directions with directions of maximum overlapping of atomic wave functions.

The interatomic distances in the neptunium metal structure are so short (and the densities so high) that one must assume at least six valence electrons and at most one 5*f* electron.

Miss Anne Plettinger and Dr Stanley Siegel gave valuable aid in calibrating the high-temperature camera and Miss Plettinger also by taking some of the diffraction patterns of neptunium metal. Sincere thanks are due Dr James C. Wallman for the use of his metal samples and Dr Sherman Fried for having made the exceptionally thin-walled capillary of fused quartz.

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# On the Structure of the Paratungstate Ion

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The structure of the complex ion in $5Na_2O.12WO_3.28H_2O$ has been determined, using a new vector-algebraic method. The formula of the ion, $W_{12}O_{46}^{20-}$, has no direct relation to the analytical formula, which would require a $W_{12}O_{41}^{10-}$-ion for the paratungstate to be a neutral salt.

## Crystals

The formula of sodium paratungstate has recently been determined as $5Na_2O.12WO_3.28H_2O$. The symmetry is triclinic, space-group $P\bar{1}$. Constants and estimated errors are:

$$\alpha=86^\circ\,0'\pm15',\ \beta=113^\circ\,20'\pm15',\ \gamma=94^\circ\,0'\pm15',$$
$$a=11{\cdot}77\pm0{\cdot}03,\ b=22{\cdot}19\pm0{\cdot}05,\ c=12{\cdot}44\pm0{\cdot}02\ \text{Å}\,.$$

There are 24 tungsten atoms in the cell (Saddington & Cahn, 1950). Single crystals of this paratungstate were prepared using the same procedure as the authors quoted. The crystal used for the X-ray investigation was prismatic with *c* as prism axis. Weissenberg photographs were taken with Cu *K* radiation and the *c* axis as rotation axis. Relative $|F|^2$ values were calculated from the estimated intensities with the help of Lu's curves (Lu, 1943). An appreciable absorption made the intensity values less valid. It was observed that reflexions with $h+k$ odd had very small intensities (the sum of their contributions was only 1·5% of the sum of all intensities). The point positions of the heavy tungsten atoms thus can be considered as corresponding to a *C*-centered unit cell, the larger dimensions being due to $Na^+$ and $H_2O$. The calculation of the three-dimensional Patterson function $P(x, y, z)$ then can be reduced to one-quarter of the unit cell. The functions $P(x, y_{n/60}, z)$ were computed on the X-RAC analogue computer for $y_n = 0$–15, and the structure was derived by a special method.

## Method of structure determination

The method of structure determination is based on the relations imposed upon the Patterson function if the structure has a centre of symmetry. Fig. 1 shows the vectors obtained for two twofold positions. They evidently form a parallelogram, where the vectors between equivalent atoms are the diagonals. The vector equations are

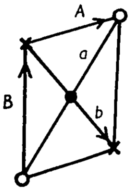

Fig. 1. Vector parallelogram produced by two twofold positions with a centre of symmetry.

$$A+B = a,\ A-B = b\,.$$

Each pair of two twofold positions will give rise to such a parallelogram in the Patterson function.

This fact indicates a simple method of analyzing the $P(x, y, z)$ vectors. Their components are tabulated and all possible vector sums are calculated. If the resulting vector sum is equal to one of the vectors in $P(x, y, z)$, the first of the vector equations is evidently fulfilled. It then remains to see if the corresponding vector difference is also found in $P(x, y, z)$.

If there are $n$ twofold positions in the unit cell, they will each form a parallelogram with the other $n-1$ positions. Each vector between equivalent atoms will then occur $n-1$ times as vector diagonal in those vector parallelograms. If there are more than $n$ vectors that have occurred $n-1$ times, because of special relations, one can find which of them are mutually combined in the parallelograms. The existence of all interatomic vectors in the structure is evidently confirmed during the derivation of the structure.

## Tungsten positions

In the case of sodium paratungstate the above method can obviously be applied only to the determination of the positions of the heavy tungsten atoms. Table 1 shows the components of all vectors obtained in $P(x, y, z)$ which possibly can be W–W vectors. (All vectors with a length $< 2{\cdot}8$ Å are excluded.) The fifth column gives the number of times that each vector has been found to be a diagonal in a vector parallelogram. Obviously there are six vectors (14, 20, 22, 38, 42, 46), as expected, which are diagonals five times or more. A control shows that these six vectors form parallelograms with all the other five vectors as the other diagonal. The 30 sides of these 15 parallelograms are found in Table 1, sixth column, and in Table 2. The six vectors (1, 6, 8, 9, 30, 36) which are sides in two parallelograms are also the highest maxima in $P(x,y,z)$, about twice as large as the maxima of the other 18 sides. The six diagonals are still smaller, each having a multiplicity only half as large as the sides (cf. Fig. 1). The 16 remaining vectors all have lower maximum values and may be explained as W–O, W–Na or O–O vectors, or as ghost maxima. The last possibility is very probable because the intensity values are not very accurate. The determination of the atomic positions from the vector diagonals is carried out by consideration of the vector relations between the point positions (Table 2). Each vector corresponds to four different point positions, e.g. 14 (0·96, 0·08, 0·54): (0·48, 0·04, 0·27), (0·98, 0·04, 0·27), (0·48, 0·04, 0·77) and (0·98, 0·04, 0·77). (0·98, 0·04, 0·77) was arbitrarily chosen as position I. Vector 22 then gives four possibilities: (0·27, 0·07, 0·46), (0·77, 0·07, 0·46), (0·27, 0·07, 0·96) and (0·77, 0·07, 0·96). Only II (0·27, 0·07, 0·96), requiring the two interatomic vectors I–II: (0·29, 0·03, 0·19) and (0·25, 0·11, 0·73), is in agreement with the vectors 6 and 18 obtained (Table 2). In the same way all the six positions were determined. The tungsten positions finally arrived at are given in Table 3.

Table 1. *Possible* W–W *vectors in* $P(x, y, z)$

| No. | Coordinates | | | Number of times that each vector occurs in a parallelogram as | |
|---|---|---|---|---|---|
| | $x$ | $y$ | $z$ | diagonal | side |
| 1 | 0·96 | 0·01 | 0·68 | — | 2 |
| 2 | 0·56 | 0·02 | 0·48 | 2 | — |
| 3 | 0·24 | 0·03 | 0·88 | 1 | 1 |
| 4 | 0·49 | 0·03 | 0·84 | 2 | 1 |
| 5 | 0·33 | 0·03 | 0·50 | 1 | 1 |
| 6 | 0·28 | 0·03 | 0·20 | — | 2 |
| 7 | 0·53 | 0·03 | 0·16 | 1 | 1 |
| 8 | 0·82 | 0·06 | 0·35 | 1 | 2 |
| 9 | 0·77 | 0·06 | 0·03 | — | 2 |
| 10 | 0·12 | 0·06 | 0·32 | — | — |
| 11 | 0·60 | 0·06 | 0·71 | — | — |
| 12 | 0·56 | 0·06 | 0·95 | — | — |
| 13 | 0·72 | 0·07 | 0·72 | 1 | 1 |
| 14 | 0·96 | 0·08 | 0·54 | 5 | — |
| 15 | 0·93 | 0·09 | 0·70 | 1 | — |
| 16 | 0·05 | 0·09 | 0·22 | 2 | 1 |
| 17 | 0·10 | 0·09 | 0·53 | 1 | 1 |
| 18 | 0·25 | 0·10 | 0·74 | 1 | 1 |
| 19 | 0·29 | 0·10 | 0·05 | 2 | 1 |
| 20 | 0·61 | 0·12 | 0·56 | 5 | — |
| 21 | 0·78 | 0·13 | 0·88 | 1 | 1 |
| 22 | 0·54 | 0·13 | 0·91 | 5 | — |
| 23 | 0·58 | 0·13 | 0·23 | 1 | 1 |
| 24 | 0·22 | 0·13 | 0·90 | — | — |
| 25 | 0·73 | 0·13 | 0·57 | 2 | — |
| 26 | 0·55 | 0·13 | 0·40 | — | — |
| 27 | 0·94 | 0·13 | 0·15 | — | — |
| 28 | 0·02 | 0·16 | 0·23 | — | — |
| 29 | 0·10 | 0·16 | 0·38 | 2 | 1 |
| 30 | 0·06 | 0·16 | 0·07 | 1 | 2 |
| 31 | 0·02 | 0·17 | 0·76 | 2 | 1 |
| 32 | 0·07 | 0·17 | 0·54 | — | — |
| 33 | 0·80 | 0·17 | 0·80 | 2 | — |
| 34 | 0·35 | 0·19 | 0·75 | — | — |
| 35 | 0·38 | 0·19 | 0·58 | 3 | 1 |
| 36 | 0·34 | 0·19 | 0·27 | 2 | 2 |
| 37 | 0·30 | 0·19 | 0·95 | 2 | 1 |
| 38 | 0·59 | 0·19 | 0·22 | 5 | — |
| 39 | 0·66 | 0·22 | 0·79 | 2 | — |
| 40 | 0·83 | 0·22 | 0·11 | 2 | 1 |
| 41 | 0·87 | 0·22 | 0·42 | 1 | 1 |
| 42 | 0·34 | 0·25 | 0·38 | 5 | — |
| 43 | 0·12 | 0·25 | 0·30 | 2 | 1 |
| 44 | 0·44 | 0·25 | 0·58 | — | — |
| 45 | 0·68 | 0·25 | 0·91 | — | — |
| 46 | 0·07 | 0·25 | 0·98 | 6 | — |

Table 2. *Interatomic vectors found during the analysis*

The numbers of the vectors are taken from Table 1.
The point positions (I–VI) are given in Table 3.

| | I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| I | 14 | 18 | 31 | 19 | 21 | 30 |
| II | 6 | 22 | 37 | 23 | 30 | 36 |
| III | 16 | 9 | 46 | 36 | 40 | 43 |
| IV | 5 | 1 | 13 | 20 | 29 | 35 |
| V | 8 | 7 | 3 | 4 | 38 | 41 |
| VI | 17 | 8 | 1 | 9 | 6 | 42 |

Table 3. *Tungsten positions*

| No. | $x$ | $y$ | $z$ |
|---|---|---|---|
| I | 0·98 | 0·040 | 0·77 |
| II | 0·26 | 0·065 | 0·95 |
| III | 0·03 | 0·130 | 0·99 |
| IV | 0·31 | 0·055 | 0·28 |
| V | 0·80 | 0·090 | 0·11 |
| VI | 0·08 | 0·120 | 0·31 |

## Oxygen positions

In the determination of the oxygen configurations in a series of polymolybdates (e.g. Lindqvist, 1950*a*, *b* and *c*) several conclusions have been drawn from the interatomic Mo–Mo distances. These investigations prove that a Mo–Mo distance of 3·0–3·5 Å corresponds to $MoO_6$ octahedra sharing edges. The same can be expected to be valid for W–W distances, as has also been found in heteropolytungstates (Keggin, 1934). Distances of 3·6 Å up to 4·6 Å have been shown to be in agreement with a Mo–O–Mo connection, the variation in length depending upon how straight the Mo–O–Mo chain is. In heteropolytungstates (Keggin, 1934) with appreciable deviations from a straight-line connection, the W–O–W distances have been found to be about 3·8 Å. In order to discuss the structure from this point of view, all W–W distances have been calculated (Table 4). It is evident that there are short W–W distances within the group I, II, III and within the group IV, V, VI, but not between these groups. In the group I, II, III three $WO_6$ octahedra share edges mutually corresponding to the structure shown in Fig. 2. In the other group only VI is connected to both the others according to Fig. 2. It then remains to link these groups together with the aid of the frequently occurring 3·7–4·1 Å vectors. This has been accomplished in Fig. 2, where I and III are linked to IV, V, and VI and II to IV and VI in accordance with Table 4. In the resulting ion, with the composition $W_{12}O_{46}^{20-}$, the six octahedra marked I, II, III are evidently parallel as are also the six marked IV, V, VI. The two groups are not, however, parallel with each other. Each of the 3+3 = 6 W–O vectors in these octahedra thus occurs 2×6 = 12 times within the ion, and may therefore show up in the *P*(*x*, *y*, *z*) function. It is, indeed, possible to find all the 6 W–O vectors, required by the structure. They are given in Table 5. The values of the W–O distances are very uncertain and the differences cannot be considered as significant. The structure is given in another representation in Fig. 3, showing the hexagonal close-packing of oxygen atoms in $W_{12}O_{46}^{20-}$. (Fig. 2 gives the wrong impression that there are holes in the middle of the ion.) The unit cell evidently contains two such $W_{12}O_{46}^{20-}$ ions, in agreement with its close to *C*-centering. No attempt has been made to determine the remaining O and Na positions.

Table 4. *The lengths of the vectors of Table* 2

(Lengths are given in Ångström units)

| | I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| I | 5·7 | 5·4 | 4·6 | 3·7 | 3·9 | 3·7 |
| II | 3·3 | 7·2 | 5·4 | 6·7 | 3·7 | 5·7 |
| III | 3·3 | 3·3 | 5·5 | 5·7 | 6·0 | 7·3 |
| IV | 5·9 | 3·8 | 4·1 | 8·1 | 5·8 | 8·0 |
| V | 5·8 | 5·7 | 3·7 | 5·7 | 8·1 | 8·0 |
| VI | 6·6 | 5·8 | 3·8 | 3·3 | 3·3 | 9·1 |

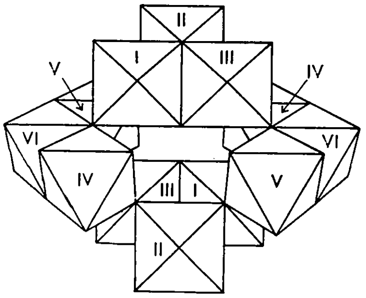

Fig. 2. Structure of the paratungstate ion shown as built up of $WO_6$ octahedra. These octahedra have the same numbers as the corresponding twofold W positions in Table 3.

Table 5. W–O *vectors found in P*(*x*, *y*, *z*)

| *x* | *y* | *z* | Length (Å) |
|---|---|---|---|
| 0·03 | 0·01 | 0·83 | 2·2 |
| 0·81 | 0·06 | 0·86 | 2·2 |
| 0·08 | 0·09 | 0·06 | 2·2 |
| 0·18 | 0·03 | 0·03 | 2·0 |
| 0·92 | 0·01 | 0·84 | 1·8 |
| 0·96 | 0·09 | 0·04 | 2·3 |

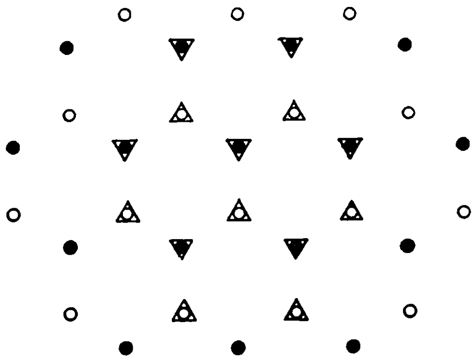

Fig. 3. The 46 oxygen atoms of the paratungstate ion showing hexagonal close-packing. The layers parallel to the plane of the figure are stacked in the order ▽ ● ○ △.

## Discussion of the structure

The formula of the ion $W_{12}O_{46}^{20-}$ has no obvious relation to the analytical formula $5Na_2O.12WO_3.28H_2O$, which, to be a neutral salt, would require a $W_{12}O_{41}^{10-}$ ion. The structure determination of the complex ion thus does not permit a direct application to the study of the conditions in aqueous solutions, as was possible in the polymolybdate case (Lindqvist, 1950*d*, 1951). The metatungstates (Illingworth & Keggin, 1935) evidently offer the same difficulty, having the formula $W_{12}O_{40}^{8-}$ instead of $W_{12}O_{39}^{6-}$. It is, however, intended to make further physico-chemical investigations in order to explain the ionic conditions in aqueous tungstate solutions.

There are other examples of large complex ions having formulae which do not correspond to neutral salts. The heteropolyacids, for example, have been discussed recently (Wells, 1950, p. 353). At present the question is left open as to the state of the excess

$H^+$ ions formed from the $H_2O$ molecules which have contributed $O^{2-}$ ions to the complex ion.

The X-ray work on this structure was carried out in Uppsala, where I was assisted by Mr Bengt Lindqvist, whom I should like to thank for his valuable aid. The Swedish Natural Science Research Council supported the investigation financially, and their support is gratefully acknowledged. The computation work took place at Pennsylvania State College, and I wish to thank Prof. Ray Pepinsky for his generous invitation to me to visit his Institute and to work with his X-RAC computer.*

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* Contract No. N 6 onr – 25916 TO 16.

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# Fourier Strips at a 3° Interval

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The production of a new set of Fourier strips to an interval of 3° is described and the uses are outlined. It is thought that this set will be of considerable service in structure-factor calculation as well as in the computation of electron-density and Patterson maps, and in the calculation of molecular Fourier transforms.

## 1. Introduction

The printed 'strips' of numbers for the evaluation of the Fourier series used in X-ray analysis were introduced by Lipson & Beevers in 1934, when a set of strips to an interval of 6° was produced. Some 75 copies of the original set were distributed to workers in many parts of the world, and they have been widely used both for the Fourier-series summation of electron densities, and for the Patterson syntheses which are being increasingly employed in the study of complex structures. They have also been used for Fourier analysis in other applications, e.g. by Ross (1943).

The original strips tabulated the values of $A \cos nh\theta$ and $A \sin nh\theta$, where $\theta$ is 6°, and $n$ takes the values 0 (1) 15 along the strip, and where $A$ has the values 0 (1) 100 on different strips. In this set the negative values of $A$ are on the reverse side of the corresponding positive-value strips. Strips having the same value of $h$ are placed in order of $A$ in one compartment of a box with sloping sides, and the different compartments of this box contain strips of the different values of $h$ from 0 to 20.

As was pointed out in one of the early papers (Lipson & Beevers, 1936), the interval $\theta = 6°$ is considered adequate for the Fourier synthesis of crystals having their greatest projection edge less than 15 Å. Modern X-ray analysis is, however, frequently concerned with projection edges considerably greater than this, at least in one direction, and therefore a finer interval of division is necessary. Furthermore, the 6° strips are inaccurate for structure-factor calculations, although a structure factor can always be reduced to summations of terms of the type $A \begin{smallmatrix}\cos\\ \sin\end{smallmatrix} nh\theta$. For this use of the strips the atomic parameters would be taken to be $h\theta$, and the contribution of the atom to the different orders would be obtained by going to different values of $n$ along the strip. With $\theta = 6°$, however, the coordinate $h\theta$ would be hopelessly inaccurate for the higher orders (larger $n$), and furthermore the limit of 20 to the value of $h$ would restrict the atom to the first third of the unit cell. These considerations limit the application of the 6° strips to structure-factor calculations.

The present paper describes the design of a further set of Fourier strips at an interval $\theta = 3°$. It is thought that this set will not only permit the strip method to be used for Fourier synthesis of unit cells up to 30 Å projection edge, but will also provide a wide field of application to structure-factor calculation (see Beevers & Lipson, 1952).

The Fourier-strip method requires the addition of