# $Cs_2K_2[Pt_{12}O_8(SO_4)_{12}]$: A New Oxide-Sulfate with the Cluster Anion $[Pt_{12}O_8(SO_4)_{12}]^{4-}$

Martin Pley and Mathias S. Wickleder

Institut für Reine und Angewandte Chemie, Carl von Ossietzky Universität, Postfach 2503, D-26111 Oldenburg, Germany

Reprint requests to Prof. Dr. Mathias S. Wickleder. Fax: +49 (0)441 798 3352. E-mail: mathias.wickleder@uni-oldenburg.de

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*Dedicated to Professor Wolfgang Jeitschko on the occasion of his 70th birthday*

Single crystals of $Cs_2K_2[Pt_{12}O_8(SO_4)_{12}]$ ($R\bar{3}$, $Z = 3$, $a = 1198.9(3)$, $c = 2768.9(9)$ pm, $R_{all} = 0.1154$) were obtained by the reaction of $Cs_2[Pt(NO_2)_4]$, $K_2[Pt(NO_2)_4]$ and conc. sulfuric acid at 400 °C in a sealed glass ampoule. The compound contains the cluster anion $[Pt_{12}O_8(SO_4)_{12}]^{4-}$. It consists of six $Pt_2^{6+}$ dumbbell shaped cations that are linked by eight oxide ions and twelve sulfate anions to form a distorted $Pt_{12}$ icosahedron. The arrangement of the cluster anions in the crystal structure provides two voids for the cations. The larger one is occupied by the $Cs^+$ ions while the $K^+$ ions reside in the smaller one. For the $Cs^+$ ions the coordination number is 15 while the $K^+$ ions have a coordination number of 13.

*Key words:* Platinum, Sulfates, Cluster, Crystal Structure, Solvothermal Reactions

## Introduction

The reactions of various platinum(II) compounds and even of elemental platinum with conc. sulfuric acids under solvothermal conditions have led to a number of new sulfates, which show as a common structural feature the existence of dumbbell shaped $Pt_2^{6+}$ ions caused by the oxidation of platinum to its trivalent state [1 – 5]. One of the most remarkable compounds that have been obtained during these investigations is the oxide-sulfate $(NH_4)_4[Pt_{12}O_8(SO_4)_{12}]$ [6]. It contains the cluster anion $[Pt_{12}O_8(SO_4)_{12}]^{4-}$ with a distorted icosahedral arrangement of the platinum atoms. These anions form a rigid arrangement in the rhombohedral unit cell providing two voids of different size for the charge balancing counter cations. In $(NH_4)_4[Pt_{12}O_8(SO_4)_{12}]$ the $NH_4^+$ ion in the larger void shows N-O distances between 296 and 385 pm and has a coordination number of 15. The ammonium ion in the smaller void has a coordination number of 13 with the N-O distances ranging from 280 up to 330 pm. In the course of our investigations on platinum sulfates we have now synthesized the second oxide-sulfate exhibiting the $[Pt_{12}O_8(SO_4)_{12}]^{4-}$ anion. In the synthesis we offered two potential counter ions of different size, $K^+$ and $Cs^+$, in order to see if there is a size depending site preference. It turned out that indeed the different voids within the cluster framework are filled selectively by different counter cations.

## Experimental Section

For the synthesis of $Cs_2K_2[Pt_{12}O_8(SO_4)_{12}]$, 0.4 g of $Cs_2[Pt(NO_2)_4]$ and 0.4 g of $K_2[Pt(NO_2)_4]$ were reacted with 2 g of conc. sulfuric acid at 400 °C in a sealed glass ampoule ($\varnothing = 10$ mm, $l = 100$ mm, thickness of the wall = 2 mm) for 72 h followed by slow cooling (3 °C/h). The nitrito platinates(II) were synthesized according to the procedure described in [7]. The product contained deep red and remarkably hygroscopic single crystals of the title compound. Several of the red crystals were selected for the X-ray investigations and mounted in glass capillaries. For the respective best specimen intensity data were collected. Data corrections were applied using the programs X-red and X-shape [8, 9]. The refinement of the crystal structure was performed with the atomic positions of platinum, sulfur, and oxygen reported for $(NH_4)_4[Pt_{12}O_8(SO_4)_{12}]$ as starting values [6] using the program SHELXL97 [10]. Two peaks of different intensities occurred in the difference Fourier map, indicating the positions of the cesium and potassium atoms, respectively. A free refinement of the site occupation factors of these atoms has

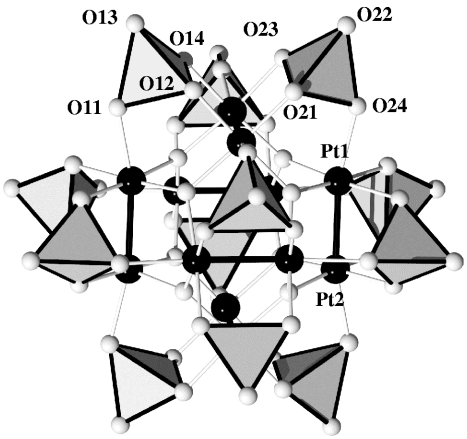


Fig. 1. The cluster anion $[Pt_{12}O_8(SO_4)_{12}]^{4-}$ in the crystal structure of $Cs_2K_2[Pt_{12}O_8(SO_4)_{12}]$. Pairs of platinum atoms (black spheres) form $Pt_2$ dumbbells (black lines) which are linked by eight oxygen atoms and twelve sulfate groups (shown as polyhedra). The twelve metal atoms form a distorted $Pt_{12}$ icosahedron.

been performed to assure that there is no mixed occupation of the sites with both atoms. Details of the refinement are given in the Tables 1 and 2, respectively.

## Results and Discussion

$Cs_2K_2[Pt_{12}O_8(SO_4)_{12}]$ crystallizes in the rhombohedral system (space group $R\bar{3}$) and contains as the characteristical structural feature the cluster anion $[Pt_{12}O_8(SO_4)_{12}]^{4-}$. Within the anion the twelve $Pt^{3+}$ ions are arranged in the form of an icosahedron which is remarkably distorted due to the formation of $Pt_2{}^{6+}$ dumbbells (Fig. 1). The Pt-Pt distance within the dumbbells is 252.7(1) pm (Table 3). This is almost the same value as found for $(NH_4)_4[Pt_{12}O_8(SO_4)_{12}]$ but is about 5 pm longer than observed for other Pt(III) sulfates [1 – 5, 11 – 13]. The distances to the other neighbouring platinum atoms within the icosahedron range from 344 up to 346 pm. The six $Pt_2{}^{6+}$ cations of the icosahedron are connected by eight $O^{2-}$ anions (O1 and O2, respectively) leading to an almost perfectly trigonal-planar coordination of the oxygen atoms by

Table 1. Crystallographic data of $Cs_2K_2[Pt_{12}O_8(SO_4)_{12}]$.

| | |
|---|---|
| Lattice parameters | $a = 1198.9(3)$ pm |
| | $c = 2768.9(9)$ pm |
| Cell volume | 3445.4(18) Å$^3$ |
| No. of formula units | 3 |
| Crystal system | rhombohedral |
| Space group | $R\bar{3}$ (No. 148) |
| Diffractometer | Stoe IPDS-I |
| Radiation | Mo-K$_\alpha$ (graphite-monochrom., $\lambda = 71.07$ pm) |
| Temperature | 20 °C |
| Data range | $4° < 2\theta < 56°$ |
| Index range | $-15 \le h \le 15$ |
| | $-15 \le k \le 15$ |
| | $-36 \le l \le 36$ |
| Rotation angle; $\varphi$-increment | $0° < \varphi < 200°$; 2.0° |
| No. of images | 100 |
| Exposure time | 5 min |
| Detector distance | 60 mm |
| Data corrections | polarization/Lorentz |
| Absorption correction | numerical [8, 9] |
| $\mu$ | 388.2 cm$^{-1}$ |
| No. of collected reflections | 19264 |
| No. of unique reflections | 1853 |
| No. of reflections with $I_o > 2\sigma(I)$ | 1526 |
| $R_{int}$ | 0.0765 |
| Structure refinement | SHELXL-97 [10] |
| Scattering factors | Intern. Tables, Vol. C [14] |
| Goodness of fit | 1.111 |
| $R1$; $wR2(I_o > 2\sigma(I_o))$ | 0.1031; 0.1407 |
| $R1$; $wR2$ (all data) | 0.1154; 0.1473 |
| Max./Min. Restelektronendichte/Å$^{-3}$ | 2,853/−2,758 |
| CSD | 416469 |

Table 2. Atomic positions and equivalent isotropic displacement parameters for $Cs_2K_2[Pt_{12}O_8(SO_4)_{12}]$.

| Atom | Wyckoff site | $x$ | $y$ | $z$ | $^aU_{eq} \cdot 10^{-1}$ [pm$^2$] |
|---|---|---|---|---|---|
| Pt1 | 18$f$ | 0.11802(8) | 0.28279(8) | 0.03271(3) | 18.9(2) |
| Pt1 | 18$f$ | 0.93410(8) | 0.12374(8) | 0.08500(3) | 19.2(3) |
| S1 | 18$f$ | 0.1825(6) | 0.3008(5) | 0.1402(2) | 21(1) |
| S2 | 18$f$ | 0.9014(6) | 0.3440(6) | 0.0453(2) | 22(1) |
| Cs | 6$c$ | 2/3 | 1/3 | 0.9187(1) | 34.8(6) |
| K | 6$c$ | 2/3 | 1/3 | 0.1268(5) | 41(2) |
| O1 | 6$c$ | 0 | 0 | 0.0917(10) | 18(5) |
| O2 | 18$f$ | 0.2043(16) | 0.1783(16) | 0.0304(5) | 19(3) |
| O11 | 18$f$ | 0.2341(17) | 0.2123(17) | 0.1393(6) | 23(3) |
| O12 | 18$f$ | 0.0364(18) | 0.2217(17) | 0.1430(7) | 27(4) |
| O13 | 18$f$ | 0.5099(16) | 0.5687(16) | 0.1539(6) | 22(3) |
| O14 | 18$f$ | 0.2139(15) | 0.3727(16) | 0.0930(6) | 20(3) |
| O21 | 18$f$ | 0.8626(16) | 0.2435(16) | 0.0857(6) | 22(3) |
| O22 | 18$f$ | 0.8693(19) | 0.4396(18) | 0.0604(7) | 28(4) |
| O23 | 18$f$ | 0.0449(16) | 0.4041(15) | 0.0380(6) | 18(3) |
| O24 | 18$f$ | 0.2817(17) | 0.4477(17) | 0.9999(7) | 27(4) |

[a] $U_{eq} = 1/3[U_{33} + 4/3(U_{11} + U_{22} - U_{12})]$ [15].

Table 3. Selected distances (pm) for $Cs_2K_2[Pt_{12}O_8(SO_4)_{12}]$.

| | | | | | | |
|---|---|---|---|---|---|---|
| Pt1 | -O2 | 198(2) | S1 | -O13 | | 144(2) |
| | -O14 | 201(2) | | -O11 | | 147(2) |
| | -O2 | 203(2) | | -O14 | | 151(2) |
| | -O23 | 204(2) | | -O12 | | 152(2) |
| | -O24 | 217(2) | | | | |
| | -Pt2 | 252.7(1) | S2 | -O22 | | 144(2) |
| | | | | -O24 | | 147(2) |
| Pt2 | -O2 | 197(2) | | -O23 | | 151(2) |
| | -O12 | 200(2) | | -O21 | | 153(2) |
| | -O21 | 201(2) | | | | |
| | -O1 | 200.8(3) | Cs | -O14 | (3×) | 309(2) |
| | -O11 | 216(2) | | -O24 | (3×) | 327(2) |
| | -Pt2 | 252.7(1) | | -O13 | (3×) | 352(2) |
| | | | | -O23 | (3×) | 353(2) |
| | | | | -O13 | (3×) | 396(2) |
| | | | | | | $\bar{d} = 347$ |
| | | | K | -O22 | (3×) | 279(2) |
| | | | | -O12 | (3×) | 303(2) |
| | | | | -O21 | (3×) | 324(2) |
| | | | | -O11 | (3×) | 327(2) |
| | | | | -O1 | | 318(3) |
| | | | | | | $\bar{d} = 309$ |

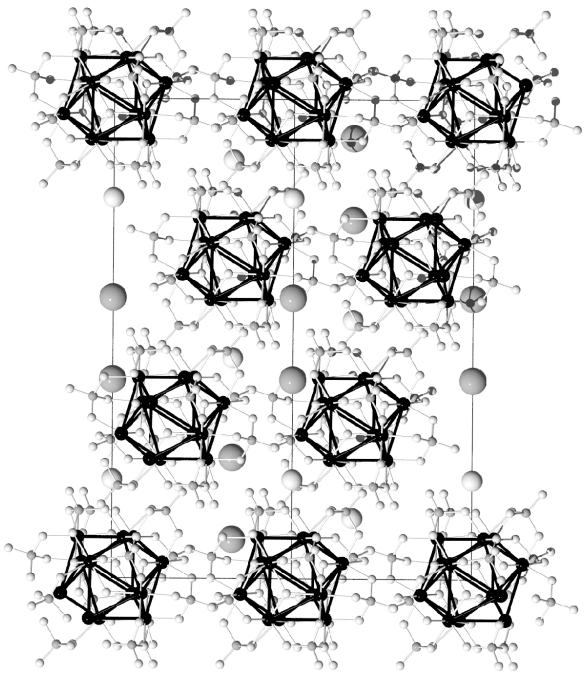

Fig. 2. Arrangement of the $[Pt_{12}O_8(SO_4)_{12}]^{4-}$ clusters in the rhombohedral unit cell (the $Pt_{12}$ icosahedra are emphasized by black lines). The large grey and white spheres are the $Cs^+$ and $K^+$ ions within the cluster framework, respectively.

three platinum atoms with Pt-O distances around 200 pm, and Pt-O-Pt angles of almost 120°. In this way eight of the twenty triangular faces of the icosahedron are centred by oxide ions. Tridentately coordinating $SO_4^{2-}$ groups are situated above the remaining twelve triangular faces. Each sulfate ion acts as a chelating ligand to one $Pt_2$ dumbbell and as a monodentate ligand to the next. One oxygen atom of the tetrahedron is not attached to a platinum atom. The different functionalities of the oxygen atoms are reflected by the S-O distances: They are found between 151 and 153 pm for the "chelating" oxygen atoms (O12, O14 and O21, O23, respectively) whereas 144 pm are observed for the non-coordinating oxygen atoms. The "monodentate" oxygen atoms (O11 and O24) show S-O distances of 147 pm. Each platinum atom is in a distorted octahedral coordination of five oxygen atoms and one further platinum atom. The distances Pt-O are 216 and 217 pm, respectively, for the oxygen atoms which are in *trans* orientation with respect to the second Pt atom (O11 and O24), while for the remaining four oxygen atoms the distances are between 197 and 204 pm. The angles O11-Pt2-Pt1 and O24-Pt1-Pt2 are 167.9(5) and 168.1(5)°, respectively, showing a severe deviation from linearity.

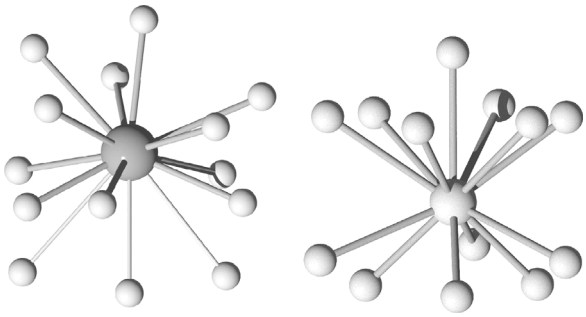

Fig. 3. Coordination of $Cs^+$ (left) and $K^+$ (right) in the crystal structure of $Cs_2K_2[Pt_{12}O_8(SO_4)_{12}]$. The three longer distances Cs-O of 396 pm are indicated by thin lines.

The $[Pt_{12}O_8(SO_4)_{12}]^{4-}$ clusters are arranged in the rhombohedral unit cell in a way that their centers are situated at the origin of the cell (Wyckoff site 3*a*) leading to $S_6$ symmetry for the anions. The cluster anions form the same rigid framework as observed for $(NH_4)_4[Pt_{12}O_8(SO_4)_{12}]$ offering two voids of different size. Because the X-ray scattering factors differ significantly for Cs and K, it could be clearly shown that the larger void is exclusively occupied by $Cs^+$ while $K^+$ resides in the smaller one. Free refinement of the site occupation factors of both sites show no deviation from complete occupation within the standard deviations.

Both $K^+$ and $Cs^+$ ions are located on the Wyckoff sites 6*c*. The $Cs^+$ ion is coordinated by 12 oxygen atoms with distances Cs-O between 309 and 353 pm. If distances up to 400 pm are taken into account, the coordination number increases to 15. The mean distances $\bar{d}$ (Cs-O) are 335 pm for coordination number 12, and 347 pm if the calculation is done for 15 oxygen ligands (Table 3). In any case these distances are remarkably longer compared to the K-O distances of the second site. The $K^+$ ion is surrounded by 13 oxygen atoms with distances between 279 and 327 pm, and the mean distance $\bar{d}$ (K-O) is 309 pm. The distances for both ions are very similar to those described for $(NH_4)_4[Pt_{12}O_8(SO_4)_{12}]$ proving the very rigid arrangement of the cluster anions, which appears to be quite independent from the respective counter cations.


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