Dalton Transactions

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Journal Name

Dalton Transactions

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Selenate as novel ligand for keplerate chemistry. New $\{W_{72}Mo_{60}\}$ keplerates with selenates inside the cavity†

Vladimir S. Korenev*[a,b], Pavel A. Abramov[a,b], Cristian Vicent[c], Artem A. Zhdanov[a,b], Alphiya R. Tsygankova[a], Maxim N. Sokolov[a,b], Vladimir P. Fedin[a,b]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

The synthesis and characterization of three novel keplerate-type compounds containing $\{W_{72}Mo_{60}\}$ mixed-metal core are reported. Complexes $(NH_4)_{72}[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]\cdot150H_2O\cdot6(NH_4)_2SeO_4$ (**1a**) and $(NH_4)_{25}(NH_2Me_2)_{47}[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]\cdot130H_2O\cdot3(NH_4)_2SeO_4$ (**1b**) were prepared by ligand substitution from the acetate anionic complex $[\{W_6O_{21}(H_2O)_5(CH_3COO)_{0.5}\}_{12}\{Mo_2O_4(CH_3COO)\}_{30}]^{48-}$ and selenate. The selenate anions in Keplerate ions $[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]^{72-}$ are very labile and easily aquate with the formation of $[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4\}_{30}(SeO_4)_{20}(H_2O)_{20}]^{52-}$, which was isolated as $(NH_4)_{20}(NH_2Me_2)_{32}[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4\}_{30}(SeO_4)_{20}(H_2O)_{20}]\cdot150H_2O$ (**2**) and structurally characterized. In the crystal structure of **2** selenate has several coordination modes, preferentially bonding to the $\{Mo_2O_4\}^{2+}$ units, and, additionally, to the $\{(W)W_5\}$ pentagonal blocks. The compounds have been characterized by elemental analysis, Raman, IR and ^{77}Se NMR spectroscopy, and by ESI mass spectrometry. Capillary electrophoresis was used for characterization of keplerates in solution for the first time.

Introduction

The keplerates are spherical polyoxometallates, whose metallic skeleton has 12 pentagonal $\{Mo(Mo_5)\}$ or $\{W(W_5)\}$ units, placed in the corners of an icosahedron, and which are linked by 30 $\{Mo_2O_4\}^{2+}$ doubly bridging units. The Mo atoms in the $\{Mo_2O_4\}^{2+}$ linkers typically coordinate a bidentate ligand in a bridging mode across the Mo-Mo bond, trans to the terminal Mo=O groups. For example, when acetate buffer is used as reaction medium, each $\{Mo_2O_4\}^{2+}$ coordinates an acetate, and the keplerate complex is isolated as $(NH_4)_{42}[\{Mo_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(CH_3COO)\}_{30}]\cdot300H_2O$.[1] These "inner" ligands can also be formate $(HCOO^-)$,[2] monocloroacetate $(ClCH_2COO^-)$,[2] hypophosphite $(H_2PO_2^-)$,[3] hydrogen phosphate (HPO_4^{2-}),[4] hydrogen sulfate (HSO_4^-)[3] and sulfate (SO_4^{2-})[5,6]: corresponding complexes were prepared and structurally characterized. In most cases they are prepared from the acetate complex by ligand exchange, and there is marked difference in the rate of substitution: whereas the exchange with the hypophosphite (at low pH) is complete at room temperature, only partial exchange with HSO_4^- was observed. The hypophosphite ligand can in turn be substituted by sulfate upon heating (~90°C), but even then only 10 sulfates enter the cavity.[5] The keplerate complex with 30 sulfates was obtained from the acetate only under reflux for 2 hours.[6] The extent of exchange strongly depends on the reaction conditions: at higher pH $[\{Mo_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SO_4)\}_{18}\{Mo_2O_4(CH_3COO)\}_{12}]^{60-}$ with 18 sulfates and 12 acetates is obtained, while with sodium sulfate and sulfuric acid instead of ammonium sulfate and hydrochloric acid $[\{Mo_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SO_4)\}_{24}\{Mo_2O_4(CH_3COO)\}_6]^{66-}$ was the product, both after heating.[6] Doubly negatively charged hydrogen phosphate HPO_4^{2-} substitutes inner acetates much easier than sulfate, and preparation of $[\{Mo_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(HPO_4)\}_{30}]^{72-}$ with 30 hydrogen phosphates requires no heating.[4]

The ability of keplerates to exchange anions is an important way to change the charge of the spherical anions, which governs such unique properties of keplerates as their self-aggregation in solution[7,8] with the formation of large spherical particles, or to regulate their cation-receptor properties[1,4,5]. The change from acetate to formate was crucial for achieving a highly ordered organization ("onion-type" structure) of the H_2O molecules inside the spherical anions.[2] The acetate ligands were exchanged for several other carboxylates, such as oxalate,[9] propionate,[10] butyrate,[11] isobutyrate[12] and pivalate[12], as a means of tuning the internal properties (such as hydrophilicity vs. hydrophobicity) of the keplerate cavity. Insertion of the azide functionality was achieved by exchange of the acetate ligands in the presence of an excess of azidoacetic acid, with the formation of $[\{Mo_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(O_2CCH_2N_3)\}_{13}\{Mo_2O_4(H_2O)_2\}_{17}]^{25-}$.[13] A 1,3-dipolar cycloaddition reaction between propiolic acid and azide functions within the cavity of the keplerate gives a mixture of 1,4- and 1,5-triazoles.[13] No reports have appeared on the ligand exchange chemistry of the tungstate-based keplerate anion, $[\{W_6O_{21}(H_2O)_5(CH_3COO)_{0.5}\}_{12}\{Mo_2O_4(CH_3COO)\}_{30}]^{48-}$ (**3**).[7]

An inorganic ligand which is analogous to hypophosphate and sulfate is selenate SeO_4^{2-}. Like sulfuric acid, selenic acid H_2SeO_4 is a strong acid and extremely soluble in water. Sodium and ammonium selenates are also highly soluble, which makes possible achieving high concentration of SeO_4^{2-} in solution in order to shift the substitution equilibrium and achieve complete substitution. An additional advantage of selenate over the sulfate lies in the possibility of doing ^{77}Se NMR. Herein we report synthesis and characterization of three new keplerates based on $\{W_{72}Mo_{60}\}$ spherical core with coordinated selenate inside the cavity.

Experimental

Reagents and chemical

The ammonium salt of $[\{W_6O_{21}(H_2O)_5(CH_3COO)_{0.5}\}_{12}\{Mo_2O_4(CH_3COO)\}_{30}]^{48-}$ (**3**) used as precursor was prepared as described in the literature[7] and characterized by IR and Raman spectroscopy. Other reagents were of commercial quality and used as purchased.

Spectral and analytical methods

Infrared spectra (4000 – 400 cm^{-1}) were recorded on a Scimitar FTS 2000 spectrophotometer in KBr pressed pellets.

Raman spectra were recorded on a Triplemate spectrometer (Spex, USA) equipped with a multichannel detector LN-1340 PB (Princeton Instruments, USA).

UV/Vis spectra were recorded on an Agilent G1600AX.

The 95.338 MHz ^{77}Se NMR spectra were recorded at room temperature from saturated aqueous solution in 5 mm o.d. tubes on a Bruker Avance 500 spectrometer. Chemical shifts are referenced to Me_2Se in $CDCl_3$.

Elemental analyses for C, H, N were performed by the Analytical Laboratory of NIIC SB RAS (Novosibirsk) on a Eurovector EA3000 CHN analyzer.

Inductively coupled plasma atomic emission spectroscopy for Mo, W, and Se was performed by the Analytical Laboratory of NIIC SB RAS (Novosibirsk) on an iCAP 6500 ICP Spectrometer (Thermo Scientific).

Capillary electrophoresis

Capillary electrophoresis experiment was carried out in a quartz capillary (L_{total} = 36 cm, L_{eff} = 28 cm) on Agilent G1600AX equipped with internal UV-vis detector under the following conditions: 10^{-3} M HCl as separation electrolyte; voltage – -15kV; wavelength – 254 nm; $2.5\cdot10^{-5}$ M aqueous solution of **1a** and **3** with pneumatic sample injection (1500 mbar×sec).

ESI-MS measurements

Electrospray Ionization mass spectrometry was performed on a Q-TOF premier mass spectrometer with an orthogonal Z-spray electrospray source (Waters, Manchester, UK). The temperature of the source block was set to 100°C and the desolvation temperature – to 200°C. A capillary voltage of 3.3 kV was used in the negative scan mode and the cone voltage was varied from low values Uc = 10 V (to control the extent of fragmentation of the identified species) ~~to 60 V to observe the intrinsic gas-phase fragmentation channels~~. TOF mass spectra were acquired in the V-mode operating at a resolution of ca. 10000 (FWHM). Mass calibration was performed using a solution of sodium iodide in 2-propanol/water (50:50) from *m/z* 50 to 3500. Sample preparation of compounds **1b** and **2** was done following the protocol described by Cronin.[14] After dissolving 5-10 mg in a minimum amount of water (typically 25 µL), a small portion of this aqueous solution was further diluted with acetonitrile 100-fold, filtered and infused via a syringe pump, directly connected to the ESI source, at a flow rate of 10 µL·min^{-1}. Sample preparation of **1a** was similar except that the 100-fold dilution step was done with 90:10 CH_3CN:H_2O mixtures to avoid precipitation which occurred in neat CH_3CN.

X-ray crystallography

The diffraction data for **2** were collected on a Bruker X8Apex-II CCD diffractometer at 150 K with MoKα radiation (λ = 0.71073 Å) by doing ω and φ scans of narrow (0.5 °) frames. The structure was solved by direct methods and refined by full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation with SHELXTL software package.[15] Absorption corrections was applied empirically with SADABS.[16] The SeO_4^{2-} anions have strongly disordered distribution inside the keplerate molecule and almost no Se positions is fully occupied, which leads to positional disorder between selenate and water inside the cavity. Occupancies of the Se positions in the non-standard coordination mode (not between molybdenum in $\{Mo_2\}$ fragments) are 5–15%, which gives the electronic density from oxygens of SeO_4^{2-} non-coordinated to metal between 1.2 and 0.4e. These values cannot be located with a good accuracy in the highly disordered structure of **2**, and such oxygen atoms were included into the formula without refinement. The data collection on keplerates is adversely affected by poor diffraction, especially if the crystal was kept in the mother liquor for more than one day. In the case of the tungsten-containing keplerates the X-ray absorption increases significantly, and dimensions of the crystal should be minimized, but the problem of low diffraction limit does not allow doing this. Due to this fact some artifacts in electronic density appear, decreasing the accuracy of an x-ray experiment. Specifically, in our case such artifacts were residual peaks up to 4e. Crystallographic data and refinement details are given in Table S1. Further details may be obtained from the Cambridge Crystallographic Data Center on quoting the depository number CCDC 1039304. Copies of this information may be obtained free of charge from http://www.ccdc.cam.ac.uk.

Experimental procedures for the synthesis of 1a, 1b and 2

$(NH_4)_{72}[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]\cdot150H_2O\cdot6(NH_4)_2SeO_4$ (1a): The acetate complex **3** (1.00 g, 0.03 mmol) was dissolved in 100 mL of H_2O under vigorous stirring to form dark brown-red solution (pH 5.1). Solid ammonium selenate (5.30 g, 30 mmol) was added, and the pH adjusted to 2.0 by a few drops of 6 M HCl. The solution was stirred for 12 h at room temperature and, if necessary, was filtered to remove any insoluble material. Then a large excess of solid ammonium chloride (10.0 g, 187 mmol) was added to produce an orange-brown precipitate. The mixture was stirred for 15 minutes and kept at 5°C for 3 h to complete precipitation. The product was isolated by filtration on a glass frit, washed successively with ethanol and diethyl ether, and dried in air. Yield 0.78 g (73% based on W). Analysis for $N_{84}H_{780}O_{738}Se_{36}Mo_{60}W_{72}$ (%) calcd: H 2.2, N 3.3, Se 8.0, Mo 16.2, W 37.2; found: H 2.1, N 3.2, Se 7.4, Mo 15.5, W 36.7. IR (cm^{-1}): 1622 (m, $\delta(H_2O)$), 1402 (s, $\delta_{as}(NH_4^+)$), 975 (m) and 943 (m, $\nu(W = O)$), 872 (s), 804 (vs), 730 (s), 650 (m), 572 (s), 480 (m). Raman (cm^{-1}): solid 300 (w), 380 (vs), 717 (vw), 866 (sh), 891 (m), 960 (sh), 972 (m); aqueous solution 297 (w), 382 (vs), 717 (vw), 867 (sh), 899 (m), 971 (m).UV/Vis (H_2O, λ, nm) 238, 373 (br).^{77}Se NMR (D_2O, r.t., δ, ppm): 1025 (s, SeO_4^{2-}).

$(NH_4)_{25}(NH_2Me_2)_{47}[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]\cdot 130H_2O\cdot 3(NH_4)_2SeO_4$ (1b): Keplerate **1a** (0.20 g, 0.0056 mmol) was dissolved in 10 mL of 0.1 M solution of ammonium selenate. Solid dimethylammonium chloride (0.50 g, 6.13 mmol) was added, causing immediate appearance of a light red-brown precipitate. The mixture was heated at 60°C until the complete dissolution (about 15 min). The dark red-brown solution was slowly cooled to room temperature. After two days dark brown crystals were collected by filtration, washed with ethanol, and dried with diethyl ether. Yield 0.14 g (69% based on W). Analysis for $C_{94}N_{75}H_{904}O_{706}Se_{30}Mo_{60}W_{72}$ (%) calcd: C 3.1, H 2.5, N 3.0; Se 7.2, Mo 16.0, W 36.7; found: C 3.1, H 2.4, N 3.0, Se 7.1, Mo 16.5, W 36.2. IR (KBr, cm^{-1}): 1621 (m, δ(H2O)), 1462 (m, $NH_2Me_2^+$), 1406 (m, $\delta_{as}(NH_4^+)$), 1019 (w, $NH_2Me_2^+$) 976 (m) and 944 (m, $\nu(W = O)$), 872 (s), 806 (vs), 731 (s), 650 (m), 572 (s), 480 (m). Raman (cm^{-1}): solid 301 (w), 380 (vs), 717 (vw), 867 (sh), 890 (m), 959 (sh), 972 (m); aqueous solution 298 (w), 381 (vs), 717 (vw), 866 (sh), 900 (m), 971 (m).

$(NH_4)_{20}(NH_2Me_2)_{32}[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4\}_{30}(SeO_4)_{20}(H_2O)_{20}]\cdot 150H_2O$ (2): Crystals of **2** were obtained in the same manner as **1b**, by working in H_2O instead of 0.1 M $(NH_4)_2SeO_4$. Yield 0.12 g (63% calculated on W). Analysis for $C_{64}N_{52}H_{820}O_{694}Se_{20}Mo_{60}W_{72}$ (%) calcd: C 2.3, H 2.4, N 2.1; Se 4.6, Mo 17.0, W 38.9; found: C 2.3, H 2.3, N 2.3 Se 4.3, Mo 17.6, W 39.1. IR (KBr, cm^{-1}): 1619 (m, $\delta(H_2O)$), 1463 (m, $NH_2Me_2^+$), 1412 (w, $\delta_{as}(NH_4^+)$), 1019 (w, $NH_2Me_2^+$) 980 (m) and 946 (m, $\nu(W = O)$), 876 (s), 809 (vs), 735 (s), 651 (m), 572 (s), 482 (m). Raman (cm^{-1}): solid 302 (w), 382 (vs), 861 (sh), 893 (m), 962 (sh), 973 (m); aqueous solution 298 (w), 381 (vs), 856 (sh), 970 (m).

Results and discussions

Compound **1a** was obtained by the ligand exchange process inside the cavity of the acetate complex **3** by treatment with an excess of ammonium selenate at pH 2. The reaction solution was kept at room temperature for 12 h and the product was precipitated by excess of ammonium chloride. **1a** was characterized by elemental analysis and ICP-AES to determine the exact formula, by spectroscopic methods (IR, Raman, UV/Vis, and ^{77}Se NMR), ESI mass spectrometry and also by capillary electrophoresis.

$$(NH_4)_{72}[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]\cdot 150H_2O\cdot 6(NH_4)_2SeO_4 \equiv (NH_4)_{72}\cdot\mathbf{1}\cdot 150H_2O\cdot 6(NH_4)_2SeO_4 \equiv \mathbf{1a}$$

The general shape of the IR spectrum of **1a** is very close to the IR spectrum of the acetate **3,** almost all peaks having very small shifts (Fig. S1). The important difference lies in the absence of the acetate characteristic bands which indicate that the ligand exchange process is complete. This conclusion was also proved by elemental analysis, showing no carbon in the sample. The selenate bands could not be observed in IR because of their overlapping with the strong bands from the keplerate metal-oxide framework between 1000 and 450 cm^{-1}.[17] However, the elemental analysis confirms that 30 acetate ligands have been replaced with 30 selenate ligands. The Raman spectra of **1a** both in solid state and in aqueous solution show practically identical shape and the location of the peaks, indicating the intactness of the keplerate cage during the ligand substitution and its stability in solution (Fig. 1a). The general shape of Raman spectrum of **1a** resembles very much that of **3**, the sole difference being that the bands assigned to $\nu_s(Mo = O)$ and $\nu_s(W = O)$ for the selenate-substituted **1a** are less intense than for acetate-substituted keplerate **3** (Fig. 1b).

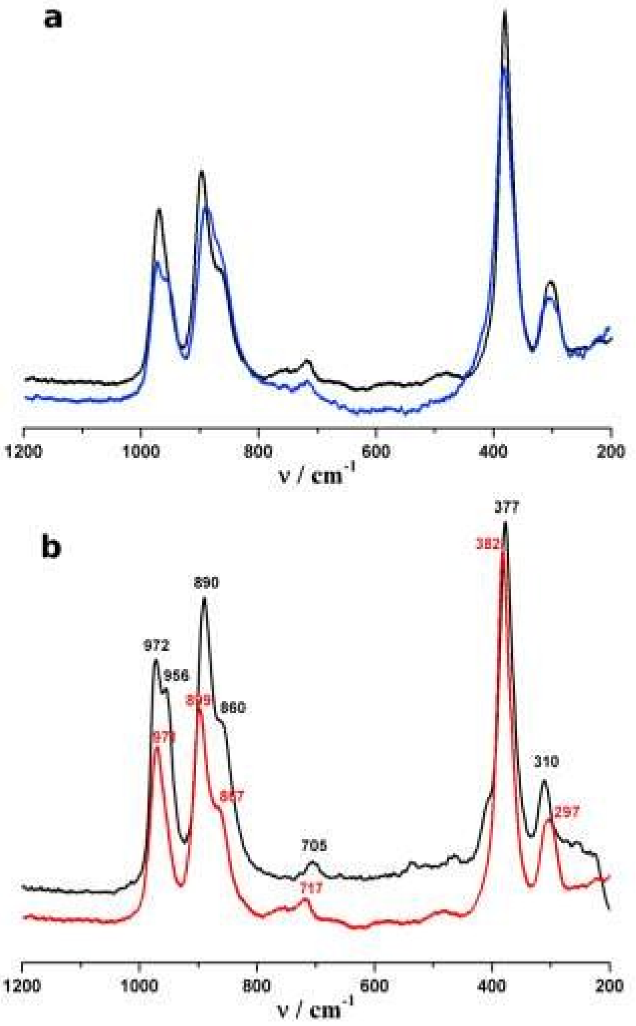


Fig. 1 (a) Raman spectra of **1a** in aqueous solution (*black*) and in solid state (*blue*). (b) Raman spectra of **1a** (*red*) and **3** (*black*) in aqueous solution.

The UV/Vis spectrum of **1a** does not differ from that of **3** (Fig. S2).

Under the conditions selected for capillary electrophoresis (*see Experimental section*) **3** migrated 2.5 minutes longer than **1a**, but the complete separation of the peaks was difficult because of the tightened trailing edge (Fig. 2). For **3** a minor broad peak-rider at the trailing edge is observed. The migration times are reproducible, and large trails may be due to close ion pairing with different number of cations, which is expected to produce sets of closely migrating species. Strong ion pairing may explain why keplerate anions in **1a**, which have higher negative charge (72-), migrate faster than in **3** (48-).

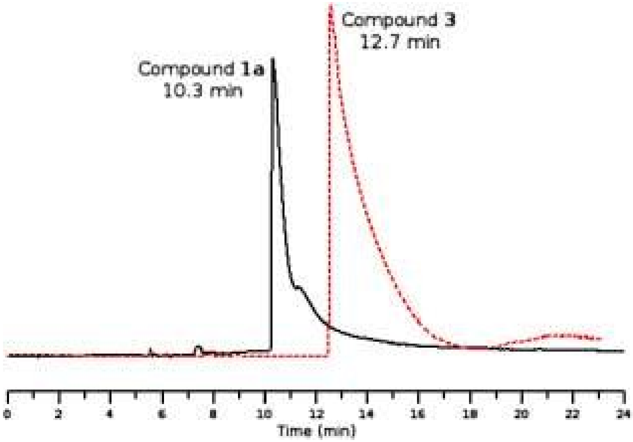


Fig. 2 Capillary electrophoresis separation of **1a** and **3**.

Compound **1b** was obtained by recrystallization of **1a** from 0.1 M aqueous solution of ammonium selenate (used to suppress the selenate loss through aquation) in the presence of dimethylammonium chloride. It was characterized by elemental analysis and vibrational spectroscopy (IR and Raman).

$(NH_4)_{25}(NH_2Me_2)_{47}[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]\cdot 130H_2O \cdot 3(NH_4)_2SeO_4 \equiv (NH_4)_{25}(NH_2Me_2)_{47}\cdot\mathbf{1}\cdot 130H_2O\cdot 3(NH_4)_2SeO_4 \equiv$ **1b**

Compound **2** was obtained by recrystallization of **1a** from water without addition of ammonium selenate, in the presence of dimethylammonium chloride. It was characterized by elemental analysis and IR and Raman spectra, and by single-crystal X-ray structure analysis. The elemental analysis gave only 20 selenates per keplerate.

$(NH_4)_{20}(NH_2Me_2)_{32}[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4\}_{30}(SeO_4)_{20}(H_2O)_{20}]\cdot 150H_2O \equiv$ **2**

The IR and Raman spectra of **1a**, **1b** and **2** are very similar. The expected difference is due to the presence of dimethylammonium bands. The Raman spectra of **2** recorded both in solid state and in aqueous solution support the stability of the anionic cage in solutions (Fig. 3a). The only difference is that the bands assigned to ν_s(Mo=O) and ν_s(W=O) in **2** were weaker and broader than in **1a** (Fig. 3b).

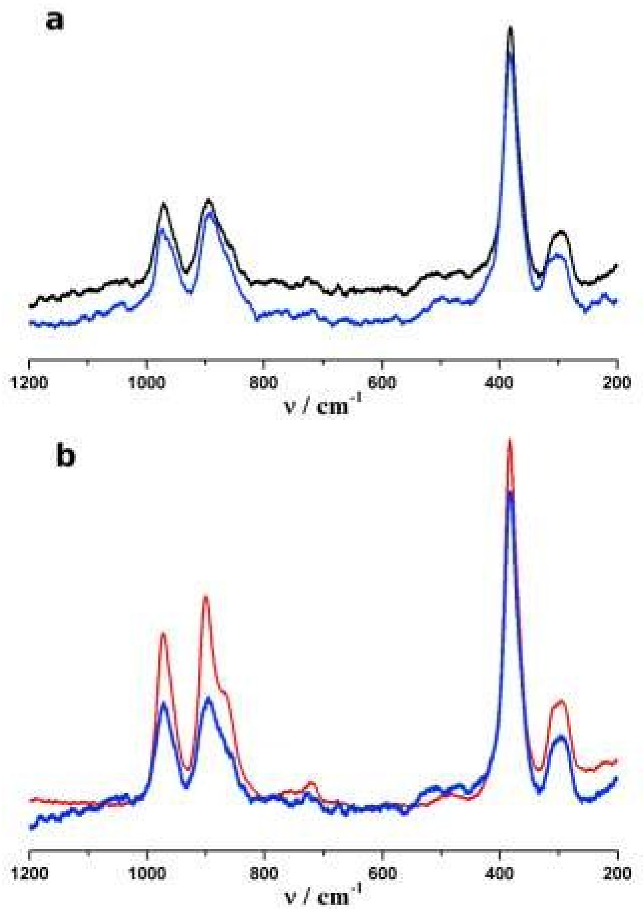


Fig. 3 (a) Raman spectra of **2** in aqueous solution (*black*) and in solid state (*blue*). (b) Raman spectra of **1a** (*red*) and **2** (*blue*) in aqueous solution.

The crystal structure of **2** is built from the large spherical $\{Mo_{60}W_{72}\}$ keplerate anions, having pentagonal $\{(W)W_5\}$ building blocks linked by $\{Mo_2(\mu\text{-}O)_2O_2\}^{2+}$ units. The available coordination sites at the $\{Mo_2O_4\}$ linkers (fig. 4a) are occupied with SeO_4^{2-} by 30–55%, which means that about 1/2–1/3 of the totally available coordination sites are occupied with water molecules. The corresponding Mo-O bond lengths are 2.366–2.397 Å. What is more interesting, SeO_4^{2-} inside the cavity, instead of occupying as much available positions at $\{Mo_2O_4\}$ linkers, also uses coordination possibilities in non-standard positions located under $\{(W)W_5\}$ building blocks. Of them the first type connects a molybdenum atom from a $\{Mo_2O_4\}$ linker (Mo-Mo(av) 2.566(1) Å) and two tungsten atoms from the pentagonal unit (Fig. 4b). The occupancies of Se positions are 3–5%, and Se-O distances lie in the range 1.6–1.8 Å. The second type of non-standard SeO_4^{2-} anion coordination connects only tungsten atoms of $\{(W)W_5\}$ building blocks with occupancies of the Se positions 5–15% (Fig. 4c). The $W\text{-}O_{SeO4}$ and WO_{H2O} bond lengths are indistinguishable and vary from 2.366 to 2.397 Å for the peripheral atoms and are much shorter, 2.260 Å, for the central atom in the pentagonal $\{(W)W_5\}$ unit.

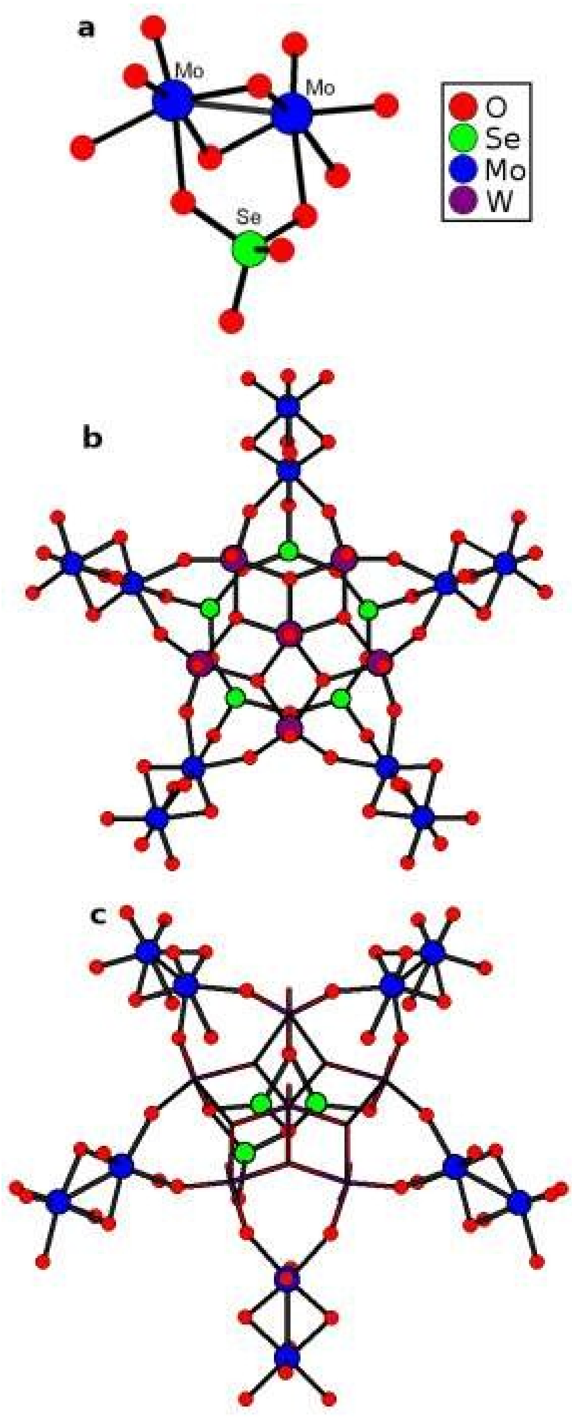


Fig. 4 Standard (a) and non-standart (b,c) coordinated SeO_4^{2-} anion in **2**.

Hence SeO_4^{2-} anions have rather random coordination which includes occupation both standard and non-standard positions. All these positions are not fully occupied with selenate, which competes with the water molecules to coordination sites, forming a dynamic system inside the keplerate anion, with full positional disorder inside the keplerate capsule. All these features point at a rather loose coordination of SeO_4^{2-} inside the keplerate cavity. Probably, in solution the selenate is constantly moving inside the keplerate cavity, filled with water, from one coordination site to another, with average environment resembling much that of free SeO_4^{2-} in water, and this explains why in ^{77}Se NMR spectrum of **1a** only one peak at 1025 pm is observed, which is virtually the same as reported for K_2SeO_4 in saturated solution (1024 pm).[18] An alternative explanation would be the complete loss of coordinated SeO_4^{2-} from the keplerate cavity into solution, but both analytical and structural data on 2 indicated that at least 2/3 of SeO_4^{2-} is retained even after heating and keeping the solution for two days, which by far exceeds the time required for a ^{77}Se NMR spectrum acquisition.

The NH_4^+ and $Me_2NH_2^+$ cations in the outer sphere of **2** are also disordered and share their positions with water molecules. The refinement reveals three types of $Me_2NH_2^+$ cations. The first type is isolated from the keplerate and form strong hydrogen bonds only with water molecules (d(N...O) = 2.7–2.8 Å). The second type forms strong hydrogen bonds to the terminal oxygen atoms of the $\{W(W_5)\}$ pentagonal building blocks. The third type occupies pores of the $\{Mo_{60}W_{72}\}$ spherical structure and competes with water for the space inside the pore (Fig. S3). The keplerate anions form a three-layered packing, with orientation of layers along [110] crystallographic direction (Fig. S4).

Electrospray Ionization mass spectrometry

Mass spectrometric characterization of Keplerate POM's clusters using soft ionization techniques has been scarcely explored. Müller and Cronin´s groups have pioneered the use of MALDI and ESI-MS, respectively, for identification of this class of polyanions.[14,19] In the present work, we address the solution characterization of new keplerates **1a, 1b** and **2** by ESI-MS. Molecular weight estimation of keplerate POM on the basis of ESI-MS analysis is not trivial because of their high molecular weight. Consequently, the isotope distribution of the anionic species detected by ESI-MS is difficult to resolve with common mass analyzers. Molecular weight estimation can be done by inspection of the spacing between adjacent multiply charged peaks observed in the ESI mass spectrum (the so-called deconvolution method). Hence, the ESI mass spectra of **1a**, **1b** and **2** are characterized by a number of signals encompassing charge states from 12- to 7- irrespective of the net charge of polyanion (72 for **1a** and **1b** and 52 for **2**) and their countercation composition. Peaks are typically broad due to the different cationic content (in this case NH_4^+, $Me_2NH_2^+$ and H^+) of each identified ion as well as to the propensity of these large polyanions to be solvated. The ESI mass spectrum of **1a** (Fig. S5) displays six broad peaks centered at m/z 2528, 2788, 3080, 3441, 3960 and 4648, encompassing charge states from 12- to 7- whereas the maximum m/z position of the envelope for compound **1b** (Fig. 5) was observed at m/z values 2632, 2877, 3176, 3536, 3999 and 4582 with decreasing charge states from 12- to 7-. Tables S2-S4 lists the m/z values at the center of each envelope observed in the negative ESI-MS of **1a**, **1b** and **2**. According to the experimentally determined m/z values for **1a** and **1b**, the distribution of charge states from 12- to 7- is produced exclusively by countercation (NH_4^+, $Me_2NH_2^+$ and H^+) adduct formation with the whole cluster $[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]^{72-}$ polyanion and water or CH_3CN molecules from the solvent (*see supporting information for detailed ESI-MS analysis*). The observed m/z values for compound **1b** are slightly higher than those observed for compound **1a**, as expected for the formation of dimethylammonium versus ammonium adducts.

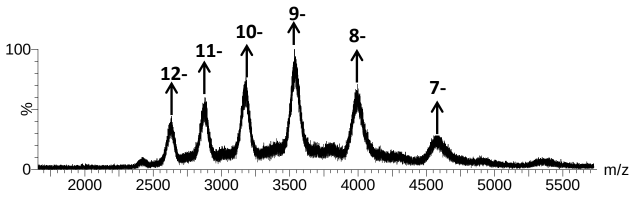


Fig. 5 Negative ESI mass spectrum CH_3CN solutions of compound **1b** recorded at low cone voltage, Uc = 10 V.

The ESI mass spectrum of **2** (Fig. S8) displayed six broad peaks centered at m/z 2561, 2803, 3097, 3450, 3900 and 4460 encompassing charge states from 12- to 7-. Like **1a** and **1b**, its ESI mass spectrum is indicative of keplerate structure preservation in the solution. A direct comparison of the m/z values determined for **1a**, **1b** and **2** was hampered because of the distinctive countercation composition that strongly influences the identity of the identified peaks and consequently their m/z values. For example, on going from **1a** to **2**, replacement of SeO_4^{2-} by H_2O occurs; however, the series of peaks in the ESI mass spectrum of **2** appears at slightly higher m/z values than those of **1a**, essentially due to the presence of Me_2NH^+ **2** and NH_4^+ in **1a**, respectively. We also note that the observation of charge states from 12- to 7-, seems to be a general characteristic of kelerate POM clusters based on pentagonal $\{(M)M_5\}$ (M = Mo, W) building blocks linked by Mo_2O_4 units. This is also manifested regardless the net charge of the polyanion, that is modulated by the ligands on the Mo_2O_4 unit, as well as the countercation.

Conclusions

A series of new keplerate complexes based on the $\{W_{72}Mo_{60}\}$ mixed-metal core with incorporated selenate ligands have been prepared. The validity of formulation has been confirmed by various methods, including complete elemental analysis, X-ray structure and ESI-mass spectrometry. The keplerate cage is stable in solutions, but SeO_4^{2-} are loosely coordinated inside the cage, show dynamic behavior in ^{77}Se NMR spectrum and are partially replaced by water in aqueous solutions. The validity of capillary electrophoresis for monitoring keplerates in solutions has been demonstrated.

Acknowledgements

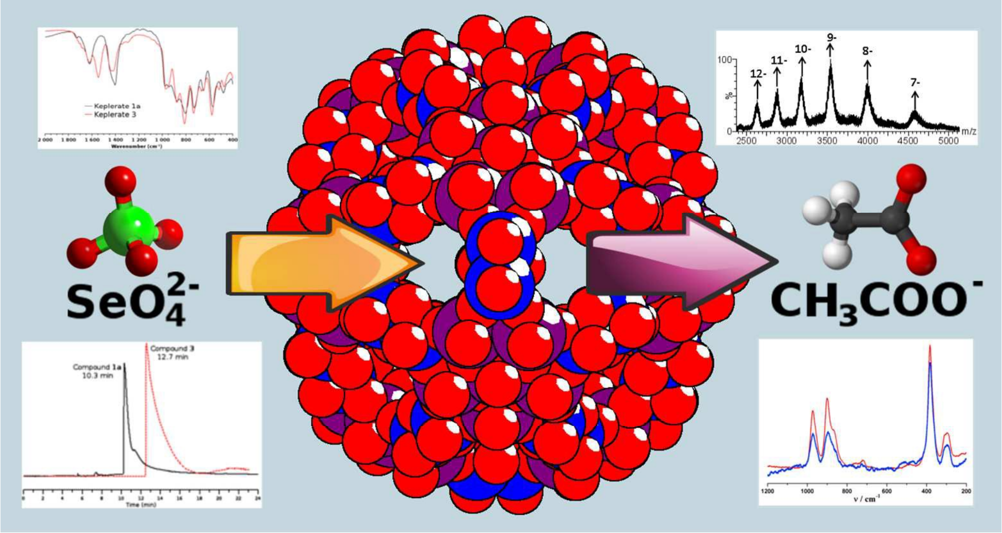
Authors thank Mr. N. B. Kompankov (NMR), ~~and~~ Dr. O. S. Koscheeva (Elemental analysis) and SCIC of the University Jaume I for their help with characterization of synthesized keplerate-type compounds. The work was partially supported by RFBR grant 12-03-31080, and the grants of the President of Russian Federation MK-4318.2013.3 and SS-516.2014.3.

Notes and references

[a] *Nikolaev Institute of Inorganic Chemistry SB RAS, Prospect Lavrentyeva 3, 630090 Novosibirsk, Russia. Fax: +7 383 330 9089; Tel: +7 383 316 5845;E-mail: wkorenev@niic.nsc.ru*
[b] *Novosibirsk State University, Pirogova street 2, 630090 Novosibirsk, Russia.*
[c] *Serveis Centrals d'Instrumentacio Cientifica, Universitat Jaume I, Avda. Sos Baynat s/n, E-12071, Castello, Spain.~~Universitat Jaume I CIF: Q-6250003-H, Av. de Vicent Sos Baynat, s/n 12071 Castelló de la Plana, Espanya.Fax: +34 964 72 90 16; Tel.: +34 964 72 80 00.~~*

† Electronic Supplementary Information (ESI) available: IR and UV/Vis spectra, electrospray ionization mass spectrometry data and crystallographic data. See DOI: 10.1039/b000000x/

1 1. A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, F. Peters, *Angew. Chem. Int. Ed.*, 1998, **37**, 3360.
2. A. Müller, V.P. Fedin, C. Kuhlman, H. Bögge, M. Schmidtmann, *Chem. Commun.*, 1999, 927.
3. A. Müller, S. Polarz, S.K. Das, E. Krickemeyer, H. Bögge, M. Schmidtmann, B. Hauptfleisch, *Angew. Chem. Int. Ed.*, 1999, **38**, 3241.
4. A. Müller, S.K. Das, S. Talismanov, S. Roy, E. Beckmann, H. Bögge, M. Schmidtmann, A. Merca, A. Berkle, L. Allouche, Y. Zhou, L. Zhang, *Angew. Chem. Int. Ed.*, 2003, **42**, 5039.
5. A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, S. Roy, A. Berkle, *Angew. Chem. Int. Ed.*, 2002, **41**, 3604.
6. A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, B. Botar, M.O. Talismanova, *Angew. Chem. Int. Ed.*, 2003, **42**, 2085.
7. C. Schäffer, A. Merca, H. Bögge, A.M. Todea, M.L. Kistler, T. Liu, R. Thouvenot, P. Gouzerh, A. Müller, *Angew. Chem. Int. Ed.*, 2009, **48**, 149.
8. M.L. Kistler, A. Bhatt, G. Liu, D. Casa, T.J. Liu, *J. Am. Chem. Soc.*, 2007, **129**, 6453.
9. A. Müller, L. Toma, H. Bögge, M. Henry, E.T.K. Haupt, A. Mix, F.L. Sousa, *Chem. Commun.*, 2006, 3396.
10. C. Schäffer, A.M. Todea, H. Bögge, O.A. Petina, D. Rehder, E.T.K. Haupt, A. Müller, *Chem.–Eur. J.*, 2011, **17**, 9634.
11. C. Schäffer, H. Bögge, A. Merca, I.A. Weinstock, D. Rehder, E.T.K. Haupt, A. Müller, *Angew. Chem., Int. Ed.*, 2009, **48**, 8051.
12. A. Ziv, A. Grego, S. Kopilevich, L. Zeiri, P. Miro, C. Bo, A. Müller, I.A. Weinstock, *J. Am. Chem. Soc.*, 2009, **131**, 6380.
13. C. Besson, S. Schmitz, K.M. Capella, S. Kopilevich, I.A. Weinstock, P. Kögerler, *Dalton Trans.*, 2012, **41**, 9852.
14. P.J. Robbins, A.J. Surman, J. Thiel, D.L. Long, L. Cronin, *Chem. Commun.*, 2013, **49**, 1909.
15. G.M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
16. G.M. Sheldrick, *SADABS*, Program for empirical X-ray absorption correction, Bruker-Nonius, 1990.
17. H.Z. Siebert, *Anorg. Allgem. Chem.*, 1954, **275**, 225.
18. E.H. Walchli, *Phys. Rev.*, 1953, **90**, 331.
19. A. Müller, E. Diemann, S.Q.N. Shah, C. Kuhlmann, M.C. Letzel, *Chem. Commun.*, **2002**, 440.


Keplerate 1a
Keplerate 3
Wavenumber (cm⁻¹)
SeO_4^{2-}
Compound 1a
10.3 min
Compound 3
12.7 min
Time (min)
12-
11-
10-
9-
8-
7-
100
%
0
m/z
2500
3000
3500
4000
4500
5000
CH_3COO^-
1200
1000
800
600
400
200
ν / cm⁻¹