**Synthesis, Crystal Structure and Magnetic Properties of the Two Polymorphs
of Novel $S = 1$ Osmate; $\text{Li}_4\text{MgOsO}_6$**

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Abstract: $\text{Li}_4\text{MgOsO}_6$ was synthesized by two different solid-state reaction procedures. The crystal structures were determined by X-ray powder diffraction technique and it was revealed that $\text{Li}_4\text{MgOsO}_6$ crystallizes in two different crystal symmetries in ordered rock salt structure type, namely monoclinic $C2/m$ and orthorhombic $Fddd$. The unit cell constants for the monoclinic system are $a = 5.1074(4) \text{ \AA}$, $b = 8.8182(4) \text{ \AA}$, $c = 5.0902(2) \text{ \AA}$, and $\beta = 109.845(4)^\circ$ and those of the orthorhombic structure are $a = 5.8485(1) \text{ \AA}$, $b = 8.3821(1) \text{ \AA}$, and $c = 17.6212(3) \text{ \AA}$. In both systems, Os^{6+} ions reside exclusively in a specific crystallographic position while Li^+ and Mg^{2+} ions exhibit mixed occupancy. The temperature dependent magnetic susceptibility data for both $S = 1$ osmate systems do not support the occurrence of any magnetic transition down to 2K. The Curie-Weiss fit to the paramagnetic regime of the magnetic susceptibility data reveal highly negative θ value (-114.81 K and -121.87 K for $C2/m$ and for $Fddd$ systems, respectively), which are indicative of predominant antiferromagnetic (AFM) interactions in both systems. The experimental effective magnetic moment (μ_{eff}) value for the monoclinic phase is $2.13 \mu_B$ and that of the orthorhombic system is $2.34 \mu_B$. Due to the rather strong AFM interactions and lack of magnetic transition down to 2K, both of these novel osmates are placed in the class of highly frustrated magnets. Low temperature magnetic susceptibility (below 2K) and dynamic magnetic properties studies (μsr studies) are in order to better understand the magnetic ground states of these two polymorphs of $\text{Li}_4\text{MgOsO}_6$.

Keywords: Structural polymorphism, Ordered rock salt structure Type, Osmates, Geometric Magnetic Frustration.

INTRODUCTION

In antiferromagnetic (AFM) materials with triangular arrangements of magnetic ions, all the spin correlations cannot be fulfilled simultaneously and conventional static magnetic ordering is inhibited. This geometric constraint results in a exotic ground states with multiple degeneracies and is known as geometric magnetic frustration (GMF).¹ However, when all the exchange interaction pathways on triangular lattice are not equally effective, the dominating interactions will govern the magnetic structure and will result in a non-frustrated ground state. The latter scenario normally results in low dimensional magnetism (LDM), instead. To verify whether a given system undergoes GMF, frustration index (f), $f = |\theta|/T_N$ is a useful measure. Absolute values of Weiss constant (θ) determine the strength of exchange interactions. Generally if exchange interactions are strong, the magnetic ordering is expected to occur at rather high temperatures (T_N). Therefore, a large f value is indicative of an intrinsic hindrance (i.e. frustration) against magnetic order (low T_N) in the presence of strong exchange interactions (high θ). Materials with $f \geq 10$ are considered highly frustrated.²

Our research group is interested in understanding the roles of various structural and electronic factors that result in either GMF or LDM in materials that comprise such triangular arrangements. The variables that affect the resultant magnetism include crystal symmetry, site symmetry, principal quantum number and spin quantum states of the magnetic ions. Ordered rocksalt structure with heavy element transition metals is an interesting class of compounds for this purpose.³⁻⁷ While they offer various triangular and tetrahedral sub-structures of magnetic ions, they bring more diverse oxidation states (especially $\geq +5$ that are rarely seen in $3d$ elements) and enable systematic alteration of the magnetic properties as a function of spin multiplicity. Moreover, the large difference between the formal charges of such magnetic ions with

diamagnetic alkali and alkali earth ions results in crystallographic cation ordering, which allows precise design of the magnetic exchange pathways. Os-based compounds have been of particular interest for us, owing to their wide range of possible oxidation states, +4 to +7, which enables formation of various spin systems in a given lattice. Li_5OsO_6 ⁸ and $\text{Li}_3\text{Mg}_2\text{OsO}_6$ ⁹ (comprising Os^{7+} and Os^{5+} , respectively) are two examples of NaCl type osmates that were studied in this respect.

Li_5OsO_6 crystallizes in a monoclinic $C2/m$ space group and is a $S = 1/2$ system, which undergoes a long range AFM ordering at ~40K and is not frustrated. This finding was in contrast with what was reported for isoelectronic and isostructural rhenium-based compound, $\text{Li}_4\text{MgReO}_6$,¹⁰ which exhibits spin glass (SG) behavior. $\text{Li}_3\text{Mg}_2\text{OsO}_6$ on the other hand crystallizes in an orthorhombic $Fddd$ space group and is a $S = 3/2$ system and undergoes an AFM transition at ~8K and is highly frustrated ($f = 13$). This was again in contrast with its $4d$ analog $\text{Li}_3\text{Mg}_2\text{RuO}_6$,¹¹ which exhibits a long range AFM order below 18K and exhibits a moderate frustration ($f = 5$).

Here we report on synthesis, crystal structure polymorphism, and magnetic properties of the $S = 1$ system, $\text{Li}_4\text{MgOsO}_6$. This study fills in the gap between the two previously studied Os^{7+} and Os^{5+} systems of the ordered rock salt structure.

EXPERIMENTAL

Synthesis

To obtain the monoclinic phase, stoichiometric amounts of Li_5OsO_6 , Osmium metal powder (Alfa Aesar, 99.95%), OsO_2 (Alfa Aesar, 99.9 %), and MgO (Acros Organics, 99.99%) were thoroughly ground in an argon-filled glove box according to the Equation 1.

The powder mixture was then pressed into a pellet and placed in an alumina crucible. The crucible was then sealed in an evacuated fused silica tube, which was placed in a box furnace and was heated at 700 °C for 24 hours. The reaction progress as a function of time was monitored by powder X-ray diffraction, which revealed formation of nearly single-phase monoclinic structure, resembling the powder pattern of Li_5OsO_6 ,⁸ with the peak positions shifted to the left. When the sample was heated for another 24 hours, additional peaks appeared which were indicative of formation of orthorhombic structure (isostructural to $\text{Li}_3\text{Mg}_2\text{OsO}_6$ ⁹). Heating the sample for longer time resulted in production of more orthorhombic phase, although a nearly single-phase orthorhombic sample was never obtained. Accordingly, effort was devoted to optimize the reaction condition towards formation of two single-phase compounds. Finally a single-phase monoclinic sample was obtained by heating a mixture based on Equation 1 at 800°C for 24 hours. The heating and cooling were done with the rate of 100°C/hr.

An alternate reaction pathway was adopted to form the nearly pure orthorhombic sample. For this purpose a mixture of Li_5OsO_6 and $\text{Li}_3\text{Mg}_2\text{OsO}_6$ with 1 : 1 ratio, based on Equation 2.

The mixture was pressed into a pellet and was sealed in an evacuated silica tube, which was then heated at 750 °C for 24 hours three times. The heating and cooling were done with the rate of 100°C/hr. After each heating cycle, the pellet was reground and repressed to ensure homogeneity.

Prior to the sample preparation, MgO was heated by H₂/O₂ flame in a silica tube under dynamic vacuum for 15 minutes to ensure the removal of trace amounts of moisture and also decomposition of carbonates. The starting material, Li₂O was prepared by heating lithium hydroxide mono-hydrate (Alfa Aesar, 98%) to 450°C in a fused quartz tube under dynamic vacuum for 18 hours and was then transferred into the glove box. To prepare Li₅OsO₆ a mixture of Li₂O and Os metal powder with 2.5: 1 molar ratio was thoroughly ground and pressed into a pellet in an-argon filled glove box. The pellet was placed in an alumina boat and heated to 500 °C in a tube furnace under dynamic argon flow. After five hours the argon flow was switched to oxygen, the temperature was raised to 800 °C and the sample was heated for twelve hours and was cooled to room temperature in ten hours. The procedure for synthesis of Li₃Mg₂OsO₆ is presented elsewhere.⁹

Crystal structure determination and sample characterization

Powder X-ray diffraction technique was used to monitor the reaction progress, phase formation and the purity of the samples. A PANalytical X'Pert Pro MPD diffractometer, equipped with a linear X'Celerator detector, with Cu-K α_1 radiation was employed for this purpose. The X-ray diffraction data were collected at room temperature in the range of $10^\circ \leq 2\theta \leq 100^\circ$ with $\sim 0.008^\circ$ steps.

The crystal structures were determined by Rietveld refinement of the powder X-ray data, using the General Structure Analysis System (GSAS) suite and EXPGUI interface.^{12, 13} The structural data from Li₄MgReO₆¹⁰ and Li₃Mg₂OsO₆⁹ were used as initial models for refinement of the monoclinic and orthorhombic structures, respectively. While the monoclinic system resembled a single-phase sample, the diffraction pattern for the orthorhombic system revealed

the presence of small amount of monoclinic phase, as well. Therefore, for refining the structure of the latter sample, two-phase refinement process approach was followed. It was found that the monoclinic phase accounted for less than 4% of the orthorhombic sample. For both refinements, pseudo-Voigt peak shape profiles were chosen and the parameters were refined to obtain the best fit to the experimental data. The residual factors for monoclinic system are $R_p = 0.0698$ and $wR_p = 0.0952$, while those of *Fddd* were minimized to $R_p = 0.0763$ and $wR_p = 0.1108$. The powder X-ray diffraction pattern along with the fit to the structural models for both polymorphs of $\text{Li}_4\text{MgOsO}_6$ are presented in Figure 1.

Figure 1. Room temperature powder X-ray diffraction pattern of monoclinic (top) and orthorhombic (bottom) variants of $\text{Li}_4\text{MgOsO}_6$. The black crosses indicate the experimental data while the Rietveld refinement fit is shown as a solid red line. The difference between these values are represented by the bottom thin blue solid line. The peak positions of the target phases are located by the green vertical tick marks and the pink vertical tick marks (bottom) represent the position of monoclinic side-product in orthorhombic sample.

Magnetic susceptibility data

Polycrystalline powders of the samples were encased in gelatin capsule, and by employing a Quantum Design MPMS SQUID magnetometer, magnetic susceptibility data were collected. Both zero-field-cooled (ZFC) and field cooled (FC) data were collected over the temperature

range of 2-400K with an applied field of 1000 Oe. Furthermore, magnetization data versus magnetic field were collected for both phases(up to 5.5 T) at 2K and 300 K.

RESULTS AND DISCUSSION

Crystal structure

Both polymorphs of $\text{Li}_4\text{MgOsO}_6$, form inordered rock salt structure type, which comprise edge-shared octahedra. The monoclinic variant (Figure 2 a) crystallizes in $C2/m$ space group and is isostructural to $S = \frac{1}{2}$ system, $\text{Li}_4\text{MgReO}_6$.¹⁰ The cell constants are $a = 5.1074(4) \text{ \AA}$, $b = 8.8182(4) \text{ \AA}$, $c = 5.0902(2) \text{ \AA}$, $\beta = 109.845(4)^\circ$, and $V = 215.64(1) \text{ \AA}^3$. Two formula units of $\text{Li}_4\text{MgOsO}_6$ are present in each unit cell. The orthorhombic system (Figure 2b) appears in $Fddd$ space group with $a = 5.8485(1) \text{ \AA}$, $b = 8.3821(1) \text{ \AA}$, $c = 17.6212(3) \text{ \AA}$ and $V = 863.84(2) \text{ \AA}^3$. It is isostructural to $\text{Li}_3\text{Mg}_2\text{RuO}_6$ ¹¹ and is composed of eight formula units per unit cell. The molar volumes of the orthorhombic phase is only 0.130(2)% larger than that of the monoclinic phase, which is indicative of nearly identical chemical compositions for the two phases. These volumes are ~3.4% larger than that of Li_5OsO_6 and ~2.0% smaller than that of $\text{Li}_3\text{Mg}_2\text{OsO}_6$. This observation is understood based on the gradual decrease of average weighted radii of Li^+ (0.76 $\text{\AA}$) and Mg^{2+} (0.72 $\text{\AA}$) in one hand and increased size of Os ions from Li_5OsO_6 (Os^{7+} : 0.525 $\text{\AA}$) to $\text{Li}_3\text{Mg}_2\text{OsO}_6$ (Os^{5+} : 0.575 $\text{\AA}$) on the other hand.¹⁴ The cell parameters and refinement parameters of both monoclinic and orthorhombic phases of $\text{Li}_4\text{MgOsO}_6$ are presented in Table 1.

Figure 2.Crystal structure of monoclinic $\text{Li}_4\text{MgOsO}_6$ (left) and orthorhombic variant of $\text{Li}_4\text{MgOsO}_6$ (right). The blue octahedra represent OsO_6^{6-} units and the yellow spheres represent mixed occupied positions by Li^+ and Mg^{2+} ions. The red spheres represent O^{2-} anions.

Table 1.Unit Cell constants and refinement parameters of two variants of $\text{Li}_4\text{MgOsO}_6$ in comparison with those of Li_5OsO_6 and $\text{Li}_3\text{Mg}_2\text{OsO}_6$

	Li_5OsO_6 ($C2/m$) ⁸	$\text{Li}_4\text{MgOsO}_6(C2/m)$	$\text{Li}_4\text{MgOsO}_6$ ($Fddd$)	$\text{Li}_3\text{Mg}_2\text{OsO}_6$ ($Fddd$) ⁹
a (Å)	5.0472(1)	5.1074(4)	5.8485(1)	5.8898(1)
b (Å)	8.7827(2)	8.8182(4)	8.3821(1)	8.4688(1)
c (Å)	5.0079(1)	5.0902(2)	17.6212(3)	17.6824(2)
β (°)	109.777(2)	109.845(4)		
V (Å ³)	208.90(1)	215.64(1)	863.84(2)	881.99(2)
Z	2	2	8	8
V/Z (Å ³)	104.45(1)	107.82(1)	107.96(2)	110.25(2)
Agreement Factors		$R_p = 0.0698$ $wR_p = 0.0952$	$R_p = 0.0763$ $wR_p = 0.1108$	

In both structures, there are four crystallographically independent cationic positions. One position in both systems is exclusively occupied by Os^{6+} ions and the other positions (denoted by M1, M2 and M3) are randomly filled by Li^+ and Mg^{2+} ions. Such selectivity for Os^{6+} is best understood based on the Pauling's rule; indicating that octahedra with highly oxidized central cations tend to avoid sharing their anions with each other (to minimize repulsive electrostatic energy). This results in site ordering for hexavalent osmium ions. In both compounds, the Os sublattice forms various corner-shared and edge-shared triangles. However, crystallographic long-range order is not in effect between monovalent Li and divalent Mg ions.

One should also note that powder X-ray diffraction technique has intrinsic limitations (when dealing with light elements such as Li), which results in the lack of high reliability for the refined occupancy factors. This limitation also applies for accurately locating the oxygen ions for which the thermal displacement factors were not refined. Atomic positions with thermal displacement parameters of all the atoms along with the site occupancies of Li/Mg for monoclinic and orthorhombic systems are provided in Table 2 and Table 3, respectively. Coordination environment of magnetic ions along with their bond valence sums¹⁵ are presented for both compounds in Table 4. The BVS values are nearly identical for both samples, and are additional structural proofs for nearly identical chemical compositions of the two phases. It should be noted that both systems exhibit tetragonal elongation (*Jahn-Teller* effect), which is well understood for the d^2 electronic configuration in octahedral crystal field.

Transformation of monoclinic unit cell to the orthorhombic supercell is schematically represented in Figure 3. The lengths of a and c parameters in monoclinic unit cell are nearly identical. Starting from four adjacent unit cells the small diagonal of one unit cell will be perpendicular to the large diagonal of the next. These diagonals form rectangle with doubled area

and represent a and b axes of new orthorhombic unit cell, respectively. In addition the b axis of the monoclinic unit cell is doubled and represent the c axis for the supercell, which is four times larger than that of the monoclinic cell.

Table 2. Atomic coordinates, occupancy factors and equivalent isotropic displacement parameters for $\text{Li}_4\text{MgOsO}_6$ refined in $C2/m$.

<i>Wyckoff</i>	<i>ATOM</i>	x	y	Z	<i>Li/ Mg Occ.</i>	$U_{iso} (\text{\AA}^2)$
$2a$	Os	0.000	0.000	0.000		0.0157(7)
$4g$	M1	0.000	0.664(2)	0.000	0.23(1)/ 0.77	0.02
$4g$	M2	0.5	0.316(3)	0.000	0.73(1)/ 0.27	0.02
$2d$	M3	0.0	0.5	0.5	0.79(3)/ 0.21	0.02
$8j$	O1	0.256(3)	0.357(1)	0.755(3)		0.015
$4i$	O2	0.258(4)	0.5	0.246(4)		0.015

Table3. Atomic coordinates, occupancy factors and equivalent isotropic displacement parameters for $\text{Li}_4\text{MgOsO}_6$ refined in $Fddd$.

		x	y	Z	<i>Li/ Mg Occ.</i>	$U_{iso} (\text{\AA}^2)$
$8a$	Os	0.125	0.125	0.125		0.0206(5)
$16g$	M1	0.125	0.125	0.3023 (8)	0.58 (1) / 0.42 (1)	0.02
$16g$	M2	0.125	0.625	0.292 (1)	0.78 (1) / 0.22 (1)	0.02
$8b$	M3	0.125	0.625	0.125	0.47(2) / 0.53 (2)	0.02
$16f$	O1	0.125	0.355 (1)	0.125		0.015
$32h$	O2	0.1112 (2)	0.377 (1)	0.2961 (5)		0.015

Table 4. Coordination sphere and Bond Valence Sums (BVS)^a of Os⁶⁺ ions in both structures of Li₄MgOsO₆.

Li ₄ MgOsO ₆ (<i>C2/m</i>)		Li ₄ MgOsO ₆ (<i>Fddd</i>)	
4xOs– O1	1.91(1) Å	2 xOs– O1	1.93(1) Å
2 xOs– O2	2.04(2) Å	4xOs– O2	1.96(1) Å
<i>BVS</i> (Os)	5.63	<i>BVS</i> (Os)	5.61

^aBVS = $\sum_{i=1}^N v_i$, $v_i = \exp[(R_0 - d_i) / 0.37]$, N is coordination number and d_i is bond distance. R_0 for Os⁶⁺ = 1.925.¹⁶

Figure 3. Schematic representation of supercell formation in a two-dimensional view. The black solid lines represent the view, along the *b* axis of four edge-shared adjacent monoclinic unit cells. The red dashed lines represent the borders of orthorhombic unit cell along the *b* crystallographic axis.

Magnetic Susceptibilities

Zero field cooled (ZFC) and field cooled (FC) magnetic susceptibility data for monoclinic and orthorhombic phases are shown in Figure 4a and Figure 4c, respectively. Both systems do not exhibit any evidence of magnetic ordering down to 2K. Inverse susceptibility data as a

function of temperature for *C2/m* and *Fddd* samples are presented in Figure 4b and Figure 4d, respectively. The paramagnetic regimes (200K – 300K) of the data fit very well to the Curie-Weiss law, $\chi = C / T - \theta$. The parameters for monoclinic system were obtained from the fit are $C = 0.57$ emu K/mol and $\theta = -115$ K while for the orthorhombic system the values are $C = 0.68$ emu K/mol and $\theta = -122$ K. The calculated effective magnetic moment ($\mu_{so} = \sqrt{8C}$) for *C2/m* system and *Fddd* system are 2.13 μ_B and 2.34 μ_B , respectively, which are both smaller than that of spin only value for a d^2 system ($\mu_{so} = \sqrt{2(2+2)} = 2.82$ μ_B). This is due to the spin-orbit coupling contribution for the electronic configuration of less than half filled. The large negative values of the Weiss constants in both systems are indicative of predominant AFM exchange interaction. However, the absence of magnetic transitions down to 2K suggests that both of these compounds are highly frustrated. These values along with those of $S = 1/2$ and $S = 3/2$ systems are summarized in Table 5. The Os– Os interactions with the shortest distances (~ 5.1 Å) for both are represented in Figure 5. The Os⁶⁺ ions in four monoclinic unit cells (Figure 5a) are shown in a similar view to the orthorhombic cell (Figure 5b). The edge-shared equilateral triangles in the monoclinic structure are extended in a two-dimensional network in only *ab* plane. In orthorhombic structure such triangles are extended in various crystallographic planes and comprise three-dimensional units such as trigonal pyramids and wedges. Despite such a clear distinction between the magnetic ion arrangement of the two structures, their static magnetic properties are very similar.

Figure 4 Temperature dependent ZFC (orange circles) and FC data (blue circles) for the monoclinic $\text{Li}_4\text{MgOsO}_6$ (a) and orthorhombic $\text{Li}_4\text{MgOsO}_6$ (c). Temperature dependent inverse susceptibility data along with the Curie-Weiss fits (dashed red lines) for $C2/m$ (b) and $Fddd$ (d) samples.

Figure 5 Representation of nearest neighbor Os – Os interactions for (a) monoclinic and (b) orthorhombic $\text{Li}_4\text{MgOsO}_6$. The monoclinic structure comprises only 2D edge-shared triangles while the orthorhombic structure is composed of other 3D motifs such as trigonal pyramids and wedges.

The field dependent magnetization data for both monoclinic and orthorhombic samples are presented in Figure 6. At 300K both systems exhibit linear dependency and at 2K both samples exhibit S-shaped behavior without hysteresis, which are additional indications of predominant AFM exchange interactions. The slight curvature at 2 K might be understood in terms of the behavior of the Brillouin function for a $S = 1$ system.

Figure 6 Field dependent magnetization data for the monoclinic $\text{Li}_4\text{MgOsO}_6$ (a) and orthorhombic $\text{Li}_4\text{MgOsO}_6$ (b) at 2K (blue circles) and at 300K (orange circles). The lack of hysteresis behavior even at 2K indicates that ferromagnetic or ferrimagnetic interactions are not present.

Table 5. Unit Cell constants and refinement parameters of two variants of $\text{Li}_4\text{MgOsO}_6$ in comparison with those of Li_5OsO_6 and $\text{Li}_3\text{Mg}_2\text{OsO}_6$

	Li_5OsO_6 ($C2/m$) ⁸	$\text{Li}_4\text{MgOsO}_6(C2/m)$	$\text{Li}_4\text{MgOsO}_6$ ($Fddd$)	$\text{Li}_3\text{Mg}_2\text{OsO}_6$ ($Fddd$) ⁹
S	$\frac{1}{2}$	1	1	$\frac{3}{2}$
θ/K	-34	-115 K	-122	-106
$\mu_{\text{so}} / \mu\text{B}$	1.73	2.82	2.82	4.24
$\mu_{\text{eff}} / \mu\text{B}$	0.92	2.13	2.32	3.37
T_N / K	40	NA	NA	8

SUMMARY

Two polymorphs of novel osmium-based compound with $\text{Li}_4\text{MgOsO}_6$ chemical compositions were synthesized by solid-state methods. The crystal structures were determined employing X-

ray powder diffraction technique. The monoclinic version, which is isostructural to Li_5OsO_6 crystallizes in $C2/m$ space group with $a = 5.1074(4) \text{ \AA}$, $b = 8.8182(4) \text{ \AA}$, $c = 5.0902(2) \text{ \AA}$, and $\beta = 109.845(4)^\circ$. The orthorhombic variant is isostructural with $\text{Li}_3\text{Mg}_2\text{OsO}_6$ with $a = 5.8485(1) \text{ \AA}$, $b = 8.3821(1) \text{ \AA}$, and $c = 17.6212(3) \text{ \AA}$. The static magnetic properties of the two forms of the novel $\text{Li}_4\text{MgOsO}_6$ are very similar. Their rather large negative Weiss constants are indicative of the strong AFM interactions, however due to the lack of any magnetic transition down to 2K they are considered highly frustrated. To better understand the nature of their magnetic ground states, low temperature magnetic susceptibility data collection (below 2K) and muon spin resonance studies are in order.

ACKNOWLEDGEMENT

P-H T. N., M. S. T., and S.D. are grateful for financial support from the U.S. Army Research Office under Contract/Grant W911NF1210076. S.D. is thankful for the fruitful discussions and experimental support that was provided by Professor Ram Seshadri at UC Santa Barbara. We are grateful for the support of the National Science Foundation through the Materials World Network grant (DMR 0909180). M. C. K. acknowledges the support of the Schlumberger Faculty for the Future Foundation Fellowship.

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