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Cyclic Tungstoselenites Based on $\{Se_2W_{12}\}$ Units

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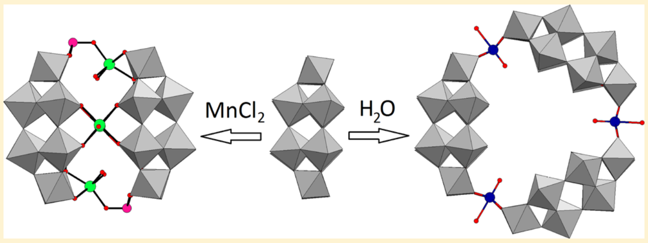
Supporting Information

ABSTRACT: The reaction of Na_2WO_4 and SeO_2 under moderately acidic conditions yielded a novel 39-tungsto-6-selenite, $[(Se_2W_{12}O_{46}(WO(H_2O))_3]^{24-}$ (**1**), isolated as $Na_{24}[H_6Se_6W_{39}O_{144}]\cdot 74H_2O$. The macrocyclic polyanion consists of three $\{Se_2W_{12}\}$ fragments connected via three *trans*-$\{WO(H_2O)\}^{4+}$ groups. The same $\{Se_2W_{12}\}$ building block is present in the structure of $[(Se_2W_{12}O_{46})_2\{Mn_2Cl(H_2O)_2\}\{Mn(H_2O)_2\}_2(SeO)_2]^{13-}$ (**2**), which was obtained from the same reagents in the presence of $MnCl_2$. The compounds were characterized by single-crystal X-ray diffraction, ^{77}Se NMR, Fourier transform infrared, and Raman spectroscopy.



1. INTRODUCTION

Polyoxometalates (POMs) are discrete polynuclear oxo complexes of transition-metal ions exhibiting a fascinating variety of structures and properties of interest for catalysis, materials science, and medicine.[1−4] POMs are usually assembled from mononuclear metal-oxo anions in aqueous acidic solutions through condensation reactions. The possibility of incorporating various heterogroups (typically tetrahedral XO_4, where X = B^{III}, Si^{IV}, Ge^{IV}, P^{V}, etc., or pyramidal XO_3, where X = Se^{IV}, Te^{IV}, As^{III}, Sb^{III}, and Bi^{III}) and heterometals in POM structures tremendously increases the structural variety of POMs, and allows for fine-tuning of their redox, catalytic, optical, and magnetic properties. In particular, lone-pair-containing heterogroups, such as pyramidal SeO_3^{2-} and TeO_3^{2-}, have attracted special attention in recent years and have become prominent building blocks in efforts by various research groups to assemble new POMs with unique structures and reactivity.[5−8] The first examples of polyoxotungstates containing selenium(IV) were reported many years ago.[9,10] Their structures are based on trilacunary Keggin $\{SeW_9\}$ units and are always stabilized by coordination to a heterometal, such as Cu^{2+}, $Fe^{2+/3+}$, or WO^{4+}: $[Cu_3(H_2O)_3(\alpha\text{-}SeW_9O_{33})_2]^{10-}$, $[Fe^{II}_3(H_2O)_3(\alpha\text{-}SeW_9O_{33})_2]^{10-}$, $[Se_2W_{21}O_{69}(H_2O)]^{4-}$, and $[Fe^{III}_4(H_2O)_{10}(\beta\text{-}SeW_9O_{33})_2]^{4-}$.[10p,q] Recently, some large tungstoselenites were added to this collection.[6,11] Most of them are based on the trilacunary $\{SeW_9\}$ unit as the main building block. These units are always generated *in situ*, and no simple salt of $[SeW_9O_{33}]^{8-}$ has been isolated and structurally characterized to date.

The presence of pyramidal XO_3 (X = Se^{IV}, Te^{IV}, As^{III}, Sb^{III}, Bi^{III}) units in POM offers a unique opportunity to explore the reactivity of the lone pair in the heteroatom (e.g., by coordination to a metal ion such as Ag^+).[7] These units are also oxidizable, and oxidation, through an increase in the coordination number of X, may lead to drastic structural changes.[6c]

Herein we report the synthesis and structures of new selenium-rich tungstoselenites, $Na_{24}[H_6Se_6W_{39}O_{144}]\cdot 74H_2O$ (**Na1**), $K_2Na_{22}[H_6Se_6W_{39}O_{144}]\cdot 57.75H_2O$ (**KNa1**), and $Na_{13}[(Se_2W_{12}O_{46})_2\{Mn_2Cl(H_2O)_2\}\{Mn(H_2O)_2(SeO)\}_2]\cdot 16H_2O$ (**Na2**). The structures of these compounds are based on the novel $\{Se_2W_{12}O_{46}\}$ building block, which is reminiscent of the hexalacunary Wells−Dawson-type 12-tungsto-2-phosphate $[H_2P_2W_{12}O_{48}]^{12-}$.

2. EXPERIMENTAL SECTION

The experiments were carried out in air. All employed reagents were of commercial quality and were used as purchased. The IR spectra (4000−400 cm^{-1}) were obtained on a Vertex 80 Fourier transform infrared spectrometer in KBr pellets. Raman spectra were recorded on Triplemate SPEX spectrometer. Thermogravimetric analysis (TGA) was done on a Netzsch TG209 F1 Iris microbalance with a heating rate of 10 K min^{-1} under a helium atmosphere (30 mL min^{-1}) in a temperature range of 20−300 °C. Elemental analysis was performed in the Analytical Laboratory of the Nikolaev Institute of Inorganic Chemistry of the Russian Academy of Sciences, Novosibirsk, Russia.

Synthesis of $Na_{24}[H_6Se_6W_{39}O_{144}]\cdot 74H_2O$ (Na1). A solution of SeO_2 (0.52 g, 4.7 mmol) in 1.0 mL of water was added to 10 mL of an aqueous solution of $Na_2WO_4\cdot 2H_2O$ (10 g, 30.3 mmol). The pH of the reaction mixture was adjusted to 4.5 with 4 M HCl. After 4 h, colorless needlelike crystals of **Na1** were separated by filtration and dried in air. Yield: 2.0 g (22% based on W). Calcd for $Na_{24}Se_6W_{39}H_{154}O_{218}$: Se, 4.00; H 1.31; Na, 4.66. Found: Se, 3.98; H, 1.37; Na, 4.71. IR (KBr,

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Table 1. Crystal Data, Data Collection and Structure Refinement Parameters for **Na1**, **KNa1**, and **Na2′**

compound	**Na1**	**KNa1**	**Na2′**
ISCD code	426040	426042	426041
empirical formula	$H_{128.50}Na_{24}O_{205.25}Se_6W_{39}$	$H_{60.75}K_2Na_{22}O_{201.75}Se_6W_{39}$	$H_{112}ClMn_4Na_{13}O_{151}Se_6W_{24}$
mol mt	11609.20	11517.13	7969.14
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	14.076(3)	14.1423(2)	13.9680(4)
b, Å	22.225(4)	22.4551(3)	15.6454(5)
c, Å	36.854(7)	35.5982(4)	18.3497(5)
α, deg	86.81(3)	88.1380(10)	77.1050(10)
β, deg	81.03(3)	79.1710(10)	69.9680(10)
γ, deg	76.40(3)	75.0520(10)	66.6280(10)
V, Å^3	11067(4)	10726.2(2)	3440.57(17)
Z	2	2	1
D_{calc}, g cm^{-3}	3.484	3.566	3.846
μ, mm^{-1}	21.317	22.026	22.098
$2\theta_{max}$, deg	55.1	59.4	76.4
temperature, K	100.0(2)	123.0(2)	100.0(2)
cryst size, mm	0.20 × 0.07 × 0.05	0.10 × 0.06 × 0.02	0.12 × 0.08 × 0.06
h, k, l ranges	$-18 \le h \le 16$, $-28 \le k \le 28$, $-47 \le l \le 34$	$-19 \le h \le 19$, $-31 \le k \le 30$, $-49 \le l \le 48$	$-23 \le h \le 24$, $-25 \le k \le 26$, $-31 \le l \le 29$
reflns measd	66925	181828	47249
unique reflns	48560	56584	33528
R_{int}	0.0405	0.0634	0.0362
obsd [$I > 2\sigma(I)$]	33250	29329	22796
no. of refined param	2257	2693	945
no. of restraints	0	0	0
R1, wR2 [$I > 2\sigma(I)$]	0.0830, 0.1675	0.0373, 0.0684	0.0469, 0.0800
R1, wR2 (all data)	0.12620.1849	0.0848, 0.0724	0.0872, 0.0915
GOF on F^2	1.075	0.774	1.003
largest diff peak/hole (e Å^{-3})	3.576/−3.675	3.109/−2.048	3.431/−2.836

cm^{-1}): 1623(s), 943(m), 897(m), 842(m), 780(s), 656(sh), 506(s). Raman (cm^{-1}): 340(m), 651(w), 818(s), 885(w), 960(vs). TGA (weight loss, %): 11.30 (−74 H_2O). The mixed potassium−sodium salt **KNa1** could be isolated by adding a small amount of KCl to the reaction solution for the preparation of **Na1**.

Synthesis of $Na_{13}[(Se_2W_{12}O_{46})_2\{Mn_2Cl(H_2O)_2\}\{Mn(H_2O)_2\}_2(SeO)_2]\cdot16H_2O$ (Na2). SeO_2 (0.10 g, 0.9 mmol) was dissolved in 0.5 mL of water and then added to 2.0 mL of an aqueous solution of $Na_2WO_4\cdot2H_2O$ (2.0 g, 6 mmol), and the pH of the reaction mixture was adjusted to 4.5 with 4 M HCl. Then 1.0 mL of an aqueous solution of $MnCl_2\cdot4H_2O$ (0.70 g, 3.5 mmol) was added to the reaction mixture. After 1 day, a yellow-orange precipitate was removed by filtration, and the filtrate was left for evaporation, giving a crop of orange crystals of **Na2** within 1 week. Yield: 1.00 g (91% based on SeO_2). Calcd for $Na_{13}Se_6W_{24}O_{116}Mn_4ClH_{44}$ (the air-dried sample): Se, 6.45; H, 0.60; Na, 4.07; Mn, 2.99. Found: Se, 6.49; H, 0.58; Na, 4.12; Mn, 3.07. IR (KBr, cm^{-1}): 1662(w), 1617(s), 1464(w), 1289(m), 943(m), 841(m), 766(s), 665(w), 510(m). Raman (cm^{-1}): 105(m), 132(m), 154(m), 222(m), 295(m), 330(m), 362(w), 410(w), 468(w), 512(w), 673(sh), 716(s), 813(s), 888(vs), 956(vs).

When taken from mother liquor, crystals of **Na2** rapidly lose water of crystallization, leading to decreasingly lower values of the water percentage as determined by TGA (%): 19.0 (−90 H_2O; a freshly isolated sample); 4.0 (−16 H_2O; air-dried sample, after keeping in air to achieve a constant sample weight).

X-ray Determination. For X-ray analysis of polyanion **1**, two different crops of single crystals designated as **Na1** and **KNa1** were used. In the case of the Mn derivative, the hydration number as determined by X-ray analysis differed from that determined by thermal and elemental analysis, and this particular composition is designated as **Na2′**. Crystallographic data and details of structure refinement for **Na1**, **KNa1**, and **Na2′** are given in Table 1. The diffraction data for **Na1** and **Na2′** were collected on a Bruker Apex DUO diffractometer with Mo Kα radiation (λ = 0.71073 Å) using φ and ω scans of narrow (0.5°) frames at 100 K. The diffraction data for **KNa1** were collected on a SuperMova (Agilent Technologies) diffractometer with Mo Kα radiation (λ = 0.71073 Å) using ω scans of 0.5° frames at 123 K at the University of Regensburg, Regensburg, Germany. All structures were solved by direct methods and refined by a full-matrix least-squares method against $|F|^2$ in an anisotropic approximation using the *SHELXTL* program set.[12] Absorption corrections were applied empirically using the *SADABS* program[13] for **Na1** and **Na2′**. For **KNa1**, absorption corrections were applied numerically based on a multifaceted crystal model using *CrysAlis* software.[14] All non-hydrogen atoms were refined anisotropically. Light atoms with site occupancies of less than 0.6−0.5 were refined in an isotropic approximation. Hydrogen atoms were not located. Solvate water molecules were differentiated from sodium or potassium cations by careful analysis of the bond distances and coordination environment. The occupation factors for the cations and oxygen atoms of the water molecules were first refined with U_{iso} = 0.05 and then fixed in the resulting values and refined in a standard way. In **Na1**, the anion $[(Se_2W_{12}O_{46}(WO(H_2O))_3]^{24-}$ was found to be disordered over two positions with relative weights of 96 and 4%. For the minor part, only 35 tungsten and 5 selenium atoms were localized and refined isotropically. Introducing disorder allowed us, however, to reduce the residual density from 8 electron peaks to 3.5, all in close proximity to heavy atoms, and the R1 value dropped by ~1%. Owing to a sufficient overlap of the disordered polyanions, oxygen and sodium atoms were treated using the ISOR instructions. The severe disorder of the cationic and solvate portions in **Na1**, **KNa1**, and **Na2′** precluded localization of all disordered solvate water molecules from the difference electron density map. Further details may be obtained

Table 2. Selected Bond Distances (Å) and Angles (deg) in Na1 and KNa1

	Na1	KNa1
W=O	1.65(2)−1.768(18)	1.697(7)−1.768(8)
W−μ_2-O_W	1.79(2)−2.087(18)	1.828(7)−2.108(8)
W−μ_2-O_{Se}	2.243(16)−2.361(18)	2.258(6)−2.326(7)
W−O_{H_2O}	2.31(2)−2.33(2)	2.335(7)−2.340(7)
Se−O_W	1.661(19)−1.716(18)	1.684(7)−1.712(7)
W−μ_3-O−W	93.4(7)−97.6(7)	93.3(2)−97.4(2)
W−μ_2-O−W	119.3(8)−122.4(8), 140.5(10)−149.8(9), 157.9(10)−174.9(10)	120.2(3)−122.5(2), 141.4(4)−155.0(5), 157.4(4)−174.2(5)
O−Se−O	98.0(9)−103.1(8)	99.7(3)−102.2(3)
W−μ_3-O−Se	114.9(9)−133.7(9)	116.0(3)−133.8(3)

from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany [fax (+49) 7247-808-666; e-mail crysdata@fiz-karlsruhe.de] upon quoting the depository numbers 426040 (**Na1**), 426041 (**Na2′**), and 426042 (**KNa1**). Bond lengths and angles are summarized in Table 2. Topologies of the anionic packing in **Na1**, **KNa1**, and **Na2′** were calculated with the *ADS* program implemented in the *TOPOS* program set for crystal chemical analysis.[15]

^{77}Se NMR Investigations. NMR experiments were performed at room temperature on a Bruker AVANCE-500 narrow-bore NMR spectrometer operating at 11.74 T. The magic-angle-spinning (MAS) ^{77}Se NMR spectra were recorded with a 4-mm H/X probe at a spinning frequency of 15 kHz and a recycle delay (d1) of 60 s. Solid H_2SeO_3 was used as the external reference (δ = 1288 ppm).[16] Solution-state ^{77}Se NMR spectra were acquired in a H_2O + 10% D_2O mixture at d1 = 1.5 s and referenced to an aqueous solution of H_2SeO_3 (δ = 1282 ppm).

3. RESULTS AND DISCUSSION

Synthesis and Structure. Synthesis of **1** was achieved by reaction of $Na_2WO_4 \cdot 2H_2O$ and SeO_2 in aqueous solution at pH 4.5−4.8. If the reaction mixture was left without stirring, large needles of **Na1** separated in 3−4 h. The hydration number in **Na1** as determined by elemental analysis and TGA were in agreement with each other, whereas X-ray structural analysis underestimated the hydration number, arriving only at composition $Na_{24}[H_6Se_6W_{39}O_{144}] \cdot 61.25H_2O$. If some KCl was introduced into the mother liquor, colorless crystals of a mixed sodium−potassium salt, **KNa1**, were obtained.

Both **Na1** and **KNa1** contain the novel, wheel-shaped polyanion $[(Se_2W_{12}O_{46}(WO(H_2O))_3]^{24-}$ (**1**) comprising three $\{Se_2W_{12}O_{46}\}$ fragments joined together by three *trans*-$\{WO(H_2O)\}^{4+}$ units, in which the apical H_2O molecule points outside the polyanion "wheel" (Figure 1). In both **Na1** and **KNa1**, the polyanions feature similar geometrical parameters (Table 2) in agreement with known tungstoselenites. Despite the idealized D_{3h} point group symmetry of the isolated polyanions, in both crystal structures the polyanions lie in general positions with space group $P\bar{1}$ and possess the lowest C_1 point group symmetry, resulting in the appearance of six crystallographically independent selenium atoms (Figure S1 in the Supporting Information, SI). The inner cavity of the polyanions is occupied by sodium cations, randomly coordinated to terminal oxygen atoms of the $\{WO_6\}$ octahedra. Only a minor portion of the cations fully occupy their positions as a result of severe disorder, and for this reason, the coordination environment for most of the sodium cations could not be identified completely. The degree of hydration based on single-crystal X-ray diffraction is therefore significantly underestimated for both **Na1** and **KNa1**. This conclusion is in agreement with elemental analysis and TGA data. An interesting fact is that in **Na1** the entire $[H_6Se_6W_{39}O_{144}]^{24-}$ wheel, constituting the largest structural unit, is disordered over two quite distant positions that are removed from each other by about 2.6 Å (Figure S2 in the SI). The major component (96%) was revealed by structural analysis in full detail, whereas for the minor position (4%), only the heavy atoms, except for a tungsten and a selenium atom, were located from the electron density map. When the minor part was included in the structure refinement, the residual electron density decreased, and the R1 value dropped by ~1%. In order to analyze the structure, we modeled the oxygen atoms of the minor component. We found that the polyanions disordered in such a way cannot coexist in the crystal packing because of the mutually prohibitive environment of their terminal oxygen atoms due to a number of too short O···O contacts of about 1 Å. The observed disorder can therefore only be explained by microblocks of a different structure, with very similar unit cell parameters, that coexists in the crystal. The coherent diffraction between them results in full interference, and therefore the structure can be described by disorder, not twinning. A similar effect was observed in another crystal and may have a systematic character. The refined values of 0.96 and 0.04 correspond to the relative weights of the domains. The overall structural arrangement of the minor domain is not yet clear because of its minor contribution to the diffraction pattern. Unfortunately, the microblock structure of the crystal cannot be further investigated by electron microscopy because the crystals

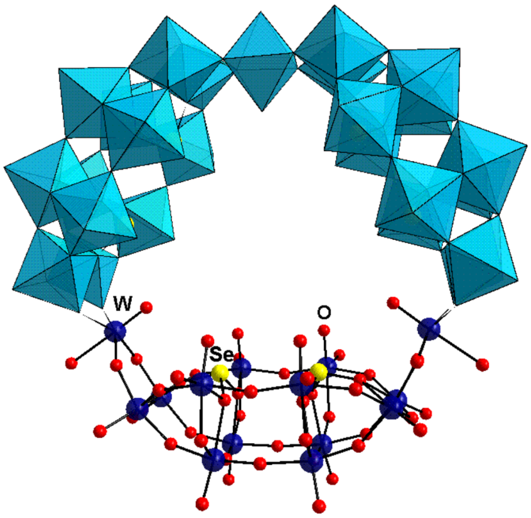

Figure 1. Representation of polyanion **1**. Color legend: WO_6, blue octahedra; Se, yellow balls; W, blue balls; O, red balls.

collapse in vacuum due to the loss of water. Further on, we will be discussing the structure of the main domain only.

The mutual arrangements of the polyanions in crystals of **Na1** and **KNa1** are very similar (see Figure S3a,b in the SI). In **Na1**, it is a two-layered hexagonal close packing (or hcp according to the O'Keeffe notation[17]) and in **KNa1** body-centered-cubic packing (bcu), both distorted to some extent (see Figure S3c,d in the SI). The hcp and bcu packings are well-known and differ only in the way in the juxtapositioning of the hexagonal layers (see Figure S3c,d in the SI). The packings are also known to allow for a continuous transition between each other via distortion. Such a distortion may relate the structures of **Na1** and **KNa1** having slightly different solvate and cationic portions because the structures show no similarities in the cationic sublattices, with the anionic packings being generally similar. Therefore, the cations and solvate water molecules adapt to either position of the polyanions to smoothen the irregularity in the anionic sublattice. Note that the structure **KNa1** is more dense than **Na1** despite the fact that in its nondistorted variant the bcu packing has a lower packing coefficient than the hcp one.

The structure of the $\{Se_2W_{12}\}$ fragments in **1** resembles that of the hexalacunary derivative of the Wells–Dawson 12-tungsto-2-phosphate $[H_2P_2W_{12}O_{48}]^{12-}$.[20] However, the presence of a lone pair on the selenium(IV) heteroatoms prevents the formation of a hypothetical plenary $\{Se_2W_{18}\}$ polyanion. Thus, each of the two belts of $\{Se_2W_{12}\}$ consists of two corner-shared W_2O_{10} units, each of which comprises a pair of edge-shared WO_6 octahedra (Figure 1). Every selenium(IV) center in $\{Se_2W_{12}\}$ is coordinated to the inner bridging oxygen atoms of both W_2O_{10} units of the belt, as well as to the oxygen atom bridging the two tungsten centers of the cap, whereas the lone pair on selenium(IV) is pointing away from the $\{Se_2W_{12}\}$ fragment. In the structure of $\{P_2W_{12}\}$, each belt consists of only one edge-shared W_2O_{10} unit, with two WO_6 fragments attached via corner-sharing on each side. This arrangement allows for tetrahedral coordination of the phosphorus(V) centers, each being bound to an oxygen atom bridging two tungsten centers in the cap, as well as an inner bridging oxygen of the W_2O_{10} group and an oxygen atom of each of the two WO_6 units of the belt.[20]

A trimeric, cyclic 39-tungsto-6-phosphate, $[\{(P_2W_{12}O_{48})WO(H_2O)\}_3]^{30-}$ (P_6W_{39}), is also known, being stabilized by coordination with various transition- and rare-earth-metal ions.[19] However, to date, all efforts to isolate the empty triangle $[H_6P_6W_{39}O_{150}]^{30-}$ have remained unsuccessful. Hence, our polyanion **1** can be of interest as a potential new POM macrocyclic ligand that could stabilize small polynuclear assemblies of transition-metal and/or lanthanide ions in the inner cavity, in analogy to the tetrameric, cyclic $[H_7P_8W_{48}O_{184}]^{33-}$, which has resulted in spectacular derivatives such as $\{Cu_{20}P_8W_{48}\}$ and $\{Fe_{16}P_8W_{48}\}$.[21] We checked this possibility by adding different transition-metal ions in the reaction mixture used for the preparation of **1**. The reaction with manganese(II) ions did not lead to the formation of the expected polyanion $\{Mn_xSe_6W_{39}\}$ but rather to the new polyanion $[(Se_2W_{12}O_{46})_2\{Mn_2Cl(H_2O)_2\}\{Mn(H_2O)_2(SeO)\}_2]^{13-}$ (**2**; Figure 2), which was isolated as a hydrated sodium salt, $Na_{13}[(Se_2W_{12}O_{46})_2\{Mn_2Cl(H_2O)_2\}\{Mn(H_2O)_2(SeO)\}_2]\cdot 16H_2O$ (**Na2**). If $MnCl_2$ was added to a mixture of Na_2WO_4 and SeO_2 in a 13:3 molar ratio, an orange solution was produced, from which the known $[Na_6(H_2O)_{18}][Mn_2(H_2O)_6(H_2W_{12}O_{42})]\cdot 6H_2O$[17] was isolated. In any case, a large excess of Mn^{2+} is necessary for the successful isolation of **Na2**: attempts to run this reaction with the stoichiometric SeO_2/Mn^{2+} ratio (i.e., 6:4) yielded only **Na1**.

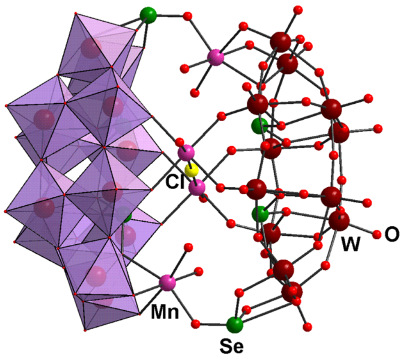

Figure 2. Combined polyhedral/ball-and-stick representation of the $[(Se_2W_{12}O_{46})_2\{Mn_2Cl(H_2O)_2\}\{Mn(H_2O)_2(SeO)\}_2]^{13-}$ polyanion.

The polyanion **2** also comprises $\{Se_2W_{12}\}$ fragments, but unlike **1**, only two of them are joined to form the macrocycle. An important difference is also that the $\{Se_2W_{12}\}$ subunits are connected together in a wheel-shaped structure not by WO_6 octahedra but by two neutral $\{Mn(H_2O)_2(SeO_3)\}$ complex units on opposite sides of the ring. Each $\{Mn(H_2O)_2(SeO_3)\}$ complex unit coordinates the $\{Se_2W_{12}\}$ fragments by two terminal oxygen atoms and by an oxygen atom belonging to one of its selenite groups. In addition, the Mn^{2+} ion coordinates an oxygen atom of a SeO_3^{2-} group, while the other two oxygen atoms of the selenite unit are shared with the $\{Se_2W_{12}\}$ framework. The inner cavity of the polyanion is occupied by a binuclear, linear fragment $\{Mn_2Cl(H_2O)_2\}^{3+}$. Each of these inner Mn^{2+} ions is coordinated to four terminal oxygen atoms of the $\{Se_2W_{12}\}$ fragments in the equatorial plane (Figure 2). All Mn^{2+} ions are coordinated in a distorted octahedral fashion. The coordination polyhedron around the peripheral Mn^{2+} ion is distorted in such a way that the bond angles $O_{Se}-Mn-O_{Se}$ between its apical sites are only 157.3(2)°, with the equatorial plane geometry being more regular. The coordination polyhedra around the inner Mn^{2+} ions are more regular. Here the distortion affects mainly the equatorial plane (Table 3), with the angle between the apical sites being 174.58(16)°. The inner Mn^{2+} ions are coordinated to oxygen atoms of the belts of the $\{Se_2W_{12}\}$ units, where the tungsten atoms are more distant from each other, leading to larger bond angles of 92.1(2) and 95.61(15)° between the *cis*-coordinated oxo groups. The geometrical parameters of the $\{Se_2W_{12}\}$ units in **2** are quite similar to those in **1** (Tables 2 and 3). The idealized point group symmetry of the discrete polyanion is D_{2h}, but in the crystal, it is reduced to C_i because the polyanion lies on an inversion center. The cationic part, together with the coordinated water molecules, is disordered in the voids of the polyanionic packing. The degree of hydration is therefore seriously underestimated by XRD, as in **1**. The mutual arrangement of the polyanions in the crystal follows the face-centered-cubic packing (**fcu**; see Figures S4 and S5 in the SI).

The formation of **1** and **2**, both based on the $\{Se_2W_{12}\}$ building block, is quite remarkable because it nicely underlines the importance of countercations in the self-assembly process of POMs. Thus, Yan et al. working under very similar conditions (the WO_4^{2-}/SeO_3^{2-} ratio in their synthesis was 5.0:1 vs 6.4:1 in our case, and their pH was 4.0 vs 4.5–4.8 in our case) isolated a $\{W_{43}Se_3\}$ tungstoselenite, whose rather

Table 3. Selected Bond Distances (Å) and Angles (deg) in Na2′

W═O	1.713(5)−1.794(5)
W−μ_2-O_W	1.729(5)−2.128(5)
W−μ_2-O_{Se}	2.263(5)−2.444(5)
Se−O_W	1.697(5)−1.729(5)
W−μ_2-O_{Mn}	2.146(5)−2.188(6)
Se−O_{Mn}	1.669(6)−1.730(5)
Mn−O_{H_2O}	2.189(6)−2.227(6)
Mn−Cl	2.5705(11)
W−μ_3-O−W	89.14(17)−96.59(18)
W−μ_2-O−W	119.9(3)−124.4(3), 141.5(3)−155.3(3), 165.1(3)−170.8(3)
O−Se−O	99.3(3)−103.0(3)
W−μ_3-O−Se	117.0(3)−135.0(3)
W−μ_2-O−Se	122.1(3)
W−μ_3-O−Mn	90.08(18), 89.49(17)
Mn−μ_2-O−Se	126.0(3)
Mn−μ_3-O−Se	122.7(3)
Mn−Cl−Mn	180
O−Mn−Cl	90.03(15)−95.61(16)
O−Mn−O	84.9(2)−99.4(2)

complicated structure is based upon {SeW_9} units as primary building blocks. The authors stressed that the presence of K^+ ions was crucial for the formation of this and related structures because these cations were trapped and ligated between the {SeW_9} units.[6a] In our case, Na^+ ions occupy the inner cavity of **Na1**, and {$Mn_2Cl(H_2O)_2$} may be regarded as a template responsible for the formation and stability of **2**. The intrinsic lability of sodium coordination in solution may be responsible for the collapse of **Na1** in water.

It is not clear whether there is a direct rearrangement pathway between the {SeW_9} and {Se_2W_{12}} building blocks. In analogy to phosphotungstate chemistry, one might hypothesize a process of pH-driven condensation of two {SeW_9} units into an unstable {Se_2W_{18}}, followed by loss of six tungstate units to give {Se_2W_{12}}. This process may well be both pH- and cation-sensitive.[20,19]

IR and Raman Spectroscopy. IR and Raman spectra of **Na1** and **Na2** show typical patterns from the presence of the W═O and W−O−W groups. Strong bands in the Raman spectra of **Na1** and **Na2** at 818 and 813 cm^{-1}, respectively, can be assigned to vibrations of the Se−O bonds in the pyramidal {SeO_3} groups of the {$Se_2W_{12}O_{46}$} fragments (which compares well with the literature data for SeO_3^{2-} ions in solution: ν_1 = 807 cm^{-1}). The characteristic Raman spectrum of **Na1** was used to study the solution behavior of polyanion **1**. A freshly prepared solution (within minutes) shows a Raman spectrum identical with that of the crystalline sample. The mother liquor in contact with the crystals also shows the same bands. However, about 1 h after sample dissolution, the initial characteristic Raman spectrum pattern decays and becomes virtually featureless, being similar to that observed for the mother liquor of **Na1** removed from contact with the crystalline solid. This observation demonstrates that the POM structure is not preserved in aqueous solution when the appropriate ionic strength, pH, and concentration range are lacking. We also recorded Raman spectra on freshly prepared solutions of **Na1** in LiCl (1.0 M), NaCl (0.5 and 0.1 M), and KCl (1.0 M). In all cases, a rapid decay was observed, which means that such salts alone are not sufficient to stabilize **1** in solution.

For **Na2**, Raman spectra show a rapid decay when a solid sample is dissolved in aqueous solution.

^{77}Se NMR. The MAS ^{77}Se NMR spectrum of **Na1** (Figure 3) shows a signal centered at 1289.9 ppm. The signal has an asymmetric shape with an ill-defined fine structure. This shape may be associated with a different local environment for each of the six selenium atoms of polyanion **1**. As the crystallographic data show (see the Results and Discussion section), in the solid state, there are indeed six structurally distinct selenium atoms, which would generate six resonance lines with slightly different chemical shifts. Upon dissolution in water, the resonance line shifts to 1271.0 ppm and then gradually decays into a set of weak NMR signals, all falling within the range of 1220−1350 ppm (see the SI), indicating the formation of unidentified products. The use of 1−2 M sodium or lithium acetate media (pH 4.5) for the solution NMR measurements did not prevent decomposition. Thus, both ^{77}Se NMR and Raman data indicate

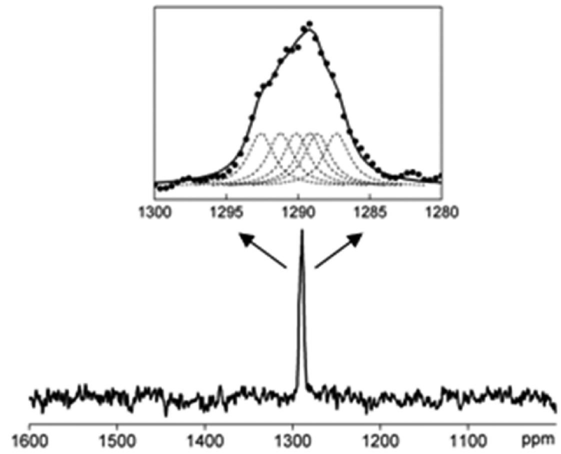

Figure 3. MAS ^{77}Se NMR spectrum for **Na1**. The experimental line shape and its representation as a superposition of six resonance lines, identical in widths and intensities, are shown in the inset by points and a solid line, respectively; the sextet components at 1287.3, 1288.7, 1289.2, 1290.1, 1291.2, and 1292.6 ppm are shown as dashed lines.

that **1** is unstable in aqueous solution (see Figures S6 and S7 in the SI). The successful synthesis and isolation of **Na1**, hence, requires a perfect balance between the pH, concentration, and ionic strength.

4. CONCLUSION

A simple method for the synthesis of two novel tungstoselenites containing the unique $\{Se_2W_{12}\}$ building unit has been demonstrated. Interaction of Na_2WO_4 with SeO_2 under moderately acidic conditions leads to the macrocyclic 39-tungsto-6-selenite $[H_6Se_6W_{39}O_{144}]^{24-}$. The structure consists of three $\{Se_2W_{12}\}$ units, which can be regarded as hexavacant derivatives of the Wells–Dawson structure type, connected by three $\{WO(H_2O)\}^{4+}$ groups. ^{77}Se NMR and Raman spectra demonstrated that it is not stable in aqueous solution and rapidly degrades into a mixture of unidentified species. When Na_2WO_4 and SeO_2 reacted in the presence of $MnCl_2$, the dimeric, cyclic polyanion $[(Se_2W_{12}O_{46})_2\{Mn_2Cl(H_2O)_2\}\{Mn(H_2O)_2\}_2(SeO)_2]^{13-}$ was formed. The structure consists two $\{Se_2W_{12}\}$ units connected by two unprecedented $\{Mn(H_2O)_2SeO_3\}$ linkers. This type of linkage indicates that selenite group in POM structures is rather flexible and may play a double role by binding not only to tungsten but also to heterometal ions, thus contributing to the extraordinary structural diversity of tungstoselenites and leaving hopes for further surprises.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, various structure representations, crystal packing, Raman and ^{77}Se NMR spectra (solution and solid state), and TGA. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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