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Keggin-type Dodecatungstocarbonate Anion Containing Carbene as a Hetero Atom

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Abstract

Single-crystal X-ray diffraction study of K^+-18-crown-6 salt of heteropolytungstic acid (CW-HPA) with carbon as a hetero atom has revealed that the compound has a formula $[K(C_{12}H_{24}O_6)]_4(CW_{12}O_{40})\cdot 2H_2O$. The anion has a Keggin structure with a carbon atom in the central tetrahedral cavity made of four oxygen atoms. The carbon atom is bonded to only two oxygen atoms with C–O single bonds (1.5(3) and 1.4(3) Å) and the O–C–O bond angle of 149(11)°. Other two C–O distances are 2.2(2) and 2.1(2) Å and cannot be considered as bondings. Therefore, the carbon atom is a carbene. ESR measurement of the crystals shows that the carbene is singlet in its ground state. The X-ray photoelectron spectrum of the starting material, CW-HPA, shows that the C 1s binding energy of the anion is 283.4 eV, which is comparable to those of graphite and polyethylene and is significantly lower than those of inorganic carbon atoms such as those in CO_2, CO or carbonate anions.

Introduction

Recently the authors have reported the synthesis of a novel heteropolytungstic acid (CW-HPA) with carbon as a hetero atom [1–3]. Infrared, Raman, ^{13}C NMR and TPD (temperature programmed decomposition) spectra indicated that the anion probably has a Keggin structure [4] containing carbon and tungsten at a 1:12 molar ratio. It was also found that the anion contains peroxo groups (–O–O–) and therefore the empirical formula of CW-HPA was $CO_2\cdot 12WO_3\cdot 7H_2O_2\cdot nH_2O$. In the present paper, the crystal structure of the K^+-18-crown-6 salt of the dodecatungstocarbonate anion, $[K(C_{12}H_{24}O_6)]_4(CW_{12}O_{40})\cdot 2H_2O$, which is prepared from the reaction of CW-HPA with $[K(C_{12}H_{24}O_6)]Cl$, is reported. The result shows that the anion is a Keggin structure with a carbon atom in the central tetrahedral cavity made of four oxygen atoms. A surprising feature of the structure is that the carbon is actually carbene having only two C–O single bonds.

Experimental

Crystals of $[K(C_{12}H_{24}O_6)]_4(CW_{12}O_{40})\cdot 2H_2O$ were prepared as follows. One g of CW-HPA [1] was dissolved in 3 ml of H_2O, to which 5 ml of aqueous solution containing 0.1 g of KCl and 0.4 g of 18-crown-6 was added. A pale yellow amorphous precipitate immediately appeared, which was removed by filtration and the filtrate was left at room temperature (r.t.) for slow evaporation. After about a week, yellow prismatic crystals appeared. *Anal.* Calc. for $[K(C_{12}H_{24}O_6)]_4(CW_{12}O_{40})\cdot 2H_2O$: C, 14.33; H, 2.46; W, 53.70. Found: C, 14.16; H, 2.39; W, 53.0%.

A crystal with approximate dimensions of 0.10 X 0.10 X 0.23 mm was subjected to a single-crystal X-ray diffraction study. The intensities were measured on a Rigaku four-circle diffractometer AFC-5R with graphite-monochromatized Mo Kα ($\lambda = 0.7107$ Å) radiation. A total of 1879 independent reflections with $|F_o| \geqslant 3\sigma(|F_o|)$ in the range $3° < 2\theta < 60°$ were used for calculation.

The crystal is tetragonal, space group $I\bar{4}$ with the following cell constants: $a = 19.404(3)$, $c = 14.931(9)$ Å; $V = 5621(4)$ Å^3 for $Z = 2$. All the atoms except hydrogens were located from a Fourier map and the parameters were refined anisotropically to the final R_1 value of 0.078 ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$).

The final atomic coordinates and the temperature parameters expressed as B_{eq} are listed in Table 1.

X-ray photoelectron spectroscopy (XPS) was measured on VG ESCA 3 with Mo Kα.

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TABLE 1. Atomic Parameters[a]

Atom	x	y	z	B_{eq}/B_{iso}
W1	720(1)	1060(1)	1662(2)	336(5)
W2	−1071(1)	720(1)	1640(2)	452(7)
W3	−342(1)	1788(1)	−53(4)	365(6)
K1	161(1)	446(1)	−4(3)	71(5)
Oc	−15(2)	73(2)	67(3)	35(10)
O1t	107(3)	155(2)	259(3)	48(14)
O2t	−158(2)	104(2)	232(3)	28(10)
O3t	−50(2)	264(2)	8(8)	59(15)
O12v	73(2)	14(2)	197(4)	61(16)
O13v	134(2)	95(2)	79(3)	44(12)
O23v	−165(4)	35(2)	83(5)	94(24)
O12e	−19(2)	107(2)	223(3)	52(14)
O13e	35(3)	173(3)	84(4)	81(20)
O23e	−100(2)	166(2)	94(4)	55(15)
Ow1	0(0)	0(0)	370(2)	25(22)
Ok1	210(2)	304(2)	13(5)	45(14)
Ok2	192(2)	384(2)	163(3)	35(10)
Ok3	200(4)	526(4)	157(5)	103(28)
Ok4	172(3)	589(2)	−7(8)	77(18)
Ok5	203(3)	517(3)	−158(4)	66(18)
Ok6	201(3)	357(3)	−160(4)	73(19)
C1	184(6)	272(6)	65(9)	114(47)
C2	217(3)	304(3)	157(4)	36(16)
C3	228(4)	404(4)	219(6)	59(25)
C4	200(5)	465(4)	237(6)	66(28)
C5	166(5)	584(5)	169(7)	75(30)
C6	187(8)	626(7)	81(9)	137(59)
C7	188(5)	623(4)	−70(6)	63(26)
C8	184(5)	601(5)	−129(7)	79(33)
C9	189(4)	498(4)	−236(5)	57(24)
C10	228(5)	433(5)	−233(7)	72(31)
C11	204(4)	282(4)	−122(5)	54(22)
C12	183(6)	275(6)	−66(8)	105(44)
Ci	−21(8)	21(8)	−4(28)	13(25)

[a]Positional parameters are multiplied by 10^4 for W, 10^3 for K, O, C. $B_{eq} = 4/3 \times a(\text{beta})a$ are multiplied by 10^2 for W, 10^1 for K, O, C.

Results and Discussion

The structure of the anion is depicted in Fig. 1. The tungsten–oxygen framework of the anion has a slightly distorted Keggin structure [4] with S_4 symmetry and is located on a $\bar{4}$ axis in the crystal lattice. The atomic distances in the anion are listed in Table 2. Although the starting material CW-HPA has 7 peroxo groups per anion [2, 3], it seems that they are completely lost during the process of crystallization. Either X-ray diffraction analysis, TPD measurement or iodometric titration of the present crystals showed there is no peroxo group in the anion. Other salts such as Ba or Cs salts of CW-HPA also seem to lose some of the peroxide groups on salt precipitation, however, their basic tungsten–oxygen framework is retained [3].

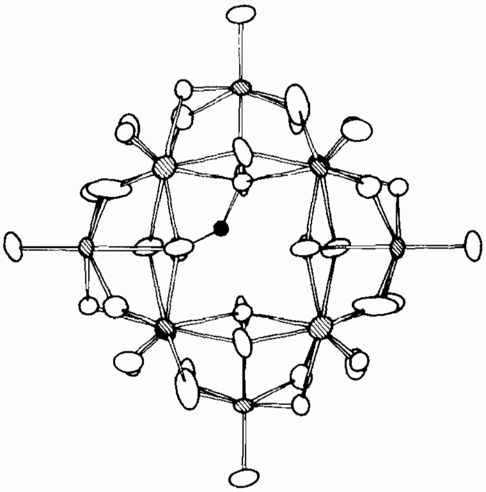

Fig. 1. Structure of $(CW_{12}O_{40})^{4-}$ observed along 4 axis. Carbon atom is shown as a filled circle. Open circles are oxygen atoms and hatched ones are tungsten atoms.

TABLE 2. Interatomic Distances within the Polyanion (Å)

Atom 1	Atom 2	Symmetry[a]	Distance	σ
Ci–Oc		(1)	1.4682	0.3231
Ci–Oc		(4)	1.5463	0.2856
Ci–Oc		(2)	2.2223	0.2449
Ci–Oc		(3)	2.0556	0.2393
W1–W2		(1)	3.5375	0.0028
W1–W3		(1)	3.5776	0.0053
W2–W3		(1)	3.5617	0.0052
W1–W3		(3)	3.4652	0.0051
W2–W1		(2)	3.5206	0.0028
W2–W1		(1)	3.5375	0.0028
W2–W3		(4)	3.4347	0.0051
W1–Oc		(1)	2.3353	0.0414
W1–O1t		(1)	1.8125	0.0455
W1–O12v		(1)	1.8436	0.0405
W1–O13v		(1)	1.7855	0.0422
W1–O12e		(1)	1.9590	0.0401
W1–O13e		(1)	1.9267	0.0589
W2–Oc		(1)	2.3004	0.0414
W2–O2t		(1)	1.5466	0.0416
W2–O12v		(2)	1.8615	0.0407
W2–O23v		(1)	1.8001	0.0715
W2–O12e		(1)	2.0395	0.0401
W2–O23e		(1)	2.1067	0.0449
W3–Oc		(1)	2.3492	0.0403
W3–O3t		(1)	1.6931	0.0411
W3–O13v		(4)	1.8326	0.0413
W3–O23v		(3)	1.7946	0.0577
W3–O13e		(1)	1.8957	0.0591
W3–O23e		(1)	1.9724	0.0519

[a]Symmetry operations: 1: x, y, z; 2: $-x, -y, z$; 3: $-y, x, -z$; 4: $y, -x, -z$.

The carbon hetero atom is located in the central tetrahedral cavity made of four oxygen atoms and is bonded to two oxygen atoms with C–O distances 1.5(3) and 1.4(3) Å, and the O–C–O bond angle is 149(11)°. The other two C–O distances are 2.2(2) and 2.1(2) Å and cannot be considered as bondings. Therefore, the carbon atom is deviated from the center of the tetrahedral cavity formed by the four oxygen atoms. The tetrahedron is somewhat flattened along the $\bar{4}$ crystal axis. The two C–O bond distances (1.5 and 1.4 Å) are larger than those in CO_2 (1.16 Å) [5] and CO_3^{2-} (1.29 Å) [6] and are considered as single bonds (single C–O bond in $(CH_3O)_4C$, 1.409(3) Å) [7]. Considering the limited volume of the central tetrahedral cavity, there is no possibility that protons are also bonded to the carbon atom. The rather unusual bonding mode of the bent CO_2 group suggests that the carbon atom is actually a carbene. In order to clarify the electronic state of the carbon atom, ESR measurement was carried out on a solid sample of the crystals from 5.5 K to r.t., since most carbenes are triplet in their ground states [8]. However, no signal was observed. Magnetic susceptibility measurement at r.t. and 77 K also showed that the compound is diamagnetic (-7.35×10^{-3} at r.t. and -4.29×10^{-1} e.m.u./g at 77 K). These facts suggest that the carbene in the poly anion is singlet at least down to 5.5 K. The existence of carbene with a singlet ground state has been theoretically predicted for many carbenes. According to *ab initio* calculations, the relative ordering of singlet–triplet states depends on the nature of the atoms X bonded to the carbene. Bonding of an atom X, which has a lone pair of π electrons, leads to dative two-electron C-X π-bonding with an empty pπ orbital on the carbene and can stabilize the singlet state substantially [9]. The existence of carbene with a singlet ground state has actually been found in HCF and FCF [10, 11].

Further supporting evidence for carbene is given by X-ray photoelectron spectroscopy of the starting material CW-HPA. The binding energy of C 1s is 283.4 eV which is comparable to that of graphite (284.3 eV) [12] or polyethylene (284.6 eV) [13]. Inorganic tetravalent carbons usually exhibit higher binding energies; CO 290.2 eV [14], CO_2 291.8 eV [15], $NaCO_3$ 289.7 eV [15]. Although there has been no report so far on the C 1s binding energy of carbene, it is reasonable that a carbon atom with a higher electron density like carbene exhibits lower binding energy than tetravalent carbons. The XPS measurement of the K^+-18-crown-6 salt was also attempted but no significant signal was obtained due to charging effect of the compound.

The carbon atom in the anion is statistically oriented to the four sites which are related by the $\bar{4}$ axis present in the center of the tetrahedral cavity with a statistical weight of 1/4. There is no possibility that the anion is actually α-metatungstate, $[(H_2)W_{12}O_{40}]^{6-}$ [12] and the electron peak ascribed to carbon is actually a ghost resulting from disorder orientation of the anion, since the latter is colorless whereas the present anion is yellow.

It should be mentioned that the basic tungsten–oxygen framework is distinctly distorted, compared with those of other Keggin-type anions so far reported. Table 3 summarizes corresponding bond distances in several Keggin anions with various hetero atoms and Fig. 2 shows oxygen classifications according to their bonding modes. From Table 3 it is evident that the distance $W–O_v$ in the present anion is significantly shorter than those in the other three anions. As a result of this shortening, $W–W_{inter}$ distances in the present anion are also shorter than those

TABLE 3. Comparison of Average Bond Distances (Å) within $(XW_{12}O_{40})^{n-}$ Keggin Anions[a]

X	C	H_2	Si	P	B
Anion Symmetry	S_4	*Td*	*Td*	*Td*	*Td*
$W–O_t$	1.67(5)	1.71(4)	1.74(6)	1.70(1)	1.69(8)
$W–O_e$	2.01(7)	1.96(9)	1.92(7)	1.92(2)	1.92(8)
$W–O_v$	1.80(7)	1.91(5)	1.91(4)	1.90(1)	1.89(7)
$W–O_c$	2.34(4)	2.22(9)	2.33(6)	2.44(1)	2.40(11)
$X–O_c$	1.4(3) 1.5(3)		1.66(13)	1.53(1)	1.48(8)
$W–W_{intra}$[b]	3.53(3)	3.33(1)	3.35(2)	3.43(2)	3.31(1)
$W–W_{inter}$[c]	3.50(3)	3.63(1)	3.70(1)	3.68(1)	3.65(1)
$O_c–O_c$	2.88(4) 2.77(4)	2.96(9)	2.70(6)	2.49(1)	2.41(13)
Reference	present work	16	17	18	19

[a] Oxygen classifications are those shown in Fig. 2. [b] Average W–W distance within W_3O_{13} unit of Keggin structure. [c] Average W–W distance between two adjacent W_3O_{13} units of Keggin structure.

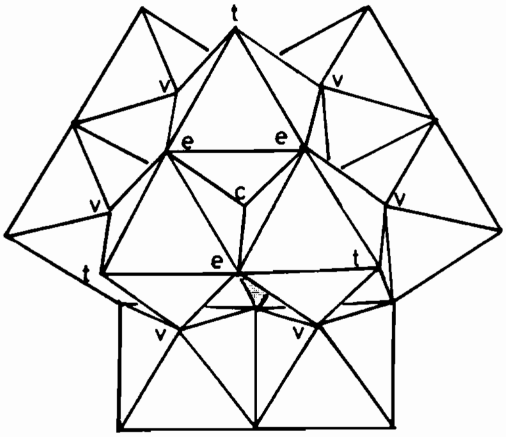

Fig. 2. Keggin structure and oxygen classifications based on their bonding modes. Each WO_6 octahedron is shown as polyhedral model.

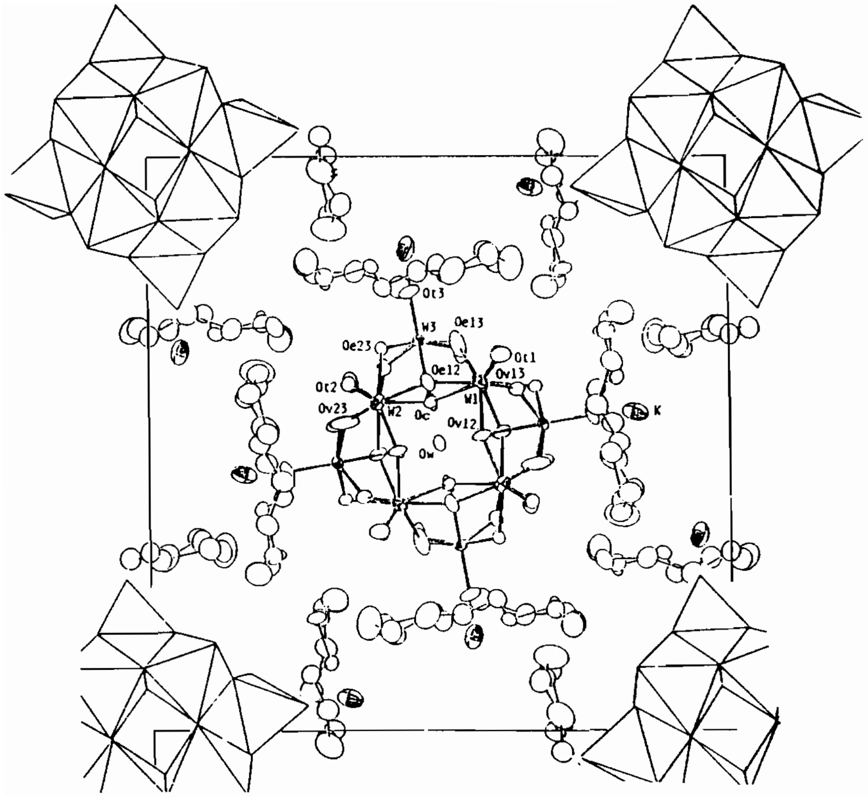

Fig. 3. Crystal structure of $[K(C_{12}H_{24}O_6)]_4[CW_{12}O_{40}]\cdot 2H_2O$ (projected along *c* axis).

of other anions. On the contrary, $W{-}W_{intra}$ distances are larger than those of the other three anions and, accordingly, $W{-}W_{intra}$ and $W{-}W_{inter}$ distances are nearly equal to one another in the present anion, the difference being only 0.03 Å on average. This is in remarkable contrast to other anions, since $W{-}W_{inter}$ distances are always significantly larger than $W{-}W_{intra}$ ones in other anions. It should be mentioned here that the rather unusual W–W distances and tungsten–oxygen framework are not the result of seeing the anion at average orientation of actually four different orientations, since the disordered orientation related by $\bar{4}$ symmetry does not affect these distances. It is shown in Table 3 that the $O_c{-}O_c$ distance in the central tetrahedral cavity is closely related to the atomic radius of the hetero atom and the distance increases with increasing radius of the hetero atom. It is therefore rational that the $O_c{-}O_c$ distance in the present anion is between those of H_2- and Si-dodecatungstate.

The crystal packing of the anions and cations is shown in Fig. 3. The K^+ ion is located 0.68 Å above the mean square plane formed by six crown-ether oxygen atoms. All the bonding distances in the crown ether and the coordination distances around the potassium atom are normal. The present study shows for the first time the preparation and crystal structure of Keggin-structure $CW_{12}O_{40}{}^{4-}$ anion. This is the first example of a carbon atom incorporated into the Keggin structure.

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