The First Sandwich-Type Heteropolytungstates Consisting of Trivacant Gallium(III)-Substituted Keggin Fragments

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The new polyoxotungstates $(NH_4)_5Na_9[Cu_4(H_2O)_2(GaW_9O_{34})_2]\cdot 22H_2O$ (**1**) and $(NH_4)_{14}[Zn_4(H_2O)_2(GaW_9O_{34})_2]\cdot 37H_2O$ (**2**) were synthesized in aqueous solution and characterized by IR and Raman spectroscopy, energy dispersive X-ray fluorescence and single-crystal X-ray analysis. Compounds **1** and **2** contain the trivacant α-B-$(GaW_9O_{34})^{11-}$ Keggin fragment, which is structurally characterized for the first time. The lacunary $(GaW_9O_{34})^{11-}$ structure exhibits a centered Ga^{III} atom, which is bound to four oxygen atoms and thus achieves a tetrahedral coordination sphere. The synthesis of **1**–**2** enlarges the class of sandwich-type polyoxoanions and enables the syntheses of a new series of gallium(III)-substituted polyoxotungstates.

Introduction

Polyoxotungstates and -molybdates[1] have been investigated extensively over the last years. Owing to their unique properties, they attract current attention in view of their potential in medicine, material science, and catalysis.[2,3] Beyond the numerous applications, polyoxoanions exhibit impressing and fascinating large structures.[4] Complex and largely unknown self-assembly reaction mechanisms are responsible for the formation of polyoxometalates and make it difficult to develop a straightforward reaction route for their syntheses. It is therefore an important challenge to synthesize polyoxoanions with novel structural features to provide an insight into building reactions. For the exact description of polyoxometalate structures, single-crystal X-ray structure analysis is the most powerful tool as the standard analytical techniques like IR, UV/Vis and elemental analysis are often insufficient.

Within the class of polyoxotungstates, the Keggin anion $(XW_{12}O_{40})^{(8-x)-}$ (where X is the central atom and x its oxidation state) and its defect fragments are the basis for an enormous number of structurally different polyoxoanions. In our work, we focused on the systematic synthesis of sandwich-type polyoxotungstates containing As, Sb and Bi.[5] Sandwich-type polyoxoanions of the $M_4X_2W_{18}$-type constitute a class of structurally interesting compounds in which two trivacant α-*B*-$(XW_9O_{34})^{n-}$ Keggin fragments (X = P^V, As^V, Si^{IV}, Ge^{IV} etc.) are connected via a belt of four transition metals M. The first anion of this type, $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, was reported in 1973 by Weakley et al.,[6] and the corresponding nickel-substituted anion was published in 1999.[7] Some analogous structures with As^V were described with M = Zn^{II}, Mn^{II}, Co^{II}, Cu^{II}, Cd^{II}, Ni^{II}.[8,5i] Kortz et al. were able expand the number of polyoxoanions of the $M_4X_2W_{18}$ structure type by synthesizing the first examples of silicotungstates $[M_4(H_2O)_2(SiW_9O_{34})_2]^{12-}$ (M = Mn^{II}, Cu^{II}, Zn^{II}) and germanotungstates $[M_4(H_2O)_2(GeW_9O_{34})_2]^{12-}$ (M = Mn^{II}, Cu^{II}, Zn^{II}, Cd^{II}).[9] Our group reported two novel anions of the $M_4X_2W_{18}$-type in which the transition metal M also can be found in the center of the α-*B*-$(XW_9O_{34})^{n-}$ fragment (M = X = Cu^{II}, Fe^{III}).[10]

The selective incorporation of diverse metals M or X is an important aim in polyoxometalate chemistry and makes it possible to modify the properties of the polyoxoanions. For example, the influence on the magnetic properties of transition metals M[11] or main group metals X[12] has been investigated during the last years as well as the effects on the polyoxoanions' catalytic properties.[5a,13] Most of the known structures contain divalent or trivalent transition metals M. Recently, some main-group substituted anions which contain In^{III} and Sn^{II} have been reported.[5h,5j,14] In this paper, we report for the first time on anions consisting of trivacant $(GaW_9O_{34})^{11-}$ Keggin fragments. Only little research was done to date on polyoxometalates containing gallium as a heteroatom. Ga^{III} is used as heteroatom, e.g. in the monovacant Keggin-type anions $[GaW_{11}Ga(OH)O_{39}]^{7-}$[15] and $[GaW_{11}O_{39}Pb]^{7-}$.[16] A Chinese group reported on polyoxoanions of the general formula $[GaW_9M_3O_{40}]^{n-}$ (with M = Mn^{II}, Co^{II}, Ni^{II}, Fe^{III}, V^V), but these compounds were not investigated by X-ray diffraction studies.[17] In 1982 Zonnevijlle characterized POMs of the general formula α-$XM^{III}(OH_2)W_{11}O_{39}{}^{n-}$ (X = B, Si, Ge, P,

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As; M = Al, Ga, In, Tl) and $X_2M^{III}(OH_2)W_{17}O_{61}{}^{7-}$ (X = P, As; M = Al, Ga, In, Tl) by elemental analysis, UV/Vis and vibrational spectroscopy.

Results and Discussion

The new polyoxotungstates $(NH_4)_5Na_9[Cu_4(H_2O)_2(GaW_9O_{34})_2]\cdot 22\,H_2O$ (**1**) and $(NH_4)_{14}[Zn_4(H_2O)_2(GaW_9O_{34})_2]\cdot 37\,H_2O$ (**2**) were synthesized in aqueous solution by reaction of $WO_4{}^{2-}$, Ga^{3+} and the divalent transition metals Cu^{2+} and Zn^{2+}, respectively. The syntheses of **1** and **2** succeeded using $Ga(NO_3)_3\cdot 9\,H_2O$ as well as Ga_2O_3 as starting material. After adding a 1 M solution of NH_4NO_3 or NH_4Cl, single crystals suitable for X-ray diffraction can be obtained by slow evaporation of the solvent. Although in most cases a stoichiometric molar ratio is the best way to synthesize polyoxoanions, we were only able to get single crystals suitable for X-ray diffraction when using an excess of gallium and tungsten.

Figure 1 shows the $[Cu_4(H_2O)_2(GaW_9O_{34})_2]^{14-}$ anion of **1**. The tetranuclear sandwich clusters $[M_4(H_2O)_2(GaW_9O_{34})_2]^{14-}$ (M = Cu^{II}, Zn^{II}) consist of two analogous α-*B*-$(GaW_9O_{34})^{11-}$ subunits, which are connected by a system of four divalent transition metal atoms. The two trivacant subunits can formally be derived from the Keggin structure by removal of three adjacent edge-sharing WO_6 octahedra. The W–O bond lengths and O–W–O bond angles summarized in Table 1 show typical values and differ only slightly from known structures of the $M_4X_2W_{18}$ type. The center of each lacunary anion is occupied by a Ga^{III} atom that is surrounded by four oxygen atoms. The Ga–O bond are in the range of 1.82(1) and 1.84(1) Å for **1** and 1.84(1) and 1.89(1) Å for **2**. We used bond valence calculations to affirm that a gallium atom is situated in the center of the Keggin fragments and to exclude an occupation of this position by the divalent transition metals. The calculated bond valences for the Ga atoms of 3.1 for **1** and 2.7 for **2** are in good agreement with the formal oxidation state +III of the gallium atoms. Modeling these atoms as copper or zinc atoms, respectively, bond valences of 2.7 for **1** and 2.5 for **2** were calculated which are obviously too high for the divalent metal atoms. The results of the elemental analyses confirm that both compounds contain gallium and copper or zinc, respectively, at a ratio of 2:4. However, we cannot exclude a slight disorder of Ga and Zn in **2** as the Ga–O bond lengths are elongated in comparison to **1**.

The two $(GaW_9O_{34})^{11-}$ Keggin fragments are connected through a $M_4O_{14}(H_2O)_2$ belt (M = Cu^{II}, Zn^{II}). The two crystallographically independent Cu atoms in **1** have a distorted octahedral coordination sphere. For Cu(1), each of the subunits provides three oxygen atoms. Cu(2) is bound to one water molecule, two oxygen atoms of one $(GaW_9O_{34})^{11-}$ subunit and three oxygen atoms of the second $(GaW_9O_{34})^{11-}$ subunit. All Cu–O distances are in the range between 1.92(1) and 2.28(1) Å. The O–Cu–O bond angles summarized in Table 1 show the distortion of the CuO_6 octahedra. In **2**, the Zn^{II} atoms are coordinated in the same way and show also an octahedral coordination sphere. The Zn^{II}–O bond lengths range between 2.00(1) and 2.19(1) Å and show that the ZnO_6 octahedra are less distorted than the CuO_6 octahedra. Figure 2 shows the Cu_4 belt in **1** and its linkage to the Ga^{III} atoms of the $(GaW_9O_{34})^{11-}$ Keggin fragments.

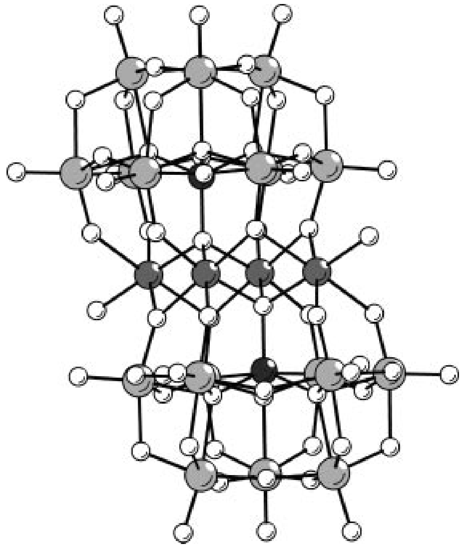

Figure 1. Ball-and-stick representation of the $[Cu_4(H_2O)_2(GaW_9O_{34})_2]^{14-}$ anion in **1**. W light gray, Ga dark gray, Cu middle gray, O white.

Table 1. Selected bond lengths [Å] and angles [°] of **1** and **2** (standard deviations in parentheses). The subscripts indicate the atoms bound to the oxygen atom, t = terminal.

	1 (X = Ga^{III}, M^{II} = Cu^{II})	**2** (X = Ga^{III}, M^{II} = Zn^{II})
$W–O_t$	1.71(1)–1.76(1)	1.72(1)–1.75(1)
$W–O_{W2}$	1.88(1)–2.09(1)	1.87(1)–2.06(1)
$W–O_{WM}$	1.75(1)–1.82(1)	1.76(1)–1.81(1)
$W–O_{WM2}$	1.82(1)–1.84(1)	1.81(1)–1.83(1)
$W–O_{XW3}$	2.19(1)–2.31(1)	2.20(1)–2.25(1)
$X–O_{XW3}$	1.82(1)–1.84(1)	1.88(1)–1.89(1)
$X–O_{XM3}$	1.83(1)	1.84(1)
$M^{II}–O_{WM}$	1.92(1)–2.25(1)	2.00(1)–2.16(1)
$M^{II}–O_{WM2}$	2.06(1)–2.28(1)	2.09(1)–2.19(1)
$M^{II}–O_{XM3}$	1.98(1)–2.06(1)	2.00(1)–2.01(1)
$M^{II}–OH_2$	1.99(1)	2.10(1)
$O–W–O_{cis}$	72.3(5)–105.3(7)	72.3(4)–104.7(5)
$O–W–O_{trans}$	156.2(5)–173.5(6)	158.8(4)–170.9(4)
O–X–O	105.8(5)–114.3(5)	105.5(4)–113.0(4)
$O–M^{II}–O_{cis}$	80.7(5)–97.1(6)	81.3(4)–95.7(4)
$O–M^{II}–O_{trans}$	169.8(5)–177.8(6)	169.9(4)–178.6(4)

The –14 charge of the gallium-substituted polyanions is balanced by nine sodium cations and five ammonium ions in **1** and 14 ammonium ions in **2**. The exact positions of the ammonium ions could not be identified by X-ray diffraction methods as they could not be distinguished from water molecules. However, the results of the elemental analyses are in complete agreement with the formulas of **1** and **2**. In addition, bond valence calculations gave no hints for protonation of the anions.[18]

In both compounds, the anions are linked by an extensive hydrogen bond network. Although the hydrogen atoms

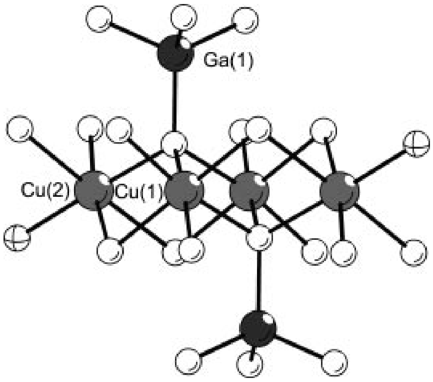

Figure 2. Ball-and-stick representation of the central $Ga_2Cu_4O_{20}(H_2O)_2$ belt in **1.** The color code is the same as in Figure 1, OH white crossed.

have not been located during the refinement, the OW···O and OW···OW distance indicates the linkage of the anions by hydrogen bonds.[18] Even though the anions in **1** and **2** contain transition metals with different chemical characteristics, the metal–metal distances in the $X_2M_4O_{20}(H_2O)_2$ belt show great similarities. The distances given in Table 2 show that these distances differ only slightly in **1** and **2**. In the rhombic M_4O_{16} (M = Cu^{II}, Zn^{II}) fragments, the side lengths of the M_4 unit differ by less than 0.1 Å for both compounds.

Table 2. Metal···metal distances [Å] in **1** and **2** (* = $-x + 1$, $-y + 1$, $-z$. ' = $-x + 2, -y + 1, -z + 1$).

	1		2
Ga(1)–Cu(1)	3.247(3)	Ga(1)–Zn(1)	3.264(2)
Ga(1)–Cu(2)	3.299(3)	Ga(1)–Zn(2)	3.299(2)
Ga(1)–Cu(1)*	3.327(3)	Ga(1)–Zn(1)′	3.310(3)
Cu(1)–Cu(1)*	3.065(4)	Zn(1)–Zn(1)′	3.032(3)
Cu(1)–Cu(2)	3.076(3)	Zn(1)–Zn(2)	3.102(2)
Cu(1)–Cu(2)*	3.140(3)	Zn(1)–Zn(2)′	3.088(2)

The synthesis of **1** and **2** enables the syntheses of a new series of gallotungstates with the general formula $[M_4(H_2O)_2(GaW_9O_{34})_2]^{n-}$. As the two crystal structures show the synthesis of the $(GaW_9O_{34})^{11-}$ Keggin defect fragments to be reproducible, we think that further anions with M = Co^{II}, Ni^{II}, Mn^{II} or Cd^{II} as heteroatoms can be synthesized.

Conclusions

Two new polyoxotungstates, $(NH_4)_5Na_9[Cu_4(H_2O)_2(GaW_9O_{34})_2]\cdot 22H_2O$ (**1**) and $(NH_4)_{14}[Zn_4(H_2O)_2(GaW_9O_{34})_2]\cdot 37H_2O$ (**2**), were synthesized and characterized by single-crystal X-ray analysis. The present work shows that the class of $M_4X_2W_{18}$ sandwich-type polyoxotungstates can be enlarged by new family of anions with $(GaW_9O_{34})^{9-}$ trivacant lacunary Keggin fragments, which has been synthesized and characterized for the first time. The two exponents of this family with M = Cu^{II} and Zn^{II} establish a new series of tungstates comparable to the known series with X = P^V, As^V, Si^{IV} and Ge^{IV}.

Experimental Section

All starting materials and chemicals were used without further purification.

Preparation of $(NH_4)_5Na_9[Cu_4(H_2O)_2(GaW_9O_{34})_2]\cdot 22H_2O$ (1): $Na_2WO_4\cdot 2H_2O$ (3 g, 9.09 mmol) was dissolved in 20 mL H_2O. The pH value of the solution was adjusted to 7 with concentrated hydrochloric acid. A solution of $Ga(NO_3)_3\cdot 9H_2O$ (0.42 g, 1 mmol) in 2 mL distilled water was added. After stirring the reaction mixture at 70 °C for 15 minutes, a solution of $Cu(CH_3COO)_2\cdot H_2O$ (0.35 g, 1.8 mmol) in 2 mL water was added dropwise. The solution was stirred at 70 °C for one hour. After cooling to room temperature, a greenish residue was removed by filtration and 1 mL of a NH_4NO_3 solution (c = 1 mol/L) was added. Green needles of **1** were obtained on slow evaporation. Yield: 388 mg (16%, based on Cu). IR: $\tilde{\nu}$ (cm^{-1}) = 3477 vs, 1627 s, 1406 m, 931 vs, 882 s, 741 s, 520 w, 455 s. Raman: $\tilde{\nu}$ (cm^{-1}) = 954 s, 780 w, 743 w, 702 w, 628 w 570 w, 512 w, 438 w, 393 w, 327 w, 217 m, 154 m, 106 m. EDX: $Cu_4Ga_2H_{68}N_5Na_9O_{92}W_{18}$ (5505.85): calcd. Cu 4.00, Ga 2.00, W 18.00; found Cu 3.80, Ga 2.15, W 18.00.

Preparation of $(NH_4)_{14}[Zn_4(H_2O)_2(GaW_9O_{34})_2]\cdot 37H_2O$ (2): $Na_2WO_4\cdot 2H_2O$ (4 g, 12.13 mmol) and NaOH (1.0 g, 25 mmol) were dissolved in 50 mL H_2O. A solution of Ga_2O_3 (0.125 g, 0.67 mmol), dissolved in 5 mL of boiling concentrated hydrochloric acid, was added dropwise and the pH was adjusted to 7. The solution was heated to 80 °C and vigorously stirred for two hours. Afterwards, the solution was cooled to room temperature and $Zn(NO_3)_2\cdot 6H_2O$ (446.2 mg, 1.5 mmol), dissolved in 6 mL of water, was added. After 20 minutes, the solution was filtered and 3 mL of a NH_4Cl solution (c = 1 mol/L) was added. Colorless single crystals of **2** were obtained on slow evaporation. Yield: 531 mg (25%, based on Zn). IR: $\tilde{\nu}$ (cm^{-1}) = 3448 vs, br, 2361 w, 2087 w, 1630 s, 1384 m, 925 s, 875 s, 738 s, 451 s. Raman: $\tilde{\nu}$ (cm^{-1}) = 949 s, 900 m, 532 w, 445 w, 351 w, 225 m, 154 m, 107 m. EDX: $Ga_2H_{134}N_{14}O_{107}W_{18}Zn_4$ (5749.40): calcd. Zn 4.00, Ga 2.00, W 18.00; found Zn 4.11, Ga 2.15, W 18.00.

Instrumentation and Analytical Procedures: IR spectra were measured with a Perkin–Elmer 683 spectrometer as KBr pellets. Raman spectra were performed with a Bruker-IFS 113-V-spectrometer. The atomic ratios of the heavy elements were determined by energy dispersive X-ray fluorescence analysis (EDX).

X-ray Crystallography and Data Collection: Diffraction experiments were performed with a STOE IPDS imaging plate system (for **1**) and a Bruker Smart Apex diffractometer with CCD detector (for **2**), both using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Structures were solved by direct methods (for **1**) or Patterson Synthesis (for **2**) with the SHELXS-97[19] and refined with the SHELXL-97 program.[20] No hydrogen atoms were included. Nitrogen atoms of ammonium cations were modeled as oxygen atoms because nitrogen atoms could not be distinguished from oxygen atoms. All metal atoms and oxygen atoms of the anions were refined anisotropically by full-matrix least-squares calculations based on F^2, the crystal water molecules were refined isotropically. The programs SADABS[21] (for **2**) and DECAY[22] (for **1**) were applied as absorption correction. As usual for polyoxometalates, the crystal structures show disorder in the crystal water molecules. Crystallographic data for **1** and **2** are summarized in Table 3.

Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldhafen, Germany; Fax: +49-7247-808-666, E-mail: crysdata@fiz-karlsruhe.de, on quoting the depository number CSD-414617 (for **1**) and CSD-414618 (for **2**).

Table 3. Crystallographic data for $(NH_4)_5Na_9[Cu_4(H_2O)_2(GaW_9O_{34})_2] \cdot 22\,H_2O$ (**1**) and $(NH_4)_{14}[Zn_4(H_2O)_2(GaW_9O_{34})_2] \cdot 37\,H_2O$ (**2**).

	1	**2**
Formula	$H_{68}Cu_4Ga_2N_5Na_9O_{92}W_{18}$	$H_{134}Ga_2N_{14}O_{107}W_{18}Zn_4$
Formula mass, M [g/mol]	5505.85	5749.40
Crystal color/habit	green needles	colorless needles
Crystal size [mm]	0.9 × 0.1 × 0.1	0.32 × 0.10 × 0.05
Crystal system	orthorhombic	triclinic
Space group	*Pccn*	$P\bar{1}$
a [Å]	21.810(4)	12.401(2)
b [Å]	17.910(4)	13.778(3)
c [Å]	20.360(4)	14.658(3)
α [°]		99.08(3)
β [°]		103.71(3)
γ [°]		102.50(3)
V [Å^3]	7953(3)	2317.0(8)
Z	4	1
$d_{\text{calcd.}}$ [g/cm^3]	4.599	4.121
μ [mm^{-1}]	27.805	23.970
T [K]	153(2)	173(2)
Measured reflections	57710	23807
Independent reflections	7781 [R_{int} = 0.1681]	11186 [R_{int} = 0.0603]
Unique refl. [$I > 2\sigma(I)$]	6394	8781
Index range	$-26 \leq h \leq 26$ $-22 \leq k \leq 22$ $-24 \leq l \leq 25$	$-16 \leq h \leq 16$ $-18 \leq k \leq 18$ $-19 \leq l \leq 19$
Parameters	356	557
2θ range [°]	$8.52 < 2\theta < 52.08$	$3.94 < 2\theta < 56.08$
R [$I > 2\sigma(I)$]	R_1 = 0.0628[a] wR_2 = 0.1510[b]	R_1 = 0.0537[a] wR_2 = 0.1164[b]
R (all data)	R_1 = 0.0757[a] wR_2 = 0.1604[b]	R_1 = 0.0732[a] wR_2 = 0.1243[b]
Goof on F^2	1.070[c]	1.030[c]
Weighting scheme	a = 0.0874 b = 236.87	a = 0.0303 b = 32.69
$(\Delta\,\rho)_{\text{max.}}$, [e$^-$Å^3]	2.658	3.406
$(\Delta\,\rho)_{\text{min.}}$, [e$^-$Å^3]	–4.640	–2.941

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; with $P = (\text{max.}\,(F_o^2, 0) + 2F_c^2)/3$. [c] Goof $= [(\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, n = number of reflections, p = parameters used.

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