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Oxalato Complexes Directly Formed by the Reaction of Interstitial Carbides with Hydrogen Peroxide

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Abstract

It is well known that ionic carbides such as CaC_2, Al_4C_3 etc. generate hydrocarbons on hydrolysis with water or acids, whereas interstitial carbides such as WC, TiC etc., in which the carbon atoms occupy interstitial positions of the metal lattice, are chemically inert. We found, however, that the latter carbides are dissolved in hydrogen peroxide aqueous solutions, generally to give oxalato complexes of W(VI) etc. This fact means that the carbon–carbon bonding is formed by a simple inorganic reaction; for the distance between carbon atoms in such carbides is far longer (about 3 Å) than the usual single bonding distance (1.5 Å). Oxalic acid can easily be isolated from the complexes as $CaC_2O_4 \cdot 2.5H_2O$. Therefore, this finding provides a new path for the total synthesis of organic compounds.

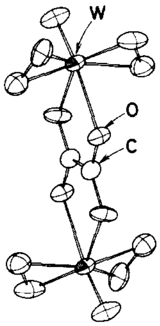

Fig. 1. Structure of $[WO(O_2)_2(C_2O_4)WO(O_2)_2]^{2-}$ determined by the single crystal X-ray analysis of its $(n\text{-}C_4H_9)_4N$ salt. Two W atoms coordinate to $(C_2O_4)^{2-}$ forming two five-membered rings, and the crystallographic inversion center is at the midlle of two carbon atoms. This anion is not identical with that in CW-HPA (the starting material) (see text).

Introduction

One of the present authors reported that tungsten carbide (WC) is dissolved with hydrogen peroxide aqueous solutions to give a new type of polytungstic acid incorporated with carbon as a heteroatom [1]. This heteropolyacid (CW-HPA) is obtained as an amorphous material with a typical empirical formula of $x\mathrm{CO_2}\cdot 12\mathrm{WO_3}\cdot 7\mathrm{H_2O_2}\cdot 25\mathrm{H_2O}$ ($x = 1$–3) [1–3]. In these earlier studies, it was believed that the carbon heteroatoms were in the form of CO_3 according to data from the ^{13}C NMR or infrared and Raman spectroscopies.

Recently, however, it was revealed by our single crystal X-ray analysis that one of the salt crystals precipitated simultaneously from a H_2O_2/H_2O solution of CW-HPA and $(n\text{-}Bu_4N)HSO_4$ is a μ-oxalato complex of W(VI) as shown in Fig. 1 [4]. This anion is not identical with that of CW-HPA because neither their carbon/tungsten ratios (see Table II below) nor peroxide/tungsten ratios (about 0.6 for CW-HPA [2]) agree with each other. Nevertheless, the fact suggests that carbon atoms in CW-HPA exist as a form of oxalato ligand. Shortly after this finding, we actually succeeded in isolating 80% of the carbon in CW-HPA as $CaC_2O_4 \cdot 2.5H_2O$ [5]. The infrared spectrum of CW-HPA can be more satisfactorily explained if it is considered that the carbon atoms form themselves into C_2O_4 ligands. The observed ^{13}C NMR shift (166.1 ppm from TMS standard) is still consistent. It is, therefore, definitive that CW-HPA is an oxalato complex of W(VI).

It would be interesting to know whether such oxalato complex formation is unique to WC, or common other carbides. In this report, we describe the results of investigations undertaken from such a point of view.

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TABLE I. Some Characters of Carbides Used in the Present Study

Carbide	Purity[a] (%)	Free carbon content[a] (%)	Particle size[a] (μm)	Lattice constant[b] (Å)	Crystal type[b]	C–C distance[b] (Å)
WC	99.9	0.04	0.92	$a_0 = 2.91, c_0 = 2.84$	α-WC	2.84
Mo_2C	99.9	na	2 ~ 3	$a_0 = 3.00, c_0 = 4.74$	β-W_2C	2.37
TiC	99.0	na	1	4.32	NaCl	3.05
ZrC	na[c]	0.12	1.8	4.70	NaCl	3.32
VC	na	0.04	1.4	4.17	NaCl	2.95
NbC	99.5	0.01	10	4.48	NaCl	3.17
TaC	99.5	0.14	1 ~ 2	4.46	NaCl	3.15
Cr_3C_2	99.0	na	5	$a_0 = 5.54, b_0 = 2.83, c_0 = 11.5$	Cr_3C_2	1.64

[a]According to the manufacturer's analytical values. [b]Based on our observations. [c]na = not available.

TABLE II. Color, Yield and Elemental Analysis for CM-HPA

Specimen	Color		Yield (g)	Analysis (weight %)				C/M (mole ratio)
	solution	solid		M	C	H	O	
CW-HPA	yellow	yellow	15	60.3	0.970	1.74	37.0	0.25
CMo-HPA	orange	orange	13	43.0	0.986	2.15	54.0	0.18
CTi-HPA	orange	brown	1.5	18.8	16.7	2.64	61.9	3.54
CZr-HPA	yellow	brown	0.1	38.0	5.04	2.01	55.0	1.0
CV-HPA	green	black	1.5	44.0	2.22	1.67	52.0	0.21
CNb-HPA	yellow	yellow	0.2	45.0	9.11	1.76	44.0	1.6
CTa-HPA	yellow	yellow	0.1	55.2	5.56	1.67	37.6	1.52
CCr-HPA	yellow	yellow	0.1	21.0	3.26	2.31	74.0	0.67

[a]Yield means grams of CM-HPA obtained from 0.06 mol of M in the starting carbide. [b]The value C/M represents the molar ratio of carbon to M in CM-HPA.

Experimental

The specimen preparation procedure was basically similar to that reported for CW-HPA [2]. Commercial carbides, listed in Table I together with their analytical data, were dissolved in 15% H_2O_2 aqueous solution. Vigorous gas evolution was observed for WC, Mo_2C, TiC, VC and NbC without being heated from outside. For ZrC, TaC and Cr_3C_2, however, heating was needed to initiate the reaction. After the gas evolution terminated, undissolved residual carbide (and gel phase generated for TiC, NbC and TaC) was filtered off using 0.45 μm filter paper. Every solution thus obtained was clear and acidic. After decomposing excess H_2O_2 with a platinized Pt net, the solution was dried under an air stream at room temperature. Non-crystalline material thus obtained was used as a specimen, denoted by CM-HPA where M stands for metal element in the starting carbide.

Contents of carbon and hydrogen were determined using a gas chromatographic CHN analyzer (Hitachi 026-type). The content of M (metal) was determined from the weight of oxide (WO_3 etc.) given by heating CM-HPA at 750 °C (600 °C for CMo-HPA) in air. The phase of each oxide was checked by X-ray diffraction. The contents of oxygen were calculated as the residual.

Infrared spectra for solid samples were recorded using a conventional KBr technique. For solution samples, spectra were recorded by sandwiching them between polished Si wafers (type: FZ-P, thickness: 1 mm, conductivity: 500–1000 cm, crystallographic orientation: (110)).

Results and Discussion

The elemental analysis results for each CM-HPA are summarized in Table II together with the yield (from 0.06 mol of M in the starting carbide) and color. Every CM-HPA contains carbon as a major constituent, the ratio of carbon to metal (C/M) ranging from 0.18 to 3.5. The analytical values of C/M for separately prepared specimens of the same CM-HPA lie in the range 0.23–0.25, 0.18–0.19 and 3.4–3.5 for M = W, V and Ti, respectively, indicating good synthetic reproducibilities. It should be noted

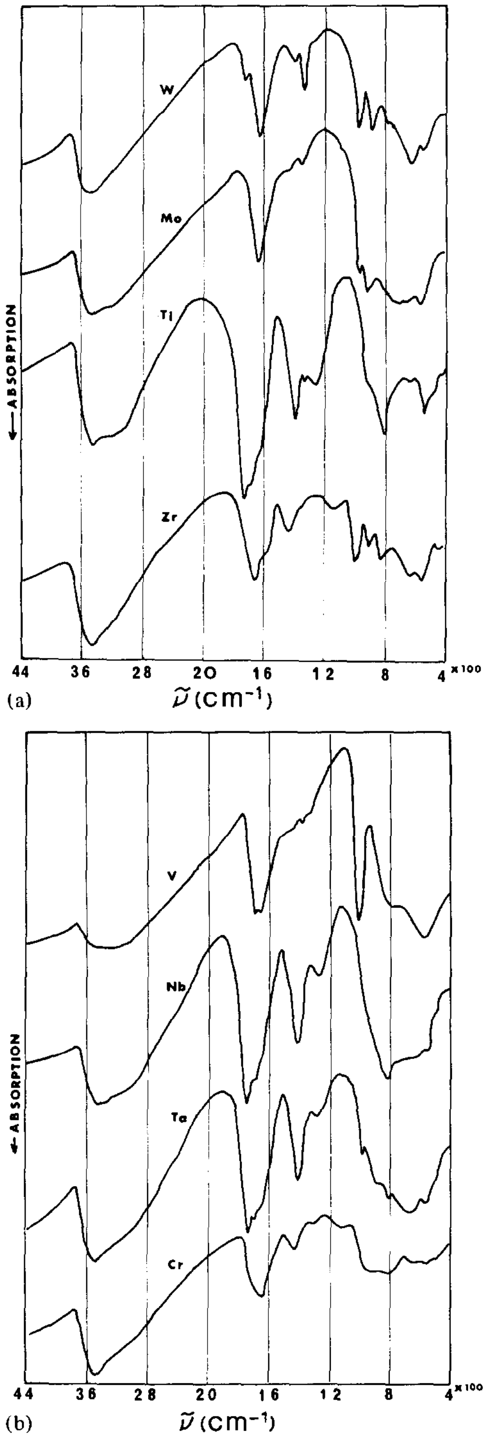
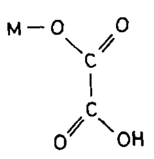


Fig. 2. Infrared spectra of (CM-HPA: (a) for M = W, Mo, Ti and Zr; (b) for M = V, Nb, Ta and Cr. The spectra were recorded using a conventional KBr pellet technique. Bands between 1200 and 1800 cm^{-1} are due to the vibrations of oxalato ligands.

that the C/M ratios in CTi-, CNb- and CTa-HPA are greater than those of starting carbides (*i.e.* 1.0). This is probably due to the disproportionation of polyanion into a carbon-free (or lean) gel phase and carbon-rich soluble species; for gel formation occurred in parallel with dissolution of carbide in these three cases.

Infrared spectra of CM-HPA are shown in Fig. 2. Absorption bands between 1200 and 1800 cm^{-1} may be due to vibrations of the oxalato ligand(s) (Ox), though the wave number region near 1630 cm^{-1} is overlapped with a vibration of water molecules in the compounds. Bands below 1000 cm^{-1} are due mostly to the vibrations of a metal–oxygen framework of polyanions. Strong and broad bands near 3400 cm^{-1} region are attributed to OH stretching vibrations. As for CW-HPA, we estimated [5] that it contains two types of Ox ligands (bidentate[III] and tetradentate[IV]), referring to infrared band classification in terms of the Ox coordination type reported for amminecobalt(III) complexes [6, 7].



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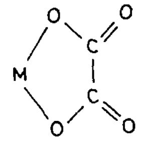

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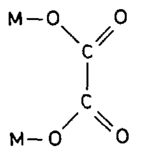

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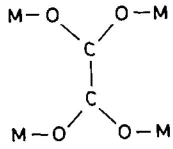

IV

To ensure this, we investigated the complexation of W-IPA, an 'iso'-version acid of CW-HPA (synthesized by the direct reaction of metallic W instead of WC with H_2O_2 [2]), with free oxalate $C_2O_4^{2-}$. Infrared spectra of solutions in the $C_2O_4^{2-}$/W-IPA system are shown in Fig. 3. Spectrum c given by a solution with C/W = 0.25 (*i.e.* C_2O_4/W = 1/8) is basically identical with that of CW-HPA with the same C/W ratio in Fig. 2, indicating that CW-HPA and the 1:8 complex in the solution are based on the same heteropolyanion(s). In spectrum b for a complex in which C/W = 0.083 (= 1/12), a band at 1400 cm^{-1} is much weaker than that at 1340 cm^{-1}. This indicates that its Ox ligands are mostly tetradentate (**IV**). As the C/W ratio is increased, bands around 1400 and 1260 cm^{-1} become stronger with a simultaneous weakening of the band at 1340 cm^{-1}. In the complex of C/W = 1.0 (spectrum e), almost all Ox ligands are considered to take a bidentate coordination (**III**). A strong band at 1700 cm^{-1} seen in spectra f and g (C/W = 2.0 and 4.0, respectively) indicates the existence of a chelating bidentate ligand (**II**). A shoulder band at 1770 cm^{-1}

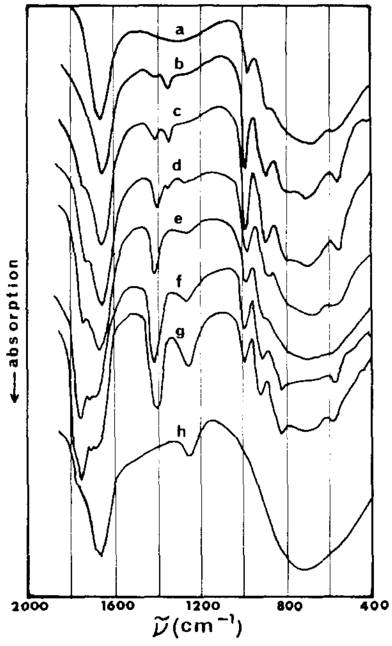

Fig. 3. Infrared spectra of solutions in the system of $C_2O_4^{2-}$/W-IPA (carbon-free iso-acid corresponding to CW-HPA). The mole ratios of carbon to tungsten in the solution are: (a) 0 (W-IPA), (b) 0.083, (c) 0.25, (d) 0.50, (e) 1.0, (f) 2.0, (g) 4.0 and (h) (almost saturated solution of $H_2C_2O_4 \cdot 2H_2O$). Sample solutions were prepared by dissolving appropriately weighed W-IPA into $H_2C_2O_4 \cdot 2H_2O$ aqueous solution.

TABLE III. C–O Stretching Vibrations (cm^{-1}) of CM-HPAs and Classification of their Oxalato Ligands in Terms of Coordination Types

M	Phase	ν(C–O) (cm^{-1})				Type[a]
W	solid	1730	1630	1400	1275	III
			1630	1340		IV
	solution	1730	1650	1400	1260	III
			1650	1345		IV
Mo	solid	1720	1630	1410	nd[b]	III
			1630	1335		IV
Ti	solid	1730	1700	1410	1260	II
			1630	1340		IV
	solution	1720	1660	1410	1260	II
Zr	solid	1650	1590	1330	nd	V
		1720	1650	1420	1240	III
V	solid	1690	1640	1420	1320	III
			1640	1360		IV
Nb	solid	1730	1650	1410	1260	III
		1700	1650	1410	1260	II
Ta	solid	1735	1650	1400	1250	III
		1695	1650	1400	1250	II
Cr	solid	1720	1640	1420	1290	III

[a] Type II, III and IV represent the chelating bidentate, the bidentate and the tetradentate oxalato ligands, respectively (see text). Type V means a ligand in a tridentate coordination. [b] nd = not detected.

seen in spectrum g is probably due to co-existing unidentate ligands (**I**). A general tendency observed for oxalato-ammine cobalt complexes [6] that the coordination type of Ox changes in the direction of **IV** → **I** with an increase of the Ox (or C)/metal ratios holds also in this system.

Examining spectra in Fig. 2 in the light of the above discussions, we may determine the coordination types of Ox in each CM-HPA as shown in Table III. As expected from the general tendency, Ox ligands in CM-HPA (M = Ti, Nb and Ta) with a large C/M ratio take, at least partly, the coordination type **II**. For CZr- and CCr-HPA with intermediate C/W ratios, the coordination type is mainly **III**, though the former contains a tridentate Ox (denoted by **V** though not illustrated). Tetradentate ligands (**IV**) always exist in the group of CM-HPA with small C/W ratios. Thus, it is obvious that every CM-HPA investigated here has carbon atoms as oxalato ligand(s).

Now we may claim that interstitial carbides generally give oxalato complexes on reacting with hydrogen peroxide*). This statement means, at the same time, that the carbon–carbon bonding is formed directly by the reaction of simple inorganic compounds. It should be emphasized that the present C–C bond formations take place during the reactions, because the C–C distance in each starting carbide (see Table I) is almost or more than twice the single bond distance except for Cr_3C_2 (which has a zigzag chain of carbons with the separation of 1.64 Å). In contrast with this, the C–C triple bonding in acetylene generated from CaC_2 on hydrolysis exists originally in the carbide; for the C–C distance in CaC_2 is 1.19 Å, being the same as that of C_2H_2. In addition, it is noteworthy that carbon is oxidized from almost zero to +3 when oxalate is formed from interstitial carbides. (It has been confirmed by ESCA study that carbon in WC is in the nearly elemental state [8]).

Oxalic acid was the first organic compound totally synthesized from dicyan by Woeler in 1824, four years before his historically famous urea synthesis, though it was believed to be an inorganic acid based on C_2O_3 at that time. However, dicyan is an intermediate compound between the inorganic and the organic one, because it has the C–C bonding in itself. The present synthesis of oxalic acid (abundantly contained in most plants) from carbides might

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*We dissolved LaC_2, an ionic carbide iso-structural with CaC_2, in a 15% H_2O_2 solution. However, no evidences indicating formation of the C_2O_4 group was obtained from the resultants (either in the solution or the solid phase).

provide the chemical evolution theories with new possibilities.

Investigations concerning the reaction mechanism are under way. Our recent finding** that corresponding nitrides (*i.e.* WN, Mo_2N and TiN) give nitro ($M\text{-}NO_2$) or nitrito(M-ONO) complexes when dissolved in an H_2O_2 solution will be helpful in solving the mechanism.

**The synthetic procedure is almost the same as that of the present oxalato complexes. The complex of W is white, but that of Mo or Ti is yellow. All complexes exhibit strong infrared bands near 1400 cm^{-1}. *Anal.* (weight %) for each complex: W, 57.4; N, 4.87; H, 2.15; O, 35.6 (N/W = 1.12 in mole ratio). Mo, 52.9; N, 4.56; H, 2.14; O, 40.4 (N/Mo = 0.59). Ti, 21.3; N, 16.2; H, 3.39; O, 58.3 (N/Ti = 2.61). Details will soon be reported elsewhere.

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