Protons attached to the remaining ring carbon atom show a quintuplet pattern near τ 8.25 p.p.m.

The infrared spectrum of the decalin analog II exhibited a N–H stretch at 3400 cm.$^{-1}$. Very strong absorption in the 1500–1300 cm.$^{-1}$ region of the infrared spectra of boron–nitrogen compounds is normally associated with the B–N stretching vibration of a covalent boron–nitrogen bond in which the free electrons of the nitrogen can participate.[16] In the spectrum of the 1,8,10,9-triazaboradecalin, three bands of unusually strong intensity were recorded at 1510, 1434, and 1320 cm.$^{-1}$. Final assignment of these modes awaits isotopic studies. The ^{11}B chemical shift of compound II was found as a singlet at −22 p.p.m. with a band width at half-maximum peak height of about 100 c.p.s.

[16] H. Beyer, J. B. Hynes, H. Jenne, and K. Niedenzu, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p. 266.

CONTRIBUTION FROM THE RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY, SCHENECTADY, NEW YORK

A Partial Study of the Ternary System Disodium Monotungstate–Tungstic Oxide–Water at 25°. The Formation of Disodium Ditungstate Pentahydrate[1]

BY EDWARD L. SIMONS

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Solubility data were obtained in the ternary system disodium monotungstate–tungstic oxide–water at 25° for mixtures in which the mole ratio of WO_3 to Na_2WO_4 was less than 7:5. The equilibrium solid phases were disodium monotungstate dihydrate, decasodium dodecatungstate 28-hydrate (sodium paratungstate), and the previously unreported disodium ditungstate pentahydrate, which is incongruently soluble. The metastable equilibriums that precede the formation of the ditungstate are described, and data are presented to show that a monohydrate is formed as a stable intermediate during the thermal dehydration of the pentahydrate. Washing and drying experiments, microscopic examination, powder X-ray diffraction patterns, chemical analysis, and thermogravimetric measurements were used to characterize both the penta- and monohydrates of disodium ditungstate.

Among the more than a dozen anhydrous and hydrated sodium isopolytungstates that have been reported in the literature since the middle of the 19th century,[2,3] only the four listed in Table I have been recognized in critical reviews[4,5] as discrete compounds.

TABLE I

COMPOSITIONS OF KNOWN SODIUM ISOPOLYTUNGSTATES[a]

Anhydrous[b]	Hydrated[c]
$Na_2WO_4 \cdot WO_3$ (Disodium ditungstate)	. . .
. . .	$5Na_2WO_4 \cdot 7WO_3 \cdot 28H_2O$ (Sodium paratungstate)
$Na_2WO_4 \cdot 3WO_3$ (Disodium tetratungstate)	$Na_2WO_4 \cdot 3WO_3 \cdot 10H_2O$ (Sodium metatungstate)

[a] Formulas are written to show the mole ratio of the components of the binary or ternary system and are not meant to inply any structural information. [b] F. Hoermann, *Z. anorg. allgem. Chem.*, **177**, 145 (1928); P. Caillet, *Compt. rend.*, **256**, 1986 (1963). [c] V. I. Spitsyn, *Zh. Obsch. Khim.*, **8**, 869 (1938); A. Lottermoser, W. Riedel, and O. Bretschneider, *Z. Elektrochem.*, **36**, 183 (1930); M. L. Freedman, *J. Am. Chem. Soc.*, **81**, 3834 (1959); K. Saddington and R. W. Cahn, *J. Chem. Soc.*, 3256 (1950); G. Schott and C. Harzdorf, *Z. anorg. allgem. Chem.*, **288**, 15 (1956); R. H. Vallance, *J. Chem. Soc.*, 1421 (1931).

Although sodium metatungstate can formally be considered as a hydrate of $Na_2WO_4 \cdot 3WO_3$, sodium paratungstate has no analog in the anhydrous binary system,[6] and complete removal of its water leads to disproportionation into a mixture of $Na_2WO_4 \cdot WO_3$ and $Na_2WO_4 \cdot WO_3$.[7,8] In 1876 Lefort[9,10] reported the crystallization of $Na_2WO_4 \cdot WO_3 \cdot 6H_2O$ from a solution of the monotungstate acidified with acetic acid, but subsequent workers have been unable either to duplicate Lefort's results[2–4,8,11] or to prepare a hydrated disodium ditungstate by other methods.[12,13]

This paper presents evidence for the formation of disodium ditungstate pentahydrate ($Na_2WO_4 \cdot WO_3 \cdot 5H_2O$) as a stable but incongruently soluble solid phase in the ternary system Na_2WO_4–WO_3–H_2O at 25° and for the formation of a monohydrate as a stable intermediate during the thermal dehydration of the pentahydrate. The phase relationships in this ternary system and the slow rate of formation of the pentahydrated ditungstate may explain the failure of previous investigators to crystallize this phase from aqueous solution.

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[1] Presented before the Inorganic Division at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

[2] Gmelin's "Handbuch der Anorganischen Chemie," S.N. 54, Verlag Chemie, G.M.B.H., Berlin, 1935, pp. 219–233.

[3] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XI, Longmans, Green and Co., London, 1931, pp. 809–812.

[4] P. Souchay, *Ann. Chim.* (Paris), [11] **18**, 61 (1943).

[5] D. L. Kepert, *Progr. Inorg. Chem.*, **4**, 199 (1962).

[6] F. Hoermann, *Z. anorg. allgem. Chem.*, **177**, 145 (1928).

[7] V. I. Spitsyn, *Zh. Obshch. Khim.*, **8**, 869 (1938).

[8] T. Dupuis, *Mikrochim. Acta*, 214 (1963).

[9] J. Lefort, *Ann. Chim. Phys.*, [5] **9**, 96 (1876).

[10] J. Lefort, *Compt. rend.*, **82**, 1182 (1876).

[11] W. Gibbs, *Am. Chem. J.*, **1**, 217 (1879).

[12] A. Lottermoser, W. Riedel, and O. Bretschneider, *Z. Elektrochem.*, **36**, 183 (1930).

[13] M. L. Freedman, *J. Am. Chem. Soc.*, **81**, 3834 (1959).

Experimental

Materials.—Disodium monotungstate dihydrate, Folin (granular), analytical reagent, Mallinckrodt. *Anal.* Calcd. for $Na_2WO_4 \cdot 2H_2O$: H_2O, 10.92; W, 55.75. Found: H_2O, 10.92; W, 55.8.

Tungstic acid, Lamp Metals and Components Department, General Electric Co. *Anal.* Calcd. for $WO_3 \cdot H_2O$: H_2O, 7.21; W, 73.59. Found: H_2O, 7.26; W, 73.4.

De-ionized water was prepared by passing laboratory distilled water through an Amberlite MB-3 mixed bed ion-exchange column.

Procedure.—Mixtures of $Na_2WO_4 \cdot 2H_2O$, $WO_3 \cdot H_2O$, and de-ionized water were prepared by direct weighing into polyethylene bottles, which were then capped, sealed with paraffin wax, and mounted on a rotating rack in a water bath maintained at 25 ± 0.01°. After at least 2 months, the solid phases were allowed to settle, and samples of the supernatant liquids were removed for determination of their water content. When two successive analyses, made at intervals of no less than 2 months, showed the same water content, the system was assumed to be at an equilibrium state, and the solution was analyzed for sodium and tungsten.

From 2 to 7 months was required to reach this state when the initial mixtures contained a mole ratio of WO_3 to Na_2WO_4 less than 7:5. More than 2 years has been insufficient for mixtures in which the ratio lies between 7:5 and 3:1. In the analogous molybdate system Byé[14,15] and Ricci and Doppelt[16] observed that weeks or months were required for equilibration of some mixtures, and that the higher the content of MoO_3, the more slowly was equilibrium reached. This paper contains no data for compositions richer in tungsten than sodium paratungstate.

Analysis.—Water was determined as the loss in weight when a sample of the solution was evaporated to dryness at 450°. Thermogravimetric measurements had shown that this temperature is high enough to ensure complete dehydration of all solids encountered in this system. To prevent spattering and decrepitation, the solid was first precipitated as a fine powder by adding to the weighed sample approximately twice its volume of ethyl alcohol. The evaporation was then carried out slowly by raising the temperature over a period of several hours. A similar technique was used to determine the water content of the wet solid phases, some of which were analyzed after they had been separated as completely as possible from their mother liquors by centrifugal or vacuum filtration and blotting with filter paper. Others were analyzed after washing, as described in a later section.

Sodium and tungsten were determined in the liquid samples and in some of the dehydrated solid samples by Lucius Pitkin, Inc., New York, N. Y. Other dehydrated solid samples were analyzed directly for the amount of WO_3 in excess of the stoichiometry of Na_2WO_4 by measuring the weight loss that occurred when they were heated at 675° with excess Na_2CO_3 in a Pt crucible in a flowing CO_2 atmosphere. Previous workers[17-20] had shown that the reaction

$$Na_2WO_4 \cdot nWO_3 + nNa_2CO_3 = (n + 1)Na_2WO_4 + nCO_2 \quad (1)$$

is complete under these conditions.

Density and pH.—Densities of aqueous solutions were measured with 1-ml. pycnometers, and pH measurements were made with a Beckman Model G pH meter using glass and saturated calomel electrodes.

X-Ray Powder Diffraction.—Photographs from which *d* values for the ditungstate phases were measured were taken in a Guinier double cylinder camera of 114.6-mm. diameter using Cu Kα radiation reflected from a quartz monochromator. The samples were wrapped in a Mylar envelope.

All other photographs were taken in a 114.6-mm. diameter Debye–Scherrer camera on 35-mm. film using Ni-filtered Cu Kα radiation. The samples were loaded as powders or as slurries of samples and their mother liquors[21] into glass capillaries, sealed at one end and tapering from an i.d. of 0.1 mm. and a wall thickness of 0.01 mm. to a flared opening at the top, which was subsequently flame-sealed to prevent dehydration of the samples during the 8-hr. X-ray exposure. Powder patterns of di- and paratungstates taken in unsealed capillaries showed marked differences from those taken in sealed capillaries.

Thermogravimetric Measurements.—A Chevenard pen-recording thermobalance was used with atmospheres of ambient air and flowing humidified air.

Karl Fischer Titrations.—A Beckman Model KF-3 Aquameter was used for the Karl Fischer titration of hydrate water in a suspension of the solid in anhydrous methanol.

Phase Relationships in the Ternary System

In Table II are listed the pertinent data on the compositions of the coexisting liquid and solid phases and of the original mixtures from which they were derived. They are summarized graphically in Fig. 1, from which actual experimental points are omitted for clarity. Each tie line, however, represents an experimental mixture.

Visual inspection of the equilibrium mixtures showed that at least two solid isopolytungstate phases had been formed in the range of compositions covered by Fig. 1. The convergence of the tie lines suggested that one phase was a hydrated ditungstate and that the other was sodium paratungstate. However, the composition of neither solid could be rigorously established from the phase diagram, because algebraic extrapolation of the tie lines was too sensitive to small errors in the analysis of the equilibrium liquid phases.

Sodium paratungstate was identified by direct analysis of the rhombohedral crystals from mixtures 5 and 6 (see Table II), which settled as a relative coarse mass from which the mother liquor could readily be removed by centrifugal filtration and blotting. The identification of the new solid phase as $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$ was less straightforward and is described in a subsequent section.

The point a on the binary boundary, Na_2WO_4–H_2O, that marks the aqueous solubility of $Na_2WO_4 \cdot 2H_2O$ also represents the isothermally invariant solution that is mutually saturated with that salt and with $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$. This same relationship was found by Byé[14,15] and by Ricci and Doppelt[16] between $Na_2MoO_4 \cdot 2H_2O$ and the salt to which they assigned the formula $Na_2MoO_4 \cdot MoO_3 \cdot 6H_2O$. The addition of even the slightest excess of $WO_3 \cdot H_2O$ to a single-phase saturated solution of Na_2WO_4 brings the system into the area in which $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$ is the saturating solid phase.

In the solutions arising from mixtures 12 through 4′, all of which were in equilibrium with the hydrated ditungstate, the weight ratio W:Na was 4.00, which

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(14) J. Byé, *Bull. Soc. Chim. France*, [5] **10**, 239 (1943).

(15) J. Byé, *Ann. Chim.* (Paris), [11] **20**, 516 (1945).

(16) J. E. Ricci and L. Doppelt, *J. Am. Chem. Soc.*, **66**, 1985 (1944).

(7) M. V. Mokhosoev and P. I. Fedorov, *Zh. Neorgan. Khim.*, **6**, 243 1961); *Russ. J. Inorg. Chem.*, **6**, 123 (1961).

8) A. E. Newkirk, *Anal. Chem.*, **32**, 1558 (1960).

(19) M. Viltange, *Ann. Chim.*, **5**, 1037 (1960).

(20) M. Viltange, *Mikrochim. Acta*, 223 (1963).

(21) Experiments with $Na_2WO_4 \cdot 2H_2O$ showed that the presence in the capillary of an aqueous tungstate solution did not alter the diffraction pattern obtained for the solid that had crystallized from that mother liquor.

TABLE II

SYSTEM Na_2WO_4–WO_3–H_2O AT 25°

	Liquid solution					Original mixture		Wet residue			
Mixture no.	Wt. ratio W:Na	Wt. % Na_2WO_4	Wt. % WO_3	Density	pH	Wt. % Na_2WO_4	Wt. % WO_3	Wt. % Na_2WO_4	Wt. % WO_3	Solid phase[a]	Method of identification
1	4.00	42.60	0.00	1.565	9.28	45.95	0.00			A	*d*
37	4.01	42.53	0.00	1.562	9.41	45.41	0.00			A	*b*
Av.		42.57	0.00	1.564	9.35						
9	4.00	42.56	0.00	1.563	9.39	45.02	0.99			A + B	*b, c, e*
36	3.99	42.54	0.00	1.561	9.34	44.46	1.51			A + B	*d, e*
10	3.99	42.59	0.00	1.564	9.31	44.01	2.00			A + B	*b, c, e*
11	4.04	42.53	0.00	1.566	9.39	43.01	2.00			A + B	*d, e*
Av.		42.56	0.00	1.564	9.36						
12		41.52	0.00	1.543	9.27	42.01	3.01			B	*d*
13	3.98	38.33	0.00	1.484	9.28	39.02	3.00			B	*b*
14		34.97	0.00	1.425	9.12	36.00	3.00			B	*b*
2	3.98	30.80	0.00	1.355	9.18	32.89	4.93	38.09	17.31	B	*d*
2′[g]						32.91	4.93			B	*b, c*
3	4.00	25.13	0.00	1.273	8.88	27.97	4.94			B	*d*
3′[g]						27.98	4.95			B	*b*
15	4.02	22.43	0.00	1.239	8.81	25.00	4.00			B	*d*
16		20.20	0.00	1.209	8.71	23.07	4.00	37.31	23.75	B	*b, c*
17		18.48	0.00	1.187	8.64	21.52	4.00			B	*b, c*
27′[h]	4.00	15.78	0.00	1.158	8.71					B	*d*
4′[h]	3.99	14.72	0.00	1.144	8.46			42.47	31.85	B	*d*
Av. (1–4′)	4.00										
4″[i]	4.07	12.08	0.18	1.117	8.48					B	*d*
5	4.14	12.14	0.33	1.119	8.30	15.00	4.99	41.08	45.06	C	*c*
Av.	4.11	12.11	0.26	1.118	8.39						
5′[g]						14.95	4.97			C	*b, f*
6	4.63	6.97	0.92	1.071	7.82	10.07	5.04	40.99	44.99	C	*c*
6′[g]						10.07	5.03			C	*b, f*
18	6.25	5.05	2.26	1.066	7.49	6.51	3.98			C	*d*
4 (metastable)	4.01	17.84	0.00	1.176	8.50	19.97	5.02			C	*d*
27 (metastable)	3.99	17.70	0.00	1.179		20.60	4.40			B + C	*d*
Av.	4.00	17.77	0.00	1.178							
3″[g] (metastable)						27.97	4.94	40.71	44.66	C	*c*

[a] A = $Na_2WO_4 \cdot 2H_2O$; B = $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$; C = $5Na_2WO_4 \cdot 7WO_3 \cdot 28H_2O$. [b] X-Ray diffraction. [c] Chemical analysis of solid washed free of mother liquor. [d] Tie line, bulk appearance, or microscopic examination. [e] Upon settling, the solid phases in the invariant region formed two distinct layers, and the fine crystals of the hydrated ditungstate could easily be separated from the underlying coarser crystals of the hydrated normal tungstate. [f] See item 3 under text heading "Metastable Equilibriums." [g] No solution analyses made on this mixture, which was prepared solely for examination of solid phase. [h] The compositions tabulated for 4′ and 27′ represent values to which the solubility had dropped spontaneously, after about 1 year, from the metastable equilibrium values of mixtures 4 and 27. [i] This mixture was prepared by adding the solution phase of mixture 5 to the solid phase of mixture 4′.

is the value of this ratio in Na_2WO_4. These solutions, therefore, contained no uncombined WO_3, and their composition was calculated from the measured water content.

In this system virtually the entire solubility curve, ab, for the ditungstate is experimentally indistinguishable from the binary boundary, Na_2WO_4–H_2O, and the salt is therefore incongruently soluble in water. $Na_2MoO_4 \cdot MoO_3 \cdot 6H_2O$, on the other hand, is congruently soluble in water, and only a portion of its solubility curve is coincident with the binary boundary.[14,15]

The dimolybdate solubility curve ends with the appearance of $Na_2MoO_4 \cdot 2MoO_3 \cdot 7H_2O$, but the terminus of the ditungstate curve, point b, is the isothermally invariant solution mutually saturated with $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$ and $5Na_2WO_4 \cdot 7WO_3 \cdot 28H_2O$. This solution has been assigned a composition that is the average of those of solutions 4″ and 5, whose tie lines, bF and bG, appear to be the limiting boundaries of the ditungstate and paratungstate regions. The solubility curve for $5Na_2WO_4 \cdot 7WO_3 \cdot 28H_2O$ was not carried beyond solution 18 because of the difficulty of reaching equilibrium when the mole ratio of WO_3 to Na_2WO_4 lay between 1.4 and 3.0.

The boundaries of the $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$ area, abF, in the ternary diagram may explain the failure of previous investigators to prepare this phase from aqueous solution. This salt crystallizes only from mixtures made by adding considerably less than the stoichiometric amount of $WO_3 \cdot H_2O$ to an aqueous solution that is more than 0.5 *M* in Na_2WO_4. Stoichiometric neutralization of an aqueous solution of Na_2WO_4 with either $WO_3 \cdot H_2O$ or a mineral acid leads to eventual precipitation of $5Na_2WO_4 \cdot 7WO_3 \cdot 28H_2O$.

Metastable Equilibriums.—The reaction between $WO_3 \cdot H_2O$ and Na_2WO_4 in aqueous solution to form $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$ was slow and proceeded through at least one intermediate solid phase. The following

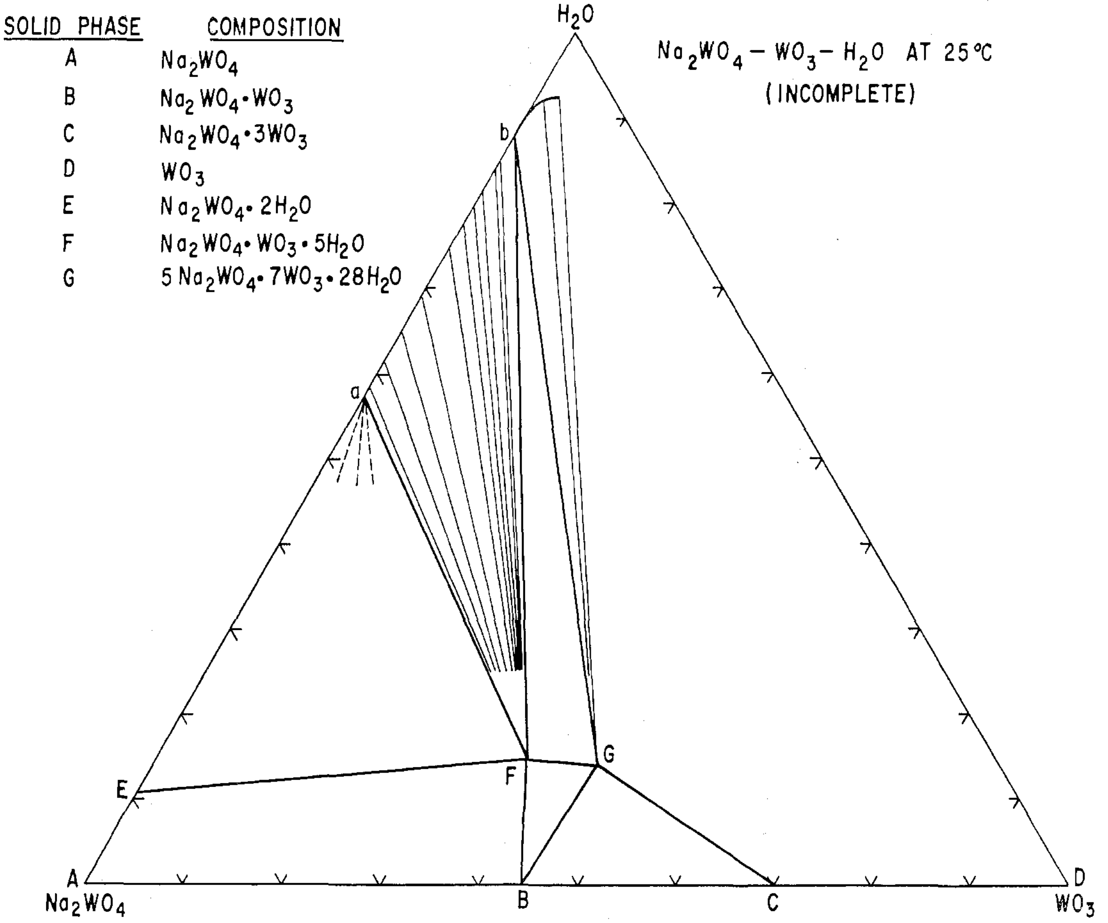

Fig. 1.—Ternary system Na_2WO_4–WO_3–H_2O at 25° (incomplete).

observations were made on mixtures that had been prepared as duplicates of numbers 2 and 3, which fall in the ditungstate region of Fig. 1, and of numbers 5 and 6, which fall in the paratungstate region.

(1) Within 1 hr. of preparation the color of the solid phase in each bottle had changed from the bright orange of $WO_3 \cdot H_2O$ to a pale yellow.

(2) The amount of solid present in bottles 2′, 3′, and 3″ after 2.5 days of mixing was much less than the amount found in the original mixtures after several months of equilibration. In their settling behavior and under microscopic examination these crystals and those in bottles 5′ and 6′ looked more like the para- than the ditungstate.

(3) All the above five solids gave the same powder X-ray diffraction pattern, which differed from that for $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$ and from that for a sample of sodium paratungstate prepared by Dr. A. E. Newkirk of this laboratory from an acidified solution of Na_2WO_4, following the method of Saddington and Cahn.[22] Analysis of a washed and blotted sample of solid 3″, however, showed its composition to be essentially the same as that of sodium paratungstate.

Powder data are not available for the sodium paratungstate sample prepared by Saddington and Cahn[22] nor are single crystal data available either for the sample prepared by Newkirk or for solid 3″. The only structural comparison made at present, therefore, is in terms of the *d* values and relative intensities listed in Table III for powder specimens of the latter two samples.

	Solid 3″	Calcd. for $5Na_2WO_4 \cdot 7WO_3 \cdot 28H_2O$
% H_2O	14.11	14.02
% Na_2WO_4	40.32	40.85
% WO_3	45.57	45.13

(4) Three weeks after preparation, bottle 2′ contained a second solid phase, which settled on standing as a distinct layer above the original solid phase. Visual and microscopic identification of the upper phase as disodium ditungstate pentahydrate was confirmed by its X-ray diffraction pattern and by chemical analysis. The lower phase still showed the X-ray diffraction pattern of the original solid phase (same as solid 3″). A few weeks more elapsed before $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$ was observed as a second phase in bottles 3′ and 3″. No second phase had appeared in bottles 5′ and 6′ after more than 2 years of mixing.

(5) Eight months after preparation, the paratungstate phase had disappeared from bottle 2′, which then contained $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$ as the only solid phase. A small amount of paratungstate still remained with the ditungstate in bottles 3′ and 3″.

There are some indications that even the equilibrium relationships shown in Fig. 1 may be metastable.

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[22] K. Saddington and R. W. Cahn, *J. Chem. Soc.*, 3256 (1950).

TABLE III

PARTIAL X-RAY DIFFRACTION DATA FOR $5Na_2WO_4 \cdot 7WO_3 \cdot 28H_2O$ PHASES[a]

Line no.	Solid 3″		Newkirk's prepn.	
	d	I/I_0	d	I/I_0
1	10.7	s	11.6	s
2	9.6	s	10.4	vw
3	8.8	vw	9.9	s
4	8.1	vw	9.3	s
5	7.6	m	8.4	vw
6	6.8	vw	8.0	s
7	5.9	w (diff.)	7.6	m
8	5.5	m	6.3	m
9	5.0	m	6.0	m
10	4.45	w	5.8	vw
11	4.14	vw	5.5	vw
12	3.99	ms	5.3	vw
13	3.9	w (diff.)	4.98	m
14	3.78	w	4.72	mw
15	3.65	m	4.50	m
16	3.6	vw (diff.)	4.31	m
17	3.51	vw	4.01	m
18	3.43	vw	3.86	w
19	3.3	w (diff.)	3.60	ms
20	3.20	m	3.47	w
21	3.15	ms	3.40	w
22	3.07	ms	3.31	m
23	2.97	ms	3.17	mw
24	2.89	ms	3.11	mw
25	2.83	ms	3.06	s
26	2.78	ms	3.00	w

[a] Cu Kα radiation, Ni filter, Debye–Scherrer camera.

(1) Mixtures 9 and 10 lie within the area, aEF, of Fig. 1 in which the equilibrium phases are $Na_2WO_4 \cdot 2H_2O$, $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$, and the isothermally invariant solution, b. The composition of the solution phase in mixture 9 remained unchanged after 4.5 years of mixing, and X-ray diffraction patterns confirmed the identity of the two solid phases still present. On the other hand, the composition of the solution phase in mixture 10, although constant for at least 2 years, had dropped after 4 years of mixing from the invariant value to 40.44% Na_2WO_4. Visual examination, X-ray diffraction, and chemical analysis showed that $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$ was the only solid phase present.

(2) After additional stirring periods of 1.5 to 4 years, the amount of dissolved solid in the solution phases of mixtures 12, 13, 14, and 18 had dropped by from 0.5 to 2% Na_2WO_4 below the values listed in Table II. The solid phases in the first three bottles still appeared to be the hydrated ditungstate, but there had been a change in solid 18. Although its ratio W:Na was still that for sodium paratungstate, its water content was only 12.8% and its X-ray powder diffraction pattern was different from that obtained for either solid 5 or solid 3″ but similar to that obtained on a partially dehydrated sample of sodium paratungstate.[23]

Identification and Some Properties of $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$

$Na_2WO_4 \cdot WO_3 \cdot 5H_2O$, as formed in this study, consisted of a white bulky mass of small pyramidal needles, approximately 28 × 1.4 μ, which showed parallel extinction under polarized light and were a uniform straw color at 45° to extinction. During centrifugal or vacuum filtration they settled as a pasty cake from which it was not possible to remove all of the mother liquor, even by subsequent blotting on a porous surface. As a result, even though the water content of $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$ is 14.63%, the wet residues listed in Table II contained enough mother liquor to bring their total water content between 25 and 45%. The composition of the equilibrium solid phase was therefore established by indirect means.

Washing Experiments and the Ratio of Na_2WO_4 to WO_3.—The slow rate at which equilibrium was reached in this system suggested that, in spite of the incongruent solubility of $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$, rapid washing of this salt with water might remove most of the mother liquor without producing any appreciable transformation to the paratungstate. Microscopic examination of a rapidly washed sample showed no apparent change in the size or shape of the crystals. Furthermore, in experiments with solids removed from some of the mixtures of Table II, the same powder X-ray diffraction patterns were obtained from a slurry of the solid with its mother liquor, from a sample of the filtered, unwashed, and blotted solid, and from a sample of the filtered, washed, and blotted solid. This pattern, whose characteristic d values and relative intensities are listed in Table IV, is different from that obtained for any previously reported isopolytungstate.[23,24] When two of these washed samples were completely dehydrated at 450° they yielded X-ray diffraction patterns that were identical with that obtained from a sample that had been prepared by fusion of an equimolar mixture of anhydrous Na_2WO_4 and WO_3.[23] This pattern, which is also tabulated in Table IV, is consistent with the single crystal data obtained by Lindqvist[25] for anhydrous $Na_2WO_4 \cdot WO_3$. By contrast, the X-ray diffraction pattern of the unwashed and completely dehydrated residue from mixture number 2 showed it to be a mixture of the anhydrous mono- and ditungstates, in conformity with the phase relationships of Fig. 1.

Finally, chemical analysis of five solid phases that had been washed and dehydrated showed that the average value for the mole ratio of Na_2WO_4 to WO_3 was 1.00 ± 0.04.

These observations show that washing with distilled water removed the mother liquor from the paste of hydrated ditungstate crystals with no detectable formation of paratungstate. The wash water, however, was just as difficult to separate from the mass of tiny crystals as the mother liquor had been, and the washed solid, like the unwashed material, still contained 25–40% H_2O after blotting. If, before filtration and washing, the solid was pulverized by using a "Wig-L-Bug," the total amount of water remaining after blotting was reduced to 20–25%.

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(23) A. E. Newkirk, unpublished X-ray powder diffraction patterns.

(24) P. Caillet, *Compt. rend.*, **256**, 1986 (1963).

(25) I. Lindqvist, *Acta Chem. Scand.*, **4**, 1066 (1950).

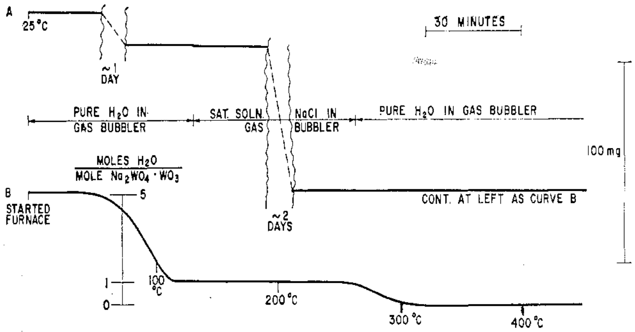

Fig. 2.—Thermogram for dehydration of $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$. Final weight of anhydrous $Na_2WO_4 \cdot WO_3$ as determined with an analytical balance after cooling was 335.5 mg.

Water Content of Hydrated $Na_2WO_4 \cdot WO_3$.—Thermogravimetric measurements and discontinuous weighing experiments, described in the following section, showed that the excess water, mechanically retained by the filtered and washed mass of crystals, could be removed by isothermal evaporation at 25–30° and an ambient relative humidity of about 75% (and possibly down to 45%). After 12–48 hr. of such exposure, samples of washed ditungstate crystals reached a weight that remained constant during continued exposure for at least 1 year. Furthermore, none of the weight so lost was regained, even when the relative humidity was increased to nearly 100%.

Table IV

Partial X-Ray Diffraction Data for Ditungstate Phases[a]

Line	$Na_2WO_4 \cdot WO_3 \cdot 5H_2O$		$Na_2WO_4 \cdot WO_3 \cdot H_2O$		$Na_2WO_4 \cdot WO_3$			
					Dried at 450°		Dried at 250°	
no.	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0
1	10.2	s	8.11	w	7.20	m+	7.61	m
2	9.19	w	6.54	s	5.96	m	6.15	m
3	8.86	m	6.26	m	5.68	vw	5.88	ms
4	8.29	vw	5.72	m	5.51	s	5.71	s
5	7.88	m	5.12	ms	4.74	vs	4.95	mw
6	7.14	ms	4.52	m	4.62	ms	4.38	s
7	5.74	vw	4.04	m	4.47	vw	4.19	m
8	5.38	vvw	3.98	ms	3.78	ms	3.85	m
9	5.02	w	3.77	mw	3.67	mw	3.80	w
10	4.88	vw	3.65	mw	3.34	vvw	3.38	mw
11	4.73	m	3.46	w	3.23	s	3.21	mw
12	4.63	m	3.33	m	3.16	ms	3.15	m
13	4.57	mw	3.27	w	3.14	ms	3.07	m+
14	4.49	w	3.03	m	3.12	ms	3.02	m
15	4.40	m	2.996	m	3.07	s	2.932	s
16	4.23	w	2.955	m	3.01	ms	2.855	m
17	3.91	w	2.855	ms	2.970	mw	2.850	w
18	3.83	w	2.810	w	2.910	m	2.753	m
19	3.63	w	2.714	m	2.791	m	2.712	m+
20	3.56	m			2.633	m	2.696	m
21	3.25	mw			2.608	m	2.577	w
22	3.18	mw			2.571	ms	2.479	mw
23	3.04	mw			2.539	m	2.433	mw
24	2.959	mw			2.521	m	2.380	w
25	2.915	m			2.448	m	2.294	w
26					2.309	m+	2.245	vw
27					2.288	mw	2.220	w
28					2.259	m	2.174	w
29					2.250	m	2.143	w
30					2.154	m	2.047	w
31					1.909	m	2.007	vw
32							1.991	w

[a] Cu Kα radiation, quartz monochromator, Guinier double cylinder camera.

The X-ray diffraction pattern after isothermal dehydration was the same as those previously obtained before and after washing, indicating no change in the solid phase. The average value for the weight loss of seven solid samples that were completely dehydrated at 450° after they had been washed and freed of their mechanically occluded water was 14.56 ± 0.18%, corresponding to a mole ratio for H_2O to $Na_2WO_4 \cdot WO_3$ of 4.97 ± 0.06.

Dehydration of $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$.—The dehydration behavior of $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$ is illustrated by the thermogravimetric tracings shown in Fig. 2 which were obtained with a sample of solid 2′ that had been washed free of mother liquor and then blotted. The upper curve shows the isothermal removal of the mechanically occluded wash water by a stream of humidified air, and the lower curve shows the subsequent dehydration at 150°/hr., still in humidified air.

An initial weight loss, which began at about 45°, culminated in a nearly horizontal plateau, extending from about 110° to about 250°, which was followed by a second and smaller weight loss; dehydration was complete by 330°. A similar thermogram was obtained in ambient air with a sample that had been washed and freed of its excess water by blotting and isothermal dehydration before being put into the thermobalance.

The shape of the thermograms suggested the formation of a second hydrate as an intermediate stage in the dehydration of the pentahydrate. Its exact stoichiometry could not be calculated from thermogravimetric data because, even in humidified air, the thermogram indicated a slow but continuous loss of weight in the region 125–250°. However, the intermediate phase is probably a monohydrate, as indicated by the fiduciary lines of Fig. 2. These composition levels are based on the assumption, confirmed by chemical analysis of the residue, that the final plateau represents anhydrous $Na_2WO_4 \cdot WO_3$, and in calculating them allowance was made for the appropriate apparent weight gain corrections that must be applied to thermogravimetric data.[26]

The qualitative and quantitative implications of this thermogravimetric behavior were confirmed by a series of static dehydration experiments.

The relatively low temperature at which dehydration began suggested that the transformation of the penta- to monohydrate might occur at room temperature if the relative humidity were low enough. Four samples of the pentahydrate, free of occluded water, were placed in a vacuum desiccator over $CaSO_4$ for 12–48 hr., during which time they lost from 10.8 to 11.4% of their weight. The transformation from penta- to monohydrate should produce a weight loss of 11.7%. Nearly complete conversion to the mono-

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[26] E. L. Simons, A. E. Newkirk, and I. Aliferis, *Anal. Chem.*, **29**, 48 (1957).

hydrate was also observed for a washed sample of the pentahydrate that had been exposed for 3 months to an atmosphere with 20–40% relative humidity. In all cases, however, the weight loss corresponding to complete conversion of the penta- to the monohydrate was achieved only by heating the sample ultimately to about 200° for 1 hr.

The solid phases produced either by isothermal dehydration or by heating to 200° gave identical X-ray diffraction patterns, which were different from those of either the pentahydrate or the anhydrous salt. The *d* values and relative intensities of this new pattern are also listed in Table IV. A sample of the pentahydrate that had been dehydrated at room temperature almost to the monohydrate level slowly regained about 40% of its total weight loss when exposed to 100% relative humidity at room temperature for 19 days. The X-ray diffraction pattern of this partially rehydrated material was the same as that of the monohydrate. A similar observation was made by Panzer[27] in his study of the dehydration of calcium acetate monohydrate (10.3% H_2O) to the half-hydrate (5.4% H_2O). Even when the sample contained 9.2% H_2O, the X-ray diffraction pattern was solely that of the half-hydrate and showed no evidence for a mixture of the mono- and half-hydrates.

The shape of the thermogram in Fig. 2 suggests that the monohydrate was undergoing slow dehydration even below 250°. This was confirmed by holding a sample of the monohydrate at 225° for 17 hr., during which time it lost two-thirds of its water. Complete dehydration could be achieved in 24 hr. at 250°, but the anhydrous $Na_2WO_4 \cdot WO_3$ thus formed gave a clear, sharp X-ray powder diffraction pattern different from that for the anhydrous salt formed either by dehydration at 450°, at 700°, or by fusion of an equimolar mixture of anhydrous Na_2WO_4 and WO_3. The pattern for this low temperature modification is also given in Table IV. The X-ray evidence suggests that this phase transition, between 250 and 450°, is different from the one reported by Hoermann[6] at 550° for $Na_2WO_4 \cdot WO_3$.

The difference in thermal stability between the penta- and monohydrate is also reflected in the results obtained by Karl Fischer titrations. Under conditions that result in complete titration of all of the water in a crystalline hydrate like disodium tartrate dihydrate, only 75% of the total water present in $Na_2WO_4 \cdot WO_3 \cdot 5H_2O$ reacted with the Karl Fischer reagent, indicating titration of 94% of the labile water. The monohydrate behaved like an anhydrous salt toward the titrant.

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[27] J. Panzer, *J. Chem. Eng. Data*, **7**, 140 (1962).

CONTRIBUTION FROM THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN,
AND THE UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

The Stereochemistry of Complex Inorganic Compounds. XXVII. Asymmetric Syntheses of Tris(bipyridine) Complexes of Ruthenium(II) and Osmium(II)

BY CHUI FAN LIU, NORA C. LIU, AND JOHN C. BAILAR, JR.

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It has been shown that asymmetric syntheses of the tris(bipyridine)ruthenium(II) ion, the tris(*o*-phenanthroline)ruthenium(II) ion, and tris(bipyridine)osmium(II) ion can be carried out simply. The ruthenium compounds can be obtained to contain as high as 63% of the levo isomer while the osmium compound can be prepared to contain 70% of the levo isomer.

The tris(bipyridine)ruthenium(II) complex was first prepared by Burstall[1] by fusing ruthenium(III) chloride with bipyridine at 250°. A more convenient method of preparation consists in refluxing an aqueous alcoholic mixture of potassium pentachlorohydroxoruthenate(IV), bipyridine, and sodium hypophosphite.[2] Since the tris(bipyridine)ruthenium(II) is octahedral, it is capable of existing in *d* and *l* forms. The resolution of this compound was carried out by Burstall.[1] The tris(bipyridine)osmium(II) complex was prepared in approximately the same manner using hexachloroosmate(IV) as starting material.[3] Unlike the ruthenium compound, however, the osmium derivative was not obtainable from aqueous solution. The resolution of the tris(bipyridine)osmium(II) ion into its optical antipodes was achieved by Burstall and coworkers.[3]

The present study deals with the asymmetric syntheses of tris(bipyridine) complexes of both ruthenium

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[1] F. H. Burstall, *J. Chem. Soc.*, 173 (1936).

[2] F. P. Dwyer, J. E. Humpoletz, and R. S. Nyholm, *J. Proc. Roy. Soc. N. S. Wales*, **80**, 212 (1946); F. P. Dwyer, *ibid.*, **83**, 134 (1949).

[3] F. H. Burstall, F. P. Dwyer, and E. C. Gyarfas, *J. Chem. Soc.*, 953 (1950).