

V-Shaped Polyoxotungstoarsenates Incorporating a Prism-Like Hexa Transition-Metals Center: $[M_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})]^{17-}$ ($M^{2+} = Mn^{2+}, Co^{2+}, Zn^{2+}$)#

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Hexa transition-metals incorporated polyoxotungstoarsenates, $[M_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})]^{17-}$ ($M^{2+} = Mn^{2+}, Co^{2+I}, Zn^{2+}$), have been prepared at pH 7–8 and characterized by elemental analysis, electrochemistry, and X-ray crystallography: $Na_{17}[Mn_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})]\cdot 41H_2O$ (**1**), $P2_1/c$, $a = 17.73(1)$ Å, $b = 22.34(1)$ Å, $c = 35.41(3)$ Å, $\beta = 95.37(3)°$, $V = 13963(14)$ Å^3, and $Z = 4$; $Na_{17}[Co_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})]\cdot 41H_2O$ (**2**), $P2_1/c$, $a = 17.65(1)$ Å, $b = 22.24(1)$ Å, $c = 34.78(2)$ Å, $\beta = 95.84(2)°$, $V = 13584(13)$ Å^3, and $Z = 4$; $Na_{17}[Zn_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})]\cdot 38H_2O$ (**3**), $P2_1/c$, $a = 17.6295(6)$ Å, $b = 22.2992(7)$ Å, $c = 34.927(1)$ Å, $\beta = 95.695(2)°$, $V = 13662.8(7)$ Å^3, and $Z = 4$. The anion of **1**–**3** consists of two B-α $[\{M(H_2O)\}M_2(AsW_9O_{34})]^{3-}$ units joined by a B-type hexa-vacant $[AsW_6O_{26}]^{11-}$ fragment, corresponding to a removal of the edge-sharing W_3O_8 moiety from B-α $[AsW_9O_{34}]^{9-}$, to form a C_{2v}-symmetric V-shaped geometry. Two edge-sharing MO_6-octahedral triads (with M···M distances 3.2–3.4 Å) are well-separated with M···M distances of 5.5–8.9 Å. Three successive electrochemically quasi-reversible two-electron Mn^{II}/Mn^{III} waves were observed in the cyclic voltammogram of **1**. M^{2+} ion with larger radius causes an elongation of the As···As distances. A single Na^+ cation coordinated by three oxygen atoms (two belonging to B-α $[AsW_9O_{34}]^{9-}$ and one belonging to B-$[AsW_6O_{26}]^{11-}$) in the crevice of the anion stabilizes the V-shaped structure.

In the presence of trivalent rare-earth ions (Ln^{3+}) and divalent transition-metal ions (M^{2+}), B-type tri-vacant fragments $[As^{III}W_9O_{33}]^{9-}$ and $[As^VW_9O_{34}]^{9-}$, which are produced by removal of three WO_6 octahedra that are edge-sharing from α-Keggin anions $[As^{III}W_{12}O_{40}]^{5-}$ and $[As^VW_{12}O_{40}]^{3-}$ respectively, self-assemble to form large-sized clusters such as $[Ce_{16}(H_2O)_{36}(WO_2)_4(W_2O_6)_8(W_5O_{18})_4(\alpha\text{-}As^{III}W_9O_{33})_{12}]^{76-}$,[1] $[K\{Eu(H_2O)_2(As^{III}W_9O_{33})\}_6]^{35-}$,[2] $[Cs\{Eu(H_2O)_2(As^{III}W_9O_{33})\}_4]^{23-}$,[2] $[\{M(H_2O)\}_3(As^{III}W_9O_{33})_2]^{12-}$ ($M = Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}$),[3–5] and $[(M)_4(H_2O)_2(As^VW_9O_{34})_2]^{10-}$ ($M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}$).[6–8] In $[\{M(H_2O)\}_3(As^{III}W_9O_{33})_2]^{12-}$, two B-$\alpha$ $[As^{III}W_9O_{33}]^{9-}$ anions, which incorporate $As^{III}O_3$ trigonal pyramids, sandwich the M_3 triangle with the D_{3h}-symmetric geometry (in an α-Keggin structural motif with the lone pair electrons of two As^{III} atoms pointing away from each other.[3–5] In $[M_4(H_2O)_2(As^VW_9O_{34})_2]^{10-}$, on the other hand, two B-α $[As^VW_9O_{34}]^{9-}$ anions, which incorporate As^VO_4 tetrahedra, sandwich the M_4 rhombohedral-like tetragon with C_i-symmetric geometry with a β-Keggin structural motif.[6–8] Figure 1 shows the D_{3h}- and C_i-symmetric sandwiched structures of $[\{M(H_2O)\}_3(As^{III}W_9O_{33})_2]^{12-}$ and $[M_4(H_2O)_2(As^VW_9O_{34})_2]^{10-}$.

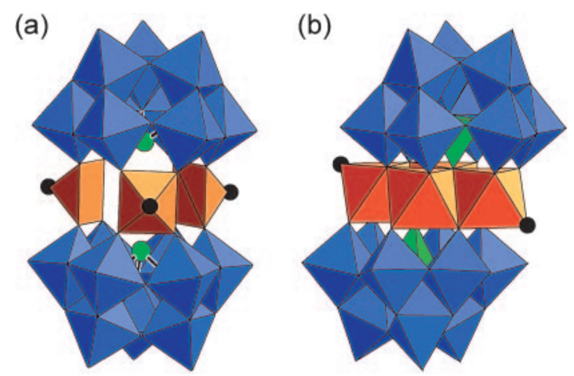

Fig. 1. Combined polyhedral/ball-and-stick representations of D_{3h}-symmetric $[\{M(H_2O)\}_3(As^{III}W_9O_{33})_2]^{12-}$ (a) and C_i-symmetric $[M_4(H_2O)_2(As^VW_9O_{34})_2]^{10-}$ (b) anions with the structure sandwiched by tri-vacant B-type fragments. Blue, green, and orange in the polyhedral representation indicate WO_6, AsO_4, and MO_5 (or MO_6) polyhedra respectively, and green and black in ball-and-stick representation indicate As^{III} and water O atoms respectively.

The use of $NaAs^{III}O_2$ instead of $Na_2HAs^VO_4$ in a preparation method of $K_{10}[Zn_4(H_2O)_2(As^VW_9O_{34})_2]\cdot 23H_2O$[6] led to the formation of $[WCo_2(H_2O)_3(As^{III}W_9O_{33})_2]^{8-}$ which has a different structure.[9] Interestingly, when $Na_2HAs^VO_4$ was used instead of $NaAs^{III}O_2$ to prepare $K_{12}[Cu_3(H_2O)_2(As^{III}W_9O_{33})_2]\cdot 11H_2O$,[3] V-shaped polyoxotungstates $Na_{17}[Mn_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})]\cdot 41H_2O$ (**1**), $Na_{17}[Co_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})]\cdot 41H_2O$ (**2**), and $Na_{17}[Zn_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})]\cdot 38H_2O$ (**3**) were afforded.[10] Complexes **1**–**3** consist of two B-α $[\{M(H_2O)\}M_2(AsW_9O_{34})]^{3-}$ fragments joined by a B-type hexa-vacant $[AsW_6O_{26}]^{11-}$ frag-

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Table 1. Crystal Data, Structure Determination, and Refinement Data for **1**, **2**, and **3**

	1	**2**	**3**
Formula	$Na_{17}Mn_6As_3W_{24}O_{137}H_{86}$	$Na_{17}Co_6As_3W_{24}O_{137}H_{86}$	$Na_{17}Zn_6As_3W_{24}O_{134}H_{80}$ [c)]
Formula weight	7636.22	7660.19	7644.82
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	17.73(1)	17.65(1)	17.6295(6)
b/Å	22.34(1)	22.24(1)	22.2992(7)
c/Å	35.41(3)	34.78(2)	34.927(1)
$\beta/^\circ$	95.37(3)	95.84(2)	95.695(2)
V/Å^3	13963(14)	13584(13)	13662.8(7)
Z	4	4	4
D_{calcd}/g cm^{-3}	3.632	3.745	3.683
$F(000)$	13576	13624	13444
μ/cm^{-1}	210.96	218.61	220.47
$2\theta_{max}/^\circ$	55	55	55
Crystal dimensions/mm^3	$0.10 \times 0.05 \times 0.03$	$0.12 \times 0.07 \times 0.04$	$0.15 \times 0.12 \times 0.10$
Temperature/°C	−100.0	−100.0	−100.0
No. data	112711	121951	131334
R(int)	0.065	0.047	0.073
No. unique data	31674	31238	32008
No. refinement data	12138	14661	15114
No. variables	1005	942	960
GOF	1.000	0.857	1.008
$R1$ [a)] $[I > 2.0\sigma(I)]$	0.049	0.043	0.065
$wR2$ [b)] $[I > 1.0\sigma(I)]$	0.087	0.099	0.161
Maximum	0.000	0.000	0.000

a) $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. c) For **3** three sodium atoms were not detected by X-ray diffraction due to the disorder. Therefore, the result of the elemental analysis was used for determination of the content of Na^+ in **3**.

ment in approximate C_{2v} symmetry. The structure is analogous to that of $Na_{16.5}Ni_{0.25}[Ni_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})]\cdot 54H_2O$ reported by Kortz et al.[11] However, our synthetic method has an advantage superior to their method: the crystallization of the present compounds occurs within a few days, in contrast with Kortz's method, which needs several months for crystallization. Hill et al. have also reported $K_{4.75}Na_{12.25}[(\{Mn(H_2O)\}Mn_2PW_9O_{34})_2(PW_6O_{26})]\cdot 12H_2O$ and $K_5Na_{12}[(\{Co(H_2O)\}Co_2PW_9O_{34})_2(PW_6O_{26})]\cdot 12H_2O$, prepared by the decomposition of the D_{3h}-symmetric sandwich-type polyoxometalate $K_{12}[\{M(H_2O)_2\}_3(A\text{-}\alpha\ PW_9O_{34})_2]$ (M = Mn, Co).[12–14] Surprisingly, when $P^VO_4{}^{3-}$ was used instead of $As^VO_4{}^{3-}$, a V-shaped anion did not form; however, a C_i-symmetric sandwich anion, $[M_4(H_2O)_2(P^VW_9O_{34})_2]^{10-}$, did form. The present paper describes the synthetic details of V-shaped compounds **1–3** together with the structural characterization involving a Na^+ cation coordinated in the crevice of the V-shaped structure.

Experimental

Synthesis. $Na_{17}[Mn_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})]\cdot 41H_2O$ (**1**) was prepared as follows. An aqueous solution (60 mL at 60–70 °C) containing $Na_2WO_4\cdot 2H_2O$ (59.5 g) and $Na_2HAsO_4\cdot 7H_2O$ (6.3 g) was acidified with 6 M HCl (60 mL), and an aqueous solution (30 mL) of $MnCl_2\cdot 4H_2O$ (6.0 g) was slowly added affording an orange-colored solution. The pH level of the mixture was adjusted to 7–8 with NaOH. The resultant solution was filtered and cooled to room temperature. Crude yellow-colored crystallites precipitated within one day. The crude product (1.0 g) was recrystallized in an aqueous solution (40 mL) of NaCl (1.0 g) and yellow-colored crystals of **1** were isolated when the solution was kept overnight at room temperature. Yield: 9.2% (based on W). Anal. Calcd for $H_{86}O_{137}Na_{17}Mn_6As_3W_{24}$: Na, 5.12; Mn, 4.32; As, 2.94; W, 57.78 wt %. Found: Na, 5.4; Mn, 4.2; As, 2.9; W, 57.5 wt %. IR (KBr disk): 949 (m), 880 (s), 831 (m), 780 (m), and 718 (s) cm^{-1}. Similar procedures by using $Co(NO_3)_2\cdot 6H_2O$ (8.8 g, 0.03 mol) and $Zn(NO_3)_2\cdot 6H_2O$ (8.9 g, 0.03 mol) instead of $MnCl_2$ gave violet-colored crystals of $Na_{17}[Co_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})]\cdot 41H_2O$ (**2**), and the colorless crystals of $Na_{17}[Zn_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})]\cdot 38H_2O$ (**3**), respectively. Yield of **2**: 11.0% (based on W), and of **3**: 7.5% (based on W). Anal. Calcd for $H_{86}O_{137}Na_{17}Co_6As_3W_{24}$: Na, 5.10; Co, 4.62; As, 2.93; W, 57.60 wt %. Found: Na, 5.0; Co, 4.7; As, 3.0; W, 57.7 wt %. IR (KBr disk): 950 (m), 885 (s), 838 (m), 777 (m), and 716 (s) cm^{-1}. Anal. Calcd for $H_{80}O_{134}Na_{17}Zn_6As_3W_{24}$: Na, 5.11; Zn, 5.13; As, 2.94; W, 57.72 wt %. Found: Na, 5.0; Zn, 5.2; As, 3.0; W, 57.6 wt %. IR (KBr disk): 953 (m), 892 (s), 834 (m), 781 (m), and 718 (s) cm^{-1}.

X-ray Structure Determination. Data collection for X-ray structural analysis was done on a Rigaku RAXIS-RAPID imaging plate diffractometer with a graphite monochromator to $2\theta_{max} = 55^\circ$ and Mo Kα radiation ($\lambda = 0.71069$ Å) generated at 50 kV and 38 mA. The structures were solved by direct methods (SHELXS-97)[15] and refined using a full-matrix least-squares refinement. Crystallographic data are given in Table 1. Lorentz polarization effects and a numerical absorption correction (the program Numabs[16] and Shape[17]) were applied to the intensity data, and H atoms were not included in the calculation. The W, As, Na, Mn, Co, and Zn atoms were refined anisotropically (except for disordered atoms), while the rest were refined isotropically. In each complex, some of the Na atoms and solvent water O atoms were disordered. The occupancies of Na16–Na19 and O136–O139 in **1**, and Na15–Na20 and O134–O141 in **2** were fixed at 1/2 throughout the refinements. For **3**, three sodium atoms were not detected by X-ray diffraction due to the disorder. Therefore, the result of the elemental analysis was used for determination of the content of Na^+ in **3**. All calculations were performed on F^2 using the CrystalStructure software package.[18] Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition numbers CSD-416593 (**1**), CSD-416594 (**2**), and CSD-416595 (**3**).

Instrumentation. Infrared spectra were recorded on a Jasco FT/IR-410 spectrometer as KBr discs. The contents of Na, As, Mn, Co, Zn, and W were determined by X-ray fluorescence analysis (with an accuracy of about 2% with a fundamental parameter method for the uniform pellet of sample) on a Shimadzu EDX-800 spectrometer. The water content was measured by thermogravimetric method on an ULVAC-TGD9600MTS9000 instrument. Cyclic voltammograms were measured with a combination of a potentiostat (Hokuto Denko HA-301) with a function generator (Nikko Keisoku NFG-3). Aqueous solutions containing 1 mM **1** (**2** or **3**) and 100 mM NaCl were purged with nitrogen gas and measured by using a glassy carbon ($\phi = 1$ mm) working electrode, a Pt-wire counter electrode, and a Ag/AgCl reference electrode. After each measurement, the working electrode was polished with 0.3 µm Al_2O_3 and rinsed with water to ensure reproducible results.

Results and Discussion

Figure 2a shows the structure of anion for **1**–**3**. The anion of **1**–**3** (with yellow color, violet, and colorless, respectively) consists of two B-α $[\{M(H_2O)\}M_2(AsW_9O_{34})]^{3-}$ units joined by a B-type hexa-vacant $[AsW_6O_{26}]^{11-}$ fragment, which corresponds to removal of the edge-sharing W_3O_8 moiety from B-α $[AsW_9O_{34}]^{9-}$, to form a V-shaped geometry with approximate C_{2v} symmetry. The $[\{M(H_2O)\}M_2(AsW_9O_{34})]^{3-}$ unit incorporates three edge-sharing M at the site for the B-α junction to form α-Keggin structure. The W–O bond distances and angles of all three structures of **1**–**3** are within the usual ranges, and all M centers are octahedrally coordinated by six O atoms with M–O bond distances of 1.97(2)–2.36(2) Å. The three M centers in each edge-sharing MO_6 octahedral triad are not equivalent, because only one (M2 or M5) of them has a terminal aqua ligand with the M2–O95 distance of 2.15(3) Å (or M5–O96 distances of 2.14(2) Å) for **1**, 2.06(2) Å (2.11(2) Å) for **2**, and 2.09(3) Å (2.08(2) Å) for **3**. Anions with analogous structures have been prepared and X-ray crystallographically characterized by other groups: $K_7Na_7[Co_6(H_2O)_2(PW_9O_{34})_2\{CoW_7O_{26}(OH)_2\}]Co(H_2O)_4 \cdot 13H_2O$,[19,20] $Na_{16.5}Ni_{0.25}[Ni_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})] \cdot 54H_2O$,[11] $Na_{17}[Ni_4Mn_2(H_2O)_2(PW_9O_{34})_2(PW_6O_{26})] \cdot 50.5H_2O$,[11] $K_{4.75}Na_{12.25}[Mn_6(H_2O)_2(PW_9O_{34})_2(PW_6O_{26})] \cdot 12H_2O$,[14] and $K_5Na_{12}[Co_6(H_2O)_2(PW_9O_{34})_2(PW_6O_{26})] \cdot 12H_2O$.[14] The V-shaped structure of the anion in **1**–**3** has As1···As3 and As2···As3 distances of 5.919(6) and 5.959(5) Å (As1···As3···As2 angle of 144.4(1)°),

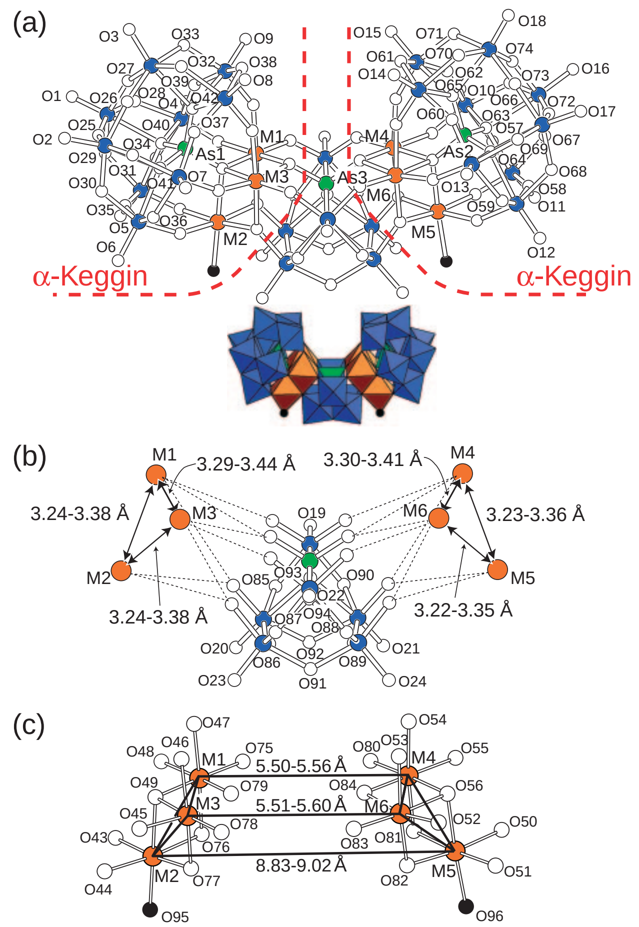

Fig. 2. Ball-and-stick and polyhedral representations of $[M_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})]^{17-}$ ($M^{2+} = Mn^{2+}$, Co^{2+}, and Zn^{2+}) and α-Keggin $[\{M(H_2O)\}M_2(AsW_9O_{34})]^{3-}$ units (a), central B-type hexa-vacant $[AsW_6O_{26}]^{11-}$ fragment coordinating two M_3 triads (b), and two M_3 triads with edge-sharing in a prism-like geometry (c). Blue, green, orange, black, and open circles indicate W, As, M, O atoms of water, and O atoms, respectively. Corresponding colors in the polyhedral representation indicate WO_6, AsO_4, and MO_6 polyhedra, respectively.

5.824(4) and 5.861(4) Å (144.40(7)°), and 5.819(5) and 5.857(5) Å (144.46(9)°), respectively. If a M^{2+} cation with a larger radius is used, elongation of As···As distances occurs, which is similar to $[Ni_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})]^{17-}$ (As···As distances of 5.776(7) and 5.816(6) Å and As1···As3···As2 angle of 144.7(1)°).[11] The edge-sharing $M_3O_{12}(H_2O)$ triads for the two α-Keggin $[\{MO(H_2O)\}(MO_2)_2(AsW_9O_{34})]^{13-}$ wings in the V-shaped geometry have M–M distances of 3.351(8)–3.443(8) Å (with M···M···M angles of 59.3(2)–61.3(2)°) in **1**, 3.217(6)–3.299(5) Å (with 59.1(1)–61.6(1)°) in **2**, and 3.244(6)–3.368(6) Å (with 58.5(1)–62.3(1)°) in **3** (Fig. 2b). These edge-sharing MO_6 octahedral M_3 triangles are linked through the B-type hexa-vacant $[AsW_6O_{26}]^{11-}$ fragment with dihedral angles of 72.635° between the M_3-triangle planes and a prism-like geometry between the two M_3 triangles and M···M distances of 5.56(1) (M1···M4), 5.60(1) (M3···M6), and 9.015(8) Å (M2···M5) in **1**, 73.226° and 5.540(6), 5.521(6), and 8.847(5) Å in **2**, and 73.254° and 5.496(7),

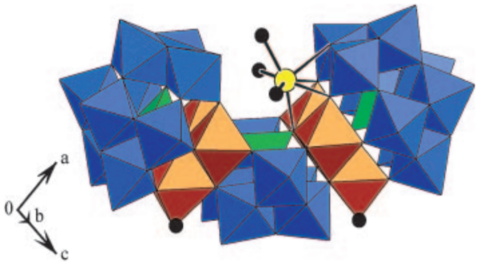

Fig. 3. Structural motif, represented by combined polyhedral/ball-and-stick, of a single Na^+ cation situated at the crevice of $[M_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})]^{17-}$. Blue, green, and orange in the polyhedral representation indicate WO_6, AsO_4, and MO_6 polyhedra respectively, and yellow and black in ball-and-stick representation indicate Na^+ and water O atoms, respectively.

5.509(7), and 8.833(6) Å in **3**. Thus, the two functionalized M_3-triangles are well-separated in the anion (Fig. 2c), as is demonstrated by the electrochemical behavior (shown below).

Similar to $[Ni_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})]^{17-}$,[11] a single Na^+ cation lies in the crevice of the V-shaped anion of **1**–**3**, stabilizing the structure and is coordinated by two oxygen atoms (O46 and O47, or O53 and O54) belonging to B-α $[AsW_9O_{34}]^{9-}$ fragment and one oxygen atom (O79 or O84) belonging to B-$[AsW_6O_{26}]^{11-}$ fragment in Na–O distances of 2.44–2.70 Å. The Na^+ cation forms the rhombohedral-like tetragon together with an alternating M_3 triangle, which can be discriminated from the M_4 tetragon with the β-junction for the sandwich-type $[M_4(H_2O)_2(As^VW_9O_{34})_2]^{10-}$ (Fig. 1b).[6–8] Figure 3 shows the Na^+ cation coordinated in the crevice of the V-shaped anion, probably as an energetic requirement for the structural stabilization. Attempts to replace the Na^+ cation in the crevice with other cations were unsuccessful, and the decomposition of the V-shaped anion occurred probably to afford the sandwich-type anion: the color of an aqueous solution containing **2** and alkaline-metal chlorides, such as KCl, RbCl, and CsCl changes from violet to blue while refluxing for 4–5 h. The IR spectra of the precipitated products are shown in Fig. 4, and the IR spectrum of the C_i-symmetric sandwich anion of $K_{10}[Co_4(H_2O)_2(AsW_9O_{34})_2]\cdot 23H_2O$[7] is included for comparison. The reaction of **2** with K^+, Rb^+, and Cs^+ resulted in the appearance of absorptions around at 770 and 840 cm^{-1} in IR spectra which suggests the formation of $[Co_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$, while refluxing with NaCl gave almost the same IR spectrum as **2**.

The redox processes of M^{2+} ($=Mn^{2+}$ and Co^{2+}) in the V-shaped anions are observed in the potential range of 0.00–1.20 V (vs Ag/AgCl). The cyclic voltammogram of **1** with a rest potential at 0.08 V in aqueous solutions had three successive Mn^{II}/Mn^{III} oxidations in the range of 0.30–0.60 V. The three quasi-reversible Mn^{II}/Mn^{III} couples at 0.32, 0.44, and 0.58 V vs Ag/AgCl for anodic peaks are accompanied by composite cathodic peaks with more negative potential for each at 30–40 mV at 0.28, 0.41, and 0.54 V, as shown in Fig. 5a. The cyclic voltammogram of $Na_{11}(NH_4)[\{Mn(H_2O)\}_3(SbW_9O_{33})_2]\cdot 45H_2O$[21] in an aqueous solution at pH of 6.5 showed three quasi-reversible one-electron Mn^{II}/Mn^{III} couples at 0.30/0.24, 0.44/0.38, and 0.56/0.50 V with about 60 mV of the potential difference between the redox peaks (Fig. 5b). In conjunction with the result of the D_{3h}-symmetric $[\{Mn(H_2O)\}_3(SbW_9O_{33})_2]^{12-}$ anion, which incorporates three $MnO_4(H_2O)$-pyramid moieties in the center, the three successive sets of the redox peaks with the potential difference of about 30 mV between anodic and cathodic peaks in cyclic voltammogram of **1** are assigned to three quasi-reversible two-electron redox processes corresponding to $2(Mn^{II}_3)/2(Mn^{II}_2Mn^{III})$, $2(Mn^{II}_2Mn^{III})/2(Mn^{II}Mn^{III}_2)$, and $2(Mn^{II}Mn^{III}_2)/2(Mn^{III}_3)$ for two well-separated edge-sharing MnO_6 octahedral Mn_3-triangles in the C_{2v}-symmetric anion (Fig. 2). The electrochemical decomposition of the anion occurred at 0.90 V for Mn^{III}/Mn^{IV} oxidation (data not shown).[22] Quasi-reversible peaks around at 1.04/0.97 V (Fig. 5c) observed for **2** suggest that occurrence of the two-electron redox process $2(Co^{II}_3)/2(Co^{II}_2Co^{III})$ occurred at the two Co_3 triangles in the anion.

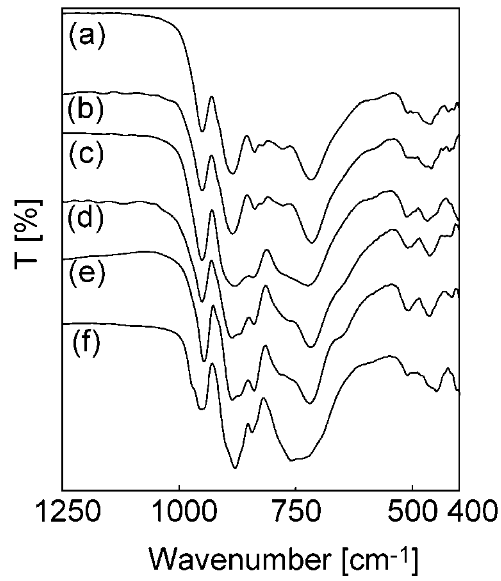

Fig. 4. Infrared spectra of **2** (a), precipitates obtained by reflux of **2** (1.0 g) in aqueous solutions (60 mL) containing NaCl (5.0 g) (b), KCl (1.5 g) (c), RbCl (1.0 g) (d), and CsCl (1.0 g) (e), and $K_{10}[Co_4(H_2O)_2(AsW_9O_{34})_2]\cdot 23H_2O$ (f).

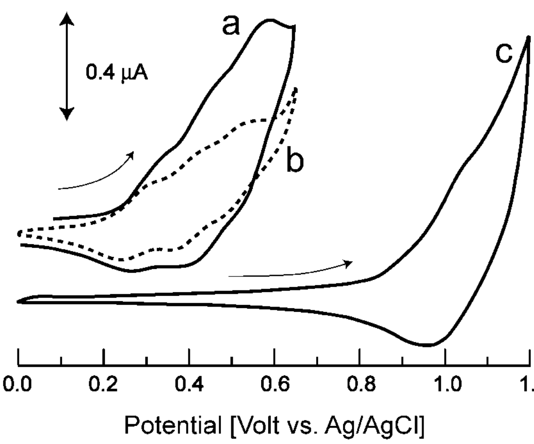

Fig. 5. Cyclic voltammograms of **1** (a), $Na_{11}(NH_4)[\{Mn(H_2O)\}_3(SbW_9O_{33})_2]\cdot 45H_2O$ (b), and **2** (c) with a scan rate of 10 mV s^{-1}.

Conclusion

The use of $Na_2HAs^VO_4$ instead of $NaAs^{III}O_2$ in the preparation of $K_{12}[Cu_3(H_2O)_2(As^{III}W_9O_{33})_2]\cdot 11H_2O$[3] led to the isolation of the C_{2v}-symmetric V-shaped polyoxotungstoarsenates $[M_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})]^{17-}$ (M = Mn **1**, Co **2**, and Zn **3**), which consist of two B-α $[\{M(H_2O)\}M_2(AsW_9O_{34})]^{3-}$ units joined by a B-type hexa-vacant $[AsW_6O_{26}]^{11-}$ fragment. A single Na^+ cation situated in the crevice of the anion structure appears to stabilize the V-shaped geometry. Approximately rhombohedral-like NaM_3-tetragon together with the edge-sharing MO_6 octahedral triad in α-Keggin $[\{M(H_2O)\}M_2(AsW_9O_{34})]^{3-}$ unit can be discriminated from the M_4 tetragon with the β-junction for the C_i-symmetric sandwich-type $[M_4(H_2O)_2(As^VW_9O_{34})_2]^{10-}$ anion, which is formed by the treatment of **1–3** with other large alkaline-metal cations (K^+, Rb^+, and Cs^+). The three successive electrochemically quasi-reversible Mn^{II}/Mn^{III} waves for the edge-sharing MnO_6-octahedral Mn_3 triad in the cyclic voltammogram of **1** are two-electron processes arising from the large separation of the two Mn_3 triads in the anion.

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9 $Na_8[WCo_2(H_2O)_3(AsW_9O_{33})_2]\cdot 29H_2O$ was prepared as follows: An aqueous solution (110 mL) containing $NaAsO_2$ (1.3 g, 0.01 mol) and $Na_2WO_4\cdot 2H_2O$ (29.7 g, 0.09 mol) was treated with an aqueous solution (110 mL) of $CoSO_4\cdot 7H_2O$ (5.90 g) and 6.4 M HNO_3 (17.2 mL). The resultant solution was refluxed for 3 h during which time the color of the solution changed from violet to green. The green solution containing NaCl (5.0 g) was concentrated to about 100 mL by using a rotary-evaporator. This solution was filtrered and cooled to room temperature. Green-colored crystals were obtained within two weeks. Potassium salts could be also obtained by adding KCl (40 g) instead of NaCl and recrystallizing from hot water. Crystallographic data as follows: triclinic, Space group $P\bar{1}$, $a = 18.87(1)$, $b = 22.94(1)$, $c = 23.94(1)$ Å, $\alpha = 84.23(2)^\circ$, $\beta = 83.66(3)^\circ$, $\gamma = 68.79(2)^\circ$, $V = 9584(9)$ Å^3, $Z = 4$. Anal. Calcd for $H_{58}O_{95}Na_8Co_{2.73}As_2W_{18.72}$: Na, 3.35; Co, 2.45; As, 2.73; W, 62.71 wt %. Found: Na, 3.95; Co, 2.48; As, 2.74; W, 62.57 wt %. IR (KBr disk) metal–oxygen stretches at $\nu = 942$ (m), 888 (s), 781 (s), 732 (s), and 601 (m) cm^{-1}.

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