Novel ligand for keplerate chemistry. Synthesis and characterization of three keplerates based on $\{W_{72}Mo_{60}\}$ spherical core with selenates introduced inside the cavity.

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Supplementary

Figure S1: Comparison of the IR-spectra of keplerates **1a** and **3**.

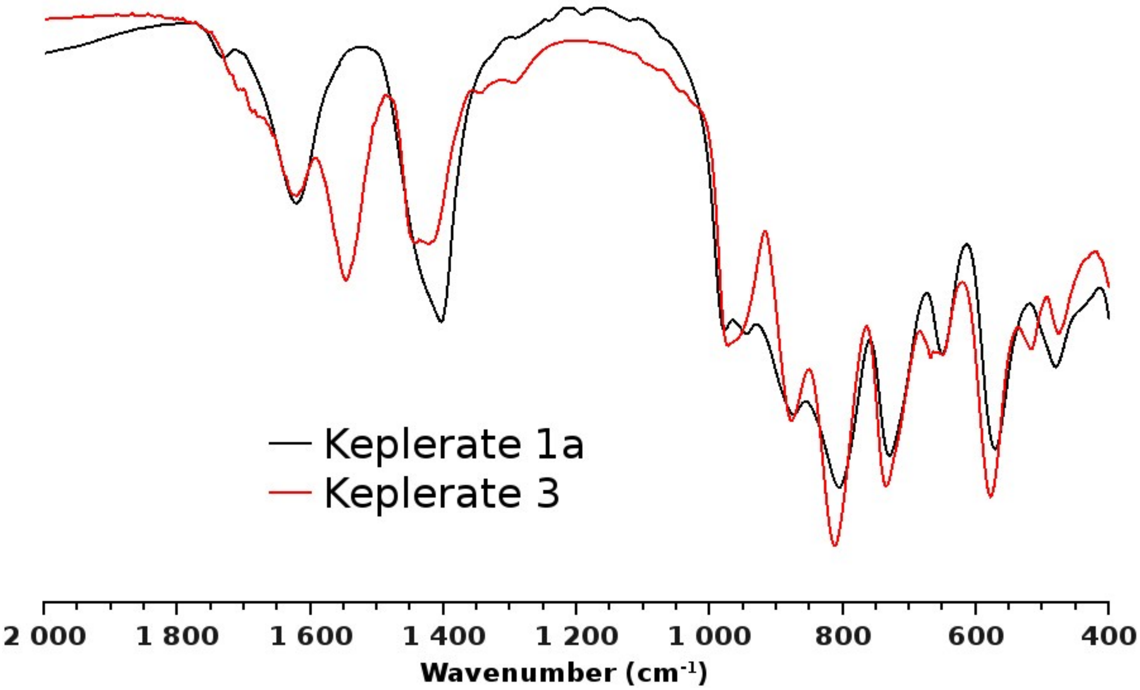

Figure S2: Comparison of the UV/Vis spectra of keplerates **1a** and **3**.

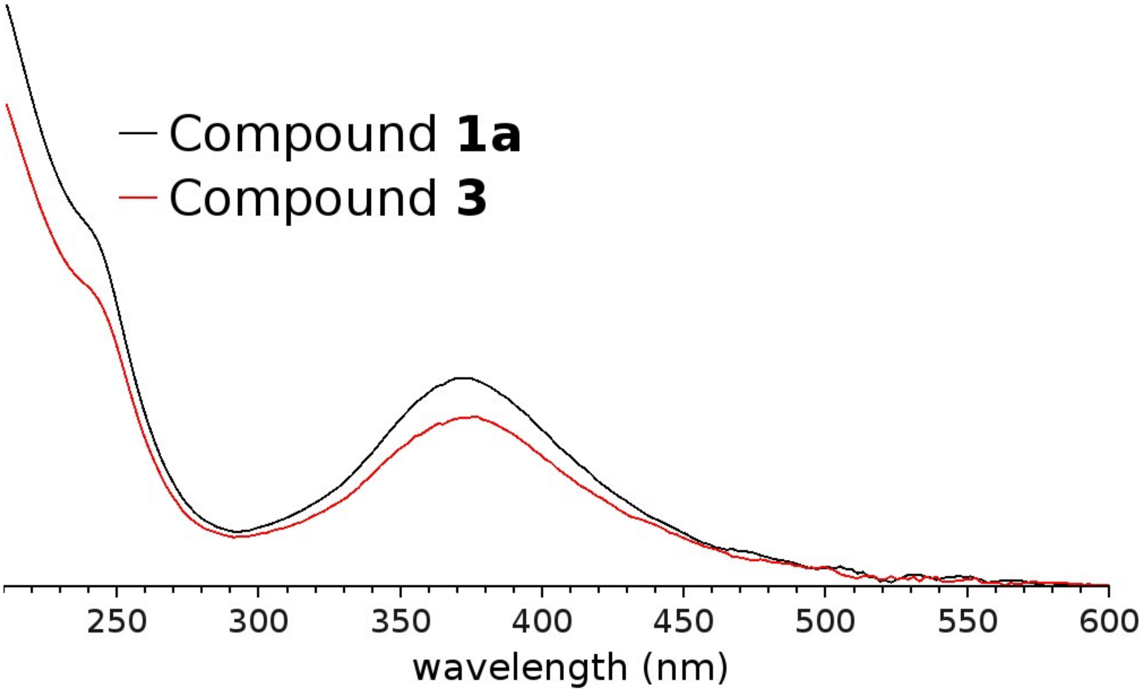

Figure S3. Location of coordinated $Me_2NH_2^+$ cations in **2**.

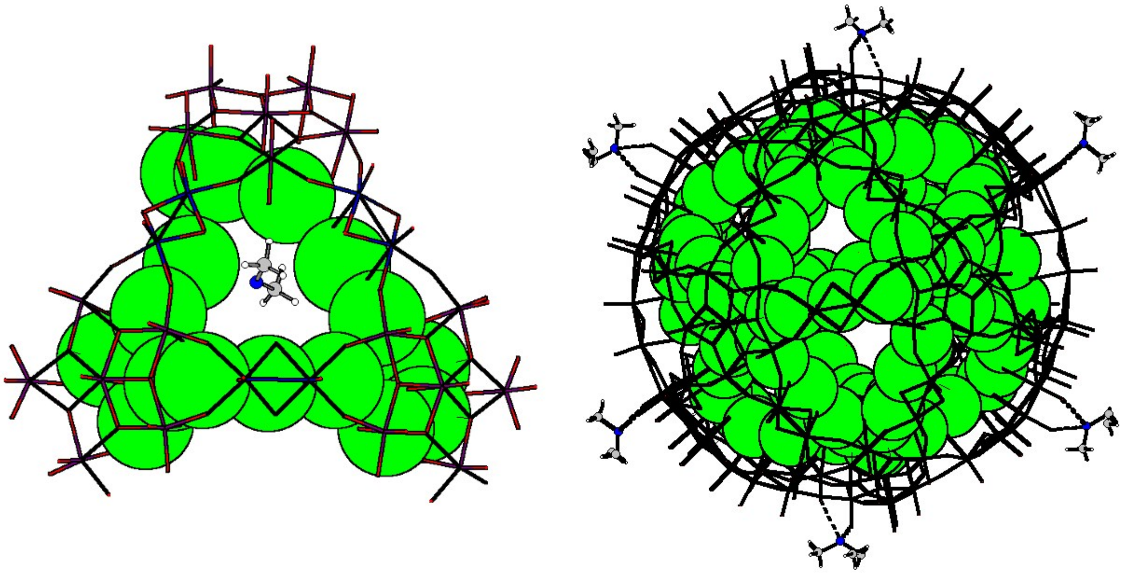

Figure S4. Three-layered crystal packing of **1a**.

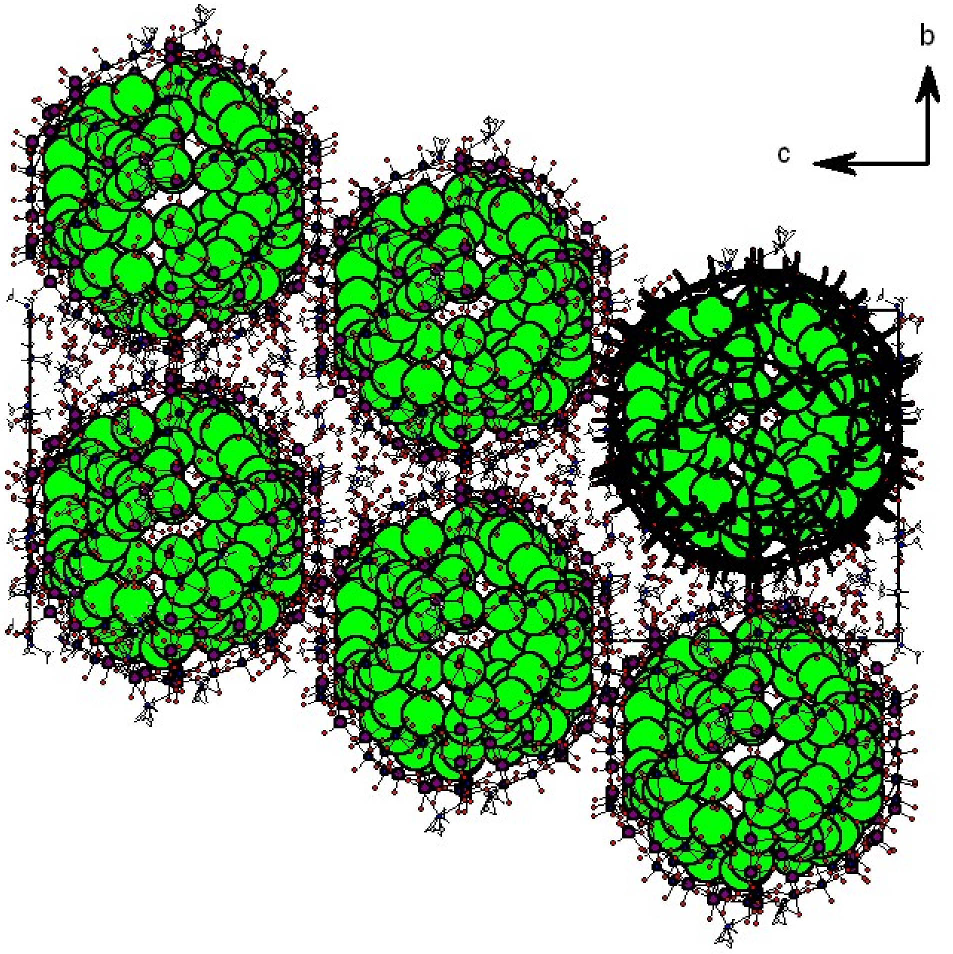

Table S1. Crystallographic data for **2**.

Chemical formula	$C_{45}H_{162}Mo_{60}N_{22.50}O_{601.26}Se_{21.57}W_{72}$
M_r	31335.89
Crystal system, space group	Trigonal, $R\bar{3}{:}H$
Temperature (K)	100
a, c (Å)	32.8171 (9), 74.653 (2)
V (Å^3)	69627 (4)
Z	3
Radiation type	Mo $K\alpha$
μ (mm^{-1})	10.58
Crystal size (mm)	0.15 × 0.12 × 0.05
Diffractometer	Bruker Nonius X8Apex CCD
Absorption correction	Multi-scan *SADABS* (Bruker-AXS, 2004)
$T_{\min}$, $T_{\max}$	0.300, 0.620
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	153672, 35539, 24563
R_{int}	0.057
θ values (°)	$\theta_{\max} = 27.5$, $\theta_{\min} = 1.5$
Range of h, k, l	$h = -36 \rightarrow 42$, $k = -42 \rightarrow 27$, $l = -96 \rightarrow 74$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.159, 1.11
No. of reflections	35539
No. of parameters	1479
H-atom treatment	H-atom parameters not defined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0899P)^2 + 157.9436P]$, where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\square_{\max}$, $\Delta\square_{\min}$ (e Å^{-3})	4.73, -3.99

Computer programs: APEX2 (Bruker-AXS, 2004), SAINT (Bruker-AXS, 2004), SHELXS2013, SHELXL2013, Diamond 3.1, CIFTAB-97 (Sheldrick, 1998).

*ESI mass spectra and peak assignments for compounds **1a** and **1b**.*

The ESI mass spectra of **1a** and **1b** (see **Figure S5** and **S6**) displayed six broad peaks centered at m/z encompassing charge states from 12- to 7-. This implies that for the $[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]^{72-}$ polyanion, from 60 to 65 negative charges must be compensated. Two posible ESI ionization mechanisms are compatible to account for the charge alleviation from the large $[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]^{72-}$ polyanion; i) cation adduct formation yielding anions of general formula $[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30+m}cat]^{n-}$ (n = 12 to 7; m = 60 to 65) or ii) cation adduct formation accompanied by m-fold releasing of SeO_4^{2-} groups that yield $[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)_{(30-m)}\} + _{(60-2m)}cat]^{n-}$ (n = 12 to 7; m = 30 to 0). This latter mechanism has been observed for the closely related keplerate POM cluster $(NH_4)_{42}[Mo_{132}O_{372}(H_2O)_6(CH_3COO)_{30}]$ that yields $(NH_4)_m[Mo_{132}O_{372}(CH_3COO)_{12}]^{n-}$ (m = 12 to 14; n = 12 to 10) upon ESI conditions. According to the experimentally determined m/z values (see **Tables S2-S3**) the distribution of charge states from 12- to 7- is produced by countercation adduct formation and solvation. Further support to this formulation comes from ESI-MS analysis of **1b** at high cone voltages (**Figure S7**) from which a m/z shift towards lower values is observed. An estimation of m/z shift is ca. 1200 that roughly account for the liberation of all 72 water molecules from the $[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]^{72-}$ polyanion. The indicated formula collected in **Tables S2-S3**, corresponds to the ion that match the m/z position at the maximum of the envelope; however, we are aware that other plausible molecular composition are also possible; for example, related ions to those included in **Table S3** at m/z 4582 may origin from replacing one Me_2NH^+ cation by the combination of $H^+ + CH_3CN$.

Figure S5. Negative ESI mass spectrum of 90:10 $CH_3CN:H_2O$ solutions of compound **1a** recorded at low cone voltage Uc = 10 V.

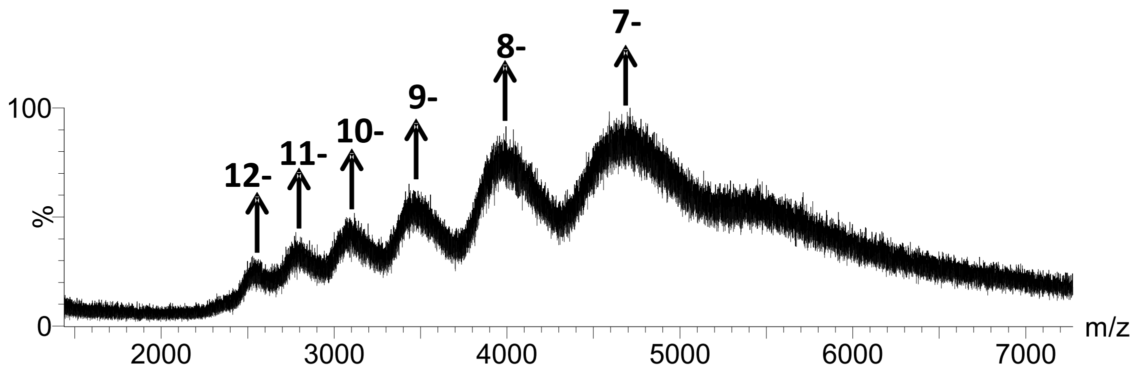

Table S2. Peak assignment of the series of peaks observed in the ESI mass spectrum shown in **figure S5** of compound **1a**.

m/z (charge state)	Envelop assignment[a]
2534 (12)	$[[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]^{72-} + 60H^+]^{12-}$
2788 (11)	$[[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]^{72-} + NH_4^+ + 60H^+ + H_2O]^{11-}$
3080 (10)	$[[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]^{72-} + 2NH_4^+ + 60H^+ + H_2O + 2CH_3CN]^{10-}$
3441 (9)	$[[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]^{72-} + 3NH_4^+ + 60H^+ + 2H_2O + 6CH_3CN]^{9-}$
3960 (8)	$[[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]^{72-} + 4NH_4^+ + 560^+ + 9H_2O + 18CH_3CN]^{8-}$
4648 (7)	$[[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]^{72-} + 5NH_4^+ + 60H^+ + 20H_2O + 35CH_3CN]^{7-}$

[a] the envelopes display different extent of cation adduct formation (where cat stands for NH_4^+ or H^+) as well as solvated water or acetonitrile molecules. For this particular simple, peaks were significantly broader than those for **1b** and **2** most likely due to the mixture of solvent used for ESI analysis.

Figure S6. Negative ESI mass spectrum CH_3CN solutions of compound **1b** recorded at low cone voltaje, Uc = 10 V.

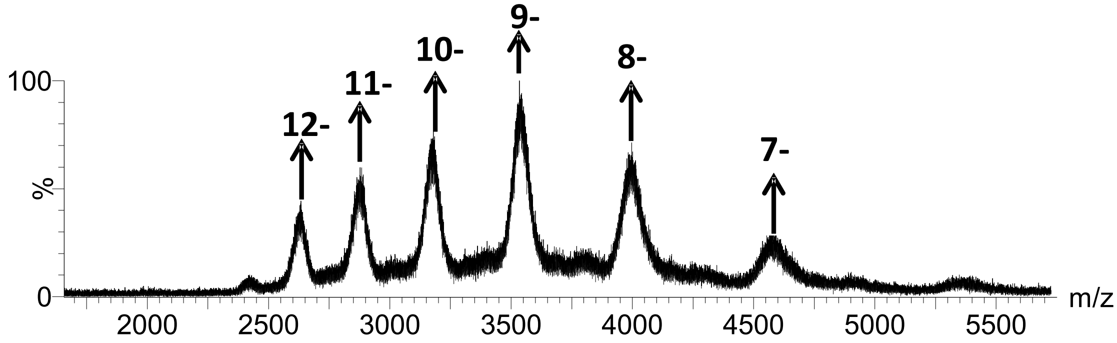

Figure S7. Negative ESI mass spectrum CH_3CN solutions of compound **1b** recorded at low cone voltaje, Uc = 10 V (bottom) and 60 V (top). Dashed lines of the same colour illustrates the shift towards lower m/z values upon increasing the cone voltage.

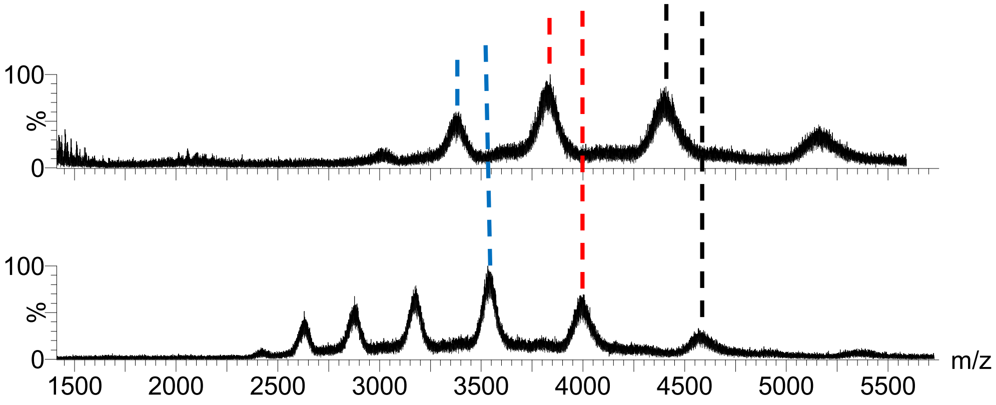

Table S3. Peak assignment of the series of peaks observed in the ESI mass spectrum shown in **Figure S6** of compound **1b**.

m/z (charge state)	Envelop assignment[a]
2632 (12)	$[[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]^{72-} + 20Me_2NH^+ + 5NH_4^+ + 35H^+]^{12-}$
2877 (11)	$[[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]^{72-} + 21Me_2NH^+ + 5NH_4^+ + 35H^+ + CH_3CN]^{11-}$
3176 (10)	$[[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]^{72-} + 22Me_2NH^+ + 5NH_4^+ + 35H^+ + 2CH_3CN]^{10-}$
3536 (9)	$[[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]^{72-} + 23Me_2NH^+ + 5NH_4^+ + 35H^+ + 2CH_3CN]^{9-}$
3999 (8)	$[[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]^{72-} + 24Me_2NH^+ + 5NH_4^+ + 35H^+ + 5CH_3CN]^{8-}$
4582 (7)	$[[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]^{72-} + 25Me_2NH^+ + 5NH_4^+ + 35H^+ + 6CH_3CN]^{7-}$

[a] The envelopes display different extent of cation adduct formation (where cat stands for Me_2NH^+, NH_4^+ or H^+) as well as solvated acetonitrile molecules, resulting in broad peaks. The indicated formula corresponds to the ion that match the m/z position at the maximum of the envelope; however, we are aware that other plausible molecular composition are also possible; for example, related ions to those included in **Table S2** at m/z 4582 may origin from replacing one Me_2NH^+ cation by the combination of $H^+ + CH_3CN$.

*ESI mass spectra and peak assignments for compound **2**.*

The ESI mass spectrum of **2** (see **Figure S8**) displayed six broad peaks centered at m/z encompassing charge states from 12- to 7-. That means that for the $[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4\}_{30}(SeO_4)(H_2O)_{20}]^{52-}$ polyanion, from 40 to 45 negative charges must be compensated and analogously to those ESI ionization mechanisms mentioned above for **1a** and **1b**, charge alleviation via cation adduct formation or m-fold releasing of SeO_4^{2-} groups are also posible. According to the experimentally determined m/z values (see **Table S4**), the distribution of charge states from 12- to 7- is produced by countercation adduct formation and solvation. The indicated formula collected in **Table S4**, corresponds to the ion that match the m/z position at the maximum of the envelope.

Figure S8. Negative ESI mass spectrum CH_3CN solutions of compound **2** recorded at low cone voltage, Uc = 10 V.

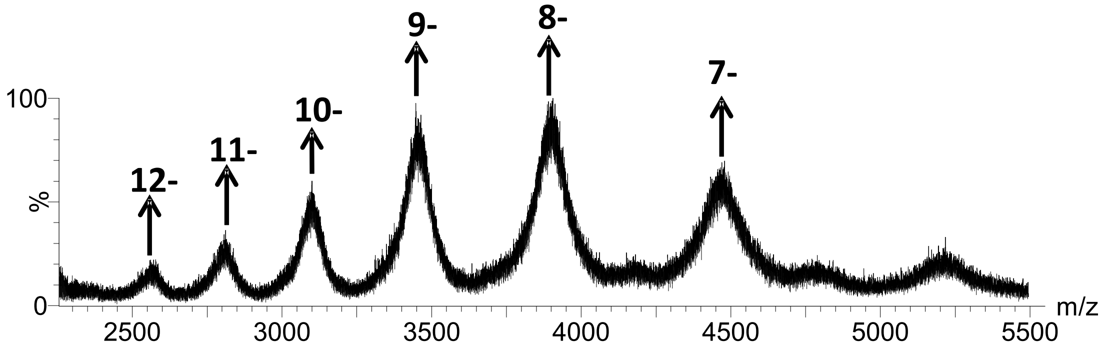

Table S4. Peak assignment of the series of peaks observed in the ESI mass spectrum shown in **Figure S8** of compound **2**.

m/z (charge state)	Envelop assignment[a]
2561 (12)	$[[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4\}_{30}(SeO_4)_{20}(H_2O)_{20}]^{52-} + 25Me_2NH^+ + 5NH_4^+ + 10H^+]^{12-}$
2803 (11)	$[[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4\}_{30}(SeO_4)_{20}(H_2O)_{20}]^{52-} + 26Me_2NH^+ + 5NH_4^+ + 10H^+ + CH_3CN]^{11-}$
3097 (10)	$[[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4\}_{30}(SeO_4)_{20}(H_2O)_{20}]^{52-} + 27Me_2NH^+ + 5NH_4^+ + 10H^+ + 3CH_3CN]^{10-}$
3450 (9)	$[[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4\}_{30}(SeO_4)_{20}(H_2O)_{20}]^{52-} + 28Me_2NH^+ + 5NH_4^+ + 10H^+ + 5CH_3CN]^{9-}$
3900 (8)	$[[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4\}_{30}(SeO_4)_{20}(H_2O)_{20}]^{52-} + 29Me_2NH^+ + 5NH_4^+ + 10H^+ + 6CH_3CN]^{8-}$
4460 (7)	$[[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4\}_{30}(SeO_4)_{20}(H_2O)_{20}]^{52-} + 30Me_2NH^+ + 5NH_4^+ + 10H^+ + 7CH_3CN]^{7-}$

[a] The envelopes display different cation adduct formation (where cat stands for Me_2NH^+, NH_4^+ or H^+) as well as solvated water molecules, resulting in broad peaks.