Notes

O-Acylation of Keggin-Type Heteropolyanions Containing Zinc(II) or Copper(II)

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Received April 23, 1991

An interesting, new development in the chemistry of heteropolyanions is the synthesis of heteropolyanions attached with organic groups.[1] Since the surface of a heteropolyanion resembles those of some metal oxides extensively used as heterogeneous catalysts for various organic reactions, organic derivatives of heteropolyanions may be useful in clarifying the mechanism of catalysis by metal oxides.

Most organic derivatives of the Keggin-type[2] heteropolyanions involve replacement of peripheral metal oxygen groups by other metal-ligand groups.[3-5] A rare type involves organic groups attached to the surface oxygen atoms of heteropolyanions.[6,7] We have found that an acyl group is attached easily to the surface oxygen atoms of Keggin- and Dawson-type heteropolyanions containing two adjacent vanadium atoms.[7] This reaction can be explained in the following way. When a hexavalent tungsten atom in a heteropolyanion is replaced by a pentavalent vanadium atom, the bridging oxygen atoms bonded to the vanadium atom get extra negative charges.[8] When there are two adjacent vanadium atoms, the bridging oxygen atom between them becomes so basic that it now reacts with acetic anhydride by an acid-catalyzed nucleophilic substitution.[7]

It occurred to us that replacing a $W^{VI}=O$ group in a Keggin anion by a divalent metal ion would make the adjacent bridging oxygen atoms sufficiently basic to be acylated. This paper reports our study on acylation of $[SiW_{11}O_{39}M(H_2O)]^{6-}$ ($M=Zn^{2+}$ or Cu^{2+}).

Experimental

Synthesis. α-$K_6[SiW_{11}O_{39}M(H_2O)] \cdot xH_2O$ ($M=Zn^{2+}$ or Cu^{2+}) was prepared according to the methods of Tézé and Hervé,[9,10] and was confirmed by its IR spectra (These compounds are denoted as SiZn and SiCu below).

Acylation. Two grams of SiM (M=Zn or Cu) was mixed with 40 m*l* of acetic anhydride (SiM does not dissolve in acetic anhydride.) Two drops of 85% phosphoric acid was added to the mixture, and the mixture was stirred for 10-12 h at 60℃. (Most of SiM had dissolved by this time.) The remaining solid was removed by filtration, and 1 g of tetrabutylammonium bromide was added to the filtrate. The solution was stirred for 10 minutes and filtered again. A solid was precipitated by addition of diethyl ether, washed with diethyl ether several times, and recrystallized in acetonitrile.[15] We have tried to grow single crystals without success. Anal. Calcd for $(TBA)_{3.3}[SiW_{11}O_{39}Zn(H_2O)(CH_3CO)_{2.7}] \cdot H_2O$: C, 18.94; H, 3.58; N, 1.25. Found: C, 18.97; H, 3.59; N, 1.21. Calcd for $(TBA)_2[SiW_{11}O_{39}Cu(H_2O)(CH_3CO)_4] \cdot 0.5(CH_3CN) \cdot H_2O$: C, 14.3; H, 2.67; N, 1.09. Found: C, 13.98; H, 2.64; N, 1.17.

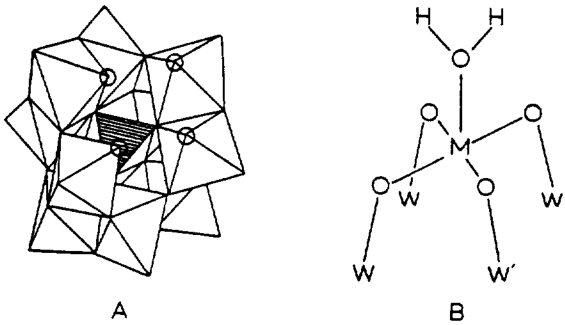


Figure 1. (A) Polyhedral representation of the lacunary anion $[SiW_{11}O_{39}]^{8-}$. Circles represent the positions of four oxygen atoms which coordinate to such divalent ions as Zn^{2+} and Cu^{2+}. (B) When Zn^{2+} forms a complex with $[SiW_{11}O_{39}]^{8-}$, four bridging oxygen atoms between the zinc atom and tungsten atoms become potential sites for acylation.

Hydrolysis. The acylated product of SiZn was dissolved in dimethyl sulfoxide. A small amount of water was added, and the solution was stirred for 1 h. A solid was precipitated by addition of a large amount of water, washed with water, and dried.

Reaction with Aniline. The acylated product of SiZn (3 g) was mixed with 50 m*l* of methylene chloride.(The solid does not dissolve in methylene chloride.) 0.4 m*l* of aniline was added, and the mixture was stirred for 6 h. The undissolved solid was separated from the solution by filtration. When the filtrate was evaporated at room temperature, white crystals formed. The IR and NMR spectra of this product agreed with those of acetanilide.

Measurements. IR spectra were obtained from KBr discs on a Shimadzu IR-400 spectrometer. ^1H and ^{13}C-NMR spectra (in deuterated dimethyl sulfoxide with tetramethylsilane internal standard) were recorded on a Bruker FT NMR (AC-300P). EPR spectra were measured using a Bruker EPR spectrometer (ER 200E) operating at 9.7 GHz.

Results and Discussion

Structural Consideration. The structure[11] of the lacunary ion $[SiW_{11}O_{39}]^{8-}$ is shown in Figure 1A. This anion, functioning as a multidentate ligand, can form complexes with various metal ions. The Zn^{2+} and Cu^{2+} ions are small enough to fit into the vacancy, and their axial positions are occupied by water molecules.

The four bridging oxygen atoms bonded to the divalent metal ion are expected to have high negative charges, and they are potential sites for acylation. It should be noted that there are two kinds of bridging oxygen atoms in a Keggin structure: one connecting two corner-sharing MO_6 octahedra and the other connecting two edge-sharing MO_6 octahedra.

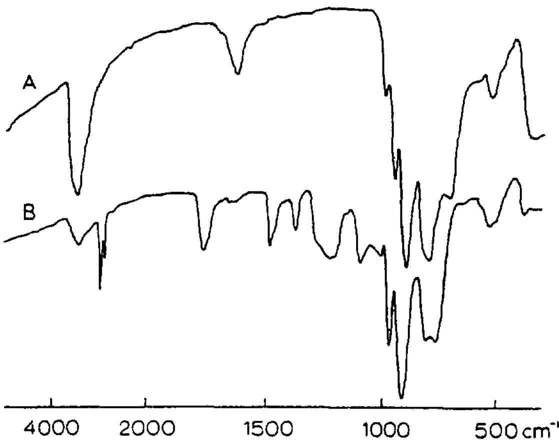


Figure 2. The infrared spectra of (A) $K_6[SiW_{11}O_{39}Zn(H_2O)]$ and (B) its acylated product. The acylated product also has the tetrabutylammonium ion.

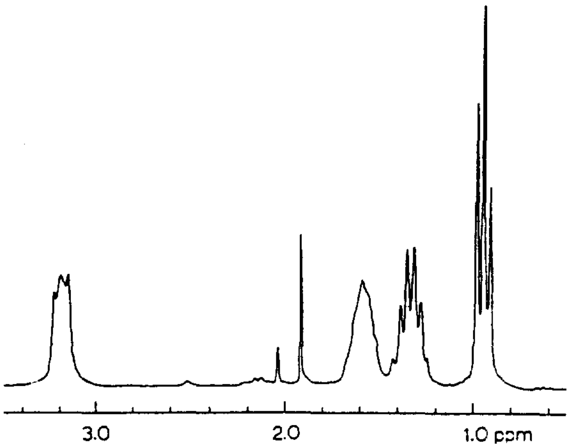


Figure 3. ^{1}H-NMR spectrum of Product Z.

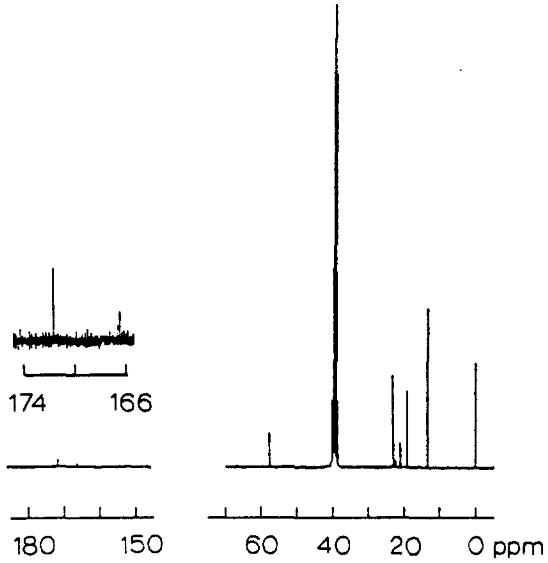


Figure 4. ^{13}C-NMR spectrum of Product Z.

Acylation of $[SiW_{11}O_{39}Zn(H_2O)]^{6-}$. The IR spectra of $K_6[SiW_{11}O_{39}Zn(H_2O)]$ and the acylated product (Product Z) are compared in Fugure 2. The bands at 700-1000 cm^{-1} are characteristic of the Keggin structure,[14] and the broad bands at 1630 and 3450 cm^{-1} originate from lattice water. The bands at 1370, 1470, 2880, and 2960 cm^{-1} for Product Z are assigned to the tetrabutylammonium ion. The new bands at 1760 and 1200-1300 cm^{-1} for Product Z may be assigned to the acetyl group attached to the heteropolyanion. The band at 1760 cm^{-1} is ascribed to the carbonyl group of CH_3CO-. The frequency of this band precludes the existence of any acylium ion (showing a carbonyl band at 2300 cm^{-1}) or a solvated acetic anhydride (showing two bands at 1800-1830 cm^{-1} and 1750-1780 cm^{-1}).

The new bands at 1200-1300 cm^{-1} are consistent with O-acylation, for such bands are expected from the $-C(=O)O-$ moiety. In fact, the IR bands of Product Z are similar to those of esters. For normal esters the $C=O$ stretch occurs at 1735 cm^{-1}, and two or more bands appear at 1100-1300 cm^{-1}. In the spectrum of vinyl acetate, the $C=O$ band is shifted to 1770 cm^{-1}. It has been suggested that the conjugation involving the single-bonded oxygen atom interferes with possible resonance with the carbonyl group leading to an increase in the absorption frequency for the $C=O$ band.[12] The high frequency of the $C=O$ band in Product Z may be explained in a similar way, for the bridging oxygen atom is bonded to three atoms, removing the possibility of resonance with the carbonyl group.

Each SiZn anion has four bridging oxygen atoms bonded to the zinc atom. Elemental analysis shows that 2.7 atoms have been acylated, indicating that Product Z is a mixture of species with different degrees of acylation.

The ^{1}H-NMR spectrum of Product Z is shown in Figure 3. The strong lines at 0.99, 1.40, 1.65, and 3.16 ppm come from the tetrabutylammonium ion. The weak impurity lines at 2.1 and 2.5 ppm may be attributed to $(CH_3)_2SO$ in the solvent and acetic anhydride or acetic acid, respectively. This leaves two lines at 1.91 and 2.03 ppm, which can be ascribed to $-CH_3$ of two different acetyl groups.[13] These chemical shifts are similar to that (1.93 ppm) of a methyl group in an ester. Two lines may be ascribed to two kinds of bridging oxygen atoms in the Keggin anion.

The ^{13}C-NMR spectrum also exhibits lines attributable to two different acetyl groups; see Figure 4. The lines at 13.45, 19.15, 23.04, and 57.51 ppm come from the tertabutylammonium ion, and the lines at 38-40 ppm from the solvent $(CD_3)_2SO$. The lines at 20.98 and 22.40 ppm may be attributed to $-CH_3$ groups, and the lines at 167 and 171.88 ppm to $>C=O$ groups of two different acetyl groups.

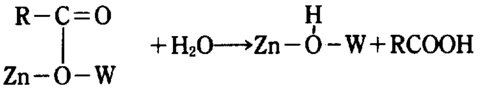
So there are three pairs of NMR lines ascribable to the acetyl group. Each pair consists of a strong line and a weak one with an intensity ratio 4 : 1, indicating that one site is favored for acylation.

	CH_3	CH_3	CO
Strong lines.	1.91	20.98	171.9 ppm
Weak lines.	2.03	22.40	167 ppm

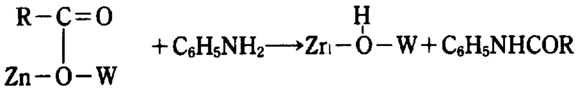
It is interesting to speculate which site is favored for acylation. The W-O-W angles are about 120° and 150° for the edge-sharing and corner-sharing modes of junction, respectively. Therefore the orbitals on the oxygen atom of the edge-sharing mode are closer to the sp^3 hybrid orbitals, and this oxygen atom is probably more favorable for acylation.

Acylation of $[SiW_{11}O_{39}Cu(H_2O)]^{6-}$. The IR spectrum of the acylated product (Product C) of $[SiW_{11}O_{39}Cu(H_2O)]^{6-}$ is quite similar to that of Product Z with new bands at 1760 and 1200-1300 cm^{-1} ascribable to the acetyl groups. Elemental analysis shows that all four bridging oxygen atoms between the copper and tungsten atoms have been acylated. No NMR spectrum was observed for Product C which is paramagnetic. The frozen solution EPR spectra show that both $g_{\parallel}$ and $A_{\parallel}$ values of the Cu^{2+} ion change when the heteropolyanion is acylated. However, no further useful information about the acylated product could be derived from the EPR spectra.

Reactions of the Acylated Products. The acyl group in Product Z can be removed easily be hydrolysis or reaction with aniline. After these reactions the IR bands at 1700 and 1200-1300 cm^{-1} and the ^1H-NMR lines at 1.92-1.98 ppm disappear from the spectra of the heteropolyanion, indicating that the acetyl group has been detached from the heteropolyanion. These reactions may be represented as follows:



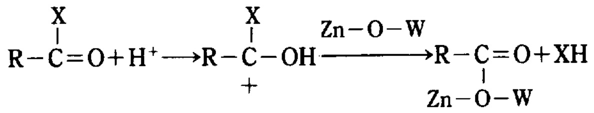
$$\begin{array}{l} R-C=O \\ \quad\;| \\ Zn-O-W \end{array} + H_2O \longrightarrow Zn-\overset{H}{\overset{|}{O}}-W + RCOOH$$



$$\begin{array}{l} R-C=O \\ \quad\;| \\ Zn-O-W \end{array} + C_6H_5NH_2 \longrightarrow Zn-\overset{H}{\overset{|}{O}}-W + C_6H_5NHCOR$$

$(R=CH_3)$

So all our experimental results are consistent with acylation of the bridging oxygen atoms between a divalent metal ion and tungsten ions in the heteropolyanions. The mechanism of acylation is probably an acid-catalyzed nucleophilic substitution with the bridging oxygen atom acting as the nucleophile.



$$R-\overset{X}{\overset{|}{C}}=O + H^+ \longrightarrow R-\underset{+}{\overset{X}{\overset{|}{C}}}-OH \xrightarrow{Zn-O-W} R-\underset{Zn-O-W}{\underset{|}{C}}=O + XH$$

$(X=CH_3COO)$

We have shown that the bridging oxygen atoms between a divalent metal ion and oxotungsten ions in some heteropolyanions can be acylated. This result suggests that the basicity of the surface oxygen atoms of heteropolyanions and metal oxides, which may play a crucial role in some reactions, can be controlled by choosing appropriate metal ions. It seems that the sum of the formal charges on two groups connected by the bridging oxygen atom is useful in estimating the basicity of the oxygen atom. For $[SiW_{12}O_{40}]^{4-}$ and $[SiW_{11}VO_{40}]^{5-}$, which do not react with acetic anhydride in the presence of acid,[7] the bridging oxygen atoms connect two $[W=O]^{4+}$ groups or one $[W=O]^{4+}$ group and one $[V=O]^{3+}$ group. For $[SiW_{10}V_2O_{40}]^{6-}$ and $[SiW_{11}O_{39}M(H_2O)]^{6-}$ ($M=Zn^{2+}$ or Cu^{2+}), which can be acylated, there are bridging oxygen atoms connecting two $[V=O]^{3+}$ groups or one $[W=O]^{4+}$ group and M^{2+} (M=Zn or Cu). So the bridging oxygen atoms in these heteropolyanions can be acylated when the sum of the formal charges on two oxometal or metal groups are less than 7. More work on other systems is needed to confirm this generalization.

Acknowledgement. The support of this research by the Ministry of Education is gratefully acknowledged.

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11. K. Y. Matsumoto and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **49**, 156 (1976).,
12. See, for example, D. L. Pavia, G. M. Lampman, and G. S. Kriz, Jr., "Introduction to Spectroscopy", W. B. Saunders Co., Philadelphia, 1979, p. 57.
13. We have observed only one ^1H-NMR line at 1.90 ppm for acylated $[Nb_2W_4O_{19}]^{4-}$ at which one bridging oxygen atom between two niobium atoms is available for acylation.
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15. Water-free solvents were used to prevent hydrolysis of the acylated product. Ether and dichloromethane were refluxed in the presence of CaH_2, and acetonitrile was stored with a molecular sieve. The reaction was carried out under a nitrogen atomosphere.

Synthetic Studies on Kainoids

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Received July 12, 1991

α-Kainic acid (**1**), isolated from the algae *Digenea simplex*[1] and *Centrocerus clavulatum*[2] has shown to possess an interesting neuronal excitatory activity.[3] Other structurally related compounds also have been isolated, namely acromelic acid (**2**) from the toxic principles of *Clitocybe acromelalga*[4] and domoic acid (**3**) and its family from the red algae *Chondria aromata*.[5a] In recent years, α-kainic acid has attracted consi-