# Gohil S. Thakur, Hans Reuter, Claudia Felser and Martin Jansen\* A new stacking variant of Na, Pt(OH),

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**Abstract:** A new stacking variant of sodium hexa-hydroxo platinate(IV), Na<sub>2</sub>Pt(OH)<sub>6</sub>, was synthesized and its structure elucidated through X-ray diffraction. The new polymorph was prepared by direct reaction of PtO<sub>2</sub> with an excess of NaOH solution applying elevated oxygen pressure at 300°C. The structure consists of layers of edge sharing Pt(OH)<sub>6</sub> and Na(OH)<sub>6</sub> octahedra. These layers are separated by an edge-to-edge distance of ~2.4 Å. The packing of the hydroxide ions corresponds to the *hcp* sequence, the title compound thus may be regarded a cation ordered variant of the Brucite structure type. During heating above  $T \sim 300^{\circ}$ C all constitutional water is released, and anhydrous Na<sub>2</sub>PtO<sub>3</sub> remains as the solid residue.

**Keywords:** crystal structure determination; hydrothermal synthesis; platinate(IV).

### **1** Introduction

Hydrothermal synthesis is among the most prolific and versatile methods in use for the preparation of solid oxide materials [1–3]. Going beyond the original definition of the term, this approach does no longer exclusively imply a supercritical state of the solvent [1], and the field of applicability has been widened significantly by taking advantage of tuning the viscosity and the hydroxide activity between concentrated to diluted aqueous solutions of hydroxides and molten hydroxides. For cases where water is added in order to adjust the solution properties of a melt, the term "hydroflux" has come into use [4]. Obviously, such procedures of preparing solid materials require to control a considerable number of experimental

parameters, and it is of particular importance to comply the technical approach with the chemical properties of the constituents of the targeted compound. Fully deprotonated oxides can be obtained from dilute alkaline solutions, in particular if the metals involved form less soluble hydroxides, or do not form hydroxides at all, which commonly holds true for noble metals. Ag<sub>2</sub>PbO<sub>2</sub> represents such an example; it can be easily obtained phase pure and as large crystals from ammoniated solutions upon addition of caustic soda lye [5].

When exploring the ternary system Ag/Pt/O at elevated oxygen pressure and under alkaline (NaOH) hydrothermal conditions, in the present work surprisingly – along with a desired deprotonated silver oxo-platinate – a sodium platinum(IV) hydroxo complex,  $Na_2Pt(OH)_6$ , had also crystallized. Its composition was confirmed by X-ray crystal structure analyses, and the hydrothermal synthesis conditions were eventually optimized, starting from PtO<sub>2</sub> and NaOH, exclusively.

 $Na_2Pt(OH)_6$  as such was first reported in 1905 [6], and its crystal structure was determined from powder X-ray [7] and neutron diffraction data (collected on a deuterated sample) [8]. The structure analysis based on neutron data enabled to localize the deuterium atoms and to assign the correct space group, which was confirmed later by X-ray single crystal studies [9].

Under the synthesis conditions applied in this work, reproducibly a new polymorph has been obtained, which is a particular stacking variant of the known polymorph [7–9]. Reducing the title compound to its binary aristotype, AX<sub>2</sub>, it becomes evident that the basic structural organization of both the modifications corresponds to the CdI<sub>2</sub> type of structure, featuring different cation ordering schemes in the different polymorphs. Due to the higher temperature applied during synthesis of the title compound, compared to the earlier reported, we regard it a high temperature modification and thus assign the prefixes according to the conventions,  $\alpha$ -Na<sub>2</sub>Pt(OH)<sub>6</sub> [7–9] and  $\beta$ -Na<sub>2</sub>Pt(OH)<sub>6</sub>, this work.

### 2 Experimental

#### 2.1 Crystal growth

Millimeter sized single crystals of  $Na_2Pt(OH)_6$  were grown by heating finely powdered PtO<sub>2</sub> and 1–2 mL of 3–5 M NaOH

**Dedicated to:** Professor Bernt Krebs on the occasion of his 80<sup>th</sup> birthday.

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solution at 300°C under high oxygen pressure. Commercially purchased powder of PtO, was used without further purification (Sigma-Aldrich 99.9%). 0.189 g of PtO, fine powder was placed in a gold crucible, flame sealed at one end, and 1.5 mL of 5 M NaOH was added on top of it. The crucible was mechanically crimped and placed inside a 20 mL stainless steel autoclave [10]. 11.2 mL of liquid oxygen was condensed into it. The said amount of oxygen generates about 2500 bars of pressure at the given temperature. After the complete condensation of oxygen, the top of the autoclave vessel was sealed by a copper bullet and fastened to make it gas-tight. The assembly was then placed in a vertical programmable furnace at  $T=300^{\circ}$ C for 4 days after which it was slowly cooled to room temperature over 24 h. Crystals were separated by means of vacuum filtrations and subsequently cleaned from any residues by ultra-sonication in alcohol.

#### 2.2 Powder X-ray diffraction

Laboratory powder X-ray diffraction (PXRD) studies at RT were performed with a HUBER G670 imaging plate Guinier camera with CuK $\alpha_1$  radiation ( $\lambda = 1.5406$  Å), in a 2 $\theta$  range of 5 – 85°. Profile refinement, a le Bail fit, was carried out with the program TOPAS (Bruker AXS; version 4.2.0.2) [11]. The refined parameters were scale factor, zero point of  $\theta$ , sample displacement (mm), and background as a Chebychev polynomial of 40<sup>th</sup> degree and 1/x function, crystallite size, microstrain, and cell constants.

#### 2.3 Single-crystal X-ray diffraction

Ambient-temperature single-crystal diffraction data of an irregularly shaped crystal fragment of appropriate size were collected on a Bruker Kappa APEX II CCD-based 4-circle X-ray diffractometer using graphite-monochromatized Mo*K* $\alpha$  radiation ( $\lambda$  = 0.71073 Å) of a fine focus molybdenum-target X-ray tube operating at 50 kV and 30 mA. Collection and reduction of data were carried out with the Bruker Suite software package [12]. Intensities were corrected for absorption effects semi-empirically from equivalents via SADABS [13]. The structure was solved by Direct Methods and refined by full-matrix least-squares fitting on  $F^2$  with the SHELXL software package [14]. Systematic absence conditions *hh2hl* only present for l=2n are consistent with the centrosymmetric space group  $P\overline{3}1c$  (No. 163) [15]) and the non-centrosymmetric one P31c (No. 159 [15]). Consequently, structure refinements were performed in both space groups, giving rise to very similar cation-anion

arrangements with the exception of disordered Na atoms in the centrosymmetric one arising from a crystallographic mirror plane through the Pt atoms. Finally, the absolute structure parameter of 0.016(11) convinced us to use the non-centrosymmetric structure model. Structure plots were drawn using DIAMOND [16].

Both hydrogen atoms were localized in a difference Fourier synthesis. Their positions were initially refined while constraining the O–H distances to 0.96 Å, and finally they were allowed to ride on the corresponding oxygen atom. During all final calculations, the lattice parameters as obtained from X-ray powder pattern refinement were used.

Crystallographic data, details of the data collection and of the structure refinement are given in Table 1, atomic coordinates, anisotropic and equivalent isotropic displacement parameters in Table 2, and bond lengths in Table 3.

Further details of the crystal structure investigation may be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata(at)fiz-karlsruhe(dot)de, on quoting the deposition number CSD-434726.

Table 1:	Crystal data and number	s pertinent to	data coll	ection	and
structure	e refinement of $\beta$ -Na,Pt(O	H) <sub>4</sub> .			

Empricial formula	Na <sub>2</sub> O <sub>6</sub> H <sub>6</sub> Pt				
M <sub>r</sub>	343.11				
Cryst. size, mm <sup>3</sup>	$0.163 \times 0.111 \times 0.083$				
Temperature, K	296(2)				
Crystal system	Trigonal				
Space group	<i>P</i> 31 <i>c</i> (no. 159)				
<i>a</i> , Å	5.8075(1)				
<i>b</i> , Å	9.3931(2)				
<i>V</i> , Å <sup>3</sup>	274.36(1)				
Ζ	2				
$D_{\text{calcd}}$ , g cm <sup>-3</sup>	4.153				
$\mu$ (Mo $K\alpha$ ), mm <sup>-1</sup>	25.7				
<i>F</i> (000), e	308				
hkl range	$-8 \le h \le 8, -8 \le k \le 8, -14 \le l \le 14$				
heta range, deg	4.052-31.982				
Refl. collected/unique	30961/647				
R <sub>int</sub>	0.0467				
Completeness to $\theta$ = 31.98°, %	100				
Absorption correction	Semi-empirical from equivalents				
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>				
Data/param. refined	647/29				
$R1/wR2 [I > \sigma(I)]$	0.0190/0.0486				
R1/wR2 (all reflexions)	0.0197/0.0490				
Extinction coefficient	0.0019(6)				
<i>x</i> (Flack)	0.016(11)				
Largest diff. peak/hole, e Å-3	3.74/-1.59				

Atom	Wyckoff site	x	у	z	<b>U</b> <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	<b>U</b> <sub>12</sub>	<b>U</b> <sub>13</sub>	U <sub>23</sub>	U <sub>eq/iso</sub>
Pt(1)	2 <i>b</i>	2/3	1/3	1/2	6(1)	6(1)	6(1)	0	0	3(1)	6(1)
Na(1)	2 <i>b</i>	1/3	2/3	0.519(1)	9(1)	9(1)	24(8)	0	0	5(1)	14(2)
Na(2)	2 <i>a</i>	0	0	0.4633(7)	19(2)	19(2)	16(3)	0	0	9(1)	18(1)
0(1)	6c	0.637(2)	0.599(3)	0.378(1)	6(3)	11(4)	13(3)	1(3)	-1(3)	7(3)	9(2)
0(2)	6 <i>c</i>	0.940(3)	0.632(3)	0.621(1)	11(4)	9(4)	10(4)	-4(3)	-3(3)	5(3)	10(2)
H(1)	6 <i>c</i>	0.5501	0.4685	0.2046							40
H(2)	6 <i>c</i>	0.7986	0.6098	0.6834							40

**Table 2:** Atomic coordinates, anisotropic and equivalent isotropic displacement parameters ( $Å^2 \times 10^{-3}$ ) for  $\beta$ -Na,Pt(OH)<sub>e</sub>.

The anisotropic displacement factor exponent takes the form:  $-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)$ ,  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table 3:** Characteristic bond lengths (Å) for  $\beta$ -Na<sub>2</sub>Pt(OH)<sub>6</sub>.

Atoms	Multiplicity	Bond length		
Pt1-01	3×	1.998(13)		
Pt1-02	3×	2.018(13)		
Na1-01	3×	2.392(14)		
Na1-02	3×	2.393(13)		
Na2-01	3×	2.367(11)		
Na2-02	3×	2.477(13)		

hydrothermal conditions, while maintaining elevated oxygen pressure (~2500 bars). Pale yellow, coarse crystalline platelets with hexagonal habit and dimensions up to 5 mm across, were obtained after vacuum filtration, see Fig. 1. The filtrate appeared slightly brownish in color indicating that some unreacted ultrafine  $PtO_2$  remained in the

#### 2.4 Thermal analysis

Thermogravimetric (TGA) analyses of  $\beta$ -Na<sub>2</sub>Pt(OH)<sub>6</sub> were carried out on a Netzsch STA 449 C analyzer. Approximately 35 mg of powdered sample was placed in a corundum crucible, which was heated and cooled back at a rate of 5 K min<sup>-1</sup> in the temperature range of 25–1000°C under dynamic argon flow.

### **3** Results and discussion

A new polymorph of Na<sub>2</sub>Pt(OH)<sub>6</sub> (the  $\beta$ -phase) has been obtained from PtO<sub>2</sub> and NaOH solution (5 M) under



**Fig. 2:** le Bail fit to the laboratory powder X-ray diffraction data  $(\lambda = 1.5406 \text{ Å})$  collected at room temperature for  $\beta$ -Na<sub>2</sub>Pt(OH)<sub>6</sub>. The black and red curves correspond to experimental and calculated data, respectively; the blue line is the difference between the two, and the vertical bars correspond to the calculated Bragg peak positions.



**Fig. 1:** Photographs of the as-grown crystals of Na<sub>2</sub>Pt(OH)<sub>6</sub> on a millimeter grid.

solution. Only large crystalline aggregates were obtained in bulk quantitative yield and no polycrystalline product was observed.

A powder X-ray diffractogram of crushed crystals shows a pattern different from that of the reported Na<sub>2</sub>Pt(OH)<sub>6</sub> ( $\alpha$ -phase). From single crystal diffraction and indexing of the powder pattern a trigonal crystal system was identified, with a le Bail fit to the PXRD resulting in lattice constants of a = 5.8075(1) and c = 9.3931(2) Å, see Fig. 2. Clearly, the c parameter is twice that of the  $\alpha$ -phase, indicating a different stacking sequence in the present compound. Single crystal diffraction data allowed to identify the different cation ordering which indeed corresponds to a new stacking variant of Na,Pt(OH)<sub>c</sub>.

The title compound has a layer structure, where the hydroxide anions follow the stacking sequence of a hexagonal closest packing and the cations occupy the octahedral voids in every second spacing, see Fig. 3. Thus, the general structural organization corresponds to the CdI<sub>2</sub> type of structure, or to the chemically more closely related Brucite structure, Mg(OH)<sub>2</sub>. The cations Na and Pt form a fully ordered distribution, where according to the ratio of 2:1, the Pt(OH)<sub>6</sub> octahedra are "isolated" and share



**Fig. 3:** Projections of the crystal structure of  $\beta$ -Na<sub>2</sub>[Pt(OH)]<sub>6</sub> along [001], left, and [010], right. Pt(OH)<sub>6</sub> octahedra in gray, Na(OH)<sub>6</sub> octahedra in green.



**Fig. 4:** Crystal structure of  $Na_2Pt(OH)_6$ , details of the layer constitution (side view, same scale) showing the structural similarity, and emphasizing the violation of the crystallographic mirror plane, in the  $\alpha$ - (above) and  $\beta$ - (below) modification of  $Na_2[Pt(OH)]_6$ . In the  $\beta$ modification all non-H atoms are drawn as displacement ellipsoids on a 90% level to relate the size of the atoms in the ball-and-stick model
of the  $\alpha$ -modification (drawn according to [9]). Numbers are indicating distances (Å) of the atoms from the planes defined by the Pt atoms.



**Fig. 5:** Stacking sequence of occupied octahedral holes [Na = green, Pt = gray)] in the [AB]/*hcp* packing of oxygen atoms [red] in the  $\alpha$ - (left, according to [8, 9]) and  $\beta$ - (right) modification of Na,Pt(OH)<sub>c</sub>.



**Fig. 6:** Thermal decomposition profile of  $\beta$ -Na, Pt(OH)<sub>6</sub> (left) and PXRD data of the solid residue (right).

common edges with six surrounding distorted  $Na(OH)_6$  octahedra, see Fig. 3.

Both polymorphs contain the same slabs, as can be seen in Fig. 4. In  $\alpha$ -Na<sub>2</sub>Pt(OH)<sub>6</sub> the slabs are stacked along the *c* axis keeping the same orientation, while in  $\beta$ -Na<sub>2</sub>Pt(OH)<sub>6</sub> the layers are shifted alternatingly by a vector of 1/3, 2/3, 0, forth and back, see Fig. 5. The *c* lattice parameter for the latter is thus twice that of the reported form of  $\alpha$ -Na<sub>2</sub>Pt(OH)<sub>6</sub> [7–9] with a similar *a* parameter. The stacking sequence found for  $\beta$ -Na<sub>2</sub>Pt(OH)<sub>6</sub> implies reduced Pt–Pt repulsion compared to the  $\alpha$ -polymorph, rendering the former electrostatically favored.

The Pt atoms occupy the centers of slightly distorted  $Pt(OH)_6$  octahedra with a mean Pt–O bond length of 2.008 Å. The  $Pt(OH)_6$  octahedra are isolated from one another and are laterally surrounded by the two types of edge sharing distorted octahedra, Na1(OH)<sub>6</sub> and Na2(OH)<sub>6</sub>, in an alternating fashion.

Thermal decomposition of  $\beta$ -Na<sub>2</sub>Pt(OH)<sub>6</sub> was monitored via DTA/TGA under argon up to  $T = 1000^{\circ}$ C, see Fig. 6 (left). The compound shows practically no weight loss up to  $T = 280^{\circ}$ C above which it loses constitutional water, three H<sub>2</sub>O molecules per formula unit, as inferred from a total weight loss of ~16.4%. According to weight calculation, the bright orange/red residue corresponds to the formula Na<sub>2</sub>PtO<sub>3</sub>, as also observed in the thermal decomposition of  $\alpha$ -Na<sub>2</sub>Pt(OH)<sub>6</sub> [9]. The dip in the DTA curve at 821°C corresponds to the melting of Na<sub>2</sub>PtO<sub>3</sub>. The X-ray diffractogram of

this residue confirms the formation of  $Na_2PtO_3$  along with a small amount of Pt metal (Fig. 6, right).

### **4** Conclusions

A new stacking variant of sodium hexa-hydroxo platinate(IV) has been obtained as coarse single crystals by hydrothermal synthesis under oxygen pressure. The general organization of the atoms corresponds to the CdI<sub>2</sub>, or Mg(OH)<sub>2</sub>, type of structure where the cations Na and Pt are fully ordered. The new  $\beta$ -Na<sub>2</sub>Pt(OH)<sub>6</sub> polymorph consists of Pt(OH)<sub>6</sub> octahedra surrounded by two types of Na(OH)<sub>6</sub> octahedra in an edge sharing fashion.

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## **Graphical synopsis**

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