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Synthesis, crystal structure and catalytic activity of Guanidinium cation directed Nickel (II)-containing open Wells–Dawson 19-tungstodiarsenate (III) $[{Ni(H_2O)_4}_2{Na(H_2O)}As_2W_{19}O_{67}(H_2O)]^{9-}$

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А new example of open Wells-Dawson type 19-tungstodiarsenate (III) $[{Ni(H_2O)_4}_2{Na(H_2O)}As_2W_{19}O_{67}(H_2O)]^9$ polyanion 1 has been synthesized in a single step reaction protocol, on interaction of nickel chloride with sodium salt of trilacunary $[B-\alpha-$ AsW₉O₃₃]⁹⁻ ligand in aqueous solution (pH ~5.8), in presence of pyridine-2,6-dicarboxylic acid. Guanidinium cation plays a structure-directing role to crystallize polyanion 1 as mixed salt of sodium and guanidinium salt in triclinic space group P-1. The solid state structure shows an open Wells–Dawson type $[As_2W_{19}O_{67}(H_2O)]^{14}$ anion containing two nickel atoms in octahedral geometry. Mixed sodium and guanidinium salt of polyanion 1 was further characterized by FT-IR, single crystal X-ray diffraction, thermogravimetric analysis, and vibrating sample magnetometry (VSM). Polyanion 1a was screened as a catalyst for oxidation of styrene.

Introduction

Polyoxometalates (POMs) are molecular entities of early transition metal MO_6 (M = W, Mo, V, Ta, etc.) octahedra generally in their high oxidation states and main group XO₄ (X = P, Si, As, etc.) tetrahedra, forming a separate class of inorganic nanoclusters. POM compounds have some important properties like wide range of structural diversity (size and shape), flexibility, acidity, solubility, thermal stability, high charge density and redox stability, due to these intrinsic properties, POMs are thoroughly studied in the area of catalysis, medicine, molecular magnets, imaging techniques, biotechnology, and materials design.¹⁻¹⁰ Keggin and Wells– Dawson type POM nanoclusters are well known, but some other molecular entities like open Wells-Dawson, Anderson, and Preyssler type polyoxoanion are not much explored. The structural flexibility of POM compounds depends on size, shape and nature of the cation, number of vacant sites, and oxidation state of heteroatom (e.g. As^{III} vs As^V). As a result, synthesis of new POM complexes in open-air aqueous medium and the diversity in structural architecture with potential applications still remains an important research objective.

Transition metal substituted POM compounds are important subclasses of metal oxide chemistry, among them lone pair containing As^{III} and Sb^{III} heteroatom containing sandwich type

complexes form a separate family for these subclass compounds. In this series, Robert et al. reported the copper containing $[As_2W_{18}Cu_3O_{66}(H_2O)_2]^{12}$ sandwich type polyanion, in which three Cu^{2+} ion are locked in the belt position and geometrically not in same environment.¹¹ Later, Kortz et al. reported a family of sandwich type complexes, as trisubstituted $[(\alpha-XW_9O_{33})_2M_3(H_2O)_3]^{12-}$ (M = Cu^{2+} , Zn^{2+} ; X = As^{II} , Sb^{III}) and disubstituted $[(\alpha-AsW_9O_{33})_2WO(H_2O)M_2(H_2O)_2]^{10-}$ (M = Co^{2+} , Mn^{2+}) polyanions.¹² Mean time Mialane et al. reported three sandwich type arsenato polytungstates $[As_2W_{18}M_3O_{66}]^{12-}$ (M = Mn^{II} , Co^{II} , and V^{IV}/V^V), in addition they also reported two Ni(II) containing

 $((CH_3)_4N)Na_7[(Mn^{III}(H_2O))_3(SbW_9O_{33})_2] \cdot 24 \cdot 5H_2O,$

 $\begin{array}{ll} Na_{8\cdot25}[(Mn^{III}(H_2O))_{2.25}(WO(H_2O))_{0.75}(AsW_9O_{33})_2]\cdot 28H_2O, & \text{and} \\ Na_3K_9[Mn^{II}(H_2O)Mn_2(AsW_9O_{33})_2]\cdot 16H_2O & \text{complexes.}^{15} \\ \text{Sandwich-type dititanium containing 19-tungstodiarsenate (III)} \\ [Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8\cdot} & \text{was also reported by one of us,} \\ \text{and used as an oxidation catalyst.}^{16} \end{array}$

Hervé et al. discovered a new molecular entity $[{K(H_2O)_3}_2{K(H_2O)_2}(Si_2W_{18}O_{66})]^{13}$, which was the first example of an open Wells-Dawson structure.¹⁷ This compound was used as a polydentate ligand and reacted with transition metals, which leads to the formation of new complexes with open Wells-Dawson structure, likewise $[\{Co(H_2O)\}\{Co(H_2O)_4\}\{K(H_2O)_2\}(Si_2W_{18}O_{66})]^{12}$ $[{M(H_2O)}(\mu-H_2O)_2K(Si_2W_{18}O_{66})]^{13-}$ (M = Co²⁺, Ni²⁺, Cu²⁺), $[\{M(H_2O)\}(\mu-H_2O)_2K\{M(H_2O)_4\}(Si_2W_{18}O_{66})]^{11} (M = Mn^{24}$ Ni²⁺), $[{KV_2O_3(H_2O)_2}(Si_2W_{18}O_{66})]^{11}$ Co^{2+} , and $[\{Fe_4(OH)_6\}(Si_2W_{18}O_{66})]^{10-} \text{ polyanions.}^{17-19} \text{ Later, Liu et al.}$ the similar structural complexes reported with germanotungstates: $K_{13}[{Co(H_2O)}(\mu \begin{array}{l} H_2O)_2K(Ge_2W_{18}O_{66})]\cdot 29H_2O \quad \text{and} \quad [\{M(H_2O)\}(\mu-H_2O)_2K\{M(H_2O)_4\}(Ge_2W_{18}O_{66})]^{11-} (M=Co^{2+}, Ni^{2+}, Mn^{2+}).^{20, 21-} \end{array}$ To till date, no such open Wells-Dawson type structure are reported for lone pair containing heteroatoms. Herein, we report a new guanidinium cation directed nickel based open Wells-Dawson 19-tungstodiarsenate (III) $[\{Ni(H_2O)_4\}_2\{Na(H_2O)\}As_2W_{19}O_{67}(H_2O)]^{9^-}$ (1) polyanion. The polyanion 1 has been synthesized by a single step reaction of nickel chloride with sodium salt of trilacunary [B-α-AsW₉O₃₃]⁹⁻ POM ligand in aqueous solution, in the presence of pyridine-2,6-dicarboxylic acid.

Experimental

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Materials and methods

The trilacunary Na₉[α-AsW₉O₃₃]·27H₂O was prepared according to the published literature procedure and its purity was confirmed by FT-IR spectrum.²² All other chemicals were commercially purchased and were used without further purification. The Fourier transform (FT-IR) spectra were recorded with Perkin-Elmer BX spectrum on KBr pellets. The abbreviations used to define the peak intensities, s = strong, m = medium, w = weak, sh = shoulder. The UV/vis spectrum in solution was recorded by an Analytic Jena Specord 250 spectrometer. Thermogravimetric analysis (TGA) were performed using a TG/DTA instrument DTG-60 Shimadzu between temperature range of 25-700 °C in a nitrogen atmosphere with a heating rate of 5 °C/min. Elemental analysis data were collected from ICP-AES instrument, ARCOS from M/s Spectro Germany. Magnetic measurements were performed on a Micro sense ADE-EV9 magnetometer from -22 to 22 kOe applied magnetic field at room temperature.

$$\label{eq:constraint} \begin{split} & [C(NH_2)_3]_5Na_4[(Ni(H_2O)_4]_2\{Na(H_2O)\}As_2W_{19}O_{67}(H_2O)]\cdot 22H \\ & _2O~(1a) \end{split}$$

0.0713 g (0.3 mmol) of NiCl₂·6H₂O was dissolved in 20 ml of H₂O with stirring. 0.0167 g (0.1 mmol) of pyridine-2,6dicarboxylic acid was added in it, a light green solution was obtained. Solution was heated to 80 °C for 60 minutes and then 0.2464 g (0.1 mmol) of Na₉[α -AsW₉O₃₃] was added to the solution with continuous stirring. A clear green solution of pH 5.8 was obtained and cooled down to the room temperature, 1 ml of 0.5 M guanidinium chloride was added and the solution was left aside. After 2-3 weeks rod like green crystals were obtained, with an yield 0.1154 g, 46.3% (based on Na₉[α -AsW₉O₃₃]·27H₂O). FT-IR: 1654(s), 946(m), 885(s), 792(sh), 746(s), 617(m), 501(m), 472(m), 441(w) (cm⁻¹). Elemental analysis (%); calcd (found): N 3.61 (3.52), Na 1.97 (1.86), As 2.57 (2.57), W 59.97 (59.87), Ni 2.02 (1.98).

Single crystal X-ray crystallography

A single crystal suitable for X-ray diffraction for compounds 1a was mounted on a capillary tube for indexing and intensity data collection at 183(2) K on an Oxford Xcalibur Ruby CCD single-crystal diffractometer (MoK_a radiation, $\lambda = 0.71073$ Å).²³ Routine Lorentz and polarization corrections were applied, and an absorption correction was performed using the ABSCALE 3 program. Pre-experiment, data collection, data reduction and analytical absorption corrections²⁴ were performed with the Oxford program suite CrysAlisPro.25 The crystal structures were solved with SHELXS-97 using direct methods.²⁶ The structure refinements were performed by fullmatrix least-squares on F2 with SHELXL-97.26 All programs used during the crystal structure determination process are included in the WINGX software.²⁷ All heavy atoms (W, Ni, As) were refined anisotropically, The atoms (Na, O, C, N) are refined isotropically. The crystal data for the polyanion 1a is summarized in Table 1.

A further detail on the crystal structure data may be obtained from CCDC 1033756 contains the supplementary crystallographic data for **1a**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.on quoting the depository number CCDC - 1033756.

Result and discussion

Synthesis and structure

The title polyanion 1a was isolated by the reaction of nickel chloride with trilacunary Na₉[B-α-AsW₉O₃₃] POM ligand in presence of pyridine-2,6-dicarboxylic acid in aqueous medium pH (~5.80). The starting materials were added in 3:1:1 molar ratio. Later, 1 ml of 0.5 M guanidinium chloride was added to the reaction mixture. Rod like green single crystalline material was collected after 2-3 weeks, and characterized as a mixed sodium - guanidinium salt of open Wells-Dawson type $[{Ni(H_2O)_4}_2 {Na(H_2O)} As_2 W_{19} O_{67}(\dot{H}_2O)]^{9-}$ (1) molecular structure. Here the guanidinium cation plays an important role for the isolation of polyanion 1a, whereas addition of caesium cation leads to the formation of $[{Ni(H_2O)}_2As_2W_{19}O_{67}(H_2O)]^{10}$ polyanion, which was earlier reported by Mialane et al.¹⁴ Such observation was previously reported by Kortz et al.28

The solid-state structure of the title polyanion **1a** reveals that the polyanion consists of two $[B-\alpha-AsW_9O_{33}]^{9}$. Keggin units which connect to an extra WO(H₂O) group, forming a dilacunary $[As_2W_{19}O_{67}(H_2O)]^{14}$ anion type moiety.^{28, 29} In addition two nickel atoms and one sodium atom are coordinated to one of the $[B-\alpha-AsW_9O_{33}]^{9}$. Keggin unit. Both the nickel atoms are coordinated to two different triads of $[B-\alpha-AsW_9O_{33}]^{9}$. Keggin unit via μ_2 -oxo bridges (Ni-O-W), and also to sodium cation by μ_2 -dioxo bridges (Ni-O-Na), the presence of sodium cation in the centre of both the nickel atom bears two terminal aqua ligand, thus leading to a distorted octahedral geometry. The other $[B-\alpha-AsW_9O_{33}]^{9}$. Keggin unit does not bond with nickel atoms but connect to nickel coordinated $[B-\alpha AsW_9O_{33}]^{9}$. Keggin unit via WO(H₂O) group, where the tungsten octahedra act as an hinge, thus forming an open molecular structure having nominal C_{2V} symmetry. [see **Fig. 1**]. Published on 04 March 2015. Downloaded by University of Pennsylvania Libraries on 04/03/2015 10:36:03

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 Table 1: Single crystal X-ray crystallographic data for compound 1a

coordinated to each nickel atom, are coordinated to sodium cation present at the centre.

Emperical Formula	$C_5As_2N_{15}Na_2Ni_2O_{91}W_{19}$
Formula weight	5532.59
Crystal system	Triclinic
Space group	P-1
<i>a</i> [Å]	13.1357(4)
<i>b</i> [Å]	16.6865(5)
<i>c</i> [Á]	26.3032(6)
α [°]	84.426(2)
β[ໆ]	84.995(2)
γ[⁹]	66.972(3)
V [Å ³]	5273.2(3)
Z	2
$\rho_{\text{calcd}} [\text{g cm}^{-3}]$	3.484
$\mu [\mathrm{mm}^{-1}]$	21.714
F_{000}	4826
Refelection collected	211119
Unique (Rint)	20751
Observed[$I > 2\sigma(I)$]	
Parameters	760
Gof	1.056
$R[I > 2\sigma(I)]^{[a]}$	0.0450
Rw(all data) ^[b]	0.1069
a] $R = \sum IIFoI - IFcII/\sum C^2)^2 / \sum w(Fo^2)^2]^{1/2}$	IFoI. [b] $R_{\rm w} = [\sum w(Fo^2) -$



Fig. 1 Ball and polyhedron representation of the polyanion $[{Ni(H_2O)_4}_2{Na(H_2O)}A_2W_{19}O_{67}(H_2O)]^{9}$ Color code: blue polyhedron: tungsten; green ball: nickel; pink ball: arsenic; orange ball: sodium; aqua ball: water molecule; red ball: oxygen.

The bond valence sum (BVS) calculations³⁰ show that both nickel atoms are present in +2 oxidation state and Ni(1)-O(68), Ni(1)-O(69), Ni(1)-O(70), Ni(1)-O(71) represents the four water molecules for Ni(1) atom, whereas Ni(2)-O(74), Ni(2)-O(75), Ni(2)-O(76), and Ni(2)-O(77) represents water molecules coordinated with Ni(2) atom. Two of the aqua ligand

Table 2: Selected bond distance (Å) for polyanion 1a								
C(1)—N(1)	1.38(3)	W(1)—O(6)	1.987(10)					
C(2)—N(6)	1.33(2)	W(2)—O(9)	1.867(9)					
C(3)—N(7)	1.31(2)	W(3)—O(25)	2.371(9)					
C(4)—N(10)	1.29(2)	W(4)—O(25)	2.281(8)					
C(5)—N(13)	1.36(2)	W(6)—O(17)	1.720(11)					
O(1)—W(1)	1.710(12)	W(6)—O(18)	1.93(1)					
O(4)—W(1)	1.975(10)	W(8)—O(21)	1.70(1)					
O(7)—W(5)	2.079(10)	W(8)—O(27)	2.390(9)					
O(8)—W(6)	2.108(10)	W(9)—O(25)	2.383(9)					
Na(1)—O(39)	2.476(11)	W(10)—O(34)	1.72(1)					
Na(1)—O(74)	2.497(11)	W(10)— O(35)	2.388(12)					
As(1)— O(25)	1.789(9)	W(11)—O(42)	1.726(11)					
As(2)— O(54)	1.800(9)	W(12)— O(45)	1.928(9)					
Ni(1)— O(39)	2.062(9)	W(16 ⁱ)—O(72)	1.719(10)					

The title polyanion **1a** closely resembles Mialane et al. reported cluster

 $K_8[Ni(H_2O)_6]_{1.5}[As_2W_{19}(H_2O)\{K(H_2O)\}\{Ni(H_2O)_4\}O_{67}]\cdot 21H_2$ O¹⁴ but with structural differences. The title polyanion **1** is an open Wells–Dawson structure, while polyanion reported by Mialane et al. is a closed sandwich type complex. In polyanion **1** the two nickel atoms are coordinated to one of the $[B-\alpha$ -AsW₉O₃₃]⁹⁻ lacunary fragments with extra tungsten centre and a sodium cation, while one nickel atom with extra tungsten and a potassium cation is present in belt position of the polyanion reported by Mialane et al.

In the solid state structure of polyanion 1a, the guanidinium cations present on the outer peripheral of the molecular cluster showing N-H···O_{POM} interactions of the guanidinium cation with terminal and bridging oxygen atoms of the polyanion [Fig. S1], and some interactions also with aqua ligands present in the crystal lattice. The H-bonding in between N3-H···O79(aqua), N5-H···O47(b), N6-H···O20(b), N7-H···O19(t), N11-H···O11(b), N15-H···O47(b) atoms, and the distances of these interactions are in the range of 2.777 - 3.057 Å [Fig. S2]. In the structure, N-H…O_{POM} interactions extended the POM unit in three-dimensional molecular structure [Fig. S1]. As a result, guanidinium cations are the essential requirement for the isolation of the polyanion 1a, such structure directing influence of guanidinium cations was previously reported in literatures.³¹⁻

Infrared spectroscopy

The FT-IR spectrum of title compound **1a** [**Fig. S3**] shows four characteristic vibration bands centred at 946, 885, 792, and 746 cm⁻¹, which are assigned for $v_{as}(W-O_t)$, $v_{as}(W-O_b)$, $v_{as}(As-O_a)$, and $v_{as}(W-O_c)$ bonds, respectively.³³ The IR frequencies of title

compound are very similar to the $[As_2W_{19}O_{67}(H_2O)]^{14}$ anion on comparison, and these observations conclude that the trilacunary $[B-\alpha-AsW_9O_{33}]^{9^-}$ anion converts to the dilacunary $[As_2W_{19}O_{67}(H_2O)]^{14^-}$ anion during the course of reaction [**Fig. S4**]. The pH of the reaction mixture ~5.80, is also evident for the transformation of POM ligand, reported in literature.³⁶ In addition three extra peaks are also observed due the presence of guanidinium cation. Two peaks centered at 3350 and 3173 cm⁻¹ are assigned to NH₂ group, and a strong peak centered at 1654 cm⁻¹ is attributed to C=N group, present in the guanidinium cation [**Fig. S3**].

UV-visible spectroscopy

The UV/vis spectrum [Fig. S5] for the polyanion 1a was also recorded in aqueous solution and we observed two absorption bands in the spectrum, first stronger band at 191 nm is due $p\pi$ - $d\pi$ charge transfer transitions of terminal oxygen atom (O_t) to d-orbitals of tungsten atoms, and a weak broad absorbance band around at 260 nm is due $p\pi$ - $d\pi$ charge transfer transitions of O_(b,c) \rightarrow W bonds present in the polyanion 1a.

Thermogravimetric analysis

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The thermogravimetric (TG) analysis of title compound **1a** was performed from room temperature to 700 °C under nitrogen flowing atmosphere with 5 °C/min heating rate [**Fig. S6**]. The compound shows four consecutive steps of weight loss due to crystal water molecules, guanidinium cation, and finally due to decomposition of the compound. The first weight loss step form room temperature to ~200 °C (9.73 %) corresponds to loss of 31 crystal water molecules. The second weight loss from 200 °C to 400 °C (6.3 %) corresponds to release of five guanidinium cations, later the compound starts decomposing from ~500 °C to 600 °C.

Vibrating sample magnetometry

Vibrating sample magnetometry (VSM) was performed for the title polyanion **1a** at room temperature, using Microsense ADE-EV9 vibrating sample magnetometer in the magnetic field from -22 to 22 kOe. A plot magnetization (M) versus applied magnetic field (H), which is named as M-H curve, is shown in **Fig. 2**. The compound shows paramagnetic behaviour and μ_{eff} value calculated from data was found to be 3.23 μ_B , which are in the range of observed μ_{eff} values for Ni²⁺ single ion. These suggest that no interaction phenomenon within the two nickel centre.



Fig. 2 Magnetization (M-H) curve of 1a at room temperature.

Catalytic oxidation of styrene

The compound 1a was tested as an oxidation catalyst for the oxidation of styrene in homogeneous medium. The catalytic reactions were performed by using styrene (2 mmol) as a substrate, catalyst **1a** (0.15 mol%), and aqueous H_2O_2 as an oxidant in acetonitrile solvent. The oxidation products of styrene were identified by comparing retention time on GC with their standard references and also confirmed by GC-MS. The results show (see Table 3) that at 60 °C temperature, H₂O₂/substrate (4:1), 30% conversion of styrene was observed with 74% selectivity of benzaldehyde and remaining byproduct's after 6h (Table 3, entry 1). When the temperature was increased to 70 °C for the same reaction conditions, conversion was improved to 50% and 72% selectivity of benzaldehyde was observed and further increase in temperature to 80 °C, conversion was increased to 82% and selectivity slightly reduced (Table 3, entry 3). The effect of oxidant (H₂O₂) was also investigated at 80 °C for the same reaction conditions, for H₂O₂/substrate (3:1) that converted styrene to benzaldehyde in 83%, with 65% selectivity (Table 3, entry 3, 4 and 6). These results show that increase in H_2O_2 /substrate ratio from 2:1 to 3:1 conversion also increased but further increase in H₂O₂/substrate ratio to 4:1, no change in conversion was observed. The conversion was also monitored at 3h and 9h for the reaction in which 3:1 (H₂O₂/substrate) was used, to see the effect of time, we found that at 3h, 61% conversion was observed with 73% selectivity of benzaldehyde, and later at 9h, 94% conversion but with decrease in selectivity (59%) (Table 3, entry 5 and 7). The selectivity of benzaldehyde decreased with time due to aerial oxidation of benzaldehyde to benzoic acid. The reaction of styrene oxidation was also performed with $Cs_6K_2[Ni(H_2O)_6][As_2W_{19}(H_2O){Ni(H_2O)}_2O_{67}] \cdot 17H_2O$ POM reported by Mialane et al. and we found that 87% conversion was observed for oxidation of styrene, with 66% selectivity for benzaldehyde at 9h by using 3:1 (H_2O_2 /substrate) (Table 3, entry 8). Styrene oxidation was also carried out separately in presence of POM ligand K14[As2W19O67(H2O)] and also NiCl₂·6H₂O at 80 °C gives 34% and 11% conversions after 6h (Table 3, entry 9 and 10) respectively, these results are comparatively poor than the polyanion 1a. In addition, the catalytic reaction was also performed in presence of both NiCl₂·6H₂O salt and K₁₄[As₂W₁₉O₆₇(H₂O)] POM ligand which gives slightly improved conversion (Table 3, entry 11), that suggests the molecular cluster polyanion 1a shows better catalytic activity. Furthermore, the styrene oxidation was also performed using the reaction conditions mentioned in the very recently reported work³⁷ by Duarte et al. of known catalysts and we found 91% conversion was obtained in 6h and benzaldehyde was obtained as a major product with 60% selectivity (Table 3, entry 12), with other minor products. We have also studied the recyclability of the catalyst (see Table S1). The catalyst can be reused up to 2 cycles with gradual decrease in conversion of styrene.

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Table 3: Catalytic oxidation of styrene in presence of catalyst **1a** and aqueous H₂O₂.^a



Entry H ₂ O ₂ /substrat	U O /substrata	Temperature (°C) Tin	Time (h)	Conversion (%) ^b	Selectivity for different products (%)					
	112Og/substrate		Time (ii)		(ii)	(iii)	(iv)	(v)	(vi)	(vii)
1	4:1	60	6	30	74	3	12	-	11	-
2	4:1	70	6	50	72	2	11	4	11	-
3	4:1	80	6	82	68	2	10	6	14	-
4	2:1	80	6	52	71	2	7	5	15	-
5	3:1	80	3	61	73	2	12	3	10	-
6	3:1	80	6	83	65	2	12	8	13	-
7	3:1	80	9	94	59	2	8	13	18	-
8	3:1	80	9	87°	66	2	8	10	11	3
9	3:1	80	6	34 ^d	76	5	10	-	9	-
10	3:1	80	6	11 ^e	94	-	6	-	-	-
11	3:1	80	6	36 ^f	72	6	10	6	6	-
12	4:1	80	6	91 ^g	60	3	11	12	14	-

^aReaction conditions: 2 mmol (styrene), 0.15 mol% **1a** catalyst, in 2 mL CH₃CN stirred for specified temperature and time. ^bConversion was determined by GC. $^{c}Cs_{6}K_{2}[Ni(H_{2}O)_{6}][As_{2}W_{19}(H_{2}O)\{Ni(H_{2}O)\}_{2}O_{67}] \cdot 17H_{2}O$ (0.15 mol%) was used as catalyst. ^dK_{14}[As_{2}W_{19}O_{67}(H_{2}O)] (0.15 mol%) was used as catalyst. $^{6}NiCl_{2} \cdot 6H_{2}O$ (5.0 mol%) was used as catalyst. $^{6}NiCl_{2} \cdot 6H_{2}O$ + K₁₄[As₂W₁₉O₆₇(H₂O)] (0.3 + 0.15) mol% used as catalyst. $^{g}1$ mmol (styrene), 0.30 mol% catalyst **1a** in 3 mL CH₃CN.

Conclusions

In conclusion, we have isolated a new guanidinium cation directed nickel based open Wells-Dawson type polyanion with containing lone pair heteroatom $[\{Ni(H_2O)_4\}_2\{Na(H_2O)\}As_2W_{19}O_{67}(H_2O)]^{9-1}$ by a one pot reaction in aqueous solution pH 5.8. The title polyanion 1a was structurally characterized by single crystal X-ray diffraction and other analytical techniques including FT-IR,

thermogravimetric analysis and VSM studies in solid state. Single crystal X-ray studies show that the title polyanion **1a** is an example of open Wells–Dawson anion, in addition the guanidinium counter cations act as a structure-directing agent. FT-IR spectroscopy shows the transformation of trilacunary [α -AsW₉O₃₃]⁹⁻ anion to dilacunary [As₂W₁₉O₆₇(H₂O)]¹⁴⁻ anion. VSM studies show the paramagnetic behaviour of title polyanion **1a** at room temperature in the presence of applied magnetic field. The polyanion **1a** was also screened as an oxidation catalyst for oxidation of styrene, and it shows good

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catalytic conversion of styrene with prominent selectivity of benzaldehyde.

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Notes and references

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[†] Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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