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The Crystal Structure of NaPt$_3$O$_4$

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The structure of a microcrystalline platinum compound is derived from x-ray data. Space group $O_h^3 - Pm3n$, $a_0 = 5.69$A, with 6 Pt at $\pm(\frac{1}{4} 0 \frac{1}{2}, \circlearrowright)$, 8 O at $\pm(\frac{1}{4} \frac{1}{4} \frac{1}{4}, \frac{1}{4} \frac{3}{4} \frac{3}{4}, \circlearrowright)$, and 2 Na at $(000, \frac{1}{2} \frac{1}{2} \frac{1}{2})$, corresponding to the formula NaPt$_3$O$_4$. The coordinations are as follows: platinum 4 O and 2 Pt, oxygen: 3 O and 2 Na, sodium: 8 O. The substance is an ionic conductor.

THE preparation of an oxide of platinum by fusion of sodium chloroplatinate with sodium carbonate has been reported by Jörgensen.[1] The oxygen content of the compound was determined by finding the weight lost on ignition with a result corresponding to the formula Pt$_3$O$_4$. Repeating this work Wöhler[2] found that all his preparations contained small and varying amounts of sodium and water in addition to platinum and oxygen. The amount of water given off upon heating was determined directly, and found to vary between 1 and 5 percent. The sodium content varied between 3 and $4\frac{1}{4}$ percent. The oxygen percentage depended on the history of the sample but was always between the extremes corresponding to PtO and PtO$_2$. Wöhler concluded that the product of the reaction described was a mixture of PtO and PtO$_2$. He did not try to account for the sodium and assumed the water to be water of hydration.

Our structure determination by x-rays shows that a compound actually is formed and that it has the composition NaPt$_3$O$_4$.

PREPARATION AND PROPERTIES

One part of finely divided anhydrous sodium chloroplatinate was thoroughly mixed with four parts of powdered anhydrous sodium carbonate. The mixture was heated in a platinum crucible, the crust forming on top being constantly pushed back into the main body of the melting material. The heating was stopped as soon as the whole mass was molten. After cooling, the unreacted sodium carbonate was dissolved in dilute nitric acid. The resulting black powder was washed with water and dried over phosphorus pentoxide. An x-ray powder diagram showed, besides other lines, those of metallic platinum. Only repeated grinding followed each time by extraction with hot aqua regia, which does not react with the compound investigated, eliminated all but traces of metallic platinum.

Analysis of the compound gave the following inconclusive results. Like Wöhler we found water to be present to the extent of 2.6 percent, even after drying for 24 hours at 110°C in a high vacuum. The platinum was determined as residue with the two results 84.69 percent and 86.51 percent which is to be compared with the theoretical value 87.07 percent for NaPt$_3$O$_4$. In order to completely eliminate the oxygen in this analysis a final introduction of hydrogen around 500°C was necessary. This produced a vigorous exothermic reaction causing the substance to heat up to a dull red and completely eliminated any sodium that had not escaped in the previous heating. No attempt was made to determine analytically the sodium content of the compound.

The compound is a jet black powder which is reasonably stable at room temperature but decomposes slowly over a period of several months. No solvent action is observed for aqua regia or concentrated mineral acids. The oxide does react, however, with reducing agents such as KI or SnCl$_2$ in a strongly acid medium. One of the reaction products appears to be colloidal platinum.

DETERMINATION OF CRYSTAL STRUCTURE

Powder diagrams taken with CrK$_\alpha$ as well as CuK$_\alpha$ radiation showed a set of very sharp lines that could be indexed on a simple cubic lattice with a unit cell of edge $a_0 = 5.69$A based on extrapolation to $\vartheta = 90°$. The first two columns of Table I contain the spacings observed together with the indices (hkl). On all our photographs there appeared a very weak diffuse line at a spacing of 4.55A. With cubic cells of twice or three times the edge of our cell this line can be indexed, but the line is diffuse and seems to vary in intensity for different preparations. There is no other evidence pointing to a larger cell.

Accurate intensities for CuK$_\alpha$ radiation were determined for $\vartheta \le 45°$ employing a Norelco Geiger counter instrument whose linearity in the range used had been established by calibration with a set of nickel foils. For each reflection counts were determined at about twenty different ϑ-values, starting and ending at a constant background. The area between a curve drawn smoothly through these points and a suitable background line was taken as a measure of the integrated intensity, and is listed in column 3 of Table I (except for a constant factor). Visual intensity data for CuK$_\alpha$ radiation were obtained by a multiple film technique.[3] These values were corrected for absorption by using as calibration points reflections (hkl) for which $h+k+l = 2n+1$. Only the Pt-atoms contribute to these reflections and they can be placed in the unit cell by the use of extinction criteria alone (compare below). The logarithms of the ratios of calculated and observed intensities were plotted

[1] S. M. Jörgensen, J. Prakt. Chem. **16**, 344 (1877).
[2] L. Wöhler, Z. anorg. u. allgem. Chem. **40**, 450 (1904).
[3] De Lange, Robertson, and Woodward, Proc. Roy. Soc. (London) A**171**, 398 (1939).

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TABLE I. The crystal structure of NaPt₃O₄.[a]

hkl	d, A	IG	Iv	Ic4		Ic1	Ic2	Ic3
—	4.55		v.v.w.					
110	4.03	334	(440)	419		566	485	566
200	2.84	68	(88)	71		111	73	48
210	2.54	1395	(1420)	1417		1417	1417	1417
211	2.32	306	(364)	342		268	259	268
220	2.00	27	(29)	26		83	64	39
310	1.79	97	(91)	93		122	155	122
222	1.64	344	(364)	305		273	286	329
320	1.58	364	(321)	321		321	321	321
321	1.52	215	(162)	175		140	160	140
400	1.42	194	(175)	165		130	124	154
411	1.34	64	(43)	37 ⎫	56	47	50	47
330	1.34			19 ⎬		24	14	24
420	1.27	30	(29)	29		39	42	22
421	1.24	325	(291)	291		291	291	291
332	1.21	37	(27)	42		34	25	34
422	1.16	21	(10)	13		31	32	18
510	1.115		51	22 ⎫	67	28	23	28
431	1.115			45 ⎬		55	53	55
520	1.055		292	101 ⎫	302	101	101	101
432	1.055			201 ⎬		201	201	201
521	1.038		45	57		47	43	47
440	1.004		162	127		104	105	120
530	0.973		26	18 ⎫	36	22	30	22
433	0.973			18 ⎬		22	25	22
600	0.947		24	5 ⎫	23	6	8	4
442	0.947			18 ⎬		23	23	15
610	0.933		83	92		92	92	92
532	0.921		86	55 ⎫	83	47	55	47
611	0.921			28 ⎬		23	25	23
620	0.898		12	12		24	30	16
541	0.876		42	42		50	49	50
622	0.857		383	266		248	238	282
630	0.848		455	117 ⎫	350	117	117	117
542	0.848			233 ⎬		233	233	233
631	0.839		59	72		60	52	61
444	0.821		286	124		105	105	119
550	0.804		252	18 ⎫		21	17	21
710	0.804			36 ⎬	125	42	42	42
543	0.804			71 ⎭		84	79	84
640	0.789		57	45		57	52	37
641	0.781		902	601 ⎫	902	601	601	601
720	0.781			301 ⎬		301	301	301

[a] IG: Geiger counter intensity; Iv: visual intensity; Ici (i=1, 2, 3, 4): calculated intensity, with i=1: contributions of Pt only; i=2: oxygens in 8e of Td⁴, u=0.322; i=3: oxygens in 8e of Oh³; i=4: final structure including Na. All forms not listed have vanishing structure factor.

for these reflections against $\sin^2 \vartheta$. A smooth curve drawn with the aid of these points served for absorption correction and is shown in Fig. 1. The visual intensities corrected in this manner are listed in column 4 of Table I. The visual values for $\vartheta \leq 45°$ are included for comparison with the Geiger counter values only and were not subsequently used in the determination of the structure.

Systematic absence of reflections (hhl) with l odd led to the probable space groups $O_h^3 - Pm3n$ and $T_d^4 - P\bar{4}3n$.[4] It was found that besides satisfying this space group criterion reflections hkl occurred if and only if one of the following conditions was satisfied: (1) $h+k+l=2n$, (2) $h=4n$, $k=4n+2$, and $l=2n+1$. These are exactly the conditions required by the two equivalent sets of 6-fold positions $6c$, $\pm(\frac{1}{4} 0 \frac{1}{2}, \circlearrowright)$ and $6d$, $\pm(0 \frac{1}{4} \frac{1}{2}, \circlearrowright)$[5]

[4] Internationale Tabellen zur Bestimmung von Kristallstrukturen, Berlin, 1935. Volumes 1 and 2.
[5] The symbol $\circlearrowright$ stands for cyclical permutation.

in O_h^3 or T_d^4.[4] Intensities calculated with Pt-atoms in one of these sets, e.g., $6c$, show satisfactory agreement with the observed values (column 6, Table I) so that there are six Pt-atoms in the unit cell. In particular, placing six more Pt-atoms in the set $6d$ would lead to unsatisfactory intensities and too short Pt-Pt distances. Another possibility not violating condition (1) would be to introduce two more Pt-atoms in positions $2a$ of O_h^3, (000, $\frac{1}{2} \frac{1}{2} \frac{1}{2}$), which would make the arrangement of Pt-atoms identical with that of W-atoms in β-wolfram.[6] It is ruled out since for it the Pt-amplitudes would cancel for ten lines which are actually present with normal intensities. The intensities calculated for Pt-atoms in positions $6c$ were used as described above to correct the visual intensities.

Even with heavy exposures, no faint lines were detected that did not satisfy either of the above extinction rules (1) and (2). Condition (1) is that for a body-centered lattice while the aggregate of conditions (1) and (2) is that of either of the two sets $6c$ and $6d$ discussed above, of which $6c$ has been filled with Pt-atoms and $6d$ is no longer available because of space requirements. The remaining atoms are thus arranged on a body-centered lattice. Nevertheless, all non-body-centered as well as body-centered 6-fold, 8-fold, and 12-fold sets of the cubic system[7] were systematically investigated in the placement of the relatively weakly scattering O-atoms. Only two possibilities were found that did not lead either to spatial difficulties or to otherwise unsatisfactory structures. These were the two related 8-fold sets $8e$ of T_d^4, (000, $\frac{1}{2} \frac{1}{2} \frac{1}{2}$) $\pm(u u u, u \bar{u} \bar{u}, \circlearrowright)$ and $8e$ of O_h^3, (000, $\frac{1}{2} \frac{1}{2} \frac{1}{2}$) $\pm(\frac{1}{4} \frac{1}{4} \frac{1}{4}, \frac{1}{4} \frac{3}{4} \frac{3}{4}, \circlearrowright)$, both of them body-centered.

The unit cell therefore contains eight oxygen atoms. Neglecting the volume of the Pt-atoms one arrives at a volume of 23A³ taken up by each O-atom. This is in fair agreement with the value of 25A³ found for PtO.[8] Indeed, taking 6A³ for the volume occupied by each Pt-atom one obtains 19A³ for the volume taken up by one O-atom in either compound, which is in excellent agreement with the values found by Zachariasen in a
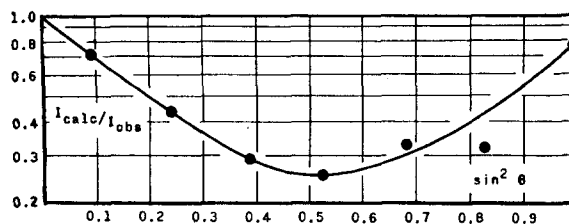

FIG. 1. Correction curve for visual intensities.

[6] A. F. Wells, Structural Inorganic Chemistry (Oxford University Press, London, 1945).
[7] R. G. Wyckoff, The Analytical Expression of the Results of the Theory of Space Groups (Washington, 1930). Sets of higher multiplicity are ruled out by volume requirements which make even a 12-fold set very unlikely (compare below).
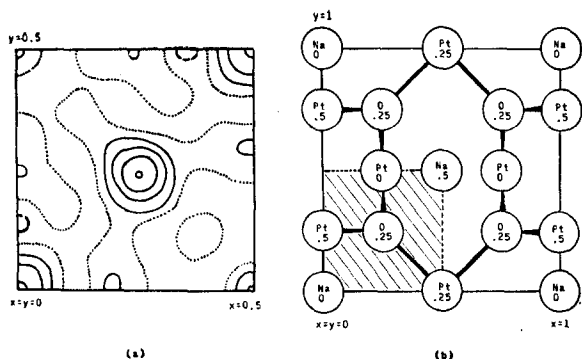[8] W. J. Moore, Jr., and L. Pauling, J. Am. Chem. Soc. 63, 1392 (1941).

Fig. 2. (a) Projection $\rho'(x, y)$ on (001) plane. Contours in arbitrary units, zero contour dotted and negative contour dashed. (b) View of unit cell along c-axis. Numbers are z-parameters, with the additional stipulation that the value 0.25 indicates an atom at $z = 0.75$ also. Only O—Pt bonds are shown.

number of oxides.[9,10] Intensities were calculated for either set of oxygen coordinates mentioned above, $8e$ of T_d^4 and $8e$ of O_h^3. These are listed in columns 7 and 8 of Table I. The parameter u for the former set was given the value 0.322, which leads to satisfactory packing and places the O-atoms at the centers of regular tetrahedra formed by the Pt-atoms. The value of the quantity

$$\frac{\sum ||F_{\text{obs}}| - |F_{\text{calc}}||}{\sum |F_{\text{obs}}|}$$

for either of the two possible oxygen positions is listed in Table II for the Geiger counter intensities alone, as well as for the whole set of intensities. The agreement is better for the set $8e$ of O_h^3 in which the oxygens are arranged on a simple cubic lattice of unit cell edge $a_0/2$.

The holes in the center of some of the oxygen cubes appeared suspicious and indeed filling these holes with some scattering matter further improved the agreement between calculated and observed intensities. It was decided to investigate this question further by the aid of a fourier projection on the xy-plane in which the platinum atoms have been removed. This was ac-

complished by using for coefficients the values of $sgn(F_{hk0}^{\text{Pt}})\{|F_{hk0}^{\text{obs}}| - |F_{hk0}^{\text{Pt}}|\}$ where $|F_{hk0}^{\text{obs}}|$ is the magnitude of the observed structure factor obtained from the intensities in the usual way, F_{hk0}^{Pt} is the structure factor for the Pt atoms alone and $sgn(F_{hk0}^{\text{Pt}})$ its sign. For the atomic structure factor of Pt an average was used of the values based on the Thomas-Fermi model[4] and those of Pauling and Sherman.[11] The intensity of reflections that superimposed was distributed in the ratios of the frequency factors among the forms involved.

Figure 2 shows (a) the resulting fourier projection for one-quarter of the unit cell and (b) for comparison, the projection of the full unit cell of the final structure. The peak at the center of the fourier projection represents two superimposed oxygen atoms. The ratio of the peak at the origin to the oxygen peak is approximately 0.7. This fits reasonably well to sodium, the only possible candidate in the reaction mixture, for which a ratio of about $0.64 = 11/16 = \text{Na}/(2 \text{ superimposed O})$ (or 10/16 for Na in the ionized state) would be expected. The fact that, if anything, the peak at the origin is somewhat higher than this, strongly indicates that practically all the holes in the oxygen cubes corresponding to the two-fold set of positions $2a$ of O_h^3 (000, $\frac{1}{2} \frac{1}{2} \frac{1}{2}$) are filled with sodium. Several minor peaks of spurious nature are also in evidence. They are probably due to such things as breaking-off error, improper apportioning of intensities for superimposed lines, and the difficulties involved in subtracting such a heavy atom as Pt. Intensities were calculated including the sodium contributions. They are listed in column 5 of Table I and appear to be in excellent agreement with the observed intensities. Significant improvement of

$$\frac{\sum ||F_{\text{obs}}| - |F_{\text{calc}}||}{\sum |F_{\text{obs}}|}$$

(Table II) over the values not including sodium is noted.

CONDUCTIVITY EXPERIMENTS

The presence in the structure of infinite strings of Pt atoms (compare below) induced us to make conductivity measurements expecting the compound to exhibit metallic conduction. A sample of about 5 mm length was placed in a glass capillary tube of about 2 mm i.d. and clamped between two spring loaded brass electrodes. The conductivity was roughly determined at $-196°C$, $30°C$, and $110°C$ and showed marked temperature de-

[9] W. H. Zachariasen, Acta Cryst. 1, 281 (1948).

[10] An oxide of the formula Pt_3O_4 has been reported by Galloni and Roffo [E. E. Galloni and A. E. Roffo, Jr., J. Chem. Phys. 9, 875 (1941)]. The diffraction pattern published by G. and R. is entirely different from that characteristic of our substance. The x-ray evidence on which the formula for their compound is based does not appear to us to be conclusive. Indeed, assuming that the compound investigated by G. and R. is a platinum oxide, one is tempted to conclude it to be PtO_2 by the following consideration. The cell volume reported is 240A³. Assuming 20A³ per O-atom one comes to 12 oxygens per unit cell. Since G. and R. show that 6 Pt-atoms in the set $6b$ of O_h^9 (reference 4) reproduce the major traits of the observed intensities one arrives at the composition PtO_2.

In a more recent publication [Z. Naturforsch. 56, 130 (1950)] R. Busch confirms the lines reported by G. and R. as due to a platinum oxide. He also refers to work on the structure of an oxide PtO_2. (Busch, Cairo, Galloni, and Raskovan, Reunion A. Fisika Arg., La Plata, 1949, to be published.) We find that the lines listed by Busch (see above) for this compound coincide with lines calculated for the unit cell of the platinum oxide whose structure, as reported by Moore and Pauling, fits the formula PtO (reference 8).

Table II. $\Sigma ||F_{\text{calc}}| - |F_{\text{obs}}||$[a]$/ \Sigma |F_{\text{obs}}|$[b] for several structures.[b]

	c_1	c_2	c_3	c_4
Geiger counter intensities	0.144	0.132	0.091	0.061
Geiger counter and visual intensities	0.168	0.166	0.126	0.102

[a] Superposed reflections were excluded.
[b] The symbols c_i ($i = 1, 2, 3, 4$) are explained in the footnote to Table I.

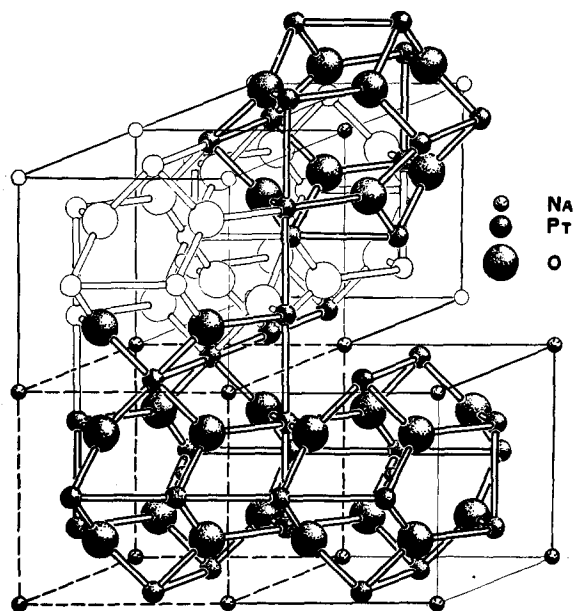[11] L. Pauling and J. Sherman, Z. Krist. 81, 1 (1932).

FIG. 3. Three-dimensional representation of relationship of atoms in $NaPt_3O_4$. Unit cube dashed at lower left corner.

pendence, being much smaller the lower the temperature. At $-196°C$ there was a steady decrease in current immediately after application of a potential to the electrodes. Replacing the emf by a short-circuit loop caused current to flow in the opposite direction. Reversing the polarity of the electrodes reversed the effect. This polarization was less marked at room temperature and still less so at 110°C. The specific resistance at room temperature was of the order of 10^4 ohm cm, but since it was impossible to obtain sintered samples no attempts were made to place the measurements on an exact basis. It is quite possible that the grains of $NaPt_3O_4$ are actually much better conductors than would correspond to this magnitude. It appears clear that the conduction is of ionic character, and that the loosely fitting Na^+-ions (compare below) are the carriers.

DISCUSSION

The crystal structure derived above corresponds to the stoichiometric formula $NaPt_3O_4$ assuming that all oxygen cubes which do not already contain Pt-atoms are filled with Na-atoms, as is strongly implied by the magnitude of the fourier peak at the origin of Fig. 2a. The formula corresponds to 3.42 percent Na 9.51 percent O and 87.07 percent Pt which is well within the values of Wöhler's and the accuracy of our analyses. The variation in the oxygen content might be due to the presence of varying amounts of an amorphous oxide or of adsorbed oxygen, in as far as it is not caused by the experimental difficulties of analysis. The same holds for the water found. Attempts to prepare a Na free compound or to replace the Na with K or Li have so far been unsuccessful. The x-ray density of the compound is calculated to be 12.13 g/cm^3.

A three-dimensional drawing of the structure is presented in Fig. 3. Infinite chains of Pt-atoms extend parallel to the edges of the unit cube. They are tied together by the O-atoms to form interlocking cages, two of which are shown by shading at the bottom of the figure and another one in different orientation at the top. At the centers of these cages are sodium ions which have as closest neighbors eight oxygen atoms at 2.46A arranged on a cube of half the unit cell edge. Each of these O-atoms has as neighbors three Pt-atoms at 2.01A forming the corners of an isosceles triangle and two Na-ions at 2.46A above and below the center of this triangle. The Pt-atoms are at the center of a square of O-atoms at 2.01A above and below which are two Pt-atoms at 2.85A, which are part of the chains of Pt-atoms already mentioned.

All atoms of a given kind are equivalent in this structure. In particular the Pt-atoms all have the unusual oxidation number 7/3. There is some covalent bonding of the Pt-atoms of a chain, the interatomic distance of 2.85A leading to a bond number 0.38.[12] The Pt—O distance corresponds essentially to a single bond between these two atoms being within 0.01A of the Pt—O distance found in PtO (2.02A).[8] It is interesting to note that this bond is not significantly shortened by a possible resonating double bond as usually formed for oxygen with trigonal hybridization. There are, however, hardly enough orbitals available in the Pt valence shell to accept such double bonds, and the p_z-lobes of the oxygen orbitals might find some compensation forming half-bonds to the sodiums towards which they are directed (compare e.g., the oxygen atom in lower left of Fig. 3). Nevertheless, the sodium must have a good deal of ionic character being responsible for the ionic conductance. The surrounding of the Na-ions by eight cubically arranged oxygens is the same as in Na_2O which has the antifluorite structure and in which the Na—O distance is 2.40A.[13] The analogous distance observed in $NaPt_3O_4$ (2.46A) indicates a somewhat looser fit of the Na-ions in $NaPt_3O_4$ than in Na_2O. The closest approach of the non-bonded O-atoms (2.85A) at the edges of these cubes as well as of the cubes containing Pt-atoms is very close to a van der Waals' contact (expected at 2.80A).

This substance reminds one somewhat of the wolfram bronzes $MeWO_3 \cdot xWO_3$, with Me an alkali metal, discussed most recently by Straumanis and co-workers,[14] and by Kupka and Sienko.[14] In the sodium bronzes the sodium is surrounded octahedrally by O-atoms at a distance of 2.72A, which is even larger than the Na—O distance in $NaPt_3O_4$. The sodium wolfram bronzes show metallic conductivity, but the lithium bronzes conduct by an ionic mechanism.[14]

[12] L. Pauling, J. Am. Chem. Soc. 69, 542 (1947).
[13] Zintl, Harder, and Dauth, Z. Elektrochem. 40, 588 (1934).
[14] M. E. Straumanis and S. S. Hsu, J. Am. Chem. Soc. 72, 4027 (1950) etc., F. Kupka and M. J. Sienko, J. Chem. Phys. 18, 1296 (1950), and reference 6.