxalato-bis(oxodiperoxotungstate)(2-), $[(n\text{-}C_4H_9)_4N]_2[WO(O_2)_2(C_2O_4)WO(O_2)_2]$

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A structure of a novel complex anion $[WO(O_2)_2(C_2O_4)WO(O_2)_2]^{2-}$ which was obtained from the reaction of H_2O_2 with WC was determined by an X-ray diffraction method. The final R-value was 0.084. This is the first example of the anion containing both C_2O_4 and O_2 groups isolated from this reaction. In this anion one $C_2O_4^{2-}$ coordinates to two W atoms forming two chelate rings, and this type of coordination is no precedent for tungsten compounds.

One of the authors has reported that tungsten carbide (WC) dissolves in diluted hydrogen peroxide and gives yellow glassy peroxotungstic acid containing carbon (CWHPA).[1-3] The C/W ratio of CWHPA has been found to be dependent on different preparative methods.[3] $[CW_{12}O_{40}]^{4-}$ has been isolated from the material C/W=1/12, and the Keggin structure of (18-crown 6-ether K)$_4[CW_{12}O_{40}]$ has been determined.[4] We used C/W=1/4 CWHPA prepared by evapolating in a short time after dissolving WC in H_2O_2, and obtained crystals of tetrabutylammonium salts. Later we found that there were at least two different kinds of crystals hard to be distinguished visually. So we carried out X-ray diffraction studies of the both crystals.[5] The mechanism of the reaction of H_2O_2 and WC has not been investigated completely, so we discuss only the structure of these crystals.

2.0 g of CWHPA (C/W=1/4) was dissolved in 3.5 ml of 30% H_2O_2. On addition of 3.0 ml of 45% $(n\text{-}C_4H_9)_4NHSO_4$ solution, pale yellow products were precipitated. The precipitate was recrystallized from suitable dichloromethane-diethyl ether mixed solvent at -10--20 °C. Colorless parallelepiped crystals appeared in 2-3 hours.

One of them was found to be $[(n\text{-}C_4H_9)_4N]_2[W_6O_{19}]$,[6] whose structure has already been reported.[7] This anion has neither peroxo part nor carbon in it. Crystallographic data and the structure shown in Fig. 1 are identical with those in literature 7).

The other one was the title compound. Crystallographic data of this compound are as follows: Formula $[(n\text{-}C_4H_9)_4N]_2[WO(O_2)_2(C_2O_4)WO(O_2)_2]$, FW=1100.64, triclinic, $P\bar{1}$, a=11.222(6), b=11.971(5), c=9.269(4) Å, α=104.48(4), β=112.52(4),

Table 1. The positional and equivalent isotropic thermal parameters

Atom	X	Y	Z	Beq.	Atom	X	Y	Z	Beq.
W	0.3354(1)	0.72151(7)	0.6011(1)	3.81	C(5)	0.853(3)	0.609(2)	0.804(3)	6.28
O(1)	0.294(2)	0.858(1)	0.549(2)	6.19	C(6)	0.672(2)	0.656(2)	0.176(2)	3.89
O(2)	0.500(2)	0.724(1)	0.772(2)	5.32	C(7)	0.767(2)	0.536(2)	0.141(3)	4.70
O(3)	0.397(2)	0.752(2)	0.828(2)	6.35	C(8)	0.681(3)	0.457(2)	0.010(3)	5.43
O(4)	0.199(2)	0.650(2)	0.443(2)	6.21	C(9)	0.779(4)	0.340(2)	-0.036(4)	8.29
O(5)	0.180(2)	0.698(2)	0.601(2)	7.25	C(10)	0.818(2)	0.783(2)	0.194(2)	3.90
O(6)	0.458(2)	0.648(1)	0.464(2)	5.01	C(11)	0.883(3)	0.885(2)	0.276(3)	5.22
O(7)	0.420(1)	0.517(1)	0.633(2)	4.03	C(12)	0.941(4)	0.915(2)	0.167(4)	7.56
N	0.744(2)	0.751(1)	0.282(2)	3.30	C(13)	0.992(3)	1.023(3)	0.234(4)	7.21
C(1)	0.508(2)	0.536(2)	0.448(2)	3.45	C(14)	0.639(2)	0.860(2)	0.321(2)	4.16
C(2)	0.847(2)	0.713(2)	0.436(2)	3.81	C(15)	0.545(3)	0.924(2)	0.182(3)	5.55
C(3)	0.788(2)	0.670(2)	0.533(3)	4.52	C(16)	0.432(3)	1.018(2)	0.232(4)	6.54
C(4)	0.903(3)	0.649(3)	0.694(3)	6.45	C(17)	0.335(4)	0.967(3)	0.241(5)	9.08

γ=72.80(4)°, V=1085.5(9) Å^3, Z=1, Dm=1.70, Dx=1.68 g cm^{-3}, μ(MoKα)=54.67 cm^{-1}. The positional and equivalent isotropic thermal parameters are listed in Table 1.[8] As is visualized in Figs. 2 and 3, this anion has the C_2O_4 part which contains a C-C bond, though there is no C-C bonding in the starting material WC. In this anion one C_2O_4 chelates to two W atoms to form two five-membered rings, and two O_2 groups and one terminal O atom coordinate to each W atom. A crystallographical inversion center is at the middle point of C(1)-C(1)' bond. This type of coordination is not very common, and only analog being $[(CH_3)_2Ga]_2(C_2O_4)$.[9] As an iso and hetero peroxotungstic acid is concerned, five structures were determined,[10-14] and among them, the structure of mononuclear oxalato complex $K_2[WO(O_2)_2(C_2O_4)]$ has been solved.[12] IR spectra of a) $(COOK)_2\cdot H_2O$, b) $K_2[WO(O_2)_2(C_2O_4)]$, and c) $[(n\text{-}C_4H_9)_4N]_2[WO(O_2)_2(C_2O_4)WO(O_2)_2]$ are compared in Fig. 4. Frequencies and shapes of the peaks due to C=O and C-O of the oxalate group in 1750-1600 and 1400-1200 cm^{-1} are quite different among these three compounds. It suggests the difference of coordination in them. Distances and angles are given in Table 2. The distances of W-O(6) and W-O(7) differ 0.31 Å. This is probably caused by the trans-influence of W-O(1). The same tendency was also recognized in $[WO(O_2)_2(C_2O_4)]^{2-}$. But W-O(7) is longer by 0.15 Å than that of

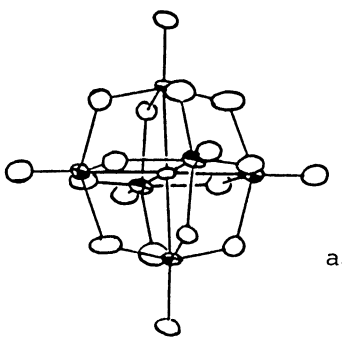

Fig. 1. Structure of $[W_6O_{19}]^{2-}$.

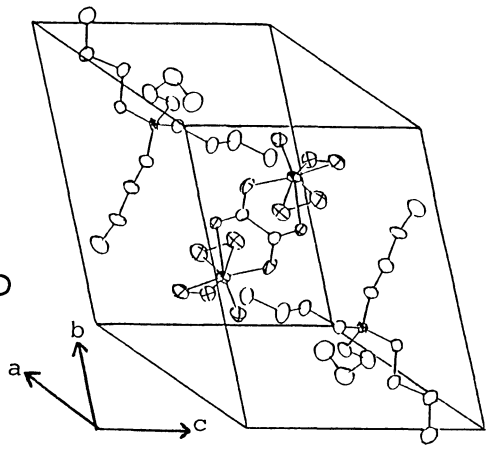

Fig. 2. Crystal structure of $[(n\text{-}C_4H_9)_4N]_2[WO(O_2)_2(C_2O_4)WO(O_2)_2]$.

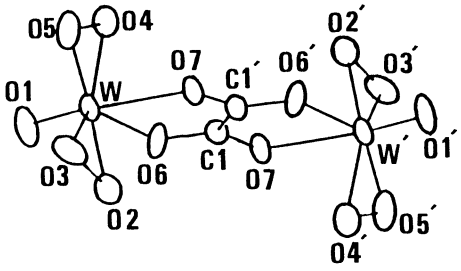

Fig. 3. Structure of $[WO(O_2)_2(C_2O_4)WO(O_2)_2]^{2-}$.

Table 2. Bond distances and angles in $[WO(O_2)_2(C_2O_4)WO(O_2)_2]^{2-}$

Bond distance/Å		Bond angle/°		Bond angle/°	
W-O(1)	1.71(2)	O(1)-W-O(2)	102.5(8)	O(4)-W-O(5)	47.0(9)
W-O(2)	1.92(2)	O(1)-W-O(3)	103.7(8)	O(4)-W-O(6)	90.3(8)
W-O(3)	1.92(2)	O(1)-W-O(4)	101.8(8)	O(4)-W-O(7)	77.9(6)
W-O(4)	1.91(2)	O(1)-W-O(5)	105.2(10)	O(5)-W-O(6)	135.6(7)
W-O(5)	1.84(3)	O(1)-W-O(6)	93.8(9)	O(5)-W-O(7)	84.3(7)
W-O(6)	2.09(2)	O(1)-W-O(7)	166.9(9)	O(6)-W-O(7)	73.2(7)
W-O(7)	2.40(1)	O(2)-W-O(3)	41.7(9)	W-O(2)-O(3)	69.4(10)
O(6)-C(1)	1.29(2)	O(2)-W-O(4)	155.3(7)	W-O(3)-O(2)	68.9(10)
O(7)-C(1)'	1.24(3)	O(2)-W-O(5)	129.0(10)	W-O(4)-O(5)	64.0(11)
C(1)-C(1)'	1.53(4)	O(2)-W-O(6)	83.3(7)	W-O(5)-O(4)	69.1(14)
		O(2)-W-O(7)	77.4(6)	W-O(6)-C(1)	120.2(18)
		O(3)-W-O(4)	134.6(10)	W-O(7)-C(1)'	111.9(15)
		O(3)-W-O(5)	90.0(10)	O(6)-C(1)-C(1)'	117.3(20)
		O(3)-W-O(6)	124.5(7)	O(7)-C(1)'-C(1)	116.8(17)
		O(3)-W-O(7)	85.0(7)	O(6)-C(1)-O(7)'	125.4(25)

the mononuclear complex anion while the length of W-O(6) agrees to the corresponding bond in the bidentate oxalato complex. On the other hand O(7)-C(1)' is 0.05 Å shorter than O(6)-C(1) in contrast to the mononuclear complex in which the length of corresponding bonds are almost equal (1.281 and 1.295 Å). The values of C-O lengths of these compounds are between those of α-anhydrous oxalic acid (1.194 and 1.289 Å).[15] The interior angles of five-membered chelate rings in the oxalatomono- and ditungstates are the same within the errors. The angles of O-C-C in $[WO(O_2)_2(C_2O_4)WO(O_2)_2]^{2-}$ are 116 and 117°, and these are very different from those of anhydrous oxalic acid in α-form (109 and 112°) because of coordination to the W atom. Around the W atom, four O atoms of the peroxo groups, O(2), O(3), O(4), and O(5) lie on the same plane from which the W atom is displaced ca. 0.4 Å towards the terminal O(1) atom. Around the oxalate group, W, O(6), O(6)', and W' are on a plane. C(1)-C(1)' bond crosses it at the center, and the angle between the plane and this bond is about 6°. C(1)' and O(7) are displaced 0.08 and 0.11 Å off this plane to the same side. The oxalate group in this anion is twisted while the C_2O_4 group lies on a plane in oxalic acid.

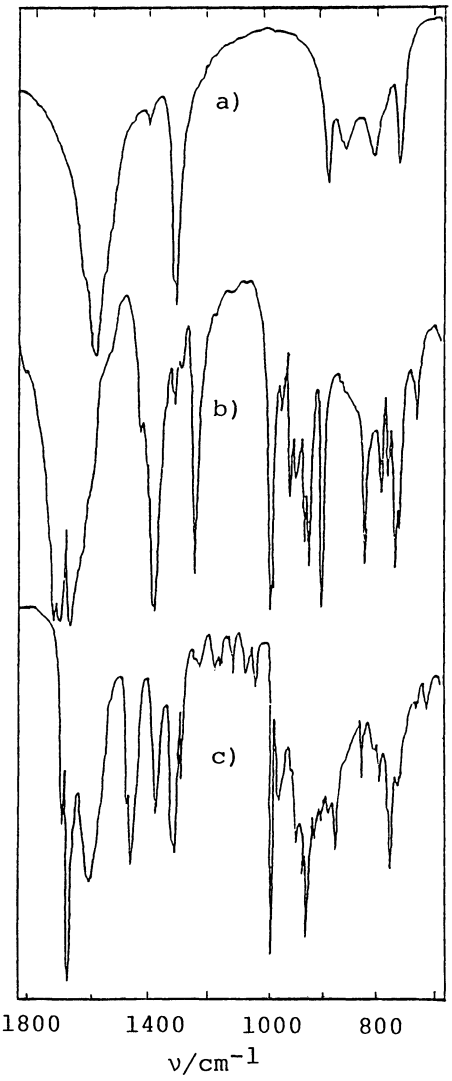

Fig. 4. Comparison of IR spectra of a) $(COOK)_2 \cdot H_2O$, b) $K_2[WO(O_2)_2(C_2O_4)]$, and c) $[(n\text{-}C_4H_9)_4N]_2[WO(O_2)_2(C_2O_4)WO(O_2)_2]$. All of the spectra were measured with KBr disks.

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4) K. Matsumoto, Y. Ozawa, Y. Sasaki, T. Kudo, and H. Okamoto, in preparation.
5) X-Ray diffraction measurement was carried out with RU-1000 X-ray generator and AFC-5R automated four-circle diffractometer in High Intensity X-Ray Facilities, Engineering Research Institute, Faculty of Engineering, The University of Tokyo, at room temperature. Calculations were carried out with UNICS-III program on HITAC M-680H/M-682H computer at the Computer Centre of the University of Tokyo.
6) Crystal dimensions were 0.35 × 0.18 × 0.15 mm^3. Intensities were collected for $4° \leqq 2\theta \leqq 50°$. 5436 reflections with $Fo \geq 2.5\sigma(Fo)$ and $Fo \geq 5.0$ were used for calculation. The positions of W atoms were determined by direct method, and all other atoms except H atoms were located from Fourier syntheses. Formula $[(n\text{-}C_4H_9)_4N]_2[W_6O_{19}]$, FW=1892.03, triclinic, $P\bar{1}$, a=19.623(4), b=12.691(2), c=12.618(3) Å, α=124.31(1), β=101.87(3), γ=93.41(2)°, V=2480(1) $Å^3$, Z=2.
7) J. Fuchs, W. Freiwald, and H. Hartl, Acta Crystallogr., Sect. B, 34, 1764 (1978).
8) Crystal dimensions were 0.38 × 0.24 × 0.17 mm^3. Intensities were collected for $4° \leqq 2\theta \leqq 50°$. 4034 points were collected, and 3361 with $Fo \geq 2.5\sigma(Fo)$ and $Fo \geq 5.0$ were used for calculation. The position of W atom was determined by Patterson function. O, N, and C atoms were located from Fourier syntheses. The positional and thermal parameters were refined by block-diagonal least-squares method. No attempt to locate 36 independent H atoms was made. The final R-value was 0.084.
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