Single crystal growth and characterization of the first reduced lanthanum molybdenum oxychloride, $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$, with an unusual trigonal prismatic MoO_6 unit

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Abstract

The use of a KCl/CsCl alkali eutectic flux under reducing conditions facilitated the crystal growth of the mixed valent Mo(V)/Mo(VI) compound $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$. $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$ crystallizes in the noncentrosymmetric hexagonal space group $P-62m$ with $a = 10.2241(2) \text{ \AA}$ and $c = 15.0768(4) \text{ \AA}$, which represents a new structure type exhibiting a three-dimensional crystal structure containing three different molybdenum coordination environments, MoO_5 square pyramids, MoO_6 trigonal prisms, and MoO_5 trigonal bipyramids. The temperature dependence of the magnetic susceptibility was measured and $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$ was found to be paramagnetic across the entire 2-300 K temperature range measured. Although noncentrosymmetric, $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$ was not found to be second harmonic generation active. $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$ was further characterized by UV/Vis spectroscopy.

1. Introduction

Crystal growth of complex oxides and related materials containing reduced early transition metals remains a relatively unexplored area in solid state chemistry owing to the synthetic difficulties involved in the crystal growth of reduced materials; however, it is an attractive area of research for the creation of new complex oxide materials containing unpaired d electrons. The presence of unpaired electrons in early transition metal cations can potentially lead to interesting electrical and magnetic properties. Known materials are predominantly limited to the simple binaries, such as VO_2 , V_2O_3 ¹⁻³, TiO ⁴, and Ti_2O_3 ⁵; ternaries such as A_xNbO_3 ($\text{A}=\text{Sr}$, Ba)^{6, 7}, $\text{Cs}_{0.33}\text{MoO}_3$ ⁸, AMoO_3 ($\text{A}=\text{K}$, Rb , Tl)^{9, 10}, $\text{Ba}_3\text{M}_5\text{O}_{15}$ ($\text{M}=\text{Nb}$, Ta)^{11, 12} and SrV_4O_9 ¹³; and some higher order oxides such as $\text{Ba}_6\text{Nb}_{14}\text{Si}_4\text{O}_{47}$ ¹⁴ and $\text{K}_2\text{Mo}_4\text{Nb}_3\text{O}_{20}$ ¹⁵. Historically, synthetic techniques used to prepare crystals of such reduced oxides have included fused salt electrolysis, chemical vapor transport, flux, and hydrothermal methods.

The lack of materials containing reduced early transition metals has motivated us to pursue synthetic routes to prepare such oxides and to measure their physical properties. An earlier approach, a two-step mild hydrothermal method, was successful for the preparation of single crystals of hybrid materials containing transition metals in a variety of reduced oxidation states.¹⁶⁻²² For the creation of new oxides we chose high temperature solution growth, a well-known method for the crystal growth of a wide variety of oxides, including some reduced ones.^{17, 23, 24} The careful selection of appropriate fluxes is critical for maintaining a redox neutral melt in which to conduct the reaction. For this reason we selected alkali metal halides, which are known to solubilize a diverse array of elements. Most oxides reported in the literature have been prepared using sealed tantalum, niobium, or fused silica tubes.^{11, 25-30} Our approach is based on the *in situ* reduction of Mo(VI) using Mo metal as a reducing agent, which was successful in

preparing, to the best of our knowledge, the first reduced lanthanum molybdenum oxychloride. A limited number of lanthanum molybdenum oxychlorides are known including $LnCl[MoO_4]$ $Ln = La, Ce, Pr, Sm - Lu$ ^{31, 32}, however these materials contain Mo(VI) exclusively.

To fully characterize this new structure type and the oxidation state of the molybdenum within the single crystals, a combination of single crystal X-ray diffraction, bond valence sum calculations (BVS), and magnetic susceptibility measurements were employed. Herein, we report the synthesis, crystal structure, and physical property characterization of $La_{20}Mo_{12}O_{63}Cl_4$.

2. Experimental Details

2.1 Reagents

CsCl (Alfa Aesar, 99+%) and LiCl (Acros, 99%) were dried at 260°C for 24 hours before use. La_2O_3 (Alfa Aesar, 99.99%) was prefired at 1000°C for 12 hours before use. MoO_3 (Alfa Aesar, 99.95%) and Mo powder ~250 mesh (Alfa Aesar, 99.9%) were used as received.

2.2 Synthesis

Single crystals of $La_{20}Mo_{12}O_{63}Cl_4$ were grown out of a molten cesium chloride/lithium chloride eutectic flux. In a typical procedure, 1 mmol of La_2O_3 (prefired at 1000°C for 12 hours), 2 mmol MoO_3 , 0.5 mmol Mo powder, and a 4x excess by weight of CsCl/LiCl (dried at 260°C for 24 hours) were placed into an 8'' long, ½'' diameter fused silica tube. The tube was evacuated to a pressure of 10^{-4} torr and flame sealed. The tube was heated in a programmable furnace to 800°C at a rate of 15°C/min, held for 24 hours, and then cooled to 400°C at a rate of 6°C/hr. At this point the furnace was shut off and allowed to cool to room temperature. The chloride flux was dissolved in water and the crystals were isolated via vacuum filtration yielding a phase pure product in approximately 80% yield based on La_2O_3 . Figure 1 shows an optical image and a scanning electron microscopy (SEM) image of representative crystals. Figure S1

displays a powder X-ray diffraction pattern (PXRD) of ground crystals of $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$ and also, for comparison, contains the calculated diffraction pattern obtained using the single crystal data, demonstrating the phase purity of the crystals.

2.3 *Energy-dispersive spectroscopy (EDS)*

Elemental analysis was performed on the single crystals using a TESCAN Vega-3 SBU SEM with EDS capabilities. The crystals were mounted on carbon tape and analyzed using a 20 kV accelerating voltage and an accumulation time of 1 minute. As a qualitative measure, EDS confirmed the presence of each reported element in the title compound.

2.4 *Single crystal X-ray diffraction (SXRD)*

X-ray intensity data from a deep blue hexagonal plate crystal were collected at 297(2) K using a Bruker SMART APEX diffractometer (Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). The raw area detector data frames were reduced and corrected for absorption effects with the SAINT+ and SADABS programs.³³ Final unit cell parameters were determined by least-squares refinement of 6928 reflections from the data set. An initial structural model was obtained with direct methods. Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2014³⁴ using the ShelXle interface³⁵.

The compound crystallizes in the trigonal / hexagonal system. No systematic absences were found in the intensity data, leaving 16 possible space groups. Eventually the noncentrosymmetric group $P\text{-}62m$ (No. 189) was confirmed by structure solution. The space group choice was checked for missed symmetry elements with the ADDSYM program, which found none.³⁶⁻³⁹ There are 18 atomic positions in the asymmetric unit: five lanthanum atoms, three molybdenum atoms, two chlorine atoms and eight oxygen atoms. All atoms are located on special positions except for three oxygens. La(1), Mo(1), O(6) and O(7) are located on mirror

planes (site $6i$, site symmetry $..m$). La(2) and La(3) are located on three-fold axes (site $4h$, site symmetry $3..$). La(4) and Mo(2) are located site $3g$ with $m2m$ site symmetry. La(5), Mo(3) and O(8) are located on site $3f$, also with $m2m$ site symmetry. The two chlorine atoms Cl(1) and Cl(2) are both located on site $2e$, with $3.m$ site symmetry. O(4) and O(5) are located on the mirror planes of sites $6k$ and $6j$, respectively, both with $m..$ site symmetry. Finally, oxygen atoms O(1), O(2), and O(3) are located on general positions (site $12l$). All atoms were refined with anisotropic displacement parameters. No deviation from full occupancy was observed for any of the metal or chlorine atoms. The final refined absolute structure (Flack x) parameter determined by the Parsons quotient method is 0.006(13).⁴⁰ Final atomic coordinates were standardized with Structure Tidy.⁴¹⁻⁴³ Crystallographic data, equivalent atomic positions, and selected interatomic distances are listed in Tables 1-3.

2.5 Powder X-ray diffraction (PXRD)

PXRD data were collected on a Rigaku D/Max-2100 powder X-ray diffractometer using Cu K α radiation. The step scan covered the angular range 5-65° 2θ in steps of 0.04°. No impurities were observed and the experimental and calculated PXRD patterns are in excellent agreement (see Figure S1).

2.6 UV-Vis diffuse reflectance spectroscopy (UV/Vis)

UV-Vis diffuse reflectance spectroscopy data of ground crystals were obtained using a PerkinElmer Lambda 35 UV-Vis scanning spectrophotometer equipped with an integrating sphere over the range of 200-900 nm. Reflectance data were transformed to absorbance via the Kubelka-Munk function.⁴⁴

2.7 Magnetic Susceptibility

The magnetic susceptibility was measured using a Quantum Design MPMS 3 SQUID magnetometer. The zero-field cooled magnetic susceptibility was measured as a function of temperature between 2-300K in an applied field of 1000 Oe. The measured magnetic data were corrected for shape and radial offset effects using the method reported by Morrison et al.⁴⁵

2.8 *Second Harmonic Generation (SHG)*

Powder SHG measurements were performed on a modified Kurtz nonlinear-optical (NLO) system using a pulsed Nd:YAG laser with a wavelength of 1064 nm. A comparison with a known SHG material was made using ground crystalline α -SiO₂. A detailed description of the equipment and methodology has been published elsewhere.^{46, 47}

3. **Results and discussion**

3.1 *Synthesis*

Crystals of La₂₀Mo₁₂O₆₃Cl₄ were grown out of a eutectic alkali metal chloride flux, which are known to be redox stable solvents suitable for the crystal growth of reduced oxides. In this work a CsCl/LiCl eutectic flux was used because of its low melting point, the long liquid range over the reaction conditions, and the low probability of incorporating either alkali metal into the product. Excluding potentially oxidizing species, such as water or oxygen, from the reaction is crucial to promote a reducing environment. For this reason the reaction was performed in an evacuated sealed fused silica tube. The hygroscopic chlorides were dried to remove water and were added to the tube immediately before sealing to minimize exposure to moisture in the atmosphere. Since lanthanum oxide is known to absorb carbon dioxide from air at room temperature to form lanthanum carbonate, which would decompose under the reaction conditions and generate significant and unsafe pressure within the tube, the La₂O₃ was pre-fired to 1000°C overnight to ensure that only the oxide was present. At 800°C all the reactants are in solution,

except for the Mo powder, which creates the reducing environment that favors the reduction of Mo(VI) to Mo(V) at the solid/liquid interface between dissolved Mo(VI) ions and Mo powder. The Mo(V) and Mo(VI) species present in solution combine with the lanthanum and chloride ions in solution during the slow cooling process to create plate crystals of $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$ as the sole product. The PXRD pattern of the ground crystals, shown in Figure S1, is in excellent agreement with the powder pattern calculated from single crystal data, confirming phase purity of the sample. Attempts to crystallize compositions containing other rare earth elements have been unsuccessful so far. Considering that lanthanum is noticeably larger than the next smaller lanthanides it is not unreasonable to assume that the inability to crystallize products containing the smaller lanthanides is due to size effects.

3.2 Structure

$\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$ represents a new structure type exhibiting a three-dimensional crystal structure containing three different molybdenum coordination environments, MoO_5 square pyramids, MoO_6 trigonal prisms, and MoO_5 trigonal bipyramids, that are connected via edge and corner sharing lanthanum polyhedra to generate the overall structure. Molybdenum in the structure segregates into two-dimensional sheets in the *ab* plane as a function of coordination environment, with MoO_5 square pyramids, MoO_6 trigonal prisms, and MoO_5 trigonal bipyramids each forming unique sheets that stack in an ABCB fashion along the *c* axis, as shown in Figure 2.

La(1) is located in a nine coordinate LaO_8Cl irregular polyhedron, shown in Figure 3, with La–O distances ranging from 2.466 Å to 2.911 Å and a La–Cl distance of 3.1523(19) Å. La(1) shares edges with La(2) through O(2) and O(3); La(3) through O(1) and O(2); La(4) through O(1) and O(7); Mo(1) through O(2), O(3), and O(7); Mo(2) through O(1); and itself through O(7) and Cl(1). La(1) also shares a corner with La(5) through O(3). La(2) is located in a

nine coordinate LaO_9 irregular polyhedron, shown in Figure 3, with La–O distances ranging from 2.516 Å – 2.991 Å. La(2) shares faces with La(3) and with itself through O(2) and O(5), respectively, forming one-dimensional infinite chains, shown in Figure 4. La(2) shares edges with La(1) through O(2) and O(3), La(5) through O(3) and O(5), and Mo(1) through O(2) and O(3). La(2) also shares a corner with Mo(3) through O(5). La(3) is located in a nine coordinate LaO_9 irregular polyhedron, shown in Figure 3, with La–O distances between 2.493 Å – 2.635 Å. La(3) shares faces with La(2) and with itself through O(2) and O(4). La(3) shares edges with La(1) through O(1) and O(2), La(4) through O(1) and O(4), and Mo(2) through O(1) and O(4). La(3) also shares a corner with Mo(1) through O(2). La(4) is located in a ten coordinate LaO_8Cl_2 irregular polyhedron, shown in Figure 3, with La–O distances between 2.399 Å – 2.721 Å and a La–Cl distance of 3.1775(19) Å. La(4) shares edges with La(1) through O(1) and O(7), La(3) through O(1) and O(4), and Mo(2) through O(1) and O(4). La(4) also shares a corner with Mo(1) through O(7). La(5) is located in a ten coordinate LaO_{10} irregular polyhedron, shown in Figure 3, with La–O distances between 2.475 Å – 2.808 Å. La(5) shares edges with La(2) through O(3) and O(5), Mo(1) through O(3), and Mo(3) through O(5), O(8), and O(6). La(5) also shares a corner with La(1) through O(3).

Mo(1) is located in a five coordinate square pyramid, shown in Figure 5, with Mo–O distances ranging from 1.753 to 1.919 Å. These distances are consistent with other reported compounds containing square pyramidal molybdenum.⁴⁸⁻⁵¹ Mo(1) shares edges with La(1) through O(3), O(7), and O(2) and La(2) through O(2) and O(3). Mo(1) also shares corners with La(4) through O(7) and La(3) through O(2). Mo(2) is located in an unusual six coordinate trigonal prism, shown in Figure 5, with Mo–O distances of 1.909 Å – 1.927 Å. Few examples of trigonal prismatic molybdenum exist in the literature, where it is usually coordinated to sulfur as

in MoS₂⁵², coordinated to sulfur or nitrogen containing organic ligands,⁵³⁻⁵⁷, or coordinated to oxygen containing organic ligands.^{58, 59} The Mo–O distances in our compound are somewhat shorter than those found in other compounds containing MoO₆ trigonal prismatic coordination environments. This is likely because the trigonal prism in our compound is highly regular while known molecular compounds contain highly distorted MoO₆ trigonal prisms. To the best of our knowledge this represents the first example of an MoO₆ trigonal prism found in a three-dimensional extended structure. Mo(2) shares edges with La(1) through O(1), La(3) through O(1) and O(4), and La(4) through O(1) and O(4). Mo(3) is located in a five coordinate trigonal bipyramid, shown in Figure 5, with Mo–O distances of 1.826 Å – 1.956 Å. These distances are consistent with several known mixed valent compounds containing similar coordination environments.^{51, 60, 61} Mo(3) shares edges with La(5) through O(5), O(6), and O(8). La(5) also shares a corner with La(2) through O(5). Given site multiplicities for Mo(1), Mo(2), and Mo(3) of 6, 3, and 3, no one site can be exclusively occupied by Mo(V) to satisfy charge neutrality, indicating at least one mixed valent Mo(V/VI) site. Bond valence analysis of each Mo site reveals Mo(1) = 5.79, Mo(2) = 5.77, and Mo(3) = 5.43 when all Mo is considered to be 6+ and Mo(1) = 5.36, Mo(2) = 5.34, and Mo(3) = 5.02 when all Mo is considered to be 5+. From this data we can reasonably conclude that the largest share of Mo(V) is located on Mo(3) and the largest shares of Mo(VI) are located on Mo(1) and Mo(2). Along the *c* axis La(1), La(4), La(5), Mo(1), Mo(2), and Mo(3) form chains shown in Figure 6. Mo(1), Mo(2), and Mo(3) form two-dimensional sheets in the *ab* plane and are shown in Figures 7-9.

3.3 *UV-vis diffuse reflectance spectroscopy (UV/Vis)*

UV-Vis absorbance data shown in Figure 10 were collected using ground crystals. The absorption edge is clearly observed in the visible region, and the band gap estimated by the onset

of the absorption edge is approximately 2.4 eV, indicating likely semiconducting behavior for the oxychloride. A broad absorbance ranging from 900 nm to 550 nm is observed, with a maximum at 551 nm and is consistent with the presence of Mo(V) cations in the structure, based on reports in the literature describing the UV-Vis absorption data collected on mixed Mo(VI)/Mo(V) containing compounds.^{62, 63}

3.4 *Magnetic Susceptibility*

The mixed valent $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$ contains Mo(V) d^1 species that give rise to paramagnetic behavior. Measurements of the temperature dependence of the magnetic susceptibility of $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$ measured in an applied field of 1000 Oe, shown in Figure 11, are consistent with simple paramagnetic behavior. This is not unexpected since the Mo(V) centers are isolated from each other. In $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$ the amount of Mo(V) is around 17% and is therefore magnetically dilute, thus no magnetic coupling is expected or observed. Down to 2K, the data do not reveal any long range magnetic order and follow the Curie-Weiss (C-W) law as expected for simple paramagnetic species. The magnetic moment calculated from the inverse susceptibilities is $1.68 \mu_B/\text{mol Mo(V)}$, which is in good agreement with the expected spin only value for $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$ of $1.73 \mu_B/\text{mol Mo(V)}$.⁶⁴

3.6 *Second Harmonic Generation (SHG)*

Although $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$ crystallizes in the noncentrosymmetric space group $P-62m$, no detectable SHG response was observed when measuring a ground polycrystalline sample. Given the roughly spherical geometry of the lanthanum coordination environments, the system does not have a large dipole moment and, as a consequence, does not efficiently generate an SHG response. It is known that compounds with large dipole moments typically exhibit large SHG responses.²²

4. Conclusion

We successfully synthesized the new lanthanum molybdenum oxychloride $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$ via a molten salt flux technique. The oxychloride exhibits a new structure type that was determined by single crystal X-ray diffraction. By utilizing a redox stable flux and Mo powder, we were able to reduce a fraction of the Mo(VI) in the reaction mixture to Mo(V). The average molybdenum oxidation state is +5.83 with a Mo(V) content of 16.67%. As a result of the magnetically dilute Mo(V) in the compound, only simple paramagnetic behavior is observed. The agreement of the experimental and theoretical magnetic moments confirms the presence and quantity of Mo(V) in the structure. The structure, while noncentrosymmetric, does not give rise to SHG behavior.

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Table 1. Crystallographic data for $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$

Formula	$\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$
Formula Weight	5079.28
Color and habit	Deep blue hexagonal plate
Crystal System	Hexagonal
Space group	$P-62m$
Temperature (K)	297(2)
a (Å)	10.2241(2)
c (Å)	15.0768(4)
Volume (Å ³)	1364.87(6)
Z	1
ρ_c (g/cm ³)	6.180
μ (mm ⁻¹)	18.226
$F(000)$	2216
Crystal size (mm)	$0.100 \times 0.060 \times 0.020$
2θ range (°)	1.351 – 35.070
Index ranges	$-16 \leq h \leq 16, -16 \leq k \leq 15, -24 \leq l \leq 22$
Reflections collected	26973
Independent reflections	2234 [R(int) = 0.0555]
GOF (F^2)	1.065
$R(F)^a$	0.0254
$R_w(F_o^2)^b$	0.0494
Flack Parameter	0.006(13)
Largest diff. peak and hole (e Å ⁻³)	1.858 and -1.492
^a $R(F) = \Sigma F_o - F_c /\Sigma F_o $. ^b $R_w(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.	

Table 2. Atomic Coordinates and equivalent isotropic displacement parameters U_{eq} for $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq} ($\text{\AA}^2 \times 10^3$)	Multiplicity
La(1)	0.2753(1)	0	0.2731(1)	10(1)	6
La(2)	$\frac{1}{3}$	$\frac{2}{3}$	0.1269(1)	10(1)	4
La(3)	$\frac{1}{3}$	$\frac{2}{3}$	0.3808(1)	8(1)	4
La(4)	0.7290(1)	0	$\frac{1}{2}$	9(1)	3
La(5)	0.7298(1)	0	0	16(1)	3
Mo(1)	0.6189(1)	0	0.2270(1)	8(1)	6
Mo(2)	0.3841(1)	0	$\frac{1}{2}$	7(1)	3
Mo(3)	0.3829(1)	0	0	7(1)	3
Cl(1)	0	0	0.1790(3)	18(1)	2
Cl(2)	0	0	0.3968(2)	17(1)	2
O(1)	0.1368(5)	0.3809(5)	0.4133(3)	10(1)	12
O(2)	0.1436(5)	0.5582(5)	0.2590(2)	10(1)	12
O(3)	0.2240(5)	0.3745(5)	0.1627(3)	13(1)	12
O(4)	0.1384(6)	0.5965(6)	$\frac{1}{2}$	10(1)	6
O(5)	0.2207(7)	0.4837(7)	0	12(1)	6
O(6)	0.4937(7)	0	0.0950(4)	14(1)	6
O(7)	0.7227(6)	0	0.3196(4)	14(1)	6
O(8)	0.2026(8)	0	0	13(2)	3

Table 3. Selected interatomic distances ($\text{\AA}$) for $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$.

La(1)-O(1) x 2	2.466(4)	La(4)-Cl(2) x 2	3.1775(19)
La(1)-O(2) x 2	2.514(5)	La(5)-O(3) x 4	2.808(4)
La(1)-O(3) x 3	2.514(5)	La(5)-O(5) x 2	2.475(6)
La(1)-O(7) x 2	2.911(4)	La(5)-O(6) x 2	2.807(7)
La(1)-Cl(1)	3.1523(19)	La(5)-O(8) x 2	2.490(2)
La(2)-O(2) x 3	2.609(4)	Mo(1)-O(2) x 2	1.919(5)
La(2)-O(3) x 3	2.669(4)	Mo(1)-O(3) x 2	1.848(4)
La(2)-O(5) x 3	2.516(4)	Mo(1)-O(7)	1.753(6)
La(3)-O(1) x 3	2.635(5)	Mo(2)-O(1) x 4	1.927(4)
La(3)-O(2) x 3	2.493(4)	Mo(2)-O(4) x 2	1.909(6)
La(3)-O(4) x 3	2.507(4)	Mo(3)-O(5) x 2	1.956(6)
La(4)-O(1) x 4	2.529(4)	Mo(3)-O(6) x 2	1.826(6)
La(4)-O(4) x 2	2.399(6)	Mo(3)-O(8)	1.843(8)
La(4)-O(7) x 2	2.721(7)		

Figure 1. Optical image of $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$ grown out of a barium chloride/sodium chloride melt and SEM image of $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$.

Figure 2. $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$ viewed down the a axis. Mo1, Mo2, Mo3, La, and Cl shown in aqua, cyan, navy, orange, and green, respectively. Oxygen atoms, La–Cl bonds, and select La–O bonds are omitted for clarity.

Figure 3. Local coordination environments of La1 – La5. La, Mo1, Mo2, Mo3, O, and Cl shown in orange, aqua, cyan, navy, red, and green, respectively. Symmetry equivalent La, O, and Cl labeled for clarity.

Figure 4. 1D chains of face sharing La2 and La3 shown about the c axis. La and O shown in orange and red, respectively.

Figure 5. Local coordination environments of Mo1, Mo2, and Mo3. Mo1, Mo2, Mo3, La, and O shown in aqua, cyan, navy, orange, and red, respectively.

Figure 6. Connectivity of La1, La4, La5, Mo1, Mo2, and Mo3 shown about the *c* axis. La, Mo1, Mo2, Mo3, Cl, and O shown in orange, aqua, cyan, navy, green, and red, respectively.

Figure 7. 2D sheet containing Mo1 square pyramids viewed down the *c* axis. La1, La2, Mo1, Cl and O shown in orange, grey, aqua, green, and red, respectively.

Figure 8. 2D sheet containing Mo2 trigonal prisms viewed down the c axis. La3, La4, Mo2, Cl, and O shown in orange, grey, cyan, green, and red, respectively.

Figure 9. 2D sheet containing Mo3 trigonal bipyramids viewed down the c axis. La2, La5, Mo3, and O shown in grey, orange, navy, and red, respectively.

Figure 10. UV/Vis absorbance spectrum for $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$.

Figure 11. Magnetic susceptibility plot for $\text{La}_{20}\text{Mo}_{12}\text{O}_{63}\text{Cl}_4$. χ and $1/\chi - \chi_0$ are shown in blue and red, respectively.