Tubular polyoxoanion $[(SeMo_6O_{21})_2(C_2O_4)_3]^{10-}$ and its transformations

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Supporting information

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Table S1. Experimental details

	Mo6Se_1	**Mo6Se_2**	**Mo8_Na**
Chemical formula	$C_6H_{42.20}Mo_{12}NNa_{10}O_{77.60}Se_2$	$C_6H_{16}Mo_{12}N_{0.50}Na_{10.50}O_{63.50}Se_2$	$C_{50}H_{111}Mo_8N_5Na_2O_{29}$
M_r	2909.31	2661.79	2059.93
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Temperature (K)	130	150	130
a, *b*, *c* (Å)	16.6045 (2), 20.8678 (3), 19.2934 (3)	10.5584 (9), 13.5966 (10), 20.6658 (16)	15.8296 (1), 18.5387 (1), 25.6801 (3)
α, β, γ (°)	90, 98.971 (1), 90	97.457 (3), 92.579 (3), 109.222 (3)	89.128 (1), 88.474 (1), 89.873 (1)
V (Å^3)	6603.37 (16)	2765.4 (4)	7532.53 (11)
Z	4	2	4
μ (mm^{-1})	3.51	4.17	1.38
Crystal size (mm)	0.30 × 0.15 × 0.15	0.28 × 0.08 × 0.04	0.20 × 0.15 × 0.15
Diffractometer	New Xcalibur, AtlasS2	Bruker D8 Venture	New Xcalibur, AtlasS2
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *SADABS* (Bruker-AXS, 2004)	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.683, 1.000	0.619, 0.746	0.990, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	39479, 15700, 13311	90226, 15526, 12078	73588, 35149, 30375
R_{int}	0.026	0.101	0.021
θ values (°)	$\theta_{max} = 29.4$, $\theta_{min} = 3.4$	$\theta_{max} = 29.7$, $\theta_{min} = 1.6$	$\theta_{max} = 29.6$, $\theta_{min} = 3.3$
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.692	0.696	0.696
Range of *h*, *k*, *l*	$-15 \le h \le 22$, $-28 \le k \le 22$, $-25 \le l \le 25$	$-14 \le h \le 14$, $-18 \le k \le 18$, $-28 \le l \le 28$	$-21 \le h \le 19$, $-22 \le k \le 25$, $-35 \le l \le 32$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.083, 1.05	0.103, 0.225, 1.12	0.035, 0.080, 1.16
No. of reflections, parameters, restraints	15700, 982, 0	15526, 848, 0	35149, 1693, 0
H-atom treatment	H-atom parameters not defined	H-atom parameters not defined	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0293P)^2 + 34.3544P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0197P)^2 + 229.1662P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0223P)^2 + 16.945P]$ where $P = (F_o^2 + 2F_c^2)/3$

$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.99, -1.11	2.69, -3.23	1.80, -0.82

Computer programs: *CrysAlis PRO* 1.171.38.41 (Rigaku OD, 2015), *APEX2* (Bruker-AXS, 2004), *SAINT* (Bruker-AXS, 2004), *SHELXS2014* (Sheldrick, 2014), *SHELXL2014* (Sheldrick, 2014), ShelXle (Hübschle, 2011), CIFTAB-2014 (Sheldrick, 2014).

Table S2. Selected geometric parameters (Å)

Mo6Se_1			
O1—Mo1	1.697 (3)	O30—Mo7	1.717 (3)
O2—Mo1	2.340 (3)	O31—Mo12	1.695 (3)
O3—Mo1	1.935 (3)	O32—Mo12	1.710 (3)
O3—Mo6	1.933 (3)	O33—Mo11	1.932 (3)
O4—Mo1	1.712 (3)	O33—Mo12	1.936 (3)
O5—Mo1	1.899 (3)	O34—Mo11	2.296 (3)
O5—Mo2	1.901 (3)	O34—Mo12	2.305 (3)
O6—Mo2	2.305 (3)	O35—Mo11	1.710 (3)
O7—Mo2	1.703 (3)	O36—Mo11	1.700 (3)
O8—Mo2	1.920 (3)	O37—Mo10	1.723 (3)
O8—Mo3	1.926 (3)	O38—Mo10	1.693 (3)
O9—Mo3	1.699 (3)	O39—Mo9	1.917 (3)
O10—Mo3	1.709 (3)	O39—Mo10	1.932 (3)
O11—Mo3	1.897 (3)	O41—Mo9	1.695 (3)
O11—Mo4	1.892 (3)	O42—Mo10	2.308 (3)
O12—Mo2	2.299 (3)	O43—Mo8	1.909 (3)
O12—Mo3	2.325 (3)	O43—Mo9	1.916 (3)
O13—Mo4	1.714 (3)	O44—Mo9	2.320 (3)
O14—Mo4	1.706 (3)	O44—Mo10	2.300 (3)
O15—Mo4	2.309 (3)	O45—Mo10	1.900 (3)
O15—Mo5	2.306 (3)	O45—Mo11	1.900 (3)
O16—Mo1	2.278 (3)	O46—Mo9	1.715 (3)
O16—Mo6	2.361 (3)	O47—Mo8	1.713 (3)
O17—Mo4	2.308 (3)	O48—Mo8	2.343 (3)
O18—Mo4	1.928 (3)	O49—Mo7	2.283 (3)
O18—Mo5	1.933 (3)	O50—Mo9	2.333 (3)
O19—Mo5	1.708 (3)	O51—Mo8	1.702 (3)
O20—Mo5	1.704 (3)	O52—Mo7	1.939 (3)
O21—Mo5	2.267 (3)	O52—Mo8	1.920 (3)
O22—Mo5	1.901 (3)	O53—Mo7	2.314 (3)
O22—Mo6	1.913 (3)	O53—Mo8	2.315 (3)
O23—Mo6	1.715 (3)	O54—Mo3	2.351 (3)
O24—Mo6	1.692 (3)	O55—Mo2	1.713 (3)
O25—Mo6	2.261 (3)	O12—Se2	1.698 (3)
O26—Mo12	2.291 (3)	O15—Se2	1.695 (3)
O27—Mo11	2.289 (3)	O16—Se2	1.698 (3)
O28—Mo7	1.698 (3)	O34—Se1	1.694 (3)
O29—Mo7	1.902 (3)	O44—Se1	1.701 (3)
O29—Mo12	1.907 (3)	O53—Se1	1.699 (3)

Mo6Se_2			
O1—Mo1	1.703 (13)	O32—Mo7	2.271 (11)
O2—Mo1	2.307 (11)	O33—Mo10	2.318 (10)
O3—Mo1	1.884 (12)	O34—Mo11	2.315 (11)
O3—Mo6	1.920 (13)	O35—Mo12	2.307 (11)
O4—Mo2	2.321 (11)	O36—Mo11	1.697 (12)
O5—Mo1	2.310 (12)	O37—Mo10	1.925 (11)
O5—Mo2	2.294 (12)	O37—Mo11	1.936 (11)
O6—Mo1	1.944 (12)	O38—Mo11	1.900 (12)
O6—Mo2	1.933 (12)	O38—Mo12	1.921 (11)
O7—Mo1	1.706 (11)	O39—Mo11	1.690 (12)
O8—Mo2	1.894 (12)	O40—Mo12	1.707 (12)
O8—Mo3	1.894 (11)	O41—Mo12	1.705 (12)
O9—Mo2	1.719 (12)	O42—Mo7	1.952 (12)
O10—Mo2	1.701 (12)	O42—Mo12	1.895 (12)
O12—Mo3	1.699 (13)	O43—Mo10	2.387 (11)
O13—Mo3	1.709 (12)	O43—Mo11	2.287 (12)
O14—Mo3	1.924 (13)	O44—Mo10	1.705 (13)
O14—Mo4	1.910 (14)	O45—Mo9	1.907 (11)
O15—Mo3	2.269 (11)	O45—Mo10	1.899 (11)
O15—Mo4	2.313 (11)	O46—Mo9	1.699 (12)
O16—Mo4	1.723 (13)	O47—Mo7	2.283 (12)
O17—Mo4	1.686 (15)	O47—Mo12	2.294 (11)
O18—Mo3	2.355 (12)	O48—Mo7	1.909 (13)
O19—Mo4	2.252 (11)	O48—Mo8	1.905 (13)
O20—Mo4	1.928 (12)	O49—Mo7	1.734 (13)
O20—Mo5	1.879 (12)	O50—Mo7	1.703 (12)
O21—Mo5	1.716 (12)	O51—Mo8	1.708 (13)
O22—Mo5	1.676 (13)	O52—Mo8	1.908 (14)
O23—Mo5	2.292 (12)	O52—Mo9	1.933 (14)
O23—Mo6	2.295 (11)	O53—Mo8	2.318 (12)
O24—Mo5	1.964 (14)	O53—Mo9	2.323 (12)
O24—Mo6	1.905 (13)	O54—Mo9	1.710 (13)
O25—Mo5	2.275 (12)	O55—Mo10	1.711 (12)
O26—Mo6	1.702 (12)	O5—Se1	1.695 (12)
O27—Mo6	2.293 (11)	O15—Se1	1.701 (11)
O28—Mo9	2.289 (11)	O23—Se1	1.693 (11)
O29—Mo8	2.289 (11)	O43—Se2	1.686 (11)
O30—Mo8	1.693 (14)	O47—Se2	1.696 (11)
O31—Mo6	1.699 (13)	O53—Se2	1.675 (12)

Mo8_Na			
O1—Mo1	1.752 (2)	O35—Mo9	1.922 (2)
O1—Mo3^{i}	2.256 (2)	O35—Mo10	1.897 (2)
O2—Mo1	1.951 (2)	O36—Mo9^{iii}	2.247 (3)
O2—Mo2	2.006 (2)	O36—Mo12	1.752 (2)
O2—Mo4^{i}	2.289 (2)	O37—Mo11	1.713 (3)
O3—Mo2	1.688 (2)	O38—Mo9	1.726 (3)
O4—Mo2	1.898 (2)	O39—Mo9	1.694 (3)
O4—Mo3	1.915 (2)	O43—Mo16	1.716 (3)
O5—Mo2	1.715 (2)	O44—Mo13	1.917 (2)
O6—Mo1	2.152 (2)	O44—Mo16	1.903 (2)
O6—Mo1^{i}	2.317 (2)	O45—Mo13	1.724 (2)
O6—Mo2	2.349 (2)	O46—Mo13	1.698 (2)
O6—Mo3	2.441 (2)	O47—Mo13	1.925 (2)
O6—Mo4	2.305 (2)	O47—Mo14	1.902 (2)
O7—Mo1	1.701 (2)	O48—Mo14	1.714 (3)
O8—Mo1	1.952 (2)	O49—Mo16	1.681 (3)
O8—Mo2^{i}	2.301 (2)	O50—Mo14^{iv}	2.277 (2)
O8—Mo4	2.011 (2)	O50—Mo15	1.950 (2)
O9—Mo4	1.693 (2)	O50—Mo16	2.018 (2)
O10—Mo4	1.717 (3)	O51—Mo15	1.696 (2)
O11—Mo3	1.928 (2)	O52—Mo13^{iv}	2.244 (2)
O11—Mo4	1.899 (2)	O52—Mo15	1.755 (2)
O12—Mo3	1.723 (2)	O53—Mo14	2.016 (2)
O13—Mo3	1.697 (2)	O53—Mo15	1.954 (2)
O17—Mo5	1.721 (2)	O53—Mo16^{iv}	2.285 (2)
O18—Mo6	1.715 (2)	O54—Mo14	1.686 (3)
O19—Mo7	1.718 (2)	O55—Mo13	2.445 (2)
O20—Mo8	1.703 (2)	O55—Mo14	2.313 (2)
O21—Mo7	1.692 (2)	O55—Mo15	2.147 (2)
O22—Mo6^{ii}	2.311 (2)	O55—Mo15^{iv}	2.308 (2)
O22—Mo7	2.015 (2)	O55—Mo16	2.354 (2)
O22—Mo8	1.954 (2)	O56—Mo10	2.012 (2)
O23—Mo5^{ii}	2.262 (2)	O56—Mo11^{iii}	2.294 (2)
O23—Mo8	1.752 (2)	O56—Mo12	1.959 (2)
O24—Mo6	2.011 (2)	O57—Mo10	1.717 (2)
O24—Mo7^{ii}	2.306 (2)	O58—Mo12	1.700 (3)
O24—Mo8	1.955 (2)	O5—Na2	2.373 (3)
O25—Mo5	2.427 (2)	O7—Na2	2.430 (3)
O25—Mo6	2.339 (2)	O10—Na2	2.409 (3)

O25—Mo7	2.345 (2)	O12—Na2	2.425 (3)
O25—Mo8	2.133 (2)	O14—Na2	2.479 (3)
O25—Mo8^{ii}	2.331 (2)	O15—Na1	2.466 (3)
O26—Mo5	1.924 (2)	O15—Na2	2.401 (3)
O26—Mo7	1.894 (2)	O16—Na1	2.385 (3)
O27—Mo5	1.692 (2)	O17—Na1	2.365 (3)
O28—Mo5	1.929 (3)	O18—Na1	2.408 (3)
O28—Mo6	1.898 (2)	O19—Na1	2.382 (3)
O29—Mo6	1.691 (3)	O20—Na1	2.467 (3)
O30—Mo10	1.699 (2)	O37—Na4	2.403 (3)
O31—Mo9	1.932 (2)	O38—Na4	2.367 (3)
O31—Mo11	1.894 (2)	O40—Na4	2.363 (3)
O32—Mo10^{iii}	2.296 (2)	O41—Na3	2.431 (3)
O32—Mo11	2.018 (2)	O41—Na4	2.482 (3)
O32—Mo12	1.958 (2)	O42—Na3	2.406 (3)
O33—Mo11	1.701 (2)	O43—Na3	2.380 (3)
O34—Mo9	2.447 (2)	O45—Na3	2.388 (3)
O34—Mo10	2.351 (2)	O48—Na3	2.403 (3)
O34—Mo11	2.346 (2)	O51—Na3	2.426 (3)
O34—Mo12	2.119 (2)	O57—Na4	2.377 (3)
O34—Mo12^{iii}	2.322 (2)	O58—Na4	2.463 (3)

Symmetry code(s): (i) -*x*+1, -*y*+2, -*z*+2; (ii) -*x*+1, -*y*+2, -*z*+1; (iii) -*x*, -*y*+1, -*z*+1; (iv) -*x*, -*y*+1, -*z*.

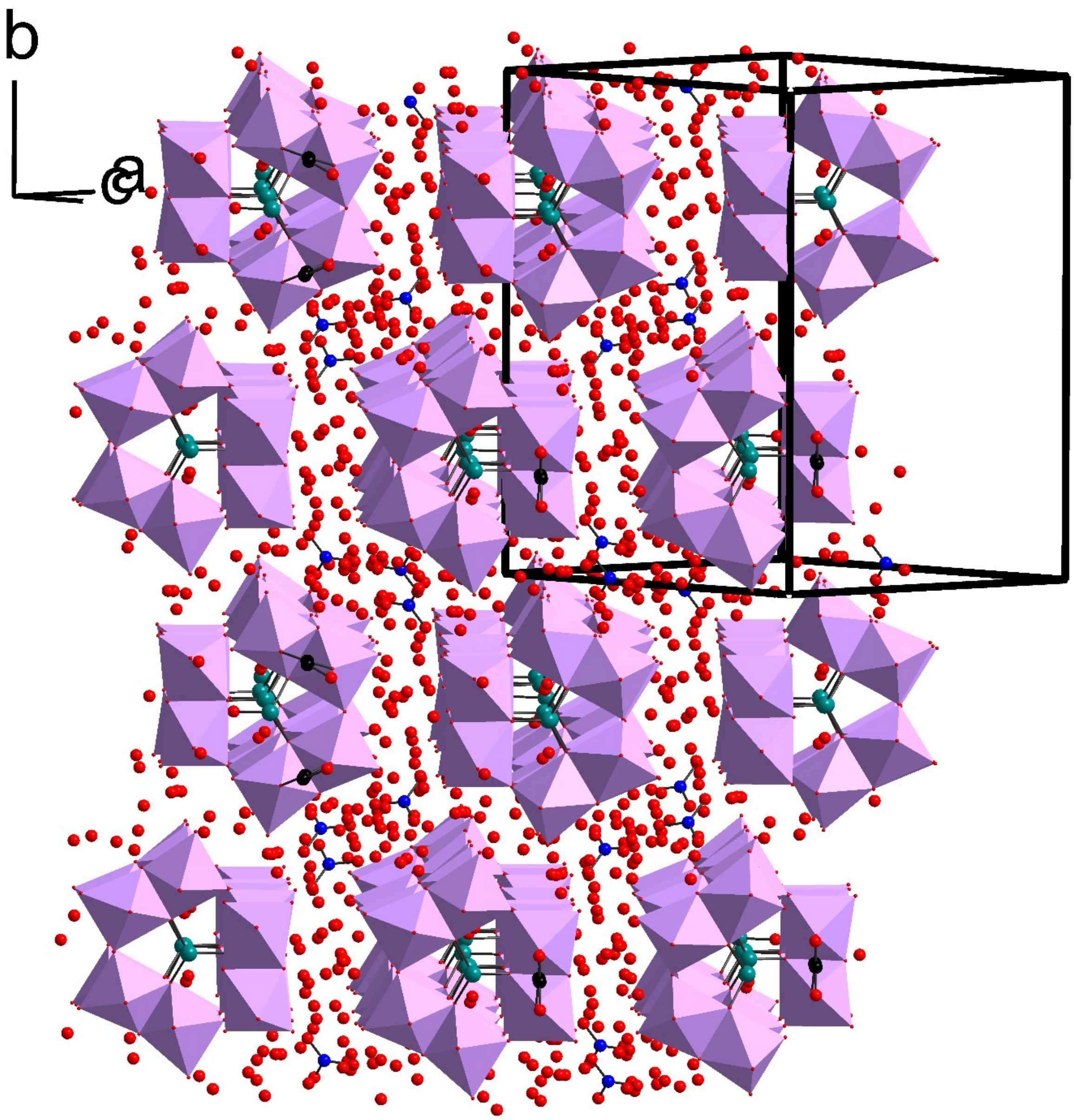

Fig. S1. The infinite tubular structures along [10-1] crystal direction in the crystal structure of Mo6Se-1.

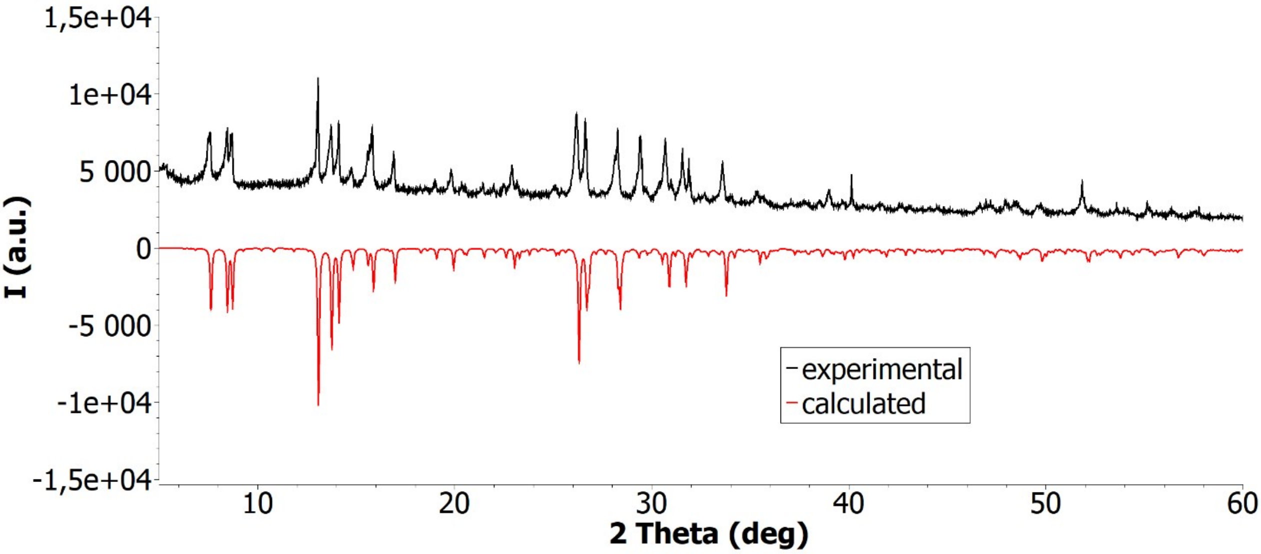

Fig. S2. Comparison of experimental and calculated powder patterns for Mo6Se-1.

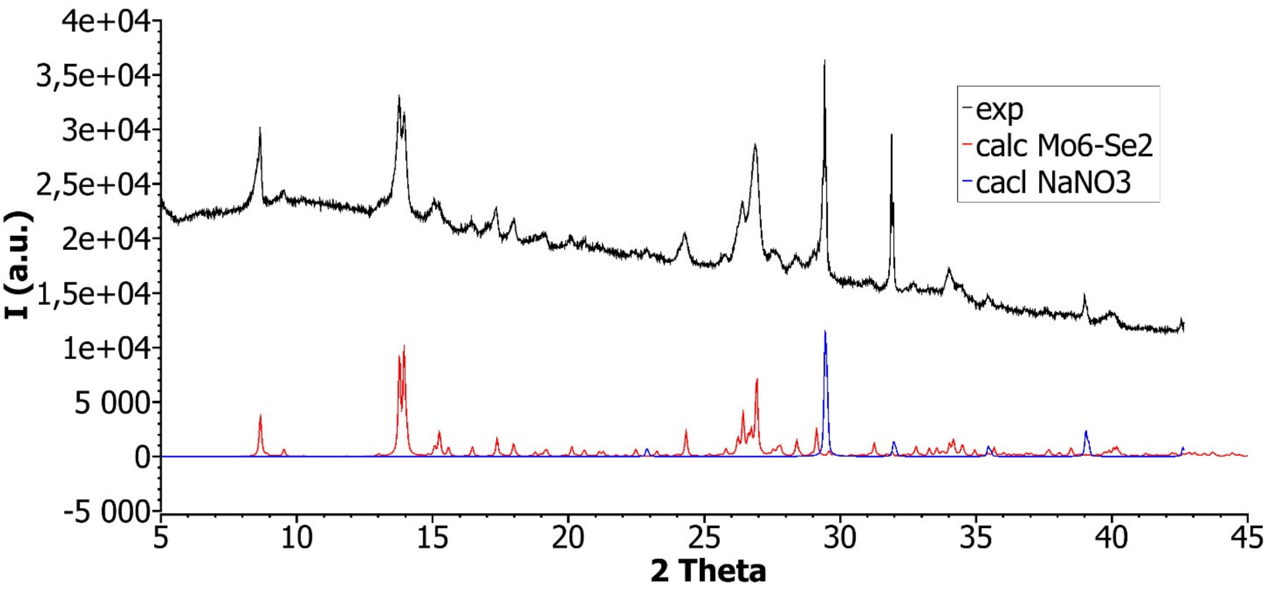

Fig. S3. XRPD patterns comparison for **Mo6Se-2**.

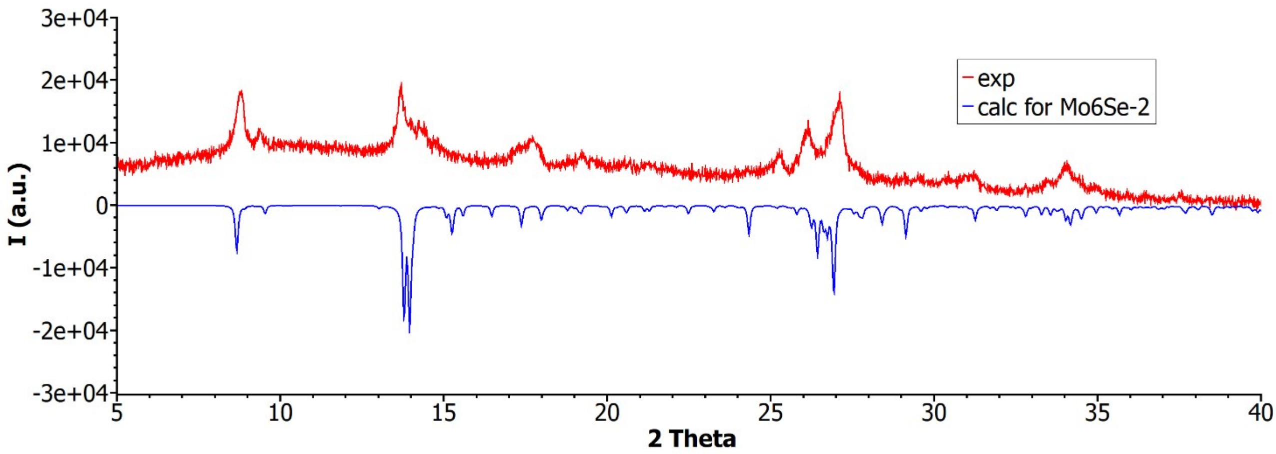

Fig. S4. XRPD patterns comparison for **Mo6Se-2** after MeOH washing.

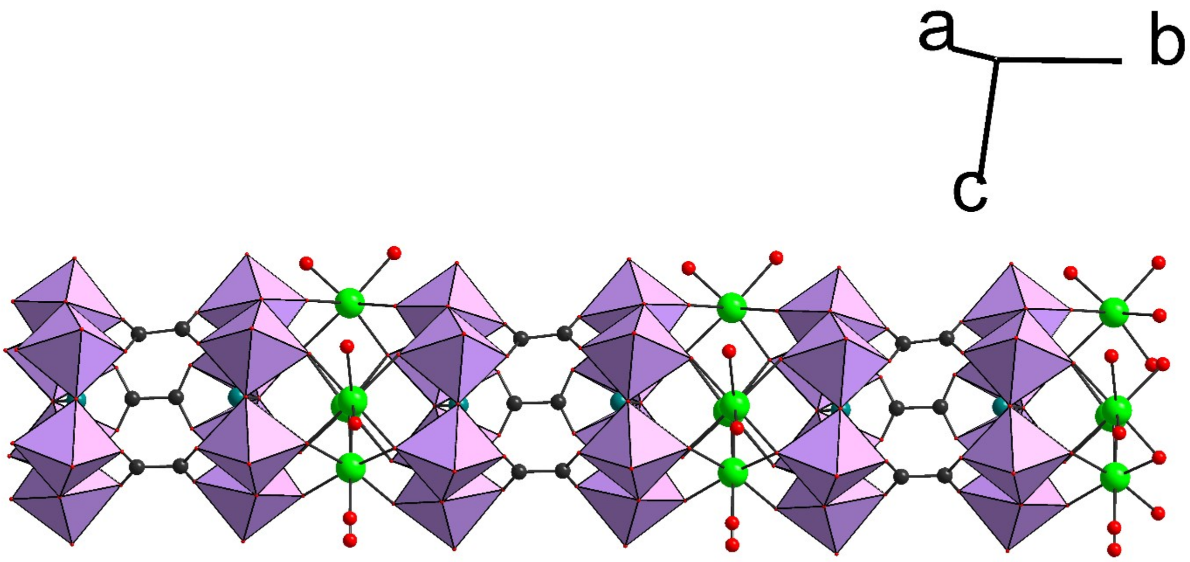

Fig. S5. Tubular aggregates in the crystal structure of Mo6Se-2.

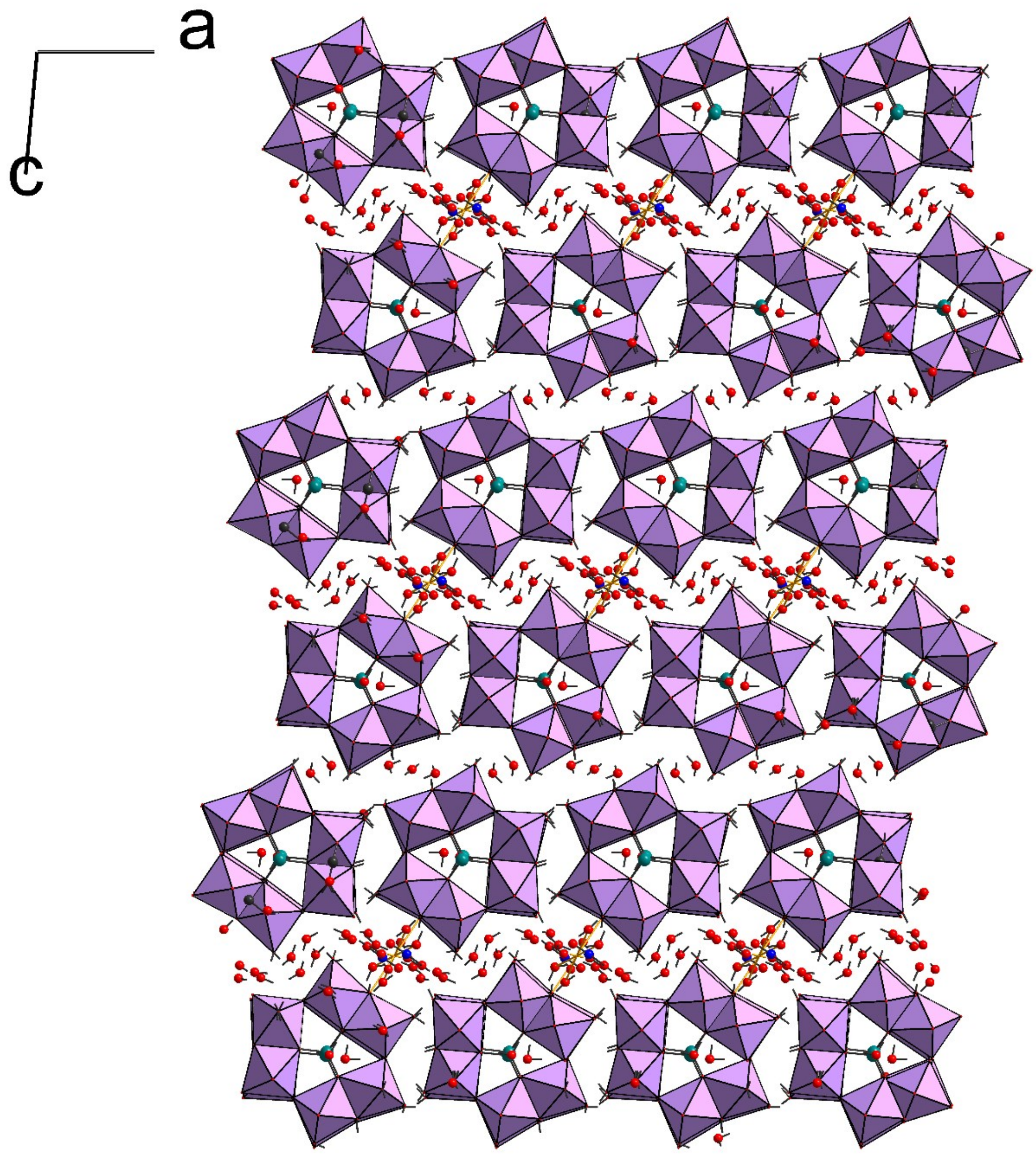

Fig. S6. Pseudo layers in the crystal structure of Mo6Se-2.

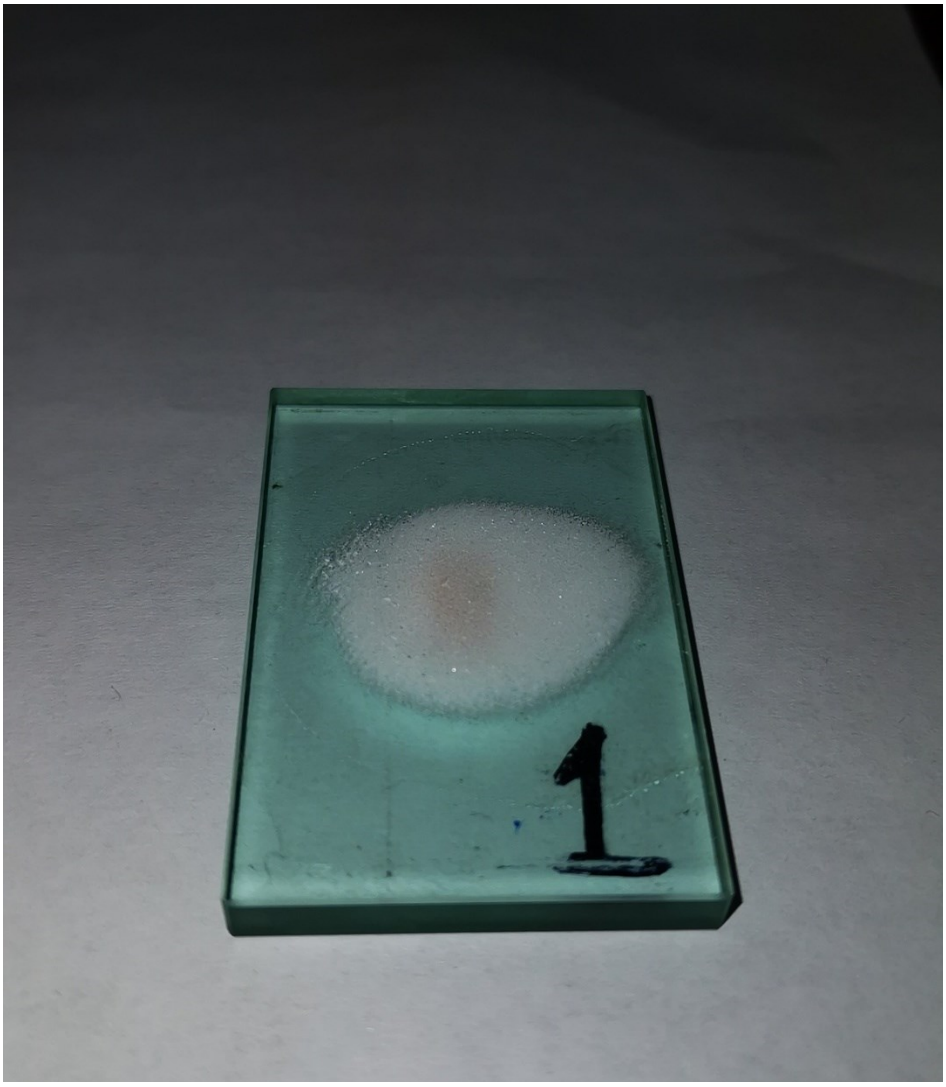

Fig. S7. The coloration of Mo6Se-2 during XRPD experiment.

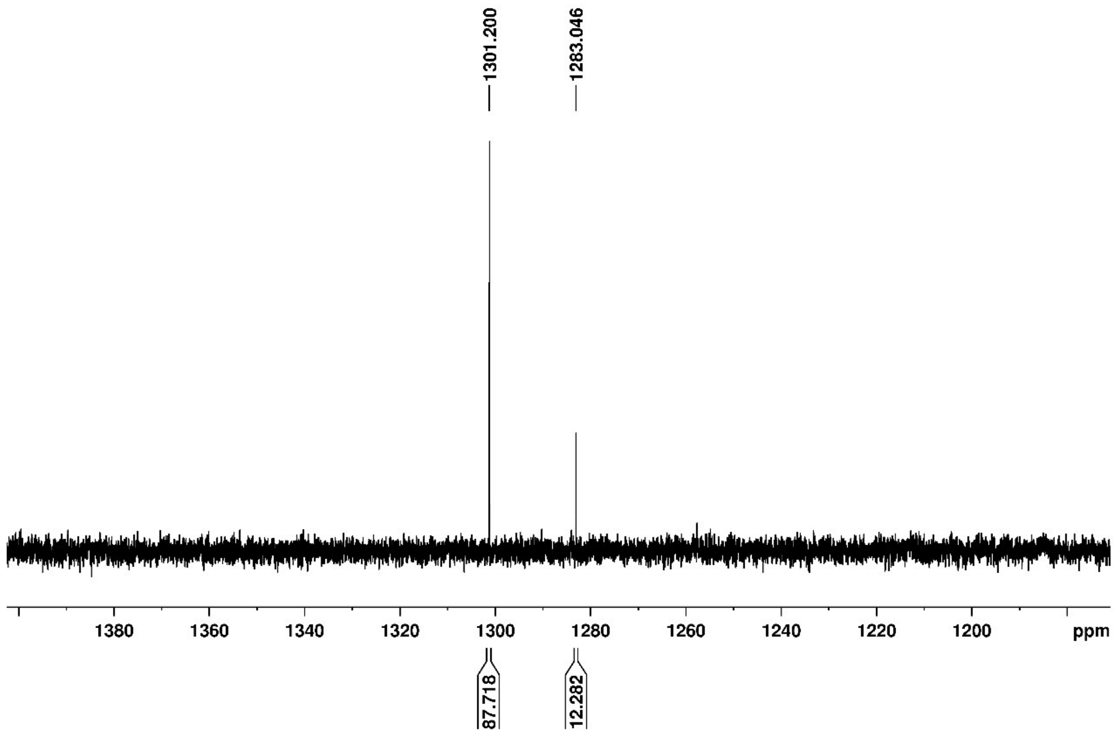

Fig. S8. ^{77}Se NMR spectrum of freshly prepared aqueous solution of **Mo6Se-2**.

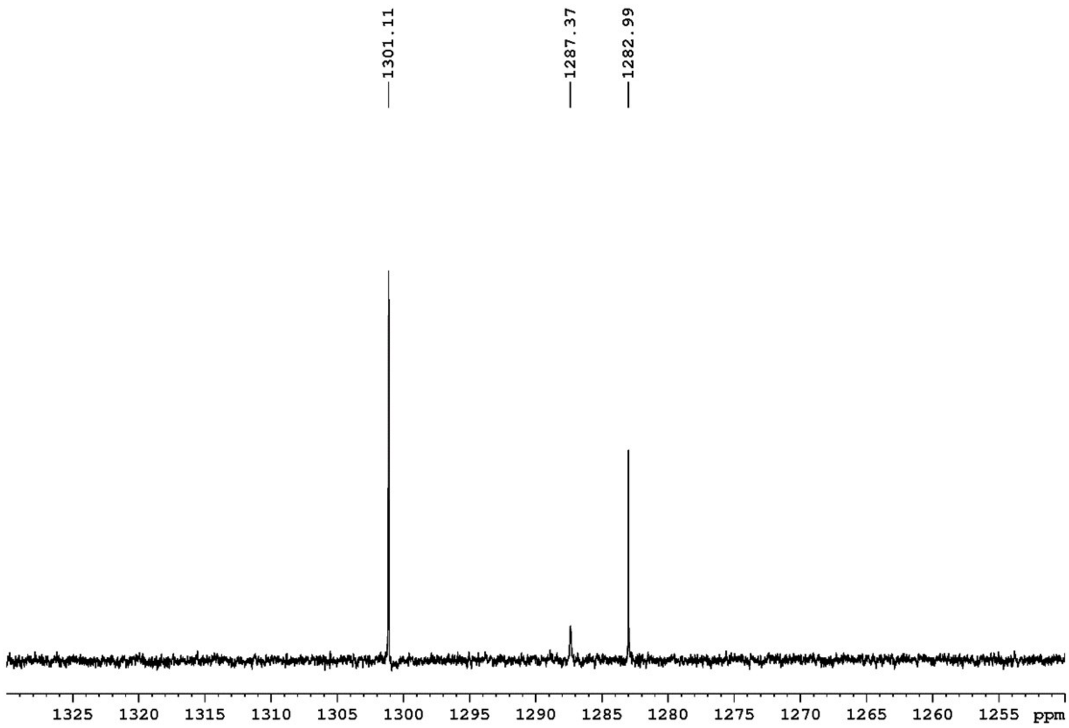

Fig. S9. ^{77}Se NMR spectrum of 22 hours aged aqueous solution of **Mo6Se-2**.

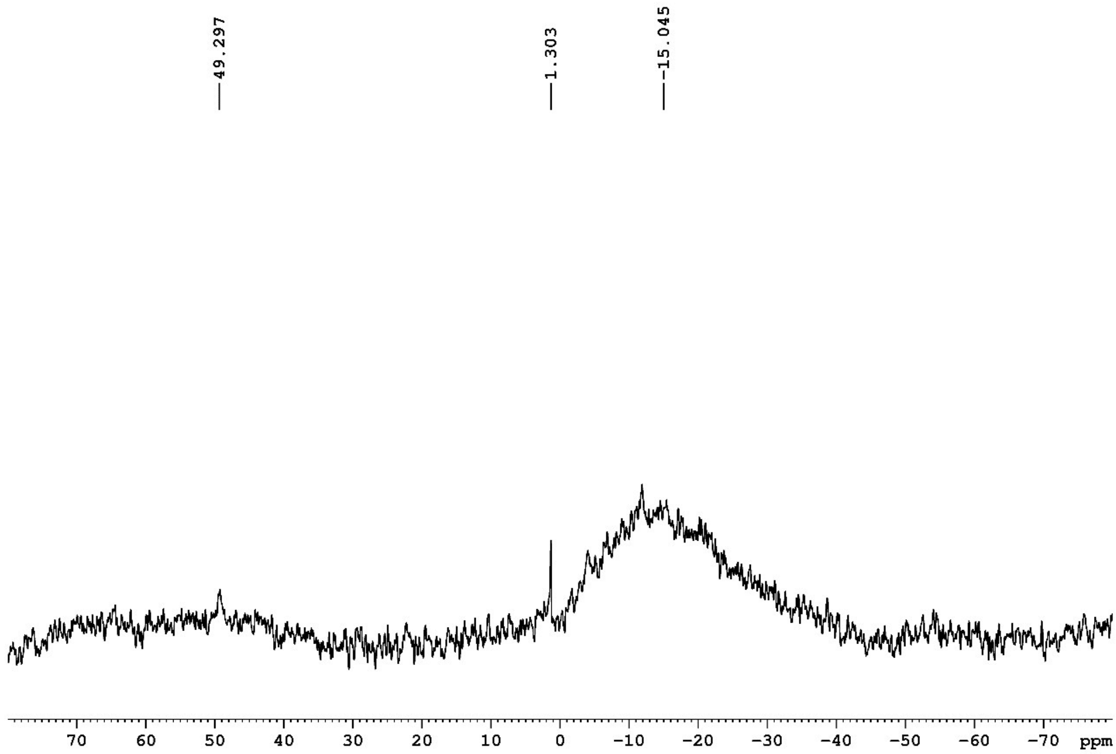

Fig. S10. ^{95}Mo NMR spectrum of an aqueous solution of **Mo6Se-2**.

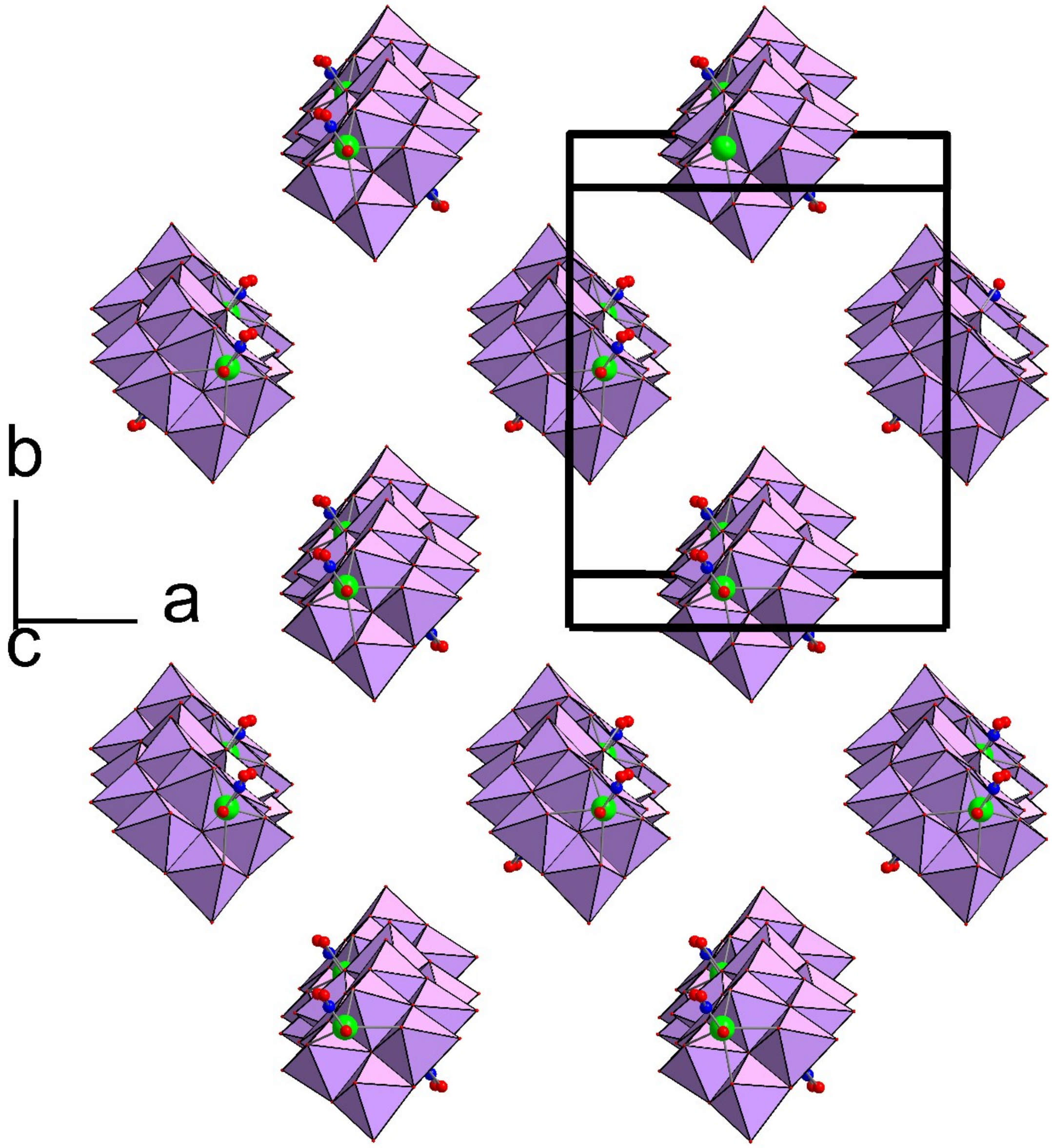

Fig. S11. 1D structures in the crystal structure of Mo8-Na.