

The Structure of Na x Pt3O4

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properties and the x-ray pattern of PtO₂ are both dependent on the heat treatment.

(2) *The substance studied by Moore and Pauling⁶ was probably not PtO.* They write: "PdO was prepared by the method of Shriner and Adams¹¹ involving fusing palladous chloride and potassium nitrate; and PtO by a similar method." . . . "The data are not sufficient to permit a rigorous structure determination to be made for PtO, but the similarity to the PdO photographs makes it highly probable that platinumous oxide has the PdO structure . . ."

The existence of PtO is questioned in Gmelin's handbook.¹² Wöhler and Frey¹³ discuss the preparation of this compound and its easy oxidability. We think the method of Shriner and Adams¹¹ applied to H₂PtCl₄ (because PtCl₂ is insoluble) would give PtO₂, because of the oxidizing properties of fused KNO₃. Moore and Pauling have not analyzed the compound obtained, so it is difficult to find out what they have actually studied.

In conclusion, the structure given for PtO is not supported by sufficient experimental evidence. It is doubtful if the authors prepared PtO or not.

(3) *It is possible to prepare the hydrate of PtO by the method of Wöhler and Frey.¹³* The dehydration of this compound gives an oxide whose composition fits well the formula PtO. The x-ray pattern is platinum-like. The only difference is that the parameters of PtO are slightly enlarged with respect to Pt. Chemically, the oxide cannot be confused with platinum because it is insoluble in aqua regia, and its density is very much lower (lying between 11.5 and 14 g/cm³). In the course of a great number of preparations of this substance, we have never found the lines reported by Moore and Pauling.

(4) *On some occasions, we have prepared the platinum oxide studied by Galloni and Roffo and have found the formula Pt₃O₄ together with the x-ray pattern reported by them.* It has been obtained by thermal decomposition of hydrated PtO₂, but it has not been possible to find a reproducible method of preparation, in spite of very numerous experiments. In two instances the right oxide has appeared, but the conditions upon which its preparation depend are not clear to us.

In conclusion, for the reasons given, we think that the compound studied by Waser and McClanahan is not Pt₃O₄Na, that the hexagonal pattern reported by Busch is caused by PtO₂, that the pattern reported by Galloni and Roffo is caused by Pt₃O₄, and finally, that the structure given to PtO by Moore and Pauling is open to discussion. Even the existence of anhydrous PtO is open to discussion.

We are indebted to Dr. J. Winkel for obtaining the spectrograms.

¹ J. Waser and E. McClanahan, *J. Chem. Phys.* **19**, 413 (1951).

² S. M. Jørgensen, *J. prakt. Ch.* **16**, 344 (1877).

³ E. E. Galloni and A. E. Roffo, *J. Chem. Phys.* **9**, 875 (1941).

⁴ R. H. Busch, *Z. Naturforschung* **5a**, 130 (1950).

⁵ W. J. Moore and L. Pauling, *J. Am. Chem. Soc.* **63**, 1392 (1941).

⁶ R. Vorhees and R. Adams, *J. Am. Chem. Soc.* **44**, 1397 (1922).

⁷ Busch, Cairo, Galloni, and Raskovan, 14a. Reunión de la Asociación Física Argentina, La Plata (1949).

⁸ Finch, Murison, Stuart, and Thomson, *Proc. Roy. Soc. (London)* **A 141**, 414 (1933).

⁹ S. Altmann and R. H. Busch, *Trans. Faraday Soc.* **45**, 720 (1949).

¹⁰ L. Pigeon, *Ann. chim. et phys.* (7), **2**, 480 (1894).

¹¹ Shriner and R. Adams, *J. Am. Chem. Soc.* **46**, 1684 (1924).

¹² Gmelin, *Handbuch der anorganischen Chemie*, eighth edition (1938), Vol. 68, part C.

¹³ L. Wöhler and W. Frey, *Z. Elektrochem.* **15**, 133 (1909).

The presence of sodium in our compound was inferred from the following facts. An electron density projection showed the presence of a concentration of scattering matter of approximately the correct magnitude for one Na-atom per each four O-atoms. This peak could not have been caused by breaking-off errors since the Pt-contributions had been subtracted from the observed *F*'s. Thus our projection contained neither Pt peaks nor the subsidiary features which ordinarily accompany large peaks and are caused by termination of the Fourier series. The analogous breaking-off features of the oxygen peaks are correspondingly smaller and have a negligible effect on the sodium peak. The inclusion of a scattering contribution from Na at the positions 2a of O_h³ significantly improved the agreement between calculated and observed intensities. The presence of Na further explains the ionic conductivity observed by us and the sodium content Wöhler reported for his preparations.³

However, as indicated in our paper, the compound NaPt₃O₄ need not be of stoichiometric nature as far as sodium is concerned. The Na-atoms (or ions) are situated in holes formed by cubes of O-atoms, and the number of holes filled in various preparations may vary. The further possibility of filling the holes with other suitable cations exists.

Our findings may thus be reconciled with those of Galloni and Busch¹ by assuming the existence of a whole series of compounds of the formula Na_xPt₃O₄, 0 ≤ x ≤ 1, all having the same framework of Pt and O-atoms described in our paper.³ A more detailed investigation is, however, required to clear up completely this question of solubility of Na and possibly other cations in Pt₃O₄.

We have now had the opportunity to analyze for sodium our original very small sample of Na_xPt₃O₄ which had been used in the x-ray experiments. The sample was treated with strong HCl containing KI followed by boiling with aqua regia. Only a portion of the sample went into solution, the exact amount dissolved being unknown. Analysis with a Beckman flame spectrophotometer showed that the original sample contained 1.3 percent Na or more. As reported previously our preparation had been extracted several times with hot aqua regia to remove traces of Pt. The Na is therefore presumed to be part of the compound.

We wish to thank Dr. R. V. Talmage for the use of the flame spectrophotometer.

¹ E. E. Galloni and R. H. Busch, *J. Chem. Phys.* **19**, 198 (1951).

² J. Waser and E. D. McClanahan, Jr., *J. Chem. Phys.* **19**, 413 (1951).

³ L. Wöhler, *Z. anorg. u. allgem. Chem.* **40**, 450 (1904).

Carrier-Free Radioisotopes from Cyclotron Targets. XXIV. Preparation and Isolation of Ir^{188, 190, 192} from Osmium*

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(Received October 26, 1951)

BOMBARDMENT of osmium with 19-Mev deuterons produces, by (*d*, 2*n*) and (*d*, *n*) reactions, several relatively long-lived, known, radioactive isotopes of iridium:^{1,2} *viz.*, Ir¹⁸⁷, Ir¹⁸⁸, two isomers of Ir¹⁹⁰, and Ir¹⁹². Radioisotopes of rhenium and osmium are also produced concurrently in relatively low yield by (*n*, *p*) and (*d*, *p*) reactions. This paper reports a method for isolation of iridium activities from irradiated osmium without the addition of stable iridium carrier.

The target was osmium metal powder (*ca.* 0.5g) in which no iridium (less than 0.01 percent) was detected by spectrographic analysis. The osmium powder was held on a grooved, water-cooled target plate by a 0.25-mil platinum foil during bombardment in the 60-inch Crocker Laboratory cyclotron.

After bombardment the osmium powder was dissolved, with heating, in a minimal amount of aqua regia. Excess nitric acid was added and the solution was heated to dryness to distill off the osmium tetroxide. Two milliliters of nitric acid were added and

The Structure of Na₂Pt₃O₄

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IN the preceding note Galloni and Busch¹ report the results of a spectroscopic analysis of a platinum oxide similar to the compound recently investigated by us.² While their compound apparently did not contain significant amounts of sodium, we had assigned the formula NaPt₃O₄ to our preparation.