696. *The Formula of Sodium Paratungstate.*

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The variations in the formulæ ascribed to the paratungstates are recalled. The results of some new chemical analyses on sodium paratungstate crystals are given, together with data obtained by goniometric measurements and by *X*-ray diffraction studies of the crystals. From these it is concluded that the crystalline salt has the composition $Na_{10}W_{12}O_{41},28H_2O$ and an attempt is made to correlate this formula with the formula $[HW_6O_{21}]^{5-}$ suggested by Jander for the paratungstate anion.

Of the numerous classes of crystalline tungstates which have been reported, three only are known for certain, *viz.* : (1) the normal tungstates in which the ratio $WO_3 : R_2O = 1$, (2) the paratungstates which have been given the formula $3R_2O,7WO_3$ by some authors, and $5Na_2O,12WO_3$ by others, and (3) the metatungstates in which the ratio $WO_3 : R_2O = 4$.

Thus Jander and Jahr (*Kolloid Beih.*, 1935, **41**, 18), despite numerous experiments, failed to obtain from alkali tungstate solutions crystals of intermediate composition; and Souchay (*Ann. Chim.*, 1943, **18**, Jan.—June issues) in a comprehensive review of the subject, has shown that the other classes previously reported are mixed crystals of the three definite classes enumerated.

For the paratungstates themselves a number of different varieties have been reported. Thus in Groth's " Chemische Kristallographie," Part II, 1908, five salts obtained by Marignac from solutions of sodium paratungstate are listed together with their crystal data. From his results Marignac claimed the existence of five forms, crystallographically different, which he formulated as different hydrates of one or other of the two formulæ $3R_2O,7WO_3$ and $5R_2O,12WO_3$. Since one such salt was obtained on one occasion only, and since in all cases the material measured was not characterised properly from a chemical standpoint, it is very doubtful whether these several compounds are in fact real and distinct. But the decision as to the correct formula of the paratungstates is difficult to make on the basis of analytical figures alone, since the salts are usually heavily hydrated and the crystals easily undergo partial dehydration in air. In addition, because of the high atomic weight of tungsten, the theoretical difference of tungsten content between the two formulæ is very small. Nevertheless by careful study of the paratungstates, Vallance (*J.*, 1931, 1421) decided in favour of the 5 : 12 formula. In his work, Vallance determined the water content by direct ignition of the crystals, and the tungsten as the trioxide after treatment of a solution of the salt with cinchonine hydrochloride followed by ignition of the precipitate thereby obtained. The content of alkali-metal oxide was obtained by difference and the ratio $WO_3 : R_2O$ used as a basis for comparison. In Souchay's work (*loc. cit.*) on the sodium salt, the water content was obtained by ignition, and the $WO_3 : R_2O$ ratio calculated from the volume of standard sodium hydroxide solution required to convert the tungstic acid portion of the acid salt into the normal salt. The results indicate the existence of a salt of ratio $WO_3 : R_2O = 2{\cdot}4$, corresponding to the 12 : 5 formula, in agreement with Vallance.

The paratungstates and paramolybdates have, in the past, often been considered as formally analogous to one another, and the same difficulty of formulation as $3R_2O,7MoO_3$ or $5R_2O,12MoO_3$ has arisen for the molybdenum compounds. *X*-Ray determination of the lattice constants and weight per unit cell of ammonium paramolybdate by Sturdivant (*J. Amer. Chem. Soc.*, 1937, **59**, 630) confirmed the analyses of Garelli and Tettamanzi (*Atti R. Accad. Sci. Torino*, 1935, **70**, 382) in assigning the heptamolybdate formula $3(NH_4)_2O,7MoO_3$,aq. to this compound. More recent analyses by Lindqvist (*Acta Chem. Scand.*, 1948, **2**, 88) have confirmed this formula.

In view of the different formulæ thus ascribed to the crystalline paratungstates and paramolybdates, and in furtherance of some work done by one of us (K. S.) on the composition of the ions formed in tungstate solutions, to which further reference will be made, it was decided to apply the *X*-ray method of analysis to the determination of the composition of crystalline sodium paratungstate. In addition some new chemical analyses on the crystals were performed.

Experimental.

A solution of sodium tungstate was prepared and its pH, originally 10·5, was adjusted to 5·2 by careful addition of nitric acid. Previous work by Jander (*Kolloid Beih.*, 1935, **41**, 21) and by Anderson and Saddington (*J.*, 1949, S 381) had shown that in such solutions the paratungstate ions are formed. The final concentration corresponded to a molar solution of the normal tungstate—a value well below that for a saturated solution of the normal salt, yet considerably in excess of the concentration corresponding to a saturated solution of the paratungstate. When the solution was kept at room temperature, therefore, crystals of sodium paratungstate slowly separated and were dried on absorbent paper ready for use in the various experiments. It was found that intergrowth of the crystals could largely be prevented by allowing them to deposit on mounds of plasticine immersed in the solution.

Chemical Analyses.—(a) *Water.* In determinations of the loss of water on heating, there was a continual decrease in weight as the temperature was increased to 300°. Further heating gave rise to no further loss in weight. The values obtained were 14·08, 13·95, 14·02, 14·05; mean 14·025%.

(b) *Sodium and tungsten.* Both metals were determined on the same samples of anhydrous salt, a separation being effected by removing the tungsten as the volatile oxychloride. A preliminary check on the efficiency of this method of separation was made with the aid of an authentic sample of anhydrous sodium tungstate.

(i) *Check on separation procedure.* A sample of recrystallised sodium tungstate (99·92% purity) was heated to constant weight at 110°. 0·5726 G. of the anhydrous salt was heated at 500—550°, in a current of hydrogen chloride; it was contained in a porcelain boat inside a hard glass tube and the tungstyl chloride, WO_2Cl_2, formed was swept along by the excess of gas. Part of the oxychloride condensed in an adaptor and the remainder was trapped in a vessel containing water. The residual sodium chloride in the boat was weighed and then tested qualitatively for tungsten. The weight of the residue obtained was 0·2280 g. (after further treatment for 60 minutes, 0·2279 g.) (theor., 0·2277 g.). The qualitative tests applied were as follows : (1) A portion of the residue was fused with ammonium hypophosphite and the cool residue moistened with water. No blue colouration was observed. (2) A further portion was dissolved in water, and hydrochloric acid was added. No precipitate of tungstic acid was obtained. (3) To a further portion dissolved in water, stannous chloride and concentrated hydrochloric acid were added. No blue coloration was obtained.

The absence of tungsten in the residue and the close agreement between the observed and the theoretical weight of the sodium chloride residue were taken as satisfactory evidence of the sufficiency of the separation procedure.

(ii) *Application to sodium paratungstate.* 0·6293 G. of the anhydrous sodium paratungstate was treated as in (i). The oxychloride fractions so obtained were combined and the tungsten precipitated as tungstic acid by the standard procedure using cinchonine hydrochloride after treatment with hydrochloric and nitric acids The precipitate was filtered off, washed, and ignited to tungsten trioxide which was then weighed. The weight of precipitate was 0·5656 g. which corresponds to 89·87% of WO_3.

The residue in the boat weighed 0·1189 g., equiv. to 0·1260 g. of Na_2O, *i.e.*, 10·02%. The theoretical weight of sodium chloride is 0·1190 g. on the basis of the 5 : 12 formula and 0·1221 g. on the basis of the 3 : 7 formula.

	Found :		Calculated for :			
	anhydrous salt.	hydrated salt.	(*a*) $3Na_2O,7WO_3,16H_2O$.*	(*b*) $5Na_2O,12WO_3,28H_2O$.*	(*c*) $3Na_2O,7WO_3$.	(*d*) $5Na_2O,12WO_3$.
H_2O	—	14·025	13·73	14·01	—	—
WO_3	89·87	—	—	—	89·72	89·98
Na_2O	10·02 (direct)	—	—	—	10·28	10·02
	$10{\cdot}02_5$ (by analysis)	—	—	—		
Ratio, $WO_3 : Na_2O$	$8{\cdot}95_8$	—	—	—	8·73	8·98
Molar ratio, $WO_3 : Na_2O$	$2{\cdot}39_7$	—	—	—	2·33	2·40

* The water contents corresponding to the other hydrates reported by Marignac (*loc. cit.*) differ from the observed value by more than 1·5%.

The whole of the residue was dissolved in water and made up to 100 ml. Portions of this solution, examined qualitatively by the tests described, showed no evidence for the presence of tungsten. Two 10-ml. portions of the solution were next analysed for sodium content by precipitation as the triple acetate with uranium and magnesium as described by Nydahl (*Lantbruks-Högskol Ann.*, 1937, **6**, 45) but using the corrected formula $NaMg(UO_2)_3,(CH_3{\cdot}CO_2)_9,6{\cdot}5H_2O$ instead of the earlier one containing $8H_2O$. The weights of the complex acetate so obtained were 0·3072 and 0·3061 g., which correspond to 10·04 and 10·01% of Na_2O respectively.

The results of the chemical analyses are summarised in the table. They appear to be in better agreement with the theoretical values corresponding to the 5 : 12 formula than with those based on the 3 : 7 formula.

In anticipation of the *X*-ray work a duplicate determination of the density of the hydrated crystals was carried out by displacement of xylene at 25°. The density was found to be 4·01 ± 0·01.

Goniometric and X-Ray Measurements.—Ten selected crystals were examined on a " Unicam " two-circle goniometer, the well-marked prismatic axis being set parallel to the axis of the vertical circle. Most of the faces gave a number of vicinal reflections of approximately equal intensity, so that it was not often possible to determine accurate interfacial angles. The best values of the angles between the prismatic faces were selected from among all the crystals examined, and a composite stereogram plotted over a 12-inch net. On this the best positions for the observed pyramidal poles were found graphically. An estimated accuracy in the positions of all poles of ±15′ was attained. The stereogram was indexed by assigning the simplest possible indices to the observed poles; the crystal was of the triclinic pinacoidal class $\bar{1}$.

The following forms were observed: 001, 010, 100, 110, $1\bar{1}0$, 011, $0\bar{1}1$, $0\bar{2}1$, $\bar{1}11$, $\bar{1}\bar{1}1$. Of these, 100 and $0\bar{2}1$ were rare and poorly developed, and 001 was almost invariably imperfect.

The habit was generally prismatic with *c* as prism axis. Rarely, *a* was the prism axis, or the crystals were plate-shaped.

Small, well-developed crystals were selected to make *X*-ray rotation photographs. They were set on the optical goniometer so that in each case one of the morphological axes was parallel to the axis of rotation. There were sufficient good faces for this to be done with an accuracy of a few minutes of arc for the *a* and *c* axes. Because of the poor quality of (100) and (001) the *b* axis was more difficult to set, and only one photograph was obtained with good layer lines. The goniometer head with the crystal in position was transferred to a Unicam *X*-ray goniometer, and a rotation photograph made with filtered copper $K\alpha$ radiation, delimited by a fine collimator. Several photographs were taken about each axis.

The diameter of the cylindrical camera (nominally 6 cm.) was accurately measured with a precision measuring microscope, and a careful mechanical check showed that the axis of rotation coincided with the camera axis within 0·1 mm. Fiducial marks made on the film before development showed the film shrinkage to be negligible to the degree of accuracy attained in the experiments.

Layer lines were found in all cases, showing that the morphological axes were also the axes of the true unit cell. The axial lengths were found by measuring the spacing of several layer lines on each photograph, and axial ratios calculated from them agreed with the optical ratios within the experimental error. The values of the axial lengths were adjusted, within the limits of this error, to make the two sets of ratios exactly consistent.

The volume of the unit cell was calculated from the crystal constants, and its molecular weight found from this and the density.

Results. The symmetry is triclinic pinacoidal $\bar{1}$, and the space-group is, therefore, $p\bar{1}$. Constants, and estimated maximum errors are: $\alpha = 86°0' \pm 15'$; $\beta = 113°20' \pm 15'$; $\gamma = 94°0' \pm 15'$; $a = 11{\cdot}77 \pm 0{\cdot}03$ A.; $b = 22{\cdot}19 \pm 0{\cdot}05$ A.; $c = 12{\cdot}44 \pm 0{\cdot}02$ A.; $a : b : c = 0{\cdot}531 : 1{\cdot}000 : 0{\cdot}560\ (\pm 0{\cdot}002)$.

These axial ratios agree, with an error of about 0·002 with those quoted by Groth (*loc. cit.*) for the compound $Na_{10}W_{12}O_{41},28H_2O$, except that, by faulty indexing, c/b was quoted as double the correct value. The measured density compares favourably with the value of 3·99 recorded by Scheibler, and quoted by Groth (*loc. cit.*).

The volume of the unit cell is given by

$$V = abc(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha . \cos \beta . \cos \gamma)^{\frac{1}{2}}$$

from which $V = (2980 \pm 30) \times 10^{-24}$ c.c.

Since the density is 4·01 at 25°, the weight of the unit cell $= 2980 \times 10^{-24} \times 4{\cdot}01$ g., and the "molecular weight of the unit cell," *i.e.*, its weight compared with that of the hydrogen atom as unity, is $(2980 \times 10^{-24} \times 4{\cdot}01)/(1{\cdot}66 \times 10^{-24}) = 7197 \pm 70$.

The molecular weights corresponding to the two formulæ which have been ascribed to sodium paratungstate are: $Na_6W_7O_{24},16H_2O$, 2098; $Na_{10}W_{12}O_{41},28H_2O$, 3598. When the molecular weight of the unit cell is divided by these values, the quotients are $3{\cdot}43 \pm 0{\cdot}03$ and $2{\cdot}00 \pm 0{\cdot}02$ respectively. Since the quotient must be an integer it is considered that the second formula is correct.

CONCLUSIONS.

The chemical analyses show that in crystalline sodium paratungstate the ratio $Na : W : H_2O = 5 : 6 : 14$.

The crystallographic results indicate that the crystal contains an asymmetric unit, which might contain more than one crystallographically distinct molecule, of gross composition corresponding to $2Na_{10}W_{12}O_{41},28H_2O$.

In addition to these facts further evidence, relating to the constitution of the ions in the solution from which the sodium paratungstate crystallises out, must be considered in order to obtain a true picture of the molecule. Jander *et al.* (*Kolloid-Beih.*, 1935, **41**, 18; *Z. physikal. Chem.*, 1942, **190**, 195) state that in solutions less than 1·2M. in tungsten the largest aggregates formed are hexatungstic ions and that the formation of a dodecatungstate ion is apparent only in stronger solutions of pH less than 3. From such solutions the crystals obtained are those of the metatungstates. The absence of a dodecatungstate ion in dilute solution is confirmed by the work of Anderson and Saddington (*loc. cit.*) whose results on the diffusion of tungsten ions, whilst not confirming unequivocally the presence of a hexatungstate ion, nevertheless do not permit the assumption of a 12-fold state of ionic aggregation.

The correlation of this evidence from studies of the salt both as solid and in solution lead to the conclusions that part of the water in the crystal is constitutional and that the composition of the unit cell in the crystal is given by $4 \times Na_5[HW_6O_{21}],\frac{27}{2}H_2O$.

These conclusions are in agreement with the chemical analyses, with the demonstration that the unit cell has a molecular weight of 7196, and with Jander's statement (*loc. cit.*) that the solutions from which the crystals are obtained contain the $[HW_6O_{21}]^{5-}$ ion. The mode of aggregation of tungstate ions in solution proposed by Jander on the basis of conductimetric and thermometric titrations and supported by Souchay (*Ann. Chim.*, 1943, **18**, 72, 178) on the basis of potentiometric titration, viz.:

$$6(WO_4,aq.)^{2-} + 7H^+ \rightleftharpoons (HW_6O_{21},aq.)^{5-} + 3H_2O$$

thus receives further support from the present work.

Finally, the formula $2Na_5[HW_6O_{21}],27H_2O$ in which one molecule of water is constitutional suggests the firmer retention of this molecule. This has not been observed; but in the experiments on the loss in weight of the crystals as a function of temperature it was impossible completely to dehydrate the salt without decomposition, leading to the formation of insoluble tungsten trioxide. The decomposition appeared to commence before all the hydrate water had been driven off.

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