Accordingly, an attempt will be made to locate the carbon atoms in other ways.

In the space group $I\bar{4}3d$ there are only two ways in which the twenty-four carbon atoms in the unit cell can be distributed among the available positions. Either the carbon atoms occupy the two sets of 12-fold positions without degrees of freedom, or they are in the 24-fold positions with one degree of freedom.

In the former case the closest Pu–C separation is 2·20 Å. This value is so much smaller than the distance 2·46 Å. observed in PuC that this distribution of the carbon atoms must be discarded as unreasonable.

The 24-fold positions for the carbon atoms are:

$$(0, 0, 0);\quad (\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})+$$
$$(y, 0, \tfrac{1}{4})\nwarrow;\ (\tfrac{1}{2}-y, 0, \tfrac{3}{4})\nwarrow;\ (\tfrac{3}{4}+y, 0, \tfrac{3}{4})\nwarrow;\ (\tfrac{3}{4}-y, 0, \tfrac{1}{4})\nwarrow.$$

If the Pu–C distance is to be 2·46 Å or greater, the parameter y must lie in the range $0{\cdot}27 \leqslant y \leqslant 0{\cdot}48$. By symmetry, values y and $\frac{3}{4}-y$ are equivalent so that only the range $0{\cdot}27 \leqslant y \leqslant 0{\cdot}375$ needs to be considered. For $y=0{\cdot}375$ two carbon atoms occupy the same site, and it is clear that y must be considerably less than $\frac{3}{8}$ if carbon atoms are to be reasonably far apart. Even if $y=0{\cdot}27$, the C–C separation is only 1·71 Å. It is therefore clear that the carbon atoms are bonded together. If the bonding corresponds to a single bond, one would expect a C–C distance of 1·54 Å, which requires $y=0{\cdot}28$.

The value $y=0{\cdot}28$ will be adopted as leading to the most reasonable structure.

Discussion of the structure

With the parameter values $x=0{\cdot}050$ and $y=0{\cdot}280$ the interatomic distances become:

Pu–3 Pu = 3·35 Å
Pu–2 Pu = 3·52 Å
Pu–6 Pu = 3·70 Å
Pu–3 C = 2·48 Å
Pu–3 C = 2·51 Å
Pu–3 C = 2·84 Å
C–1 C = 1·54 Å
C–2 Pu = 2·48 Å
C–2 Pu = 2·51 Å
C–2 Pu = 2·84 Å

In PuC each plutonium atom is bonded to six carbon atoms with Pu–6 C = 2·46 Å. The distances Pu–C in Pu_2C_3 are thus quite reasonable. The Pu–Pu distances are all sufficiently large, but it is difficult to state whether or not there is direct Pu–Pu bonding.

It is seen that carbon atoms are bonded together into pairs. The bond distance of 1·54 Å was assumed, and the actual bond length may possibly be a little shorter than assumed.

Thanks are due to Dr E. F. Westrum for the loan of micro preparations of plutonium carbides and Miss Anne Plettinger for having taken the X-ray diffraction patterns.

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Acta Cryst. (1952). **5**, 19

Crystal Chemical Studies of the 5*f*-Series of Elements. XVI. Identification and Crystal Structure of Protactinium Metal and of Protactinium Monoxide

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(*Received* 11 *May* 1951)

X-ray diffraction examination shows that Sherman Fried, P. Sellers and R. E. Elson have succeeded in producing protactinium metal by reduction of the tetrafluoride with barium.

Investigations of the micro preparations showed the presence of small amounts of PaO_2 and of two other phases not previously encountered. One of these phases is identified as PaO, and the other as Pa metal.

Protactinium metal is tetragonal body-centered with two atoms in a cell of dimensions

$$a_1 = 3{\cdot}925 \pm 0{\cdot}005,\quad a_3 = 3{\cdot}238 \pm 0{\cdot}007\ \text{Å}.$$

The calculated density is $\rho = 15{\cdot}37 \pm 0{\cdot}08$ g.cm.$^{-3}$.

Each metal atom has ten next neighbors, eight at a distance of 3·212 Å and two at 3·238 Å. The metallic radius of protactinium for co-ordination number twelve is 1·63 Å. The results on thorium, protactinium and uranium show that there are no 5*f*-electrons in the metals.

PaO has the sodium chloride type of structure with $a = 4{\cdot}961 \pm 0{\cdot}003$ Å. The calculated density of PaO is $\rho = 13{\cdot}43$ g.cm.$^{-3}$.

The first compounds of protactinium to be prepared and conclusively identified were PaO_2, Pa_2O_5, $PaCl_4$, PaOS and PaF_4 (Zachariasen, 1949, 1950). In all cases the chemical identity was established through interpretation of X-ray diffraction patterns of the micro preparations.

The preparation of the tetrafluoride was of considerable interest, in that this compound is relatively nonvolatile and hence is excellently suited as starting material in reduction experiments designed to produce metal. Sherman Fried, P. Sellers and R. E. Elson made two separate attempts to obtain metal by reduction of protactinium tetrafluoride with barium. Both experiments were carried out on the 50 μg. scale. Microscopic examination indicated that the experiments had been successful. In each of the two experiments the reaction product consisted of a tiny metallic-looking globulet. This paper reports the results of X-ray diffraction investigations of the two globulets.

The X-ray diffraction data

The X-ray diffraction patterns were taken with Cu *K* radiation filtered through nickel foil. The globulet was contained in a thin-walled, flat-bottomed capillary.

The first X-ray diffraction patterns were taken using the original globulets and merely transferring them from the microcrucibles to the capillaries. Although these patterns were extremely weak, they showed that the products of the two reduction experiments were essentially the same. The only significant difference was that the diffraction lines of PaO_2 were quite prominent in the pattern of one globulet but hardly visible in that of the other.

Because of the extremely high absorption coefficient, the observed diffraction pattern is due only to the surface layer of the globulet. In order to improve the intensity of the pattern it was therefore essential to increase the surface area of the sample. Because of the microscopic size it was obviously out of the question to increase the surface area by filing. As a feasible substitute for filing it was decided to try to flatten the globulet into a disk. The flattening into nearly circular disks was successfully carried out by Dr Sherman Fried.

Table 1 gives the observed intensities and sine squares. No correction has been applied to the observations. As a consequence of absorption and excentricity effects, the observed sine squares are too large at small angles. The diffraction lines are quite diffuse at large scattering angles.

Interpretation of the diffraction pattern

The diffraction lines 1 and 7 of Table 1 can be interpreted as two of the strongest lines of the PaO_2 pattern. Lines 3 and 5 coincide with PaO_2 lines, but their intensities are too high relative to those of lines 1 and 7. Accordingly, lines 3 and 5 must correspond also to

Table 1. *Diffraction data*

	Observed		Calculated					
			PaO_2		Phase I		Phase II	
No.	Int.	$\sin^2\theta$	$H_1H_2H_3$	$\sin^2\theta$	$H_1H_2H_3$	$\sin^2\theta$	$H_1H_2H_3$	$\sin^2\theta$
1	*vw*	0·0599	111	0·0588	—	—	—	—
2	*ms*	0·0731	—	—	111	0·0725	—	—
3	*w*	0·0787	200	0·0784	—	—	110	0·0772
4	*vs*	0·0975	—	—	200	0·0966	101	0·0953
5	*w+*	0·1567	220	0·1568	—	—	200	0·1544
6	*wm*	0·1945	—	—	220	0·1933	—	—
7	*vvw*	0·2174	311	0·2156	—	—	—	—
8	*vw*	0·2293	—	—	—	—	002	0·2268
9	*s*	0·2511	—	—	—	—	211	0·2497
10	*ms*	0·2679	—	—	311	0·2658	—	—
11	*vw*	0·2917	—	—	222	0·2899	—	—
12	*ms*	0·3064	—	—	—	—	112 220	0·3040 0·3088
13	*m*	0·3841	—	—	400	0·3866	202 310	0·3812 0·3860
14	*w−*	0·4051	—	—	—	—	301	0·4041
15	*w*	0·4599	—	—	331	0·4590	—	—
16	*w+*	0·4841	—	—	420	0·4832	—	—
17	*w*	0·536	—	—	—	—	222	0·536
18	*w*	0·550	—	—	—	—	103	0·549
19	*w+*	0·557	—	—	—	—	321	0·559
20	*w−*	0·580	—	—	422	0·580	—	—
21	*m*	0·613	—	—	—	—	312 400	0·613 0·618
22	*w*	0·652	—	—	511 333	0·652	—	—
23	*s*	0·704	—	—	—	—	330 213	0·695 0·703
24		0·712	—	—	—	—	411	0·713
25	*w−*	0·772	—	—	440	0·773	420	0·772
26	*wm*	0·842	—	—	531	0·846	402	0·844
27	*w−*	0·860	—	—	—	—	303	0·858
28	*vw*	0·872	—	—	600 442	0·870	—	—
29	*vw−*	0·905	—	—	—	—	004	0·907
30	*w*	0·921	—	—	—	—	332	0·922

reflections due to another phase present in the sample. It is shown in Table 1 that all diffraction lines, apart from the two faint PaO_2 lines, can be assigned to two other phases.

Phase I

One of these phases has a face-centered cubic translation lattice with a unit cell constant

$$a = 4{\cdot}961 \pm 0{\cdot}003 \text{ Å}, \quad = 4{\cdot}951 \pm 0{\cdot}003 \text{ kX}.$$

The reflection (420) is definitely stronger than the neighboring reflection (331). This observation strongly suggests that phase I is not protactinium metal but rather the compound PaO with sodium chloride type of structure. This suggestion gets additional support when one makes comparisons with the monoxide of neighboring elements, as discussed later in this paper. Indeed, the direct and indirect evidence for the identification of phase I as PaO is so strong as to leave no room for doubt.

The calculated density of PaO is $\rho = 13{\cdot}43$ g.cm.$^{-3}$.

Phase II

The second phase is tetragonal body-centered with dimensions

$$a_1 = 3{\cdot}925 \pm 0{\cdot}005 \text{ Å} = 3{\cdot}917 \pm 0{\cdot}005 \text{ kX.},$$
$$a_3 = 3{\cdot}238 \pm 0{\cdot}007 \text{ Å} = 3{\cdot}232 \pm 0{\cdot}007 \text{ kX.}$$

It is seen from Table 1 that the observed intensities require just two metal atoms per unit cell. The volume per metal atom is 24·9 Å^3 as compared with 28·0 Å^3 in phase I. In thorium metal the atomic volume is 32·8 Å^3 and in uranium metal it is 20·7 Å^3.

In view of these observations and of the small metal–metal distances one is led to the conclusion that phase II is protactinium metal.

A number of observations corroborate the conclusion. The solid metallic-looking globulet was ductile, since it could be flattened into a disk. When it was heated in hydrogen, a reaction took place. X-ray diffraction patterns of the reaction product showed the presence of PaO_2, of phase I, and of a phase isostructural with UH_3, while there was no trace of phase II.

Discussion of the results

The density of protactinium metal is calculated to be $\rho = 15{\cdot}37 \pm 0{\cdot}08$ g.cm.$^{-3}$. The structure of the metal is not like that of any other element. However, the structure can be regarded as being derived from the cubic body-centered structure by compressing the latter along a fourfold axis so that the axial ratio is decreased from the ideal value of unity to 0·825. If this ratio were $\sqrt{\frac{2}{3}} = 0{\cdot}817$, each metal atom would have ten neighbors at exactly the same distance. As it is, each metal atom has eight neighbors at a distance of 3·212 Å and two at 3·238 Å. The next four neighbors are at the much greater distance of 3·925 Å.

The radius of the protactinium metal atom for co-ordination number ten is thus 1·609 Å. This corresponds to a radius of 1·63 Å for co-ordination number twelve. The metallic radius of thorium is 1·80 Å, and for uranium it is 1·54 Å. (The radius in body-centered uranium is 1·50 Å, and the correction in going from co-ordination eight to twelve is 0·04 Å.)

The metallic radii for thorium, protactinium and uranium show the rapid decline with atomic number characteristic of entrance of electrons into the *d* subshell. The presence of 5*f*-electrons in these metals is definitely excluded. Thus a radius of 1·76 Å for protactinium would be expected if one of the five outer electrons were a 5*f*-electron.

The monoxides of all elements from thorium to americium are now known. The interatomic distances are:

Th–O	2·60 Å	Np–O	2·50 Å
Pa–O	2·48 Å	Pu–O	2·48 Å
U–O	2·44 Å	Am–O	2·48 Å

The binding in these compounds is definitely metallic in character, and their existence cannot be regarded as evidence of a divalent state.

The help given by Sherman Fried, P. Sellers and R. E. Elson, who did the chemical work, and by Anne Plettinger, who took the diffraction patterns, is gratefully acknowledged.

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