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Rapid communication

Hydroxide flux synthesis and crystal structure of the ordered palladate, $LuNaPd_6O_8$

Samuel J. Mugavero III, Mark D. Smith, Hans-Conrad zur Loye*

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, USA

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Abstract

We report the single crystal structure of $LuNaPd_6O_8$ grown from a sodium hydroxide flux. The utilization of a hydroxide flux has led to the preparation of the first ordered substitution of a lanthanide metal and an alkali metal on the *A*-site in a platinum group oxide and the first palladate to contain both a lanthanide metal and an alkali metal. The 1:1 ordered substitution of Lu^{3+} and Na^+ in place of the commonly observed divalent cation leads to slabs of LuO_8 and NaO_8 cubes bridged together by PdO_4 square planes. The compound crystallizes in the cubic space group *Pm*-3 (#200) with $a = 5.72500(10)$ Å and is structurally related to other cubic palladium oxides.

Keywords: Palladium; Lanthanide; Hydroxide flux; Single crystal

Oxides containing platinum group metals have been studied and characterized for many years and are represented by a multitude of new materials with diverse structures and exhibiting a wide range of properties [1–5]. Within this group, complex palladium oxides, containing palladium in either the +2 or +4 oxidation state, are only sparsely represented. The oxidation state of palladium in these oxides is heavily dependant upon the method of synthesis. For example, divalent palladium compounds such as the ternary alkaline-earth palladates Sr_2PdO_3, $SrPd_3O_4$, and $CaPd_3O_4$ [6] and the rare-earth palladates Ln_4PdO_7 ($Ln =$ lanthanide) [7–10] and $La_2Pd_2O_5$ [8–10] have been synthesized using traditional high-temperature solid-state techniques. Although not as common as ternary palladates, a number of quaternary phases are known, for example, the alkaline-earth palladate $CaBa_2Pd_3O_6$ [11] and the rare-earth palladates $BaPdLn_2O_5$ ($Ln =$ lanthanide) [12], which were isolated from a $BaCl_2$ flux. When palladates with higher oxidation states are desired, high-pressure techniques have been employed resulting in the synthesis of mixed valent palladates, such as $LnPd_2O_4$ ($Ln =$ lanthanide) [13,14], trivalent palladates, such as the $LaPdO_3$ perovskite, [15] and tetravalent palladates, such as the 2-H perovskite-related oxides Ca_4PdO_6 and Sr_4PdO_6 [16], the pyrochlores $Ln_2Pd_2O_7$ ($Ln =$ lanthanide) [17], and the inverse spinel Zn_2PdO_4 [18]. High-pressure techniques are one example that illustrates how utilizing a different synthetic technique can result in the preparation of a new material.

We have been studying the reactivity of lanthanide and platinum group metals in alkali metal hydroxide fluxes as a means for growing high quality single crystals of new oxide materials. Several years ago, we reported the hydroxide flux synthesis and subsequent crystal growth of $SrPd_3O_4$ and $CaPd_3O_4$ [19]. Since then our investigation of hydroxide fluxes has led to the crystal growth and discovery of many new oxides of both known and novel structure types, including the double perovskites, $Ln_2MM'O_6$ ($Ln =$ La–Eu; $M =$ Li, Na; $M' =$ Ir, Ru, Os) [2,20–24], perovskite-related oxides, $La_{2.5}K_{1.5}IrO_7$ [25] and $La_9RbIr_4O_{24}$ [1] and the defect fluorites, Ln_3MO_7 ($Ln =$ Sm–Gd; $M =$ Ru, Os) [26,27].

In an effort to further explore the chemistry of palladium in hydroxide fluxes we have succeeded in growing high quality single crystals of $LuNaPd_6O_8$ from a sodium hydroxide flux. The ability to dissolve both lanthanide and platinum group metals in sodium hydroxide fluxes has

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*Corresponding author. Fax: +1 803 777 8508.
E-mail address: ZurLoye@mail.chem.sc.edu (H.-C. zur Loye).

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been previously demonstrated [20,22–24,26,27] therefore, sodium hydroxide was chosen as the flux for use with our reagents. Although many platinum group metal oxides have been prepared from hydroxide fluxes, palladates remain relatively unexplored. This compound is of interest because it not only represents a rarely reported synthetic approach for preparing complex palladium oxides but also because it is, to the best of our knowledge, the first example of a platinum group oxide with an ordered substitution of a lanthanide and an alkali metal in place of a divalent alkaline-earth metal.

$LuNaPd_6O_8$ crystallizes in the cubic space group *Pm*-3 with lattice parameter $a = 5.72500(10)$ Å and is structurally related to $SrPd_3O_4$ [6,19,28], $CaPd_3O_4$ [6,19,29], and $NaPt_3O_4$ [30]. The cubic morphology of a typical single crystal of $LuNaPd_6O_8$ is shown in the SEM micrograph in Fig. 1. The arrangement of the lutetium and the sodium cations in the crystal structure of $LuNaPd_6O_8$ is best described as being of the caesium chloride type. Eight lutetium atoms are arranged in a cubic coordination environment, each located at a corner of the cubic unit cell. At the centre of the unit cell, one sodium atom sits in a cubic coordination environment and corner-shares to the eight LuO_8 cubes as shown in Fig. 2. The palladium atoms are in a square planar coordination environment, which corner-share with each other and simultaneously edge-share with the LuO_8 and NaO_8 cubes to create an infinite, ordered network as shown in Fig. 3. The Lu–O and Na–O bond lengths of the LuO_8 and NaO_8 cubes are 2.371(5) and 2.587(5) Å, respectively. The Pd–O bond length is 2.0271(3) Å, the two *cis*-O–Pd–O bond angles are 85.0(2)° and 94.9(2)°, while the *trans*-O–Pd–O bond angle is 176.3(2)°, each deviating slightly from the ideal square planar geometry. The palladium atom is shifted 0.067(4) Å out of the plane of the oxygen atoms. This deviation from

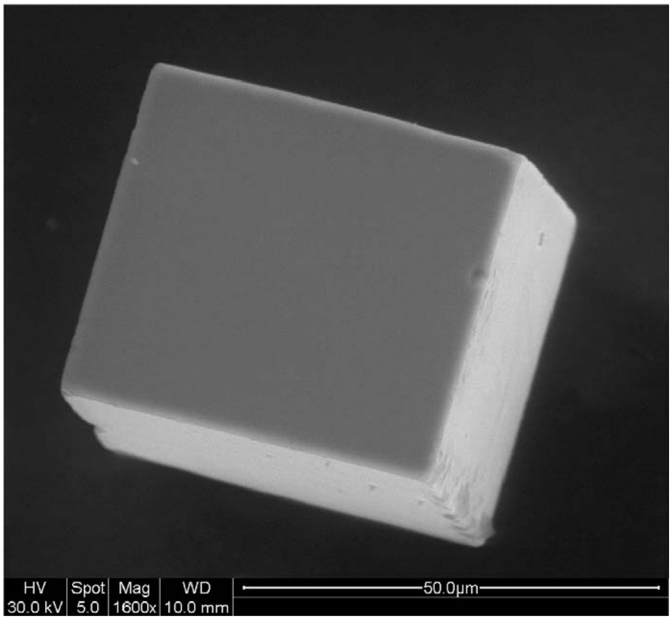

Fig. 1. Scanning electron micrograph of $LuNaPd_6O_8$.

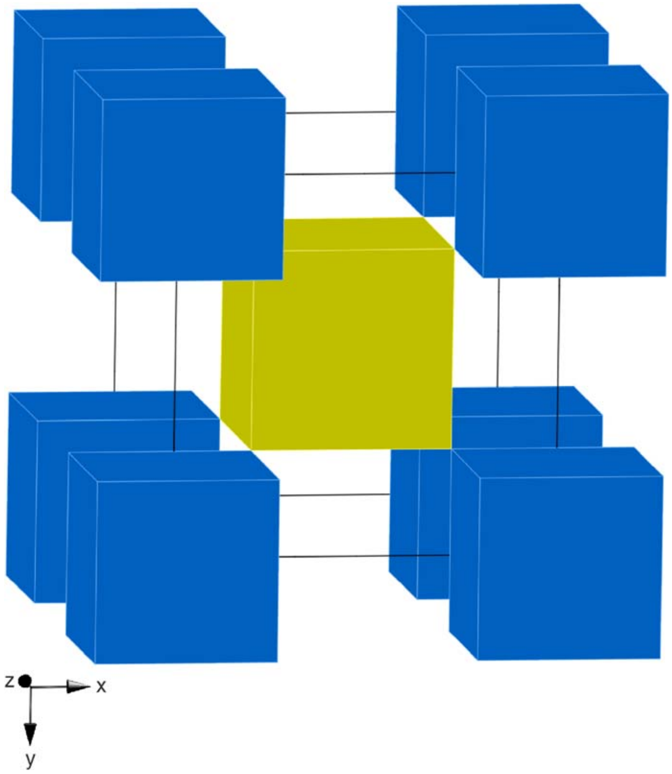

Fig. 2. Corner-shared connectivity of LuO_8 cubes (dark grey) and NaO_8 cubes (light grey) viewed along the *z*-direction in the unit cell of $LuNaPd_6O_8$.

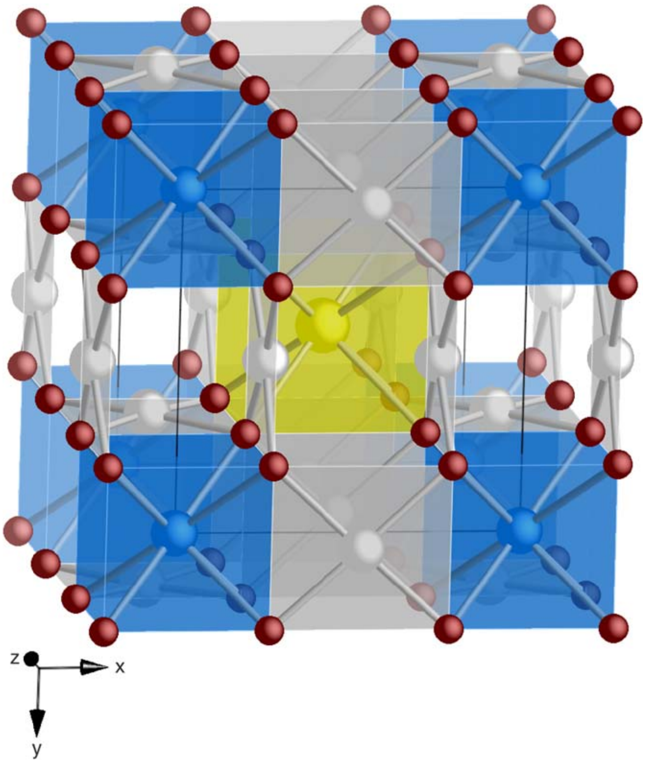

Fig. 3. Unit cell of $LuNaPd_6O_8$ viewed along the *z*-direction. The Pd^{2+} cations (light grey) reside in a square planar coordination environment and connect the slabs of LuO_8 (dark grey) and NaO_8 (medium grey) cubes. Oxygen atoms are represented as black spheres.

ideality can be attributed to the fact that the corner-shared NaO_8 and LuO_8 cubes are of different dimensions, which causes the PdO_4 square planes to be slightly puckered.

$LuNaPd_6O_8$ differs from the APd_3O_4 (A = Ca, Sr) palladates [6,19,29] in that, in place of two Ca^{2+} or Sr^{2+} cations, we observe a 1:1 ordered arrangement of Lu^{3+} and Na^{+} cations. As a result of this ordered cation substitution, the APd_3O_4 unit cell effectively doubles to $A_2Pd_6O_8$. The total charge on the A-site becomes +4 and is maintained by one Lu^{3+} and one Na^{+} cation. The substitution of a lanthanide and a sodium cation for an alkaline-earth cation, such as strontium or calcium, has been demonstrated in other systems, for example, in the 2H-perovskite-related oxides described by the general formula $A_{3n+3m}A'_nB_{3m+n}O_{9m+6n}$ [31–33]. Typically, the A-site cation is an alkaline-earth metal as observed in the A_4BO_6-type 2H-perovskites Sr_4PtO_6 [34], Sr_4PdO_6 and Ca_4PdO_6 [16] or the $A_3A'BO_6$-type, Ca_3MgIrO_6 [35]. In this family of oxides, $(NaLa_2)NaPtO_6$ was the first example in which an A-site substitution of an alkaline-earth metal cation by a lanthanide and an alkali metal cation had been accomplished [36]. Since then several other A-site substituted 2H-perovskite-related oxides with the general formula $(A_{3-x}Na_x)NaBO_6$ (A = La, Pr, Nd; B = Rh, Pt) have been reported [37]. In these compounds, the Ln^{3+} and Na^{+} cations in an eight-coordinate environment are disordered on the A-site. Interestingly, while the charge difference between the constituent lanthanide and sodium is significant, it does not appear to be sufficient to cause cation ordering. Typically, ordering occurs when there is a large size and/or charge difference between the cations. Size considerations show that in an eight-coordinate environment, La^{3+}, Pr^{3+}, and Nd^{3+} (1.16–1.109 Å) [38] are very close in size to Na^{+} (1.18 Å) [38], which potentially promotes cation mixing on the same site. In $LuNaPd_6O_8$, on the other hand, the substitution of a lanthanide metal and alkali metal in place of an alkaline-earth metal, leads to an ordered substitution arrangement of Lu^{3+} and Na^{+} for Sr^{2+} or Ca^{2+} cations on the A-site. Apparently, Lu^{3+}/Na^{+} ordering is observed because of their size and charge differences, specifically the difference in size between the Lu^{3+} (0.977 Å) [38] and the Na^{+} (1.18 Å) [38] cation is large and, most likely, the dominant contributor for ordering. We can further examine the structural relationship of $LuNaPd_6O_8$ and the APd_3O_4 (A = Ca, Sr) phases if we compare the Pd–O, Lu–O, and Na–O bond lengths in $LuNaPd_6O_8$ with the Ca–O and the Pd–O bond lengths in the $CaPd_3O_4$ phase. In both compounds, the Pd–O bond lengths are virtually identical, 2.0271(3) Å in $LuNaPd_6O_8$ and 2.0278(1) Å in $CaPd_3O_4$. The Lu–O and Na–O bond lengths in $LuNaPd_6O_8$ are 2.371(5) and 2.587(5) Å, while the Ca–O bond length in $CaPd_3O_4$ is 2.4836(1) Å. Interestingly, if we consider the average of the Lu–O and Na–O bond lengths (2.479(5) Å), we see that this distance is almost identical to the Ca–O bond length (2.4836(1) Å) again demonstrating why Lu^{3+} and Na^{+} can effectively substitute for Ca^{2+}. Work is currently underway to grow single crystals of analogous $LnNaPd_6O_8$ (Ln = small lanthanide) phases, as well as to investigate the reactivity of palladium in other alkali metal hydroxides. A full report of the synthesis and characterization of analogous $LnNaPd_6O_8$ phases will be presented in the near future.

Supplemental information: Experimental details and relevant crystallographic information is included as Supplemental Information. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; E-mail: crystdata@fiz-karlsruhe.de) on quoting the depository number CSD-416619.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.07.025.

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