Inorg. Chem. **2003**, *42*, 947–949

Inorganic Chemistry
Communication

Crystal Growth of Novel Osmium-Containing Triple Perovskites

Katharine E. Stitzer,[†] Ahmed El Abed,[‡,§] Mark D. Smith,[†] Matthew J. Davis,[†] Seung-Joo Kim,[†] Jacques Darriet,[‡] and Hans-Conrad zur Loye*,[†]

Department of Chemistry and Biochemistry, University of South Carolina,
Columbia, South Carolina, 29208, and Institut de Chimie de la Matière Condensée
de Bordeaux (ICMCB-CNRS), 87 Avenue du Dr. Schweitzer, 33608 Pessac Cedex, France

Received October 22, 2002

Single crystals of two new osmium-containing triple perovskites, $Ba_3LiOs_2O_9$ and $Ba_3NaOs_2O_9$, were grown from reactive molten hydroxide fluxes in sealed silver tubes. They crystallize in the space group $P6_3/mmc$ with lattice parameters of $a = 5.8025(1)$ Å, $c = 14.1468(4)$ Å for $Ba_3LiOs_2O_9$ and $a = 5.8858(1)$ Å, $c = 14.3451(5)$ Å for $Ba_3NaOs_2O_9$. The magnetic susceptibility of these osmates indicates significant Os–Os coupling within the octahedra pair.

Oxides are ubiquitous in nature and exist for virtually all elements, where typically several binary and many ternary and quaternary compositions are known. There are, of course, exceptions (the noble gases, for example), however; even among the metals, there are cases (for example gold) where very few oxides have been prepared and structurally characterized. This, surprisingly, is also true for osmium, which forms the well-known tetroxide, but for which there are few known complex oxides, and an even smaller number that have been fully structurally characterized and/or synthesized as single crystals. Most of the past research has focused on the preparation of ternary phases including $Cd_2Os_2O_7$,[1–4] $Tl_2Os_2O_7$,[5] $Hg_2Os_2O_7$,[6] $Ca_2Os_2O_7$,[7–9] $AOsO_3$ (A = Ca, Sr, and Ba),[7,10] M_2OsO_3 (M = Li, Na),[11] $La_4Os_6O_{19}$,[12,13] $La_3Os_2O_{10}$,[14] $Ln_2Os_2O_7$ (Ln = Pr, Nd, Sm, Eu, Tb, Ho, Lu, and Y),[15] $NdOsO_4$,[16] La_3OsO_7,[17] $MOsO_4$ (M = Na, K, Rb, and Cs),[18] Cd_3OsO_6,[19] $Sr_{11}Os_4O_{24}$,[20] and M_5OsO_6 (M = Li, Na).[21] Quaternary osmium-containing oxides are even more rare, and only a few examples, including Sr_2MOsO_6 (M = Li, Na, Mg, Ca, Sr, Fe, Co, Sc, Cr, In, and Ga),[22] Ba_2MOsO_6 (M = Pr, Nd, Sm−Lu, Y),[23] Ba_2MOsO_6 (M = Co, Ni),[24] and Ba_2MOsO_6 (M = Li, Na),[22,25] are known. Of these examples, a small number have been reported as single crystals, such as $La_3Os_2O_{10}$,[14] $NdOsO_4$,[16] $La_4Os_6O_{19}$,[12] and $Cd_2Os_2O_7$,[1,4] which were grown in sealed silica tubes using $KClO_3$, $Sr_{11}Os_4O_{24}$,[20] which was grown from a KO_2 flux in a closed Ag bomb, and Na_5OsO_6,[21] which was grown from a Na_2O/NaOH flux. We recently reported the single crystal synthesis of Ba_2MOsO_6 (M = Li, Na)[25] from hydroxide fluxes in covered crucibles, and in an effort to expand the number of known complex osmium-containing oxides, we have continued to explore the growth of complex osmium-containing oxide single crystals using high temperature solutions.

High temperature solution growth has been extremely effective for the growth of oxide single crystals containing virtually every element in the periodic table.[26] Fluxes

---

* To whom correspondence should be addressed. E-mail: zurloye@sc.edu.

[†] University of South Carolina.

[‡] Institut de Chimie de la Matière Condensée de Bordeaux.

[§] Permanent address: Mohamed I University, Faculté des Sciences, Oujda, Morocco.

(1) Sleight, A. W.; Gillson, J. L.; Weiher, J. F.; Bindloss, W. *Solid State Commun.* **1974**, *14*, 357.
(2) Reading, J.; Weller, M. T. *J. Mater. Chem.* **2001**, *11*, 2373.
(3) Sarkozy, R. F.; Chamberland, B. L. *Mater. Res. Bull.* **1973**, *8*, 1351.
(4) Mandrus, D.; Thompson, J. R.; Gaal, R.; Forro, L.; Bryan, J. C.; Chakoumakos, B. C.; Woods, L. M.; Sales, B. C.; Fishman, R. S.; Keppens, V. *Phys. Rev. B* **2001**, *63*, 195104.
(5) Sleight, A. W.; Gillson, J. L. *Mater. Res. Bull.* **1971**, *6*, 781.
(6) Reading, J.; Gordeev, S.; Weller, M. T. *J. Mater. Chem.* **2002**, *12*, 646.
(7) Chamberland, B. L. *Mater. Res. Bull.* **1978**, *13*, 1273.
(8) Shaplygin, I. S.; Lazarev, V. B. *Thermochim. Acta* **1977**, *20*, 381.
(9) Reading, J.; Knee, C. S.; Weller, M. T. *J. Mater. Chem.* **2002**, *12*, 2376.
(10) Shaplygin, I. S.; Lazarev, V. B. *Russ. J. Inorg. Chem.* **1976**, *21*, 1279.
(11) Lazarev, V. B.; Shaplygin, I. S. *Russ. J. Inorg. Chem.* **1978**, *23*, 802.
(12) Abraham, F.; Tréhoux, J.; Thomas, D. *Mater. Res. Bull.* **1977**, *12*, 43.
(13) Shaplygin, I. S.; Lazarev, V. B. *Dokl. Akad. Nauk SSSR* **1978**, *241*, 420.
(14) Abraham, F.; Tréhoux, J.; Thomas, D. *J. Solid State Chem.* **1979**, *29*, 73.
(15) Shaplygin, I. S.; Lazarev, V. B. *Mater. Res. Bull.* **1973**, *8*, 761.
(16) Abraham, F.; Tréhoux, J.; Thomas, D. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1627.
(17) Lam, R.; Wiss, F.; Greedan, J. E. *J. Solid State Chem.* **2002**, *167*, 182.
(18) Levason, W.; Tajik, M.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1985**, 1735.
(19) Lazarev, V. B.; Shaplygin, I. S. *Russ. J. Inorg. Chem.* **1979**, *24*, 128.
(20) Tomaszewska, A.; Müller-Buschbaum, H. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1738.
(21) Betz, T.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1985**, *524*, 17.
(22) Sleight, A. W.; Longo, J.; Ward, R. *Inorg. Chem.* **1962**, *1*, 245.
(23) Treiber, V. U.; Kemmler-Sack, S. *Z. Anorg. Allg. Chem.* **1981**, *478*, 223.
(24) Treiber, V. U.; Kemmler-Sack, S. *Z. Anorg. Allg. Chem.* **1980**, *470*, 95.
(25) Stitzer, K. E.; Smith, M. D.; zur Loye, H.-C. *Solid State Sci.* **2002**, *4*, 311.
(26) Elwell, D.; Scheel, H. J. *Crystal Growth from High-Temperature Solutions*; Academic Press: New York, 1975.

10.1021/ic026124p CCC: $25.00

employed for the growth of oxide single crystals have included alkali and alkaline earth carbonates, halides, peroxides, super oxides, and hydroxides. Of these diverse solvent systems, hydroxides have been particularly advantageous for obtaining oxides containing elements in unusual or high oxidation states as demonstrated by systems such as Ni(IV) in $Ba_6Ni_5O_{15}$,[27] Rh(V) in Sr_3NaRhO_6,[28] and more recently the mixed valent Ru(V/VI) in $Ba_3NaRu_2O_9$.[29]

As the volatility of OsO_4 is both a safety and a synthetic concern, we have explored the use of sealed silver tubes for the crystal growth of complex osmium-containing oxides in an attempt to avoid loss of osmium during the synthesis. This work has resulted in the preparation of two new triple perovskites, $Ba_3MOs_2O_9$ (M = Li, Na), containing osmium in a mixed formal oxidation state of +5/+6.

Single crystals of $Ba_3MOs_2O_9$ were grown from molten hydroxide fluxes in sealed Ag tubes. For $Ba_3LiOs_2O_9$,[30] $Ba(OH)_2{\cdot}8H_2O$ (Fisher, ACS reagent) and Os metal powder (J & J Materials, Inc., 99.98%) (1.6:1 molar ratio) were mixed with $LiOH{\cdot}H_2O$ (Alfa Aesar, reagent) and KOH (Fisher, ACS reagent) in a 5.5-fold mass excess. In the case of $Ba_3NaOs_2O_9$,[31] $Ba(OH)_2{\cdot}8H_2O$ and Os metal powder (1.6:1 molar ratio) were mixed with NaOH (Fisher, ACS reagent) in a 10-fold mass excess. The reactant constituents were placed inside a 0.5 in. diameter silver tube, which had been flamed sealed at one end and crimped and folded at the other. The tube was heated at 2.5 °C/min to the reaction temperature of 600 °C, held for 24 h, and then quickly cooled to room temperature, by shutting off the furnace. Shiny black crystals were extracted from the flux matrix by sonication in methanol.

Hexagonal pyramids and double pyramid shaped crystals were isolated from both batches of $Ba_3MOs_2O_9$ (M = Li, Na) crystals. The double pyramid crystal morphology appears to be characteristic for this structure type as we have observed it for other triple perovskite oxides, including $Ba_3MRu_2O_9$[29] and $Ba_3MIr_2O_9$[32] (M = Li, Na) systems as well. Energy dispersive spectroscopy (EDS, Philips XL 30 ESEM microscope) was used to analyze the elemental content of the crystals and to verify the presence of barium, osmium, and oxygen for both compounds, and sodium for $Ba_3NaOs_2O_9$. Lithium cannot be observed as it falls below the elemental cutoff for the instrument. Furthermore, within the detection limits of the instrument, no other extraneous elements were identified.

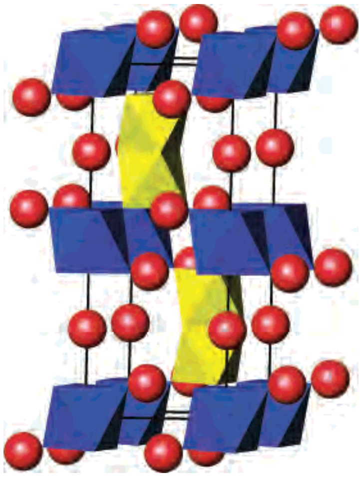

Figure 1. Approximate [110] view of the structure of $Ba_3MOs_2O_9$ (M = Li, Na) consisting of yellow Os_2O_9 octahedra pairs and blue MO_6 (M = Li, Na) octahedra singles. Ba cations are shown as red spheres.

An approximate [110] view of $Ba_3MOs_2O_9$ (M = Li, Na) is shown in Figure 1. The oxide is isostructural with the 6H-$BaTiO_3$[33] structure, also referred to as the triple perovskite structure. It consists of face-sharing Os_2O_9 octahedra pairs, which in turn share six vertices to six MO_6 (M = Li, Na) octahedra. In terms of stacking of close packed layers, the triple perovskite is a combination of hexagonal (ABAB) and cubic (ABCABC) stacked layers, creating the face-shared octahedra pairs and the vertex-shared octahedra, respectively. The barium atoms are located in 12-fold coordination sites.

The alkali metal to oxygen distances measure 2.154(5) Å for LiO_6 and 2.259(5) Å for NaO_6 and are in good agreement with M−O distances observed for the osmium-containing double perovskite Ba_2MOsO_6 (M = Li, Na).[25] There are two different Os−O distances within the octahedra pair; three long distances measuring 2.032(4) and 2.041(6) Å for the lithium and sodium analogues, respectively, and three short distances of 1.873(3) and 1.852(5) Å for the lithium and sodium analogues, respectively. The short and long grouping of metal−oxygen distances for the face-shared octahedra pairs is typical for the triple perovskite structure and has been observed for numerous other compositions.[29] The long Os−O distance is formed by the set of three oxygens that are located in the shared face of the octahedra pair, and the short distance is to the outer set of six oxygens that corner share to the sodium (lithium) containing octahedra. The short Os−O distances are comparable to distances measured for OsO_6 octahedra with osmium in a high formal oxidation state,

---

(27) Campá, J. A.; Gutiérrez-Puebla, E.; Monge, M. A.; Rasines, I.; Ruíz-Valero, C. *J. Solid State Chem.* **1994**, *108*, 230.

(28) Reisner, B. A.; Stacy, A. M. *J. Am. Chem. Soc.* **1998**, *120*, 9682.

(29) Stitzer, K. E.; Smith, M. D.; Gemmill, W. R.; zur Loye, H.-C. *J. Am. Chem. Soc.* **2002**, *124*, 13877.

(30) Crystal data for $Ba_3LiOs_2O_9$: formula $Ba_3LiOs_2O_9$, MM = 943.38 g/mol, hexagonal, space group $P6_3/mmc$, $a = 5.8025(1)$ Å, $b = 5.8025(1)$ Å, $c = 14.1468(4)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$, $V = 412.50(2)$ Å^3, $Z = 2$, $T = 293$ K, $\lambda = 0.71073$ Å, $D_c = 7.593$ g/cm^3, crystal size $0.10 \times 0.11 \times 0.07$ mm^3, $\mu = 44.82$ mm^{-1}, $\theta_{max} = 31°$, independent reflections 291 ($R_{int} = 0.1108$), data/restraint/parameters 291/0/22, final $R(F) = 0.0312$, $wR(F^2) = 0.0642$. Atomic coordinates (x, y, z) and equivalent isotropic displacement parameters: Ba1 (0, 0, $^1/_4$), 0.0076(2) Å^2; Ba2 ($^1/_3$, $^2/_3$, 0.91276(6)), 0.0085(2) Å^2; Li (0, 0, 0), 0.007(6) Å^2; Os ($^1/_3$, $^2/_3$, 0.15792(3)), 0.0049(2) Å^2; O1 (0.4885(7), 0.9770(10), $^1/_4$), 0.007(2) Å^2; O2 (0.1763(5), 0.3530(10), 0.4136(4)), 0.010(1) Å^2.

(31) Crystal data for $Ba_3NaOs_2O_9$: formula $Ba_3NaOs_2O_9$, MM = 959.41 g/mol, hexagonal, space group $P6_3/mmc$, $a = 5.8858(1)$ Å, $b = 5.8858$ (1) Å, $c = 14.3451(5)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$, $V = 430.37(2)$ Å^3, $Z = 2$, $T = 293$ K, $\lambda = 0.71073$ Å, $D_c = 7.404$ g/cm^3, crystal size $0.12 \times 0.08 \times 0.05$ mm^3, $\mu = 43.013$ mm^{-1}, $\theta_{max} = 42°$, independent reflections 648 ($R_{int} = 0.0395$), data/restraint/parameters 648/0/22, final R1(all data) = 0.0354, wR2(all data) = 0.0793. Atomic coordinates (x, y, z) and equivalent isotropic displacement parameters: Ba1 ($^2/_3$, $^1/_3$, 0.0883(1)), 0.012(1) Å^2; Ba2 (0, 0, $^1/_4$), 0.010(1) Å^2; Na (0, 0, 0), 0.011(1) Å^2; Os ($^1/_3$, $^2/_3$, 0.1611(1)), 0.006(1) Å^2; O1 (0.1808(5), 0.3617(11), 0.0910(4)), 0.012(1) Å^2; O2 (0.0206(16), 0.5103(8), 1/4), 0.012(1) Å^2.

(32) Kim, S.-J.; Smith, M. D.; zur Loye, H.-C. Unpublished results.

(33) Burbank, R. D.; Evans, H. T. *Acta Crystallogr.* **1948**, *1*, 330.

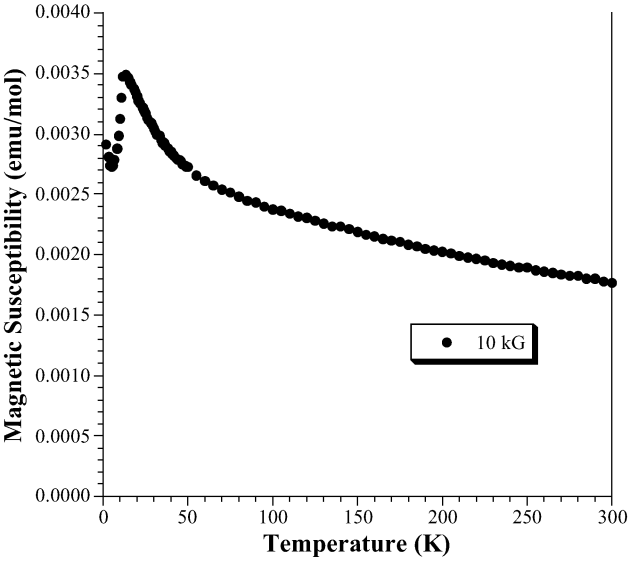

Figure 2. Temperature dependence of the magnetic susceptibility of loose crystals of $Ba_3LiOs_2O_9$ at an applied field of 10 kG. A diamagnetic correction of the atoms using Pascal's constants was applied to the data.

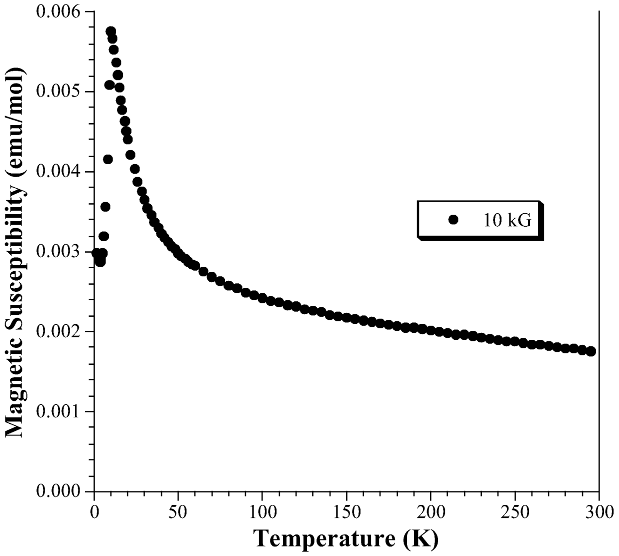

Figure 3. Temperature dependence of the magnetic susceptibility of loose crystals of $Ba_3NaOs_2O_9$ at an applied field of 10 kG. A diamagnetic correction of the atoms using Pascal's constants was applied to the data.

such as +5, +6, or +7.[16,20,21,25] The Os−O distance measuring ~2.03 Å is typical for this set of M−O separations in triple perovskites. Interestingly, the Os−Os interatomic distances of 2.6053(6) and 2.5490(8) Å for the lithium and sodium analogues, respectively, are noticeably shorter than the Os−Os distances in osmium metal (2.675 Å), favoring metal−metal interactions.

Using batches of single crystals, the magnetic susceptibility[34] of these new triple perovskites was investigated. The temperature dependence of the ZFC magnetic susceptibility of $Ba_3LiOs_2O_9$ is shown in Figure 2. At low temperatures, there is an increase in the susceptibility to a maximum at 13 K followed by a decrease in susceptibility, indicative of antiferromagnetic correlations. There is a beginning of a second magnetic transition at 5 K, below which the susceptibility begins to increase again. Fitting the high temperature portion of the susceptibility data (150 K $\leq T \leq$ 300 K) to the Curie−Weiss law yields a Curie constant of 1.403 emu·K·mol^{-1} with $\mu_{\text{eff}} = 3.34\ \mu_B$ and $\theta = -490$ K. This very large, negative Weiss constant suggests strong short-ranged osmium−osmium interactions within the face-sharing octahedra, while the downturn in the susceptibility at 13 K is most likely caused by long range magnetic interactions. The effective moment is significantly lower than the theoretical spin only moment for an Os(V/VI) system of 4.78 μ_B, which is most likely a result of spin−orbit coupling in the osmium.

The temperature dependence of the ZFC magnetic susceptibility for $Ba_3NaOs_2O_9$ is shown in Figure 3. Similar to that of the lithium analogue, there is an increase in susceptibility at low temperatures to a maximum at 10 K whereupon the susceptibility decreases and levels out at 6 K. Here also, the large negative Weiss constant of $\theta = -462$ K suggests strong short-ranged osmium−osmium interactions within the face-sharing octahedra, while the downturn in the susceptibility at 10 K is most likely caused by long-range magnetic interactions. Fitting the high-temperature portion of the susceptibility data (150 K $\leq T \leq$ 300 K) yields $C = 1.33$ emu·K·mol^{-1} with $\mu_{\text{eff}} = 3.25\ \mu_B$. Again, the effective moment is considerably lower than the theoretical spin only moment.

It is our belief that this method for preparing single crystals of osmates is quite general, and hence, work toward the flux growth of other complex osmates is underway.

Acknowledgment. Financial support from the National Science Foundation through Grant DMR:0134156 is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic information for $Ba_3LiOs_2O_9$ and $Ba_3NaOs_2O_9$ in CIF format. Details of the X-ray structure determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

IC026124P

---

(34) Magnetic measurements: The magnetic susceptibility of $Ba_3MOs_2O_9$ (M = Li, Na) was measured on samples of loose single crystals using a Quantum Design MPMS XL SQUID magnetometer. Temperature dependence measurements were taken at a field of 10 kG.