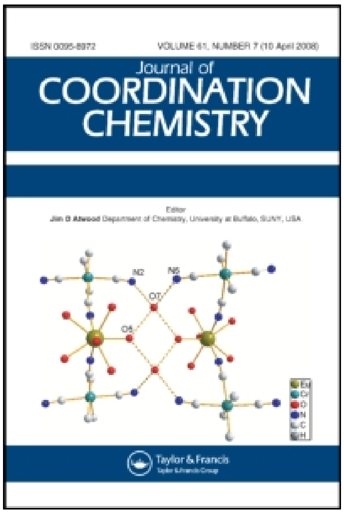

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Sandwich-type polyoxoanions based on A-β-$GeW_9O_{34}^{10-}$. Synthesis and characterization of $[(A\text{-}\beta\text{-}GeW_9O_{34})_2(MOH_2)_3CO_3]^{13-}$ ($M = Y^{3+}$, Sm^{3+}, and Yb^{3+}) polyoxoanions

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The title complexes were synthesized at room temperature by the reaction of A-β-$GeW_9O_{34}^{10-}$ with MCl_3 ($M = Y^{3+}$, Sm^{3+}, and Yb^{3+}) in $0.1\,mol\,L^{-1}$ sodium carbonate solution and characterized by elemental analysis, FT-IR, UV, ^{13}C- and ^{183}W-NMR spectroscopies, and thermogravimetric analysis (TGA). Two-line ^{183}W-NMR spectrum with 2 : 1 intensity ratio confirms that $[(A\text{-}\beta\text{-}GeW_9O_{34})_2(MOH_2)_3CO_3]^{13-}$ contains an anion of D_{3h} symmetry. The difference of the two chemical shifts $\Delta\delta = 30.56$ affirms the presence of A-β-$GeW_9O_{34}^{10-}$. The chemical shift of the single-line ^{13}C-NMR spectrum of $[(A\text{-}\beta\text{-}GeW_9O_{34})_2(MOH_2)_3CO_3]^{13-}$ and frequencies of stretching vibrations of all three complexes affirm the presence of coordinated carbonate. TGA shows that the complexes are thermally stable up to 430°C.

Keywords: Polyoxoanions; Sandwich type; A-β-GeW_9O_{34}; Trivalent yttrium, samarium, and ytterbium ions; ^{183}W-NMR spectroscopy

1. Introduction

The lacunary polyoxometalate as a multiple oxygen donor with multiple coordination and oxophilic properties of trivalent lanthanide ions enables synthesis and design of suitable building blocks. Such lanthanide–polyoxometalates have tremendous structural variety and interesting properties which are useful in catalysis, magnetism, luminescence, and material science [1–6]. The vacant lacunary polyoxometalates derived from Keggin-type polyoxometalates, $XW_{12}O_{40}^{n-}$ ($X = As^{5+}, Ge^{4+}, P^{5+}, Si^{4+} \ldots$), are the major precursors of these fields. Phosphorous and silicon containing polyoxoanions are the most intensively studied systems so far because they exhibit a large variety of lacunary precursor species, but the number of germanium-containing polyoxoanions is relatively small. Herve and Teze [7] reported the first monolacunary germanotungstate

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$[GeW_{11}O_{39}]^{8-}$ in 1977, and now most germanium-containing polyoxoanions are based on monovacant germanotungstates. These derivatives can be considered as pentadentate ligands, but close inspection of the structures of the above species indicates that the lanthanides are too big to enter the respective vacancies fully. They usually sit somewhat above the lacunary hole and are coordinated to the four equatorial oxo-donors of the polyoxoanion. The coordination sphere is usually completed by another ligand to form *bis*(undecatungstogermanate) lanthanides or by terminal water; of course, these monomeric species have a strong tendency to oligomerize in the presence of suitable ligand, such as acetate or oxalate, polymerizing to form 1-D chains, 2-D layers, and 3-D networks [8–15].

The $[GeW_9O_{34}]^{10-}$ polyoxoanion is tri-vacant, first reported by Herve and Teze [7] in 1977, and has six unsaturated oxygens available for coordination with a positive metal. Generally, metal ions react with $[GeW_9O_{34}]^{10-}$ to form tri-substituted dimeric complexes, such as $[Fe_6(OH)_3(A\text{-}\alpha\text{-}GeW_9O_{34}(OH)_3)_2]^{11-}$ [16], sandwich-type complexes, such as $[Na_2(UO_2)_2(A\text{-}\alpha$ or $\beta\text{-}GeW_9O_{34})_2]^{14-}$ [17], and $[Zr_3O(OH)_2(\alpha\text{-}GeW_9O_{34})(\beta\text{-}GeW_9O_{34})]^{12-}$ [18], weakly type sandwich complexes, such as $[M_4(H_2O)_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{12-}$ ($M = Mn^{2+}$, Cu^{2+}, Zn^{2+}, and Cd^{2+}) [19] and more recently, the banana-shaped polyoxoanion, such as $[((CoOH_2)Co_2GeW_9O_{34})_2(GeW_6O_{26})]^{20-}$ [20]. The weakly type sandwich complexes are thermally stable and suitable precursors for preparation of inorganic–organic composite polyoxoanions, such as $[Cu(en)_2(H_2O)]_2[Cu(en)_2(H_2O)_2]\{[Cu(en)_2]_3[Cu_4(GeW_9O_{34})_2]\} \cdot 10H_2O$, $(H_2en)\{[Zn(en)_2]_4[Zn_4(Hen)_2(GeW_9O_{34})_2]\} \cdot 10H_2O$, $[enH_2][C_8N_4H_{22}]_3H_2[Co_4(enH)_2(GeW_9O_{34})_2] \cdot 6H_2O$, $[Co(en)_3]_2H_6[Co_4(enH)_2(GeW_9O_{34})_2] \cdot 14H_2O$ (en = ethylenediamine), and $K_4Na_4[Cu_2(H_2O)_8Cu_4(H_2O)_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]14H_2O$ [21–23]. The $[GeW_9O_{34}]^{10-}$ has seven oxygens available for bonding (the Bα form). A study of the interaction of A-$[GeW_9O_{34}]^{10-}$ with lanthanides has not been reported. There are several reports about the interaction of $[XW_9O_{34}]^{n-}$ ($X = P$, $n = 9$; $X = Si$, $n = 10$; and $X = As(V)$, $n = 9$) with lanthanide ions. In 2003, lanthanide complexes of $[(XW_9O_{34})_2Ln_3O_3(OH_2)_2]^{15-}$, where $Ln = Ce^{3+}$, La^{3+}, and $X = P^{5+}$ and As^{5+} were reported [24]. Hill *et al.* [25] reported the first examples of sandwich-type polyoxoanions that encapsulate a dianion (CO_3^{2-}) in the center $[(A\text{-}PW_9O_{34})_2(YOH_2)_3CO_3]^{11-}$. We synthesized the first lanthanide derivatives of this category, $[(A\text{-}AsW_9O_{34})_2(MOH_2)_3CO_3]^{11-}$ ($M = Y^{3+}$, Sm^{3+}, and Yb^{3+}) [26] and $[(A\text{-}SiW_9O_{34})_2(MOH_2)_3CO_3]^{13-}$ ($M = Y^{3+}$ and Yb^{3+}) [27]. These complexes are formed by the reaction of $A\text{-}XW_9O_{34}^{n-}$ with M^{3+} ions in aqueous Na_2CO_3 solution in modest yield and high purity. Herein, we report the first examples of sandwich complexes with trivalent transition and lanthanide ions based on $[A\text{-}\beta\text{-}GeW_9O_{34}]^{10-}$ polyoxanions. The sandwich-type complexes, $[(A\text{-}\beta\text{-}GeW_9O_{34})_2(MOH_2)_3CO_3]^{13-}$ ($M = Y^{3+}$, Sm^{3+}, and Yb^{3+}), are synthesized in an aqueous carbonate solution and at room temperature. Spectroscopic studies suggest that polyoxoanions have a sandwich-type structure (figure 1), similar to the structure of the $[(A\text{-}\beta\text{-}SiW_9O_{34})_2(MOH_2)_3CO_3]^{13-}$ ($M = Y^{3+}$ and Yb^{3+}) complexes reported by us [27]. Structure of the complexes consists of two lacunary $A\text{-}\beta\text{-}GeW_9O_{34}^{10-}$ Keggin moieties, which are linked by a $(H_2OM)_3CO_3$ belt into an assembly of virtual D_{3h} symmetry. Their synthesis, chemical behavior, and spectroscopic characterization are reported.

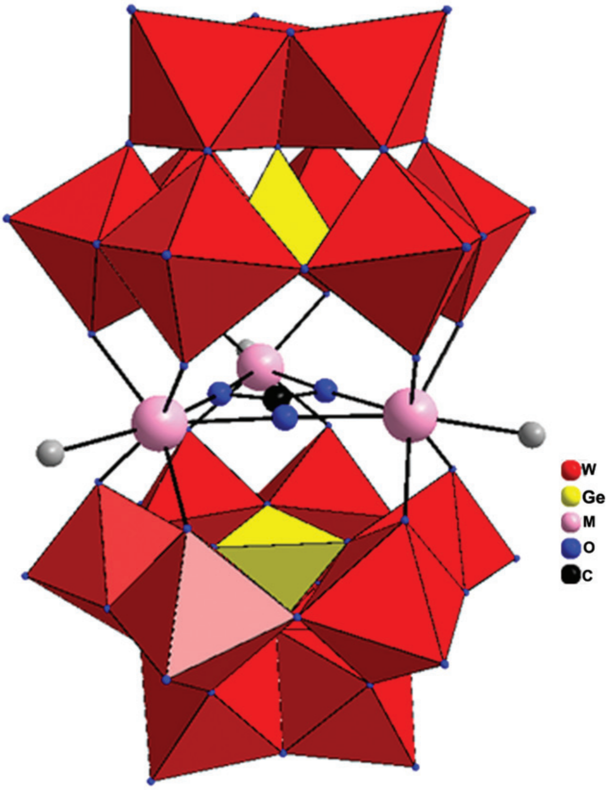

Figure 1. Proposed structure of **1**, **2**, and **3**.

2. Experimental

2.1. *Chemical and apparatus*

All reagents were commercially obtained and used without purification. $YCl_3 \cdot 6H_2O$, and $YbCl_3 \cdot 6H_2O$ were purchased from Acros Company and $SmCl_3 \cdot 6H_2O$ from Alfa Aesar Company. Infrared (IR) spectra were recorded as KBr pellets on a Thermo Nicolet FT-IR model Nexus-670. The ^{13}C- and ^{183}W-NMR spectra were recorded on a DRX-500 AVANCE spectrometer. Resonance frequency is 125.75 MHz and chemical shifts were given with respect to chloroform as external standard for ^{13}C-NMR. Resonance frequency is 12.505 MHz for ^{183}W-NMR and chemical shifts were given with respect to $2\,mol\,L^{-1}$ sodium tungstate solution. Thermogravimetric analysis (TGA) was carried out using a PL-1500 TGA apparatus. Electronic spectra were recorded on a Varian, CARY 1E UV-Vis spectrophotometer. Inductively coupled plasma (ICP) was used for elemental analysis of yttrium, samarium, ytterbium, and tungsten, whereas flame photometry was used for the elemental analysis of sodium and potassium. TGA was used for the analysis of carbon and crystallization water.

Strongly acidic (Dowex HCR-W2 H^+ form) and basic (Amberjet 4200 Cl^- form) resins packed into a column (20 cm length; 1 cm diameter) were used for ion exchange chromatography. For cation exchange, first $1\,mol\,L^{-1}$KOH was eluted through the acidic form of the cationic resin followed by distilled water, and then solutions of the complexes were eluted through it. For anion exchange, solutions of the complexes were eluted through the anion exchange resin column. The eluants were collected and studied by IR spectroscopy after solvent evaporation.

2.2. *Preparation*

$Na_9H[A\text{-}\beta\text{-}GeW_9O_{34}]\cdot xH_2O$ was prepared according to the literature [7] with some variations. First, 1.06 g (10 mmol) of GeO_2 was dissolved in 35 mL of NaOH (5%, 10 mmol), and then 30.0 g of $Na_2WO_4\cdot 2H_2O$ (90 mmol) in 40 mL of cool water was added with stirring. The solution was transferred to an ice bath and then hydrochloric acid ($6\,mol\,L^{-1}$, 16 mL) was slowly added to the vigorously stirred solution. The solution was filtered and left to stand in a refrigerator (5°C). The sodium salt slowly crystallized after some days. Yield: 13.2 g, 44% based on $Na_2WO_4\cdot 2H_2O$.

2.2.1. $K_{10}Na_3[(A\text{-}\beta\text{-}GeW_9O_{34})_2(YOH_2)_3(CO_3)]\cdot 21H_2O$ (1). A 0.48-g (1.6 mmol) sample of $YCl_3\cdot 6H_2O$ was dissolved in 20 mL of twice distilled water and 2 mL of $1\,mol\,L^{-1}$ Na_2CO_3 was slowly added with stirring. Solid $Na_9H[A\text{-}\beta\text{-}GeW_9O_{34}]\cdot xH_2O$ (2.00 g, 1.0 mmol) was quickly added with vigorous stirring. The solution was stirred at room temperature (30°C) for 60 min and then centrifuged for removal of insoluble material. Solid KCl (0.45 g) was added and the solution was cooled in an ice water bath and then filtered off. The crude product was recrystallized at least twice in hot water. Yield: 1.7 g (57%). Anal. Calcd for $K_{10}Na_3[(A\text{-}\beta\text{-}GeW_9O_{34})_2(YOH_2)_3(CO_3)]\cdot 21H_2O$: C, 0.21; Na, 1.19; K, 6.73; W, 56.92; Y, 4.59; and H_2O, 7.43. Found: C, 0.22; Na, 1.12; K, 6.48; W, 56.01; Y, 4.20; and H_2O, 7.48%.

2.2.2. $K_{10}Na_3[(A\text{-}\beta\text{-}GeW_9O_{34})_2(SmOH_2)_3(CO_3)]\cdot 22H_2O$ (2). The procedure for **1** was repeated, but using $SmCl_3\cdot 6H_2O$ (0.59 g) instead of $YCl_3\cdot 6H_2O$ and 0.65 g instead of 0.45 g of KCl. Yield: 1.3 g (42%). Anal. Calcd for $K_{10}Na_3[(A\text{-}\beta\text{-}GeW_9O_{34})_2(SmOH_2)_3(CO_3)]\cdot 22H_2O$: C, 0.20; Na, 1.15; K, 6.50; W, 55.05; Sm, 7.50; and H_2O, 7.48. Found: C, 0.19; Na, 1.00; K, 6.60; W, 54.95; Sm, 7.40; and H_2O, 7.46%.

2.2.3. $K_{10}Na_3[(A\text{-}\beta\text{-}GeW_9O_{34})_2(YbOH_2)_3(CO_3)]\cdot 22H_2O$ (3). The procedure for **1** was repeated, but using $YbCl_3\cdot 6H_2O$ (0.62 g) instead of $YCl_3\cdot 6H_2O$ and 0.62 g instead of 0.45 g of KCl. Yield: 1.5 g (35%). Anal. Calcd for $K_{10}Na_3[(A\text{-}\beta\text{-}GeW_9O_{34})_2(YbOH_2)_3(CO_3)]\cdot 22H_2O$: C, 0.20; Na, 1.13; K, 6.43; W, 54.42; Yb, 8.54; and H_2O, 7.40. Found: C, 0.18; Na, 1.13; K, 6.48; W, 54.14; Yb, 8.87; and H_2O, 7.34%.

3. Results and discussion

3.1. *Synthesis and stability*

$[A\text{-}\beta\text{-}GeW_9O_{34}]^{10-}$ at room temperature reacts with MCl_3 ($M = Y^{3+}$, Sm^{3+}, and Yb^{3+}) in aqueous Na_2CO_3 solution ($0.1\,mol\,L^{-1}$) to form **1**, **2**, and **3** in medium yields.

The syntheses of the complexes require the presence of CO_3^{2-}. When solutions of the complexes are eluted through the cation-exchange resin column (K^+ form), no retention of the complexes is observed. The IR spectrum of each individual eluant is the same as that of the eluted parent complex. On the other hand, when solutions of the complexes are eluted onto an anion-exchange column (Cl^- form), the anionic complexes are retained into the column [24, 28]. As expected, results of control experiments with aqueous solutions of MCl_3 show that the lanthanide ions were retained on the cation-exchange column but passed through the anion-exchange column. These observations provide good evidence for inner-sphere bonding of the M^{3+} cations to $[A\text{-}\beta\text{-}GeW_9O_{34}]^{10-}$. Complexes of **1** and **3** are stable under reflux in unbuffered water while **2** is unstable. Experimental results show that **1** and **3** are stable from pH 3 ($10^{-3}\,mol\,L^{-1}$ HCl) to 11 ($10^{-3}\,mol\,L^{-1}$ NaOH), while the best pH range stability for **2** is 5–9. Preliminary syntheses of isostructural complexes with La^{3+}, Ce^{3+}, and Pr^{3+} were unsuccessful.

3.2. *IR spectroscopy*

IR spectra of **1**, **2**, and **3** are similar, confirming that the complexes have similar structures (Supplementary material). Comparing IR spectra of the complexes with the trivacant lacunary $[A\text{-}\beta\text{-}GeW_9O_{34}]^{10-}$, (1) bands at 935 and $973\,cm^{-1}$ are assigned to the asymmetric stretching vibrations of W–O_d. For the complex, these bands shifted 5 and $10\,cm^{-1}$ to higher frequencies, (2) the band at $880\,cm^{-1}$ is assigned to the asymmetric stretching vibrations of W–O_b–W, (3) the W–O_c–W vibrations split into two bands at 710 and $780\,cm^{-1}$ for the complexes and shifted symmetrically by 5 and $65\,cm^{-1}$ to lower and higher frequencies, respectively, and (4) (Ge–O_a) vibrations for complexes are overlapped by (W–O_b–W) and (W–O_c–W) vibrations (O_d is a terminal oxygen, O_b is a bridging oxygen between corner-sharing octahedra, and O_c is a bridging oxygen between edge-sharing octahedra) [29, 30]. IR spectra of the complexes show bands at $1477\text{–}1486\,cm^{-1}$ for **1** and **3** and $1469\text{–}1481\,cm^{-1}$ for **2**, assigned to the doubly degenerate ν_3 mode of coordinated CO_3^{2-} with a partial splitting of $10\,cm^{-1}$. This splitting is commonly observed in carbonate complexes [25–27] and attributed to distortion of the CO_3^{2-} group. The ν_3 stretching frequencies increase with coordination of carbonate to M^{3+} in comparison to free carbonate. As a result, we conclude that CO_3^{2-} coordinates more strongly in **1** and **3** than **2**. This appears in hydrolytic and thermal stabilities; **1** and **3** are hydrolytic and thermally more stable than **2**. Attempts to synthesize similar complexes with La^{3+}, Ce^{3+}, Pr^{3+}, and Nd^{3+} were unsuccessful. Although ionic radii variations are small from La^{3+}–Sm^{+3}, they do affect the properties and reactivity of the lanthanide ions [31]. Formation of sandwich-type polyoxoanions containing carbonate is a function of the lanthanide ion size. The other two IR active modes, ν_2 and ν_4, of CO_3^{2-} overlap with the W–O stretching bands.

3.3. *NMR spectroscopy*

^{183}W-NMR spectroscopy has become a powerful routine method for structural characterization of polyoxoanions in solution [32]. As polyoxoanion **1** is diamagnetic, we performed ^{183}W- and ^{13}C-NMR studies in solution. The ^{183}W-NMR spectrum of **1** shows a singlet at -110.22 ppm and a doublet at -140.37 and -141.19 ppm with a 2 : 1

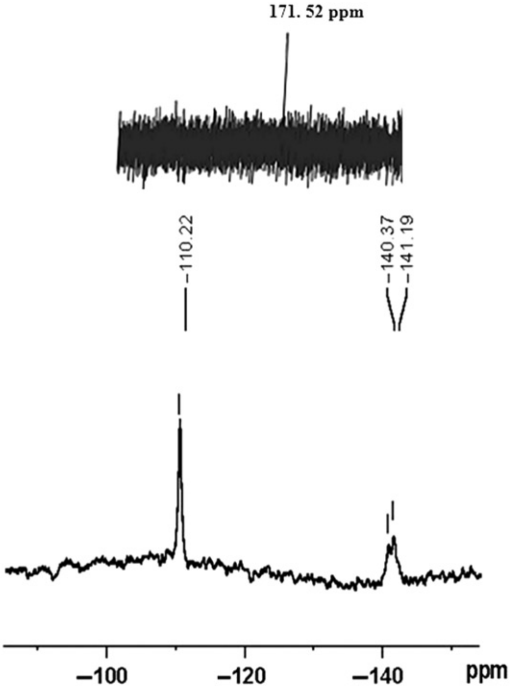

Figure 2. ^{183}W-NMR spectrum (bottom) and ^{13}C-NMR spectrum (top) of solutions of **1**.

intensity ratio (figure 2). A two-line spectrum would be consistent with a structure of D_{3h} symmetry. The peak at −110.22 ppm can be attributed to the six equivalent tungstens in a "belt" and the doublet at −140.37 and −141.19 ppm to the three tungstens in capping each $[A\text{-}\beta\text{-}GeW_9O_{34}]$ unit (≈0.8 Hz). The ^{183}W pattern for **1** is consistent with the observed pattern for other 3 : 2 sandwich complexes, such as $[(A\text{-}SiW_9O_{34})_2(HOZr)_3]^{11-}$ [33] and $[(SiW_9O_{34})_2Sn_3]^{14-}$ [34]. The $\Delta\delta = \delta_{belt} - \delta_{cap}$ can be used in distinguishing A-α or A-β isomers of $[A\text{-}GeW_9O_{34}]$. The $\Delta\delta(A\text{-}\alpha) > \Delta\delta(A\text{-}\beta)$ and generally, for A-β isomer a $\Delta\delta < 50$ is observed [35]. A $\Delta\delta \approx 30$ for **1** indicates that the $[GeW_9O_{34}]$ units have the same A-β structure as the precursor trilacunary polyoxoanion. The ^{13}C-NMR spectrum of **1** shows a peak at 171.52 ppm attributed to encapsulated CO_3^{2-} (figure 2). The two-line ^{183}W-NMR with 2 : 1 intensity ratio indicates that symmetry of the complex is not affected significantly by coordination of carbonate, suggesting that CO_3^{2-} is encapsulated in the Y_3^{3+} plane and on mirror plane of two $[A\text{-}\beta\text{-}GeW_9O_{34}]$ units. In order to obtain a solution of **1** that was concentrated enough for ^{183}W- and ^{13}C-NMR spectroscopy, it was necessary to convert the potassium salt to the lithium salt by the addition of $LiClO_4$. The ^{183}W- and ^{13}C-NMR results show that the lithium salt of **1** is stable.

3.4. *Thermal properties: TGA*

TG analyses were carried out under N_2. The TGA curves exhibit two weight loss steps from 35°C to 500°C, first, 35°C to 300°C with 7.48%, 7.46%, and 7.34% weight loss attributed to the loss of all the lattice and coordinated water molecules (24, 25, and 25 molecules for **1**, **2**, and **3**, respectively), and second, 430–500°C with approximately 0.68%, 0.75%, and 0.63% weight loss for **1**, **2**, and **3**, respectively, are assigned to loss of one CO_2 from the decomposition of CO_3^{2-}. The TGA curve of **2**, as an example, is shown in Supplementary material. The TGA analysis shows that the complexes are thermally stable to 430°C.

3.5. *Electronic spectroscopy*

UV-electronic spectra of compounds exhibit two characteristic bands at 200 and 250 nm, assigned to $O_d \rightarrow W$ and $O_b \rightarrow W$ charge transfer transitions, respectively [26, 27]. These bands are shifted to lower frequencies (higher wavelengths) on comparison with the A-β-$GeW_9O_{34}^{10-}$ due to the coordination of M^{3+}. Comparison of the UV spectra of **2** and that of precursor $[A\text{-}\beta\text{-}GeW_9O_{34}]^{10-}$ are shown in Supplementary material.

4. Conclusion

Three new polyoxoanions $[(A\text{-}\beta\text{-}GeW_9O_{34})_2(MOH_2)_3CO_3]^{13-}$ ($M = Y^{3+}$, Sm^{3+}, and Yb^{3+}) were synthesized by the reaction of M^{3+} ions with the trilacunary $[A\text{-}\beta\text{-}GeW_9O_{34}]^{10-}$ in aqueous Na_2CO_3 solution. Spectroscopic studies suggest that polyoxoanions have a sandwich-type structure (figure 1), similar to the structure of $[(A\text{-}\beta\text{-}SiW_9O_{34})_2(MOH_2)_3CO_3]^{13-}$ ($M = Y^{3+}$ and Yb^{3+}) [27]. Furthermore, evidence has been presented for the influence of the trivalent lanthanide radii on stability and formation of complexes.

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