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Crystal Growth of Novel Lanthanide-Containing Platinates $K_4[Ln_6Pt_2O_{15}]$ (Ln = La, Pr, Nd, Sm) with a Unique Framework Structure

Hans-Conrad zur Loye,*,† Tara J. Hansen,† Qingbiao Zhao,† Samuel J. Mugavero III,† Ray L. Withers,‡ and Mark D. Smith†

Department of Chemistry and Biochemistry, University of South Carolina,
Columbia, South Carolina 29208, and Research School of Chemistry,
The Australian National University, Canberra ACT 0200, Australia

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Crystals of a new family of lanthanide-containing platinum oxides with a unique framework structure were grown out of molten hydroxide fluxes. The structure consists of a crystallographically well-behaved $[Ln_6Pt_2O_{15}]^{4-}$ framework permeated by channels filled with disordered atoms along the [100] and equivalent directions. Open-channel structures are rare in oxides and apparently unknown in platinate chemistry.

Oxides containing platinum group metals have been extensively studied because of their interesting physical properties and the existence of a wide variety of possible structure types.[1−9] Typically, these compounds are prepared by conventional solid-state synthesis of the constituent elements. To synthesize new compositions, however, other synthetic techniques are often necessary to aid in the discovery of these compositions and to prepare compounds exhibiting new structure types. The use of molten salts for the growth of single crystals is well established,[6,7,10,11] and our group has investigated, in particular, the use of alkali-metal hydroxides[1,2,5,13−19] and carbonates[12] as fluxes to aid in the incorporation of lanthanides and platinum group metals into a wide range of new metal oxide structures.

Recently, we reported three new rare-earth-containing platinates, La_3NaPtO_7, Nd_3NaPtO_7, and La_4PtO_7, grown as single crystals in Na_2CO_3 and K_2CO_3 carbonate fluxes.[20] As expected, when the reactive Na_2CO_3 flux was used, the Na^+ cations incorporated into the Ln_3NaPtO_7 (Ln = La, Nd) structure, as Na^+ (1.18 Å; eight-coordination environment) and La^{3+} and Nd^{3+} cations (1.16 and 1.11 Å; eight-coordination environment), are similar in size and readily substitute for one another. The larger K^+ cations from the K_2CO_3 flux, on the other hand, did not incorporate into the La_4PtO_7 structure because the size difference between K^+ (1.51 Å; eight-coordination environment) and La^{3+} was too

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

† University of South Carolina.

‡ The Australian National University.

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(23) Crystal data for $K_4Ln_6Pt_2O_{15}$ (Ln = La, Pr, Nd, Sm), respectively: $Im\bar{3}m$, a = 12.1552(1), 11.9610(1), 11.9083(1), and 11.7983(1), Å; R1 [F, $I > 2\sigma(I)$] = 0.0251, 0.0251, 0.0265, 0.0563; wR2 [F^2, $I > 2\sigma(I)$] = 0.0479, 0.0626, 0.0507; 0.1058; GOF = 1.129, 1.184, 1.233, 1.320.

10.1021/ic801789e CCC: $40.75

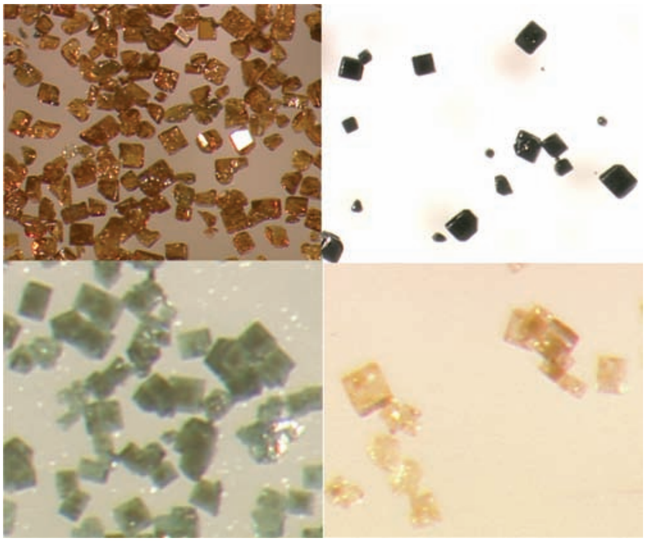

Figure 1. Optical images of $K_4[La_6Pt_2O_{15}]$ (top left), $K_4[Pr_6Pt_2O_{15}]$ (top right), $K_4[Nd_6Pt_2O_{15}]$ (bottom left), and $K_4[Sm_6Pt_2O_{15}]$ (bottom right). The crystals are approximately 0.1−0.2 mm in size.

great. Similarly, crystals of $(NaLa_2)NaPtO_6$ were grown using a reactive NaOH flux, resulting in a 2H perovskite-related oxide.[1] However, when the same reaction conditions were repeated with KOH as the flux, crystals with the approximate composition $K_4[Ln_6Pt_2O_{15}]$ (Ln = La, Pr, Nd, Sm) were formed. These oxides crystallize in an unusual 3D channel structure, similar to what is found for zeolites and quite unexpected for platinum oxides. While the potassium from the flux is incorporated into the crystal, it is not located in the framework itself but rather in the channels of the framework, where it provides charge balance.

Crystals of the $K_4[Ln_6Pt_2O_{15}]$ (Ln = La, Pr, Nd, Sm) series were grown from molten potassium hydroxide fluxes. For the synthesis of $K_4[La_6Pt_2O_{15}]$ and $K_4[Nd_6Pt_2O_{15}]$, KF was added as a mineralizer. In the case of $K_4[La_6Pt_2O_{15}]$, as the ratio of KF to KOH was increased from 1:9 to 2:3, the size of the crystals decreased, while for $K_4[Nd_6Pt_2O_{15}]$, the addition of 10 wt % KF resulted in an increase in crystal formation. The addition of KF to the rest of the members of the series had little or no effect on the crystals produced. The crystals formed as cubes varying in color from dark red ($K_4[La_6Pt_2O_{15}]$), black ($K_4[Pr_6Pt_2O_{15}]$), blue-green ($K_4[Nd_6Pt_2O_{15}]$), to yellow ($K_4[Sm_6Pt_2O_{15}]$) (Figure 1). Crystals can be obtained at temperatures as low as 600 °C and as high as 750 °C; however, the crystal quality is best when a growth temperature of 650 °C is used.

Single-crystal X-ray diffraction revealed that $K_4[Ln_6Pt_2O_{15}]$ (Ln = La, Pr, Nd, Sm) crystallizes in a 3D framework structure, containing disordered cations and anions in the channels (Figure 2). Elemental analysis by energy-dispersive spectroscopy (EDS) consistently gave a sample composition of approximately $K_4[Ln_6Pt_2O_{15}]$, while elemental analysis indicated a composition of approximately $(Ln_{0.8}O_{2.8})(K_4[Ln_6Pt_2O_{15}])$; it is possible that some O atoms in the channels are, in fact, hydroxide ions, thus achieving charge balance.

High-quality crystals of $K_4[Ln_6Pt_2O_{15}]$ (Ln = La, Pr, Nd, Sm) were used for the structure determination. All reflections could be indexed to a body-centered-cubic unit cell with *a* = 12.1552(1) Å (La), 11.9610(1) Å (Pr), 11.9083(1) Å (Nd), and 11.7983(1) Å (Sm). Examination of the reflection data showed no systematic absences other than those caused by the lattice centering. A reasonable structural model was obtained by direct methods in the space group $Im\bar{3}m$ (No. 229). The structure consists of a crystallographically well-behaved Ln−Pt−O framework permeated by channels of disordered atoms along [100] and equivalent directions. The asymmetric unit of the framework consists of one rare earth, one platinum, and two oxygen sites. These atoms were successfully refined with anisotropic displacement param-

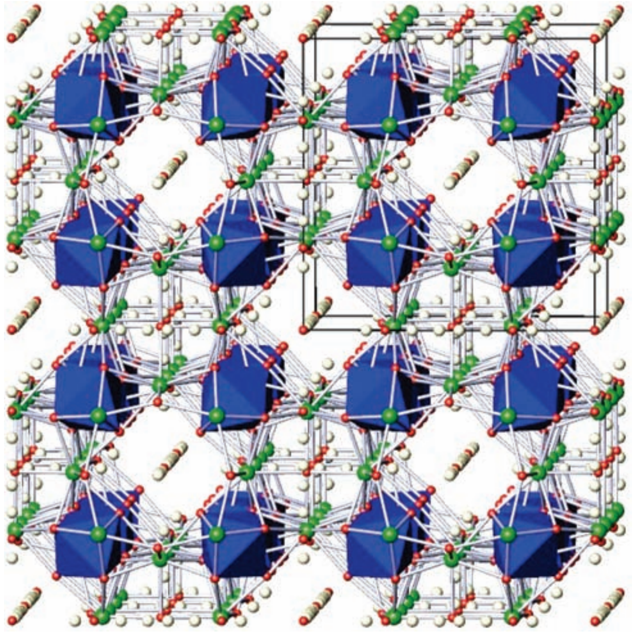

Figure 2. Structure of the $K_4[Ln_6Pt_2O_{15}]$ framework depicting the disordered K ions residing in the channels. PtO_6 octahedra are shown in blue, La atoms in green, O atoms in red, and K atoms in gray.

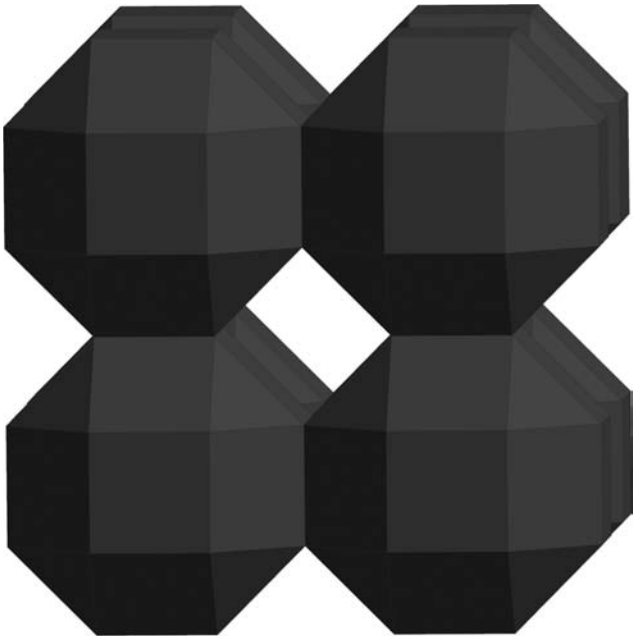

Figure 3. Arrangement of eight sodalite-like cages in $K_4[Ln_6PtO_{15}]$. The cages are connected via common rare-earth cations in an arrangement that generates a 3D channel structure. The apexes of the gray building blocks identify the locations of the Ln ions.

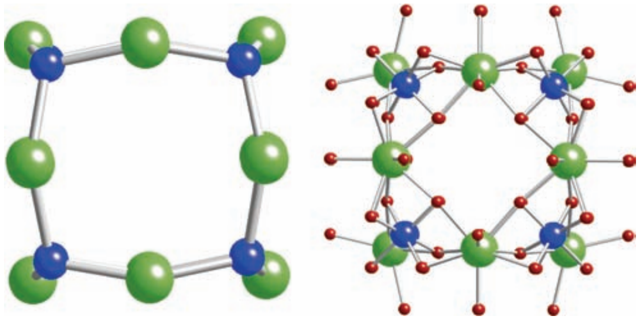

Figure 4. (left) Structure of the $Ln_{12}Pt_8$ core of the main building block. The Pt atoms (blue) are at the corner of a cube. The 12 Ln atoms (green) bridge the Pt atoms along the 12 cube edges. (right). Structure of the $Ln_{12}Pt_8O_{72}$ cluster with Pt (blue), Ln (green), and O (red). The 24 outer O atoms (6 × 4) are shared between adjacent clusters.

eters. This 3D Ln−Pt−O framework is anionic, with composition and charge of $[Ln_6Pt_2O_{15}]^{4-}$. Within the channels in the framework, an essentially continuous distribution of electron density was observed. The channels must contain some K ions based on the qualitative elemental analysis (EDS) results, which consistently indicated the presence of four K atoms or possibly other positively charged species (e.g., H^+, La^{3+}). Unfortunately, because of the extreme disorder of the ions occupying the channels, the composition and precise structural features inside these channels are undetermined from the X-ray single-crystal analysis. The general refinement strategy to deal with this disorder is covered in detail in the Supporting Information.

The $[Ln_6Pt_2O_{15}]^{4-}$ framework consists of linked building blocks that are reminiscent of sodalite cages (Figure 3).

Each such cage contains 8 PtO_6 octahedra that are surrounded by 36 Ln atoms, 24 of which (6 × 4) are shared with the 6 surrounding cages. This leaves a cubic $Ln_{12}Pt_8$ core (Figure 4) consisting of 8 Pt atoms at the corners and 12 Ln atoms roughly in the middle of each cube edge, thereby bridging adjacent Pt atoms. In the core, each Pt is in an octahedral PtO_6 environment, while each Ln is in a distorted bicapped trigonal-prismatic LnO_8 coordination environment. The inside of each channel is “lined” with O atoms that coordinate to the cations in the channel, which provide charge balance for the $[Ln_6Pt_2O_{15}]^{4-}$ framework (Figure 4). The Ln−Pt−O cages connect in three dimensions to form channels in the *a*, *b*, and *c* directions; at each of the six junctions, four Ln and four O atoms are shared.

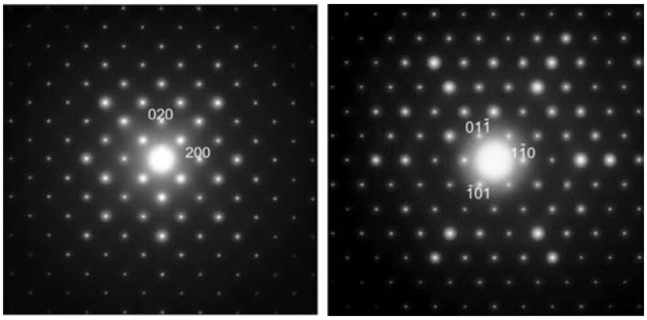

Figure 5. Electron diffraction patterns for $K_4[La_6Pt_2O_{15}]$ demonstrating the cubic symmetry and the absence of any type of superstructure and of any incommensurate modulation.

To further investigate the crystals, electron diffraction studies were carried out to confirm the cubic symmetry and to establish that the crystals are not incommensurately modulated. The electron diffraction patterns (Figure 5) confirm the cubic nature of $K_4[La_6Pt_2O_{15}]$ and, consistent with the single-crystal X-ray diffraction data, demonstrate the absence of any superstructure or structural modulation.

The success in preparing crystals of this new structural family provides additional impetus to further explore the Ln−Pt−O phase space, particularly with the smaller rare-earth cations, to see if related structural motifs can be obtained. Furthermore, exploring the synthesis of the sodium and lithium analogues, with perhaps improved cation order in the channels, is an obvious goal.

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Supporting Information Available: X-ray crystallographic data in CIF format, synthesis, and crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

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