

Syntheses, properties and biological activity of organogermanium substituted heteropolytungstates

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Abstract

Six new compounds [(RGe)XW₁₁O₃₉]ⁿ⁻ (R = HOOCCH₂CH₂, HOOCCH₂(*m*-NO₂C₆H₄)CH); X = Ge, Si, P) have been prepared and their Keggin structures determined by elementary analysis, IR, UV, ¹H NMR and ¹⁸³W NMR spectrometry. The results show that the complexes retain Keggin structure with organogermanium group grafting on the polyoxometalate surface. The complexes exhibit antitumoral activity in vitro as shown by MTT experiment.

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Our recent work involves studies in both the antitumoral activity and catalytic activity of substituted heteropolyorganometallic complexes. Polyoxometalates (POMs) have attracted much attention because of their potential applications in catalysis, medicine and material science [1–3]. Hill has pointed out that the versatility of the POMs and grafting organic and organometallic groups onto the polyoxometalate surface can significantly increase their catalytic or medical applications. In addition, organogermanium acids HOOCRGeCl₃ are potent antiviral agents and exhibit some certain catalytic ability. To date, the reaction of lacunary polyoxotungstates with organogermanium acid has been reported rarely [4–9], and to the best of our knowledge, there is no report on the antitumoral activity of organogermanium substituted heteropoly complexes. As part of our continuing investigation of POMs containing organometallic groups, we have systematically synthesized the [HOOCRGe]³⁺ substituted heteropolytungstates

[10] and investigated their antitumoral activity in vitro. Also, the syntheses of these six new compounds opened up another avenue of synthesizing novel magnetic materials.

Elementary analytical data, the observed frequencies of the main IR and tentative assignments of UV bands of the title complexes are given in supporting information.

Compared with XW₁₂O₄₀⁴⁻, the IR spectra of the substituted heteropolyanions still have the four characteristic peaks of $\nu_{\text{as(W-Od)}}$ (Od, terminal oxygen), $\nu_{\text{as(W-Ob-W)}}$, $\nu_{\text{as(W-Oc-W)}}$ (Ob, Oc, bridging oxygen) and $\nu_{\text{as(X-Oa)}}$ (Oa, central oxygen), indicating that the new complexes retain the basic frame of the Keggin structure. However, the terminal oxygen vibrations for [(RGe)XW₁₁O₃₉]ⁿ⁻ are shifted to low energy relative to the terminal oxygen vibration for XW₁₂O₄₀⁴⁻. This is due to an increase of negative charge on the polyanion. The $\nu_{\text{as(W-Oc-W)}}$ of the complexes exhibit splitting, most probably resulting from the change of anion symmetry [14].

The IR spectra display a single, sharp absorption in the 1700–1730 cm⁻¹ region. This feature is characteristic of the

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C=O stretch. In the 3430–3440 cm^{-1} region, the O–H stretches show the existence of COOH. These both show the existence of organogermanium acid group in the complexes.

The title anions absorb at ca. 200 ± 2 nm and 260 ± 2 nm. The first band at higher energy has been assigned to the $\text{O}_{b/c} \rightarrow \text{W}$ charge transfer band. The second band at lower energy is characteristic of 12-heteropolytungstates and has been attributed to the $\text{O}_d \rightarrow \text{W}$ charge-transfer band [15].

The ^1H NMR and ^{183}W NMR spectra are listed in Tables 1 and 2.

The title complexes gave clean ^1H spectra. In the $\text{HOOCCH}_2\text{CH}_2\text{GeCl}_3$ (^1H NMR data are 2.19 (t, CH_2COOH), 2.86 (t, CH_2GeCl_3), 9.95 (s, COOH) ppm, respectively), the Ge atom links with three chlorine atoms, the H chemical shift of GeCH_2 is 2.86 ppm. When $\text{HOOCCH}_2\text{CH}_2\text{GeCl}_3$ reacted with SiW_{11} for example, the electron density on Ge was affected by the heteropoly

Table 2
 ^{183}W NMR data (ppm) of the compounds

Anions	^{183}W		
$[\text{SiW}_{11}\text{O}_{39}(\text{GeCH}_2\text{CH}_2\text{CO}_2\text{H})]^{5-}$	–65.31 (2)	–95.48 (2)	–121.47 (4)
	–128.31 (1)	–201.17 (2)	
$[\text{PW}_{11}\text{O}_{39}(\text{GeCH}_2\text{CH}_2\text{CO}_2\text{H})]^{4-}$	–42.38 (2)	–73.42 (2)	–101.91 (2)
	–105.29 (2)	–110.30 (1)	–178.862
$[\text{GeW}_{11}\text{O}_{39}(\text{GeCH}_2\text{CH}_2\text{CO}_2\text{H})]^{5-}$	–94.14 (2)	–95.96 (2)	–108.21 (2)
	–113.94 (2)	–117.28 (2)	–192.43 (2)

anion so the electron density on Ge increased, so the H chemical shift of GeCH_2 shifted to highly magnetic field (1.30 ppm). The other H chemical shifts also changed (^1H NMR shifts are 12.20 (COOH), 2.37 (t, $2 \times \text{CH}_2\text{COOH}$) ppm, respectively). This can demonstrate that $[\text{RGe}]^{3+}$ group incorporated with the tungstosilicates and organic group did not separate from the Ge atom.

Table 1
 ^1H NMR data (ppm) of the compounds

Anions	^1H					
$\alpha\text{-SiW}_{11}\text{GeR}_1$	1.12 (2)	2.53 (2)	12.0 (1)	3.28 (60)		
$\alpha\text{-SiW}_{11}\text{GeR}_2$	2.98 (1)	3.09 (2)	7.45–8.04 (4)	3.26 (60)		
$\text{GeW}_{11}\text{GeR}_1$	1.29 (3)	2.46 (2)	3.18 (48)	11.87 (1)	2.55 (3)	
$\text{GeW}_{11}\text{GeR}_2$	2.91 (2)	3.08 (1)	6.55–7.98 (4)	11.71 (1)	3.14 (48)	2.55 (3)
$\text{PW}_{11}\text{GeR}_1$	1.35 (2)	2.56 (2)	3.24 (48)	2.62 (9)	12.26 (1)	
$\text{PW}_{11}\text{GeR}_2$	2.93 (1)	3.02 (2)	7.46–8.01 (4)	12.0 (1)	3.13 (48)	2.60 (6)

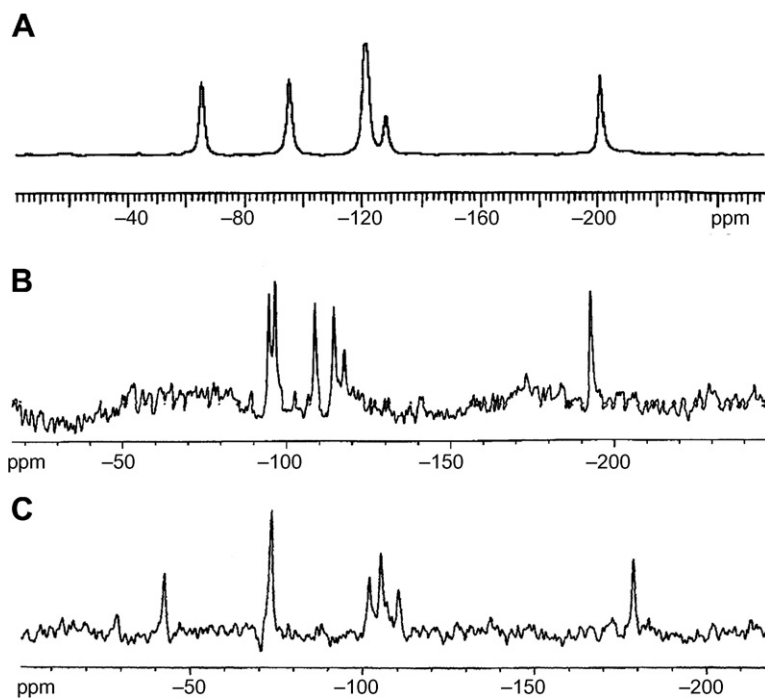


Fig. 1. ^{183}W NMR of the compounds: (A) for $(\text{Me}_4\text{N})_5[\text{SiW}_{11}\text{O}_{39}(\text{GeCH}_2\text{CH}_2\text{CO}_2\text{H})] \cdot 8\text{H}_2\text{O}$ (B) for $(\text{Me}_4\text{N})_4[\text{PW}_{11}\text{O}_{39}(\text{GeCH}_2\text{CH}_2\text{CO}_2\text{H})] \cdot 1.5\text{DMSO}$ (C) for $(\text{Me}_4\text{N})_5[\text{GeW}_{11}\text{O}_{39}\text{GeR}_1] \cdot \text{DMSO}$.

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