Electronic Supplementary Information for: Crystallization of a Keplerate-type polyoxometalate into a superposed kagome-lattice with huge channels

Masaki Saito and Tomoji Ozeki*

Department of Chemistry and Materials Science, Tokyo Institute of Technology
2-12-1-H-63 O-okayama, Meguro-ku, Tokyo 152-8551, Japan.
Fax +81-3-5734-2442; Tel +81-3-5734-2442; E-mail:tozeki@cms.titech.ac.jp

List of contents

Details of the crystal structure determinations

Compound 1:
A dark red crystal with the dimension of 0.26×0.28×0.30 mm was mounted on a Rigaku Mercury CCD system equipped with a rotating target X-ray generator. The diffraction images were collected by using *CrystalClear*[1] and processed by using *HKL2000*.[2] The structure was solved by the direct methods using *SHELXS97* and refined by the full-matrix least-squares with *SHELXL97*.[3] Large solvent accessible voids remain in the structure. They are presumably filled with severely disordered water molecules, which could not be modeled by the present analysis. *PLATON*[4] SQUEEZE routine reports that the volume of total potential solvent accessible void is 11,552 Å^3 per unit cell, which exceeds one quarter of the unit cell volume of this compound, 45,647 Å^3. Estimated number of electrons within the void is reported to be 2,149 electrons/cell, which corresponds to roughly 60 water molecules per Mo_{132} cluster. The least-squares refinement against the intensities corrected by SQUEEZE converged to the final $R_1 = 0.0607$ ($I > 2\sigma(I)$) and $wR(F^2) = 0.1959$ (all data). However, the refinement against the SQUEEZE'd reflection data was not employed here because a) the void volume is too large compared with the volume of the unit cell and b) the atomic parameter file used for the SQUEEZE calculation did not contain the hydrogen atoms. These conditions considerably reduce the applicability of the SQUEEZE procedure. Therefore, the formula of the compound reported here is based on the water molecules determined by the X-ray diffraction using intensities not corrected by SQUEEZE and the number of water molecules is very likely to be underestimated.

Compound 2:
A dark red crystal with the dimension of 0.10×0.22×0.22 mm was mounted on a Rigaku Mercury CCD system installed at the NW2A beamline of the Advanced Ring (AR) of Photon Factory (PF), High Energy Accelerator Research Organization (KEK). The diffraction images were collected by using *CrystalClear*[1] and processed by using *HKL2000*.[2] The structure was solved by the direct methods using *SHELXS97* and refined by the full-matrix least-squares with *SHELXL97*.[3] Large solvent accessible voids remain in the structure. They are presumably filled with severely disordered water molecules, which could not be modeled by the present analysis. *PLATON*[4] SQUEEZE routine reports that the volume of total potential solvent accessible void is 114,279 Å^3 per unit cell, which exceeds the half of the unit cell volume of this compound, 209,497 Å^3. Estimated number of electrons within the void is reported to be 23,500 electrons/cell, which corresponds to roughly 220 water molecules per Mo_{132} cluster. The least-squares refinement against the intensities corrected by SQUEEZE converged to the final $R_1 = 0.0678$ ($I > 2\sigma(I)$) and $wR(F^2) = 0.2168$ (all data). However, the refinement against the SQUEEZE'd reflection data was not employed here because a) the void volume is too large compared with the volume of the unit cell and b) the atomic parameter file used for the SQUEEZE calculation did not contain the hydrogen atoms. These conditions

considerably reduce the applicability of the SQUEEZE procedure. Therefore, the formula of the compound reported here is based on the water molecules determined by the X-ray diffraction using intensities not corrected by SQUEEZE and the number of water molecules is very likely to be underestimated. The Sr^{2+} cations are also disordered. Their occupancy refinement converged to the total number of Sr^{2+} cations fewer than that required to balance the anionic charge of $\{Mo_{132}\}$. This unbalance was estimated to be neutralized by NH_4^+ that are disordered with water molecules of crystallization. However, atomic scattering factor for oxygen was uniformly used for the atoms in the solvent area, since the NH_4^+ are hardly distinguished from H_2O.

References:

1 *Crystal Clear*, Molecular Structure Corporation, Orem, UT, 2001.
2 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276A**, 307-326.
3 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112-122.
4 A. L. Spek, *Acta Crystallogr., Sect D,* 2009, **65**, 148-155.

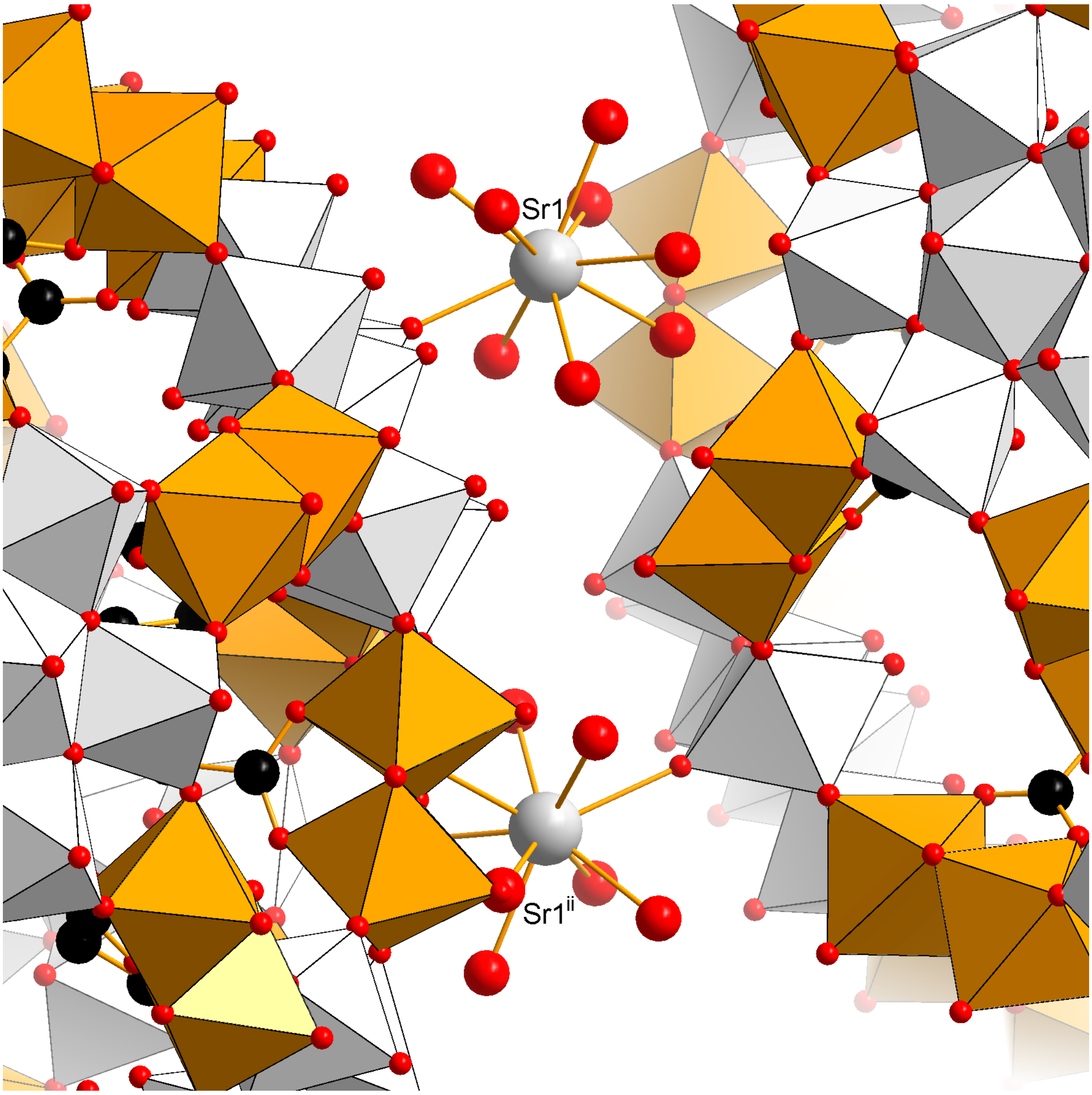

Figure S1. Second shortest interactions between two {Mo_{132}} anions in compound **1**. Distance between two {Mo_{132}} is 31.807 Å. The cluster shown left is located at (0, 0, 0) and the one shown right is at (1/2, 1/2, 1). Note that these anions are related by the inversion centre at (1/4, 1/4, 1/2). White polyhedra represent the coordination sphere of Mo atoms in $[Mo^{VI}_6O_{21}(H_2O)_6]^{6-}$ and orange polyhedra represent those in $[Mo^{V}_2O_4(CH_3COO)]^{+}$. Symmetry code: ii) 1/2–*x*, 1/2–*y*, 1–*z*.

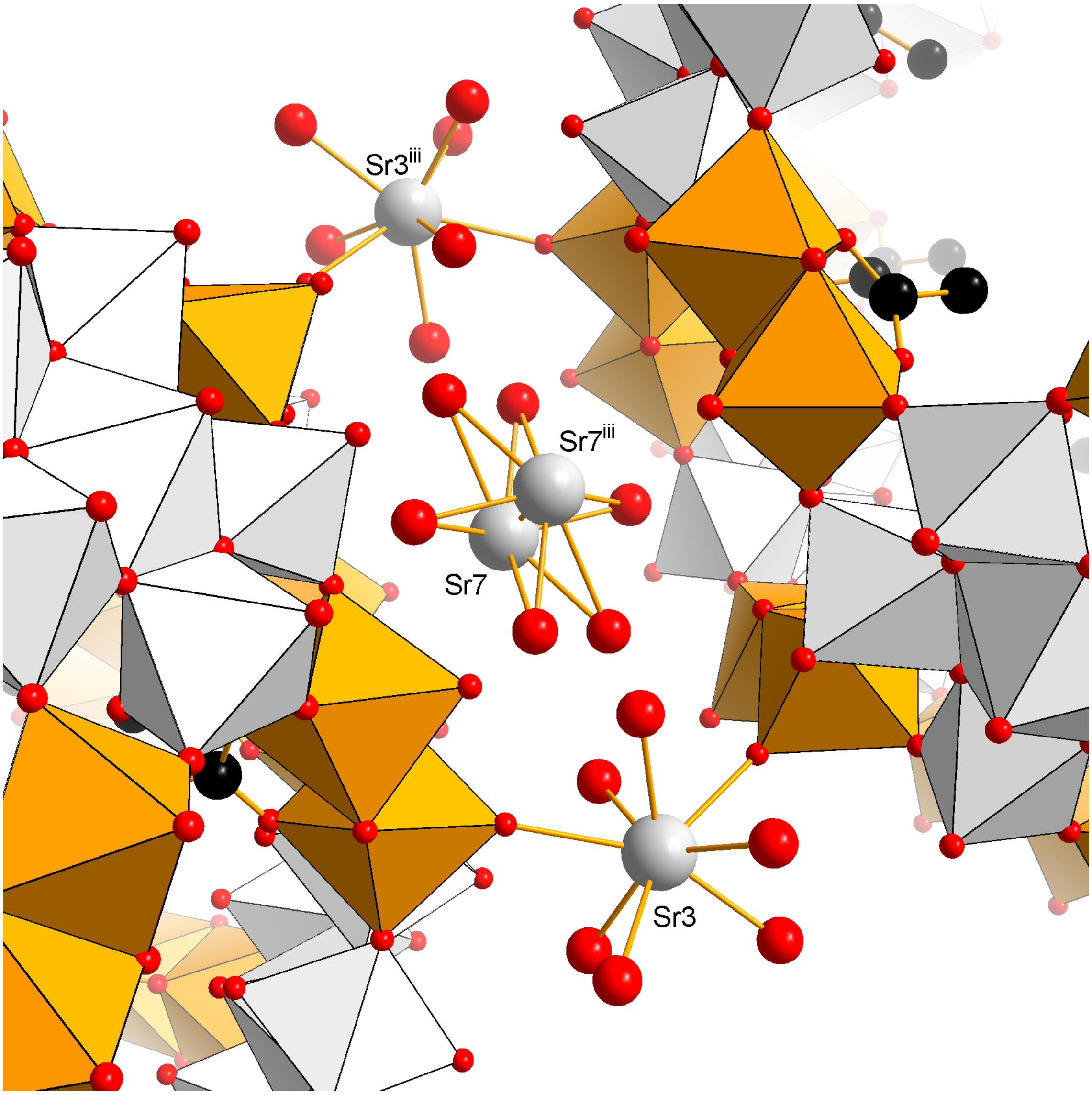

Figure S2. Third shortest interactions between two {Mo_{132}} anions in compound **1**. Distance between two {Mo_{132}} is 32.331 Å. The cluster shown left is located at (0, 0, 0) and the one shown right is at (0, 0, 1). Note that these anions are related by the inversion centre at (0, 0, 1/2). White polyhedra represent the coordination sphere of Mo atoms in $[Mo^{VI}_6O_{21}(H_2O)_6]^{6-}$ and orange polyhedra represent those in $[Mo^{V}_2O_4(CH_3COO)]^{+}$. Symmetry code: iii) $-x, -y, 1-z$.

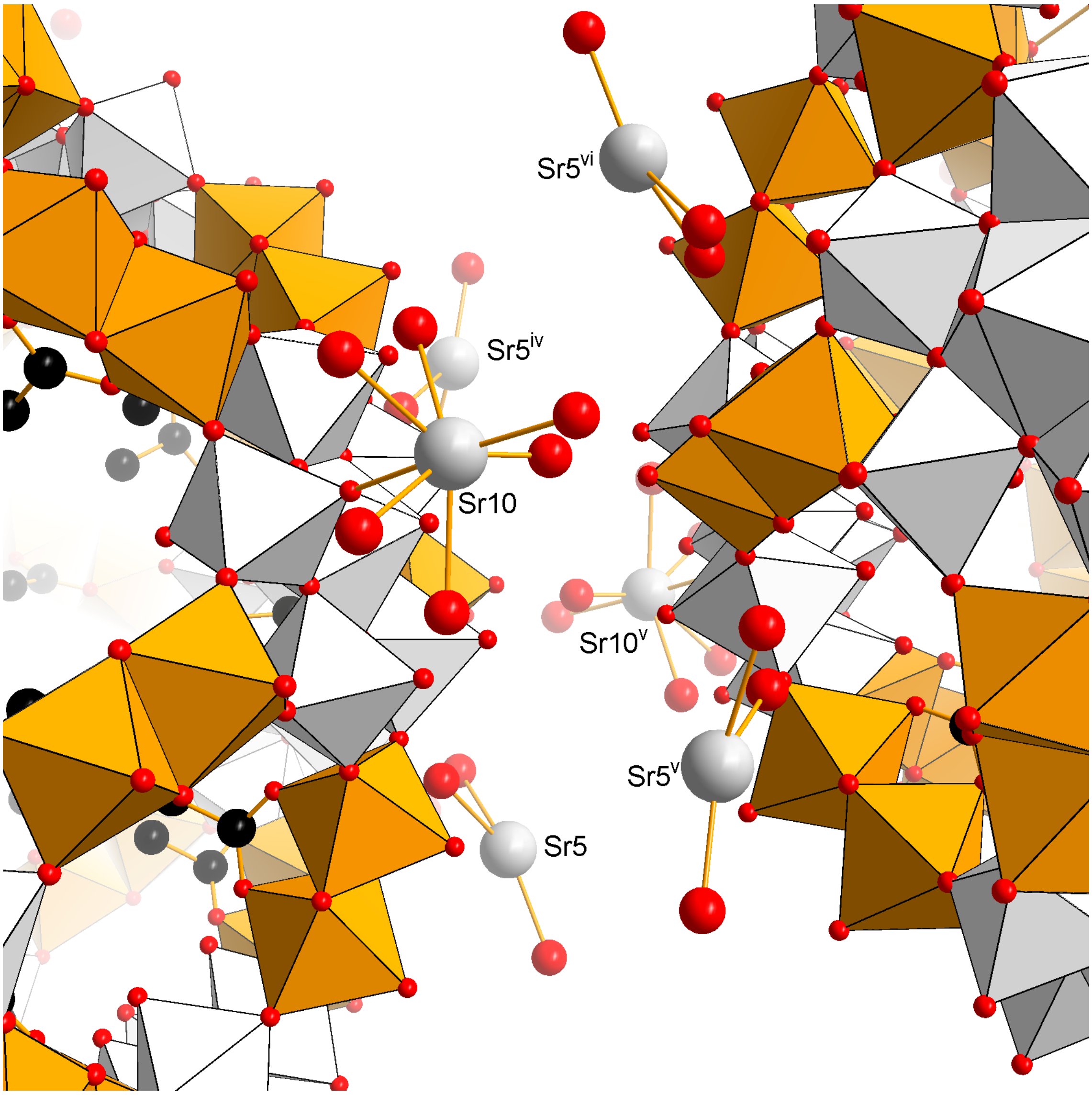

Figure S3. Fourth shortest interactions between two {Mo_{132}} anions in compound **1**. Distance between two {Mo_{132}} is 32.331 Å. The cluster shown left is located at (0, 0, 0) and the one shown right is at (1, 0, 1). Note that these anions are related by the inversion centre at (1/2, 0, 1/2). White polyhedra represent the coordination sphere of Mo atoms in $[Mo^{VI}_6O_{21}(H_2O)_6]^{6-}$ and orange polyhedra represent those in $[Mo^{V}_2O_4(CH_3COO)]^{+}$. Symmetry codes: iv) $x, -y, z$; v) $1-x, y, 1-z$; vi) $1-x, -y, 1-z$.

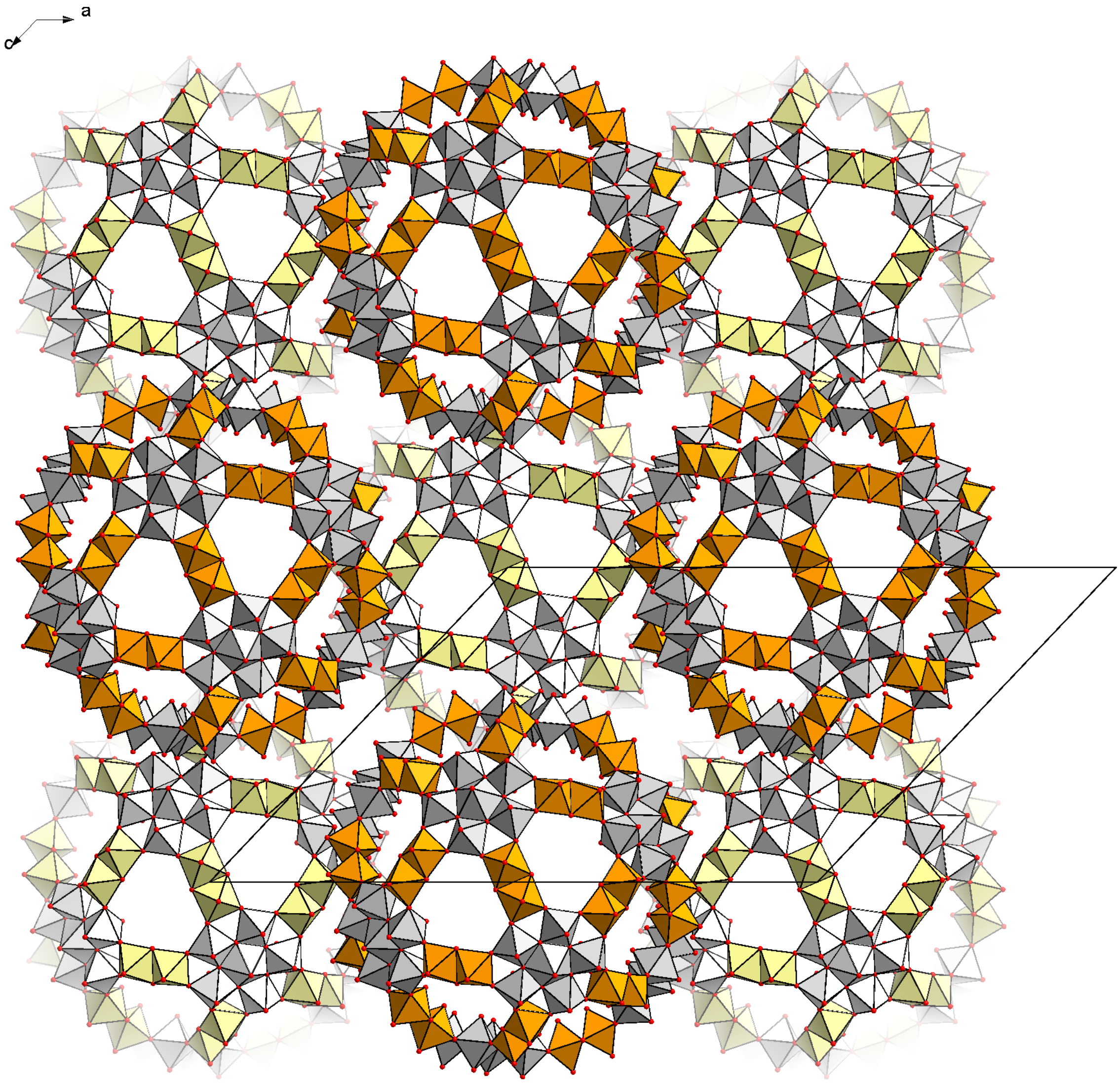

Figure S4. Packing diagram of compound **1** viewed along the crystallographic *b* axis. Only the MoO_x polyhedra in the $\{Mo_{132}\}$ anions are shown for clarity. Those with centroids at $y = 0.5$ are shown in darker colour and those with centroids at $y = 0$ are shown in lighter colour.

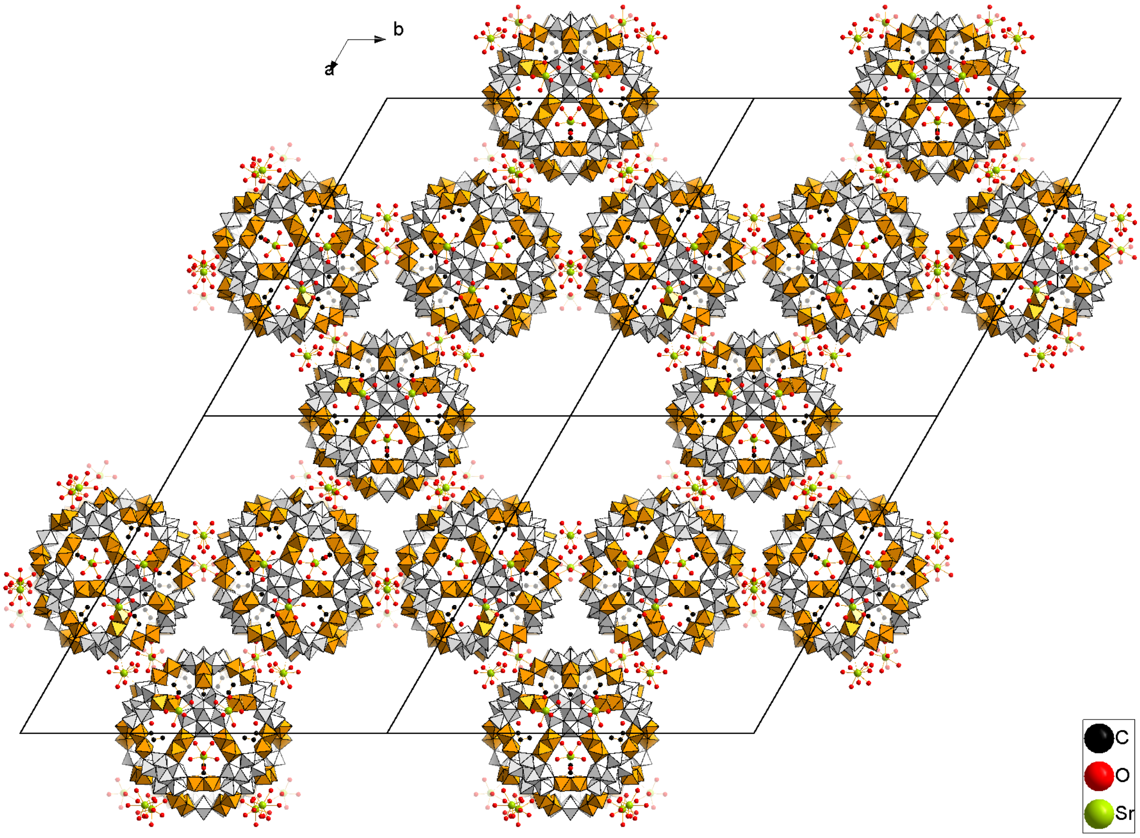

Figure S5. 2D kagome-lattice sheet of {Mo$_{132}$} in compound **2** that is spanning parallel to the crystallographic *ab* plane. Only the {Mo$_{132}$} anions, Sr^{2+} cations that are connecting {Mo$_{132}$}, and its hydration spheres are shown for clarity.