Preparation of Polychlorophosphazene from Perchloro-1-phosphinyldiphosph(V)azadiene (III)

5.93 g of the phosphorus oxide dichloride derivative (III) were heated in a current of dry nitrogen (bath temperature 200°) for 4 h when 2.19 g $POCl_3$ (92.6% theoretical) were liberated. The residue was a dark chlorophosphazene rubber.

Found, %: N 11.38, 11.34; Cl 59.9, 60.3.

Calculated for $PNCl_2$, %: N 12.06; Cl 61.2.

Preparation of Polychlorophosphazene from Higher Perchloro-1-phosphinylpolyphosphazenes†

(a) 6.5 g phosphorus oxide dichloride derivative with average composition $Cl(PNCl_2)_{10}POCl_2$ were heated gradually at 2.5 mm Hg to 280° (bath temperature). 1.1 g of a mixture of phosphorus oxide dichloride derivatives with b.p. 100°–200° at 2.5 mm Hg were distilled, 0.4 g of $POCl_3$ was collected in a trap cooled with dry ice, and 4.4 g of a dark rubber-like polychlorophosphazene remained behind.

(b) 2.47 g of phosphorus oxide dichloride derivatives with average composition $Cl(PNCl_2)_4POCl_2$ were heated in a current of dry nitrogen to 160°–214° when 0.717 g of $POCl_3$, apparently contaminated with $Cl_3P=N-POCl_2$, collected in the trap and 1.42 g of polymer remained as a viscous oil, soluble in benzene.

Found, %: N 0.49, 0.49.

Preparation of Polymer from the Monomethyl Ether (IV)

5.96 g (15.6 mmoles) of compound (IV) were heated at 140° in a current of dry nitrogen for 2 h, when 1.56 g of phosphoryl(V) chloride, mixed with some carbon-containing substances, were collected in a trap cooled with dry ice in acetone.

Found, %: Cl 67.38, 67.39; C 1.30, 1.33; H 0.84, 0.87.

This substance redistilled almost completely at 100°–103°.

Found, %: Cl 68.79, 68.33; C 1.08, 1.00; H 0.58, 0.60.

Calculated for $POCl_3$, %: Cl 69.57.

The residue in the reaction flask was heated at 100° and 2–3 mm Hg for 2 h to give a resinous polymer.

Found, %: C 3.07, 3.08; H 0.92, 0.93; P 28.26, 28.41; N 10.15, 9.91; Cl 48.45, 48.60.

0.2 g of liquid was collected in a trap cooled with a mixture of dry ice and acetone.

Found, %: C 3.42, 3.56; H 0.88, 0.88; Cl 61.43, 61.37.

Calculated for a mixture of 39% methyl chlorophosphate and 61% phosphoryl(V) chloride, %: C 3.14; H 0.78; Cl 60.9.

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† The polymer from the higher phosphorus oxide dichloride derivatives was prepared by T. I. Lopushinskaya.

SUMMARY

1. A new method has been developed for preparing polychlorophosphazenes, based on the thermal splitting of phosphoryl(V) chloride from perchloro-1-phosphinylpolyphosphazenes according to the scheme: $Cl(PNCl_2)_nPOCl_2 \rightarrow POCl_3 + [(PNCl_2)_n]_m$. This reaction also takes place with a number of substituted phosphorus oxide dichloride derivatives.

2. Hydrolysis of perchloro-1-phosphoranyldiphosph(V)azadiene gives the monohydroxy-derivative $(P_3N_2Cl_6O_2H)_3$; this, when heated undergoes polycondensation with the loss of HCl and the formation of an oxygen-containing phosphazene polymer.

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SOLUBILITY AND ACID–BASE PROPERTIES OF TANTALUM AND NIOBIUM HYDROXIDES

A. K. Babko, V. V. Lukachina, and B. I. Nabivanets

The absence of quantitative results on the acid–base properties and the dissociation of tantalum and niobium hydroxides makes it difficult to discuss the chemistry of their dissolution in acids and alkalis, particularly as this is accompanied by the formation of complex ions and, at higher concentrations, of polyions. This information is important for tantalum and niobium complexes, for which quantitative stability data are lacking. This is because it has not previously been possible to determine or calculate the equilibrium concentration of tantalum or niobium ions not combined in a complex. The absence of a standard state corresponding to a particular concentration of known tantalum or niobium ions in solution and of a standard electrode have meant that for the many tantalum and niobium complexes, only relative and, for the most part, qualitative stability data are available.

We have measured the solubility of freshly precipitated tantalum and niobium hydroxides (tantalic and niobic acids) in order to establish the composition of the ions in solution and to obtain the quantitative acid–base properties of the compounds.

Tantalic or niobic acids were precipitated by adding nitric acid to pH 4–5 to a known quantity of an alkaline solution of potassium tantalate or niobate and diluting with water; HNO_3 or KOH were then added to secure the required pH, which was measured potentiometrically with a glass electrode. In solutions with $[HNO_3] < 1 N$, potassium nitrate was added to keep the ionic strength at $I = 1$. The total volume of solution and precipitate was 100 ml.

Preliminary experiments showed that variations in temperature between $17°$ and $25°$, in holding time between 10 and 40 days, or in the quantity of solid phase had little effect on the solubility of the acids. Accordingly, the precipitates were kept in the solutions at $18°–20°$ for 2–3 weeks; the total quantity of tantalic or niobic acids (as suspension and true solution) corresponded to a concentration of 2×10^{-3} M in the final volume.

The precipitates were separated from the equilibrium solutions by centrifuging and the equilibrium concentration of tantalum was determined photometrically from the reaction with pyrocatechol in the presence of oxalic acid[1,2] and that of niobium from the reaction with Xylenol Orange[3]. The acidity was determined potentiometrically to ±0.05 pH units or by titrating with alkali.

We studied the influence of the centrifuging (rev/min and duration) on the completeness of precipitation. From solutions with pH ≥ 1, the precipitates settled rapidly, but at $[HNO_3] > 0.1 N$, stable colloidal solutions were formed. We therefore followed the influence of centrifuging conditions in more detail with solutions at pH 3 and $[HNO_3] = 3 N$, which showed that minimal constant solubilities of tantalic and niobic acids were obtained when precipitates were separated at 8000–10 000 rev/min for 45–60 min.

The pH dependence of solubility, Fig. 1, shows that the "isoelectric range" of tantalic acid lies at pH 9 to 2 and that for niobic acid at pH 7 to 0, the metallic character of

tantalum being more marked than that of niobium, according to their position in the Periodic Table. The results also confirm the suggestion[4] that niobium has a greater affinity for oxygen than has tantalum.

The solubility of niobic acid in the isoelectric range is 1.4×10^{-5} M and that of tantalic acid 6.0×10^{-6} M. The latter value is slightly lower than that found earlier[2], because previously the centrifuging was at 1500–2000 rev/min which fails to give complete separation of the precipitate.

In concentrated nitric acid the solubility of niobic acid is less than that of tantalic acid, confirming that tantalum hydroxide is more basic than niobium hydroxide. The opposite relationship is observed in hydrochloric and sulphuric acids[5], presumably because the formation of chloro- and sulphato-complexes is easier for niobium than for tantalum.

The slope of the curves, Figs. 2–4, suggests important conclusions regarding the tantalum and niobium ions in equilibrium with the solid phase during the dissolution of the respective acids. If this dissolution is accompanied by the formation of only monomeric ions, the H^+ (or OH^-) concentration should influence the solubility to the power $m \geq 1$, in accordance with the equations (e.g. for tantalum):

$$Ta(OH)_5 + mH^+ \rightleftarrows Ta(OH)_{5-m}^{+m} + mH_2O$$
$$\uparrow \downarrow \text{ solution}$$
$$Ta(OH)_5$$
$$\text{solid phase} \uparrow \downarrow$$
$$Ta(OH)_5 + mOH^- \rightleftarrows Ta(OH)_{5+m}^{-m}.$$

If, however, polyions are formed, m should be < 1. For example, the dissolution of tantalic acid with the formation of dimeric cations would be expressed by the equation

$$Ta(OH)_5 + 0.5H^+ \rightleftarrows Ta(OH)_{4.5}^{+0.5} + 0.5H_2O$$

or

$$2Ta(OH)_5 + H^+ \rightleftarrows Ta_2(OH)_9^+ + H_2O.$$
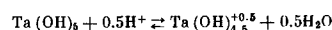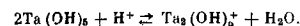
In the calculations we should take account only of that fraction of the tantalum (or niobium) which is present in solution in the form of ions. The concentration of molecules can be taken as equal to the solubility of tantalic (or niobic) acid in the isoelectric range, where ionic forms are present only in very small quantities. The concentration of ionic forms $(M^{\pm})$ will thus be

$$[M^\pm] = [M^V]_{total} - [M^V]_{isoelectric\ range}.$$

The results of the calculations are given in Tables 1 and 2 and Figs. 2–4. The slope of the curve in Fig. 2 (tan $\alpha = 1$) shows that in acid medium, during the initial stage of dissolution, monomeric cationic forms of tantalum are produced and $m = 1$:

$$Ta(OH)_5 + H^+ \rightleftarrows Ta(OH)_4^+ + H_2O. \tag{1}$$
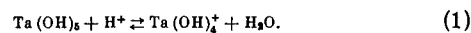
Increase in the tantalum concentration, in accordance with published results[6], leads to the formation of polycations, since in this range $m < 1$.

For niobium, in the initial stage of dissolution, m is slightly greater than unity (Fig. 3)†, because at nitric acid concentrations greater than $2 N$ there is a marked increase in the mean activity coefficient of the acid, but we were
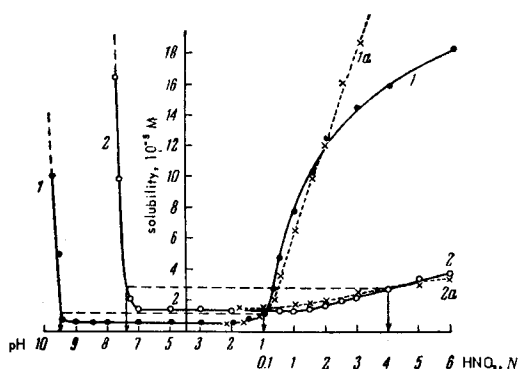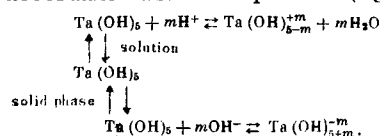

Fig. 1. Solubility of tantalic (1) and niobic (2) acids: 1a), 2a) solubilities calculated from the basic dissociation constants of tantalic and niobic acids respectively.

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† Other experiments showed that increase in the concentration by the addition of KNO_3 has no influence on the solubility of niobic acid, so that the slope of the curve in Fig. 3 is determined by the removal of OH^- groups solely under the influence of H^+ ions and nitrato-complexes are not formed.
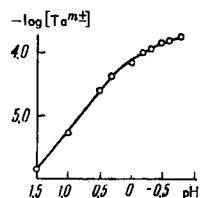
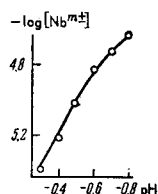Fig. 2. Influence of pH on the solubility of tantalic acid in acidic medium.

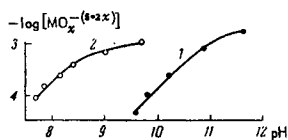Fig. 3. Influence of pH on the solubility of niobic acid in acidic medium.

Fig. 4. Influence of pH on the solubility of tantalic (1) and niobic (2) acids in alkaline medium.

TABLE 2. pH dependence of the solubility of niobic acid: $[Nb^{m\pm}] = [Nb^V]_{total} - [Nb^V]_{isoelectric\ range}$; $[Nb^V]_{isoelectric\ range} = 1.4 \times 10^{-6}$ M.

pH	$10^6 [Nb^V]_{total}$ M	$10^6 [Nb^{m\pm}]$ M	$-\log[Nb^{m\pm}]$	pH	$10^6 [Nb^V]_{total}$ M	$10^6 [Nb^{m\pm}]$ M	$-\log[Nb^{m\pm}]$
7.00	1.4	0.0	—	0.00	1.4	0.0	—
7.67	9.7	8.3	4.081	−0.30	1.8	0.4	5.398
7.82	16.4	15.0	3.824	−0.40	2.0	0.6	5.222
8.15	24.0	22.6	3.646	−0.48	2.3	0.9	5.046
8.40	37.8	36.4	3.439	−0.60	2.9	1.5	4.824
9.00	66.0	64.6	3.192	−0.70	3.3	1.9	4.721
9.73	106.0	104.6	2.981	−0.78	3.8	2.4	4.620

unable to allow for this in the absence of quantitative information. The dissolution of niobic acid in the initial stage can be expressed, by analogy with tantalum, by the equation

$$Nb(OH)_5 + H^+ \rightleftarrows Nb(OH)_4^+ + H_2O. \qquad (2)$$
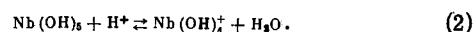
The slope of the curves, Fig. 4, shows that in the initial stage of dissolution in alkali, monomeric anionic forms of tantalum and niobium are formed and $m = 1$:

$$Ta(OH)_5 + OH^- \rightleftarrows TaO_3^- + 3H_2O, \qquad (3)$$

$$Nb(OH)_5 + OH^- \rightleftarrows NbO_3^- + 3H_2O. \qquad (4)$$
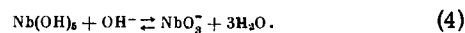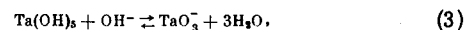
Increase in the concentration of tantalum (or niobium) leads to the formation of polyanions ($m < 1$), in agreement with published results [6,7].

We also confirmed the production of anionic forms in alkali and cationic forms in nitric acid by electromigration.

The results in Fig. 1 and Tables 1 and 2 can be used to calculate the constants for the basic and acidic dissociation of tantalic and niobic acids. In accordance with Eqns. (1) and (2), the basic dissociation of tantalum and niobium hydroxides can be represented:

$$Ta(OH)_5 \rightleftarrows Ta(OH)_4^+ + OH^-,$$
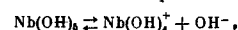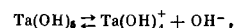
$$Nb(OH)_5 \rightleftarrows Nb(OH)_4^+ + OH^-,$$

$$K_{base,\,Ta} = \frac{[Ta(OH)_4^+][OH^-]}{[Ta(OH)_5]}, \qquad (5)$$

$$K_{base,\,Nb} = \frac{[Nb(OH)_4^+][OH^-]}{[Nb(OH)_5]}. \qquad (6)$$

In accordance with Eqns. (3) and (4), the acidic dissociation of tantalum and niobium hydroxides can be represented:

$$Ta(OH)_5 \rightleftarrows TaO_3^- + H^+ + 2H_2O,$$

$$Nb(OH)_5 \rightleftarrows NbO_3^- + H^+ + 2H_2O,$$
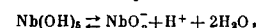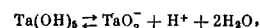
$$K_{acid,\,Ta} = \frac{[TaO_3^-][H^+]}{[Ta(OH)_5]}, \qquad (7)$$

$$K_{acid,\,Nb} = \frac{[NbO_3^-][H^+]}{[Nb(OH)_5]}. \qquad (8)$$

Eqns. (5)–(8) show that their basic and acidic dissociation constants are equal to the OH⁻ or H⁺ concentrations at which

$$[Ta(OH)_4^+] = [Ta(OH)_5], [Nb(OH)_4^+] = [Nb(OH)_5]$$

or

$$[TaO_3^-] = [Ta(OH)_5], [NbO_3^-] = [Nb(OH)_5].$$

TABLE 1. pH dependence of the solubility of tantalic acid: $[Ta^{m\pm}] = [Ta^V]_{total} - [Ta^V]_{isoelectric\ range}$.

pH	$10^5 [Ta^V]_{total}$ M	$10^5 [Ta^{m\pm}]$ M	$-\log[Ta^{m\pm}]$	pH	$10^4 [Ta^V]_{total}$ M	$10^4 [Ta^{m\pm}]$ M	$-\log[Ta^{m\pm}]$
9.50	0.6	0.0	—	1.00	1.1	0.5	5.302
9.60	5.0	4.4	4.357	0.50	3.0	2.4	4.620
9.80	10.6	10.0	4.000	0.30	4.8	4.2	4.377
10.20	26.0	25.4	3.595	0.00	7.8	7.2	4.143
10.85	82.0	81.4	3.090	−0.18	10.6	10.0	4.000
11.60	158.0	157.5	2.803	−0.30	12.2	11.6	3.936
				−0.48	14.5	13.9	3.857
2.00	0.6	0.0	—	−0.60	16.0	15.4	3.813
1.50	0.7	0.1	6.000	−0.78	18.4	17.8	3.750

TABLE 3.   Instability constants of hydroxo-complexes of tantalum(V) and niobium(V)*.

$$k = \frac{[M(OH)_{n-1}^{6-n+1}][OH^-]}{[M(OH)_n^{5-n}]}; \quad K = \frac{[M(OH)_{5-n}^{n+}][OH]}{[M(OH)_5]};$$

$$n \leqslant 5; \; M = Ta, \, Nb$$

Hydroxo-complex	k	pk	K	pK
Ta(OH)⁴⁺	$2.5 \cdot 10^{-30}$	29.6	$2.5 \cdot 10^{-30}$	29.6
Ta(OH)₂³⁺	$2.5 \cdot 10^{-27}$	26.6	$6.3 \cdot 10^{-57}$	56.2
Ta(OH)₃²⁺	$4.0 \cdot 10^{-23}$	22.4	$2.5 \cdot 10^{-79}$	78.6
Ta(OH)₄⁺	$2.0 \cdot 10^{-18}$	17.7	$5.0 \cdot 10^{-97}$	96.3
Ta(OH)₅	$1.0 \cdot 10^{-13}$	13.0	$5.0 \cdot 10^{-110}$	109.3
Nb(OH)⁴⁺	$6.3 \cdot 10^{-34}$	33.2	$6.3 \cdot 10^{-34}$	33.2
Nb(OH)₂³⁺	$1.6 \cdot 10^{-30}$	29.8	$1.0 \cdot 10^{-63}$	63.0
Nb(OH)₃²⁺	$6.3 \cdot 10^{-26}$	25.2	$6.4 \cdot 10^{-89}$	88.2
Nb(OH)₄⁺	$1.3 \cdot 10^{-20}$	19.9	$8.3 \cdot 10^{-109}$	108.1
Nb(OH)₅	$2.5 \cdot 10^{-15}$	14.6	$2.1 \cdot 10^{-123}$	122.7

   * The constants underlined are those found experimentally; the other constants were obtained by calculation.
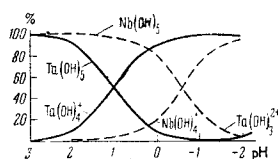
Fig. 5.   Distribution of the soluble fraction of tantalic and niobic acids between various forms in acidic solutions (in the absence of polyions).

These conditions correspond to a twofold increase in the tantalum (or niobium) concentration above the precipitate. The arrows in Fig. 1 mark the OH⁻ and H⁺ concentrations at which the solubility of tantalic and niobic acids is doubled. From these results we obtain values for the constants (5)–(8):

$$K_{base, Ta} = 1.0 \times 10^{-13}, \quad K_{base, Nb} = 2.5 \times 10^{-15},$$

$$K_{acid, Ta} = 2.5 \times 10^{-10}, \quad K_{acid, Nb} = 4.0 \times 10^{-8}.$$

The basic dissociation constants were used to calculate the solubility of tantalic and niobic acids in acid. The results (broken curves 1a and 2a in Fig. 1) show that in the range of monomeric forms of tantalum and niobium, the solubilities calculated are very close to the experimental ones, confirming that our constants are correct.

The basic dissociation constants are also the instability constants of the corresponding hydroxo-complexes:

$$K_{base} = k_5 = \frac{[M(OH)_4^+][OH^-]}{[M(OH)_5]},$$

where k_5 is the fifth individual instability constant of the hydroxo-complex M(OH)₅ (M = Ta, Nb). Using the relationship between the negative logarithms of the individual

instability constants (pk) derived from electrostatic characteristics[8], we calculated the individual (k) and total (K) instability constants of the hydroxo-complexes of tantalum and niobium. The calculation was made for the "quintuply-charged central ion–singly-charged ligand" system. The constants obtained are given in Table. 3.

Using these instability constants, we constructed a diagram showing the percentage distribution of tantalum and niobium, between various forms, in relation to the hydrogen ion concentration, by Kleiner's method[9]. The results refer to conditions in which polymeric forms are absent from the solution, and the curves, Fig. 5, show that, in acid solutions (in the absence of complex-forming reagents), the ionised fraction of the tantalum and niobium is present as Ta(OH)₄⁺ and Nb(OH)₄⁺ cations (or TaO₂⁺ and NbO₂⁺). Acidic solutions contain only insignificant quantities of more highly charged monomeric tantalum and niobium cations. Our results show that, at a definite acidity, the solution in equilibrium with the solid hydroxide phase contains tantalum and niobium ions of definite composition, the concentration of which can be calculated from the acidic and basic dissociation constants. Tantalum and niobium hydroxides can therefore be taken as standard states for quantitative calculation of the dissociation constants of tantalum and niobium complexes.

SUMMARY

1. The solubility of freshly precipitated tantalum and niobium hydroxides has been measured in the [H⁺] range 1×10^{-11} to 6 N (nitric acid). The "isoelectric range" of tantalic acid lies at pH 9 to 2 and that of niobic acid at pH 7 to 0, indicating that tantalum is more metallic than niobium. The solubility of tantalic acid in the isoelectric range is 6.0×10^{-6} M; that of niobic acid, 1.4×10^{-5} M.

2. The effect of H⁺ and OH⁻ concentration on the solubility of the acids has been calculated. Monomeric tantalum and niobium ions are formed in both acidic and alkaline media in the initial stage of dissolution. The pH values corresponding to a twofold increase in the solubility have been used to calculate the basic and acidic dissociation constants of tantalum and niobium hydroxides:

$$K_{base, Ta} = \frac{[Ta(OH)_4^+][OH^-]}{[Ta(OH)_5]} = 1.0 \times 10^{-13},$$
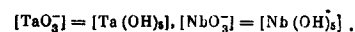
$$K_{base, Nb} = \frac{[Nb(OH)_4^+][OH^-]}{[Ta(OH)_5]} = 2.5 \times 10^{-15},$$

$$K_{acid, Ta} = \frac{[TaO_3^-][H^+]}{[Ta(OH)_5]} = 2.5 \times 10^{-10},$$

$$K_{acid, Nb} = \frac{[NbO_3^-][H^+]}{[Nb(OH)_5]} = 4.0 \times 10^{-8}.$$

3. The electrostatic characteristics and the basic dissociation constants have been used to calculate the instability constants of tantalum and niobium hydroxo-complexes. Diagrams showing the distribution of these elements between different hydrolysed forms in acidic solutions have been constructed.

4. The influence of centrifuging conditions (duration and rate of rotation of the centrifuge) on the completeness of separation of tantalum and niobium hydroxide precipitates has been observed.

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COMPOUNDS OF THALLIUM(III) WITH 4,7-PHENANTHROLINE

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The preparation and properties of many complexes of thallium(III) with 1,10-phenanthroline have been described[1-5], but compounds with 4,7-phenanthroline were unknown. This paper partly supplies this information. The starting materials were 4,7-phenanthroline, purified by recrystallisation from water or alcohol, and thallium(III) chloride and nitrate[6].

Preparation of $TlCl_3 \cdot p$-Ph† and $TlCl_3 \cdot p$-Ph.$2H_2O$

9–10 ml 0.5 M alcoholic 4,7-phenanthroline were added with vigorous stirring to 12–13 ml 0.5 M $TlCl_3 \cdot 4H_2O$ in anhydrous methanol. The pale yellow precipitate was filtered off, washed with alcohol, and dried in a desiccator over $CaCl_2$. The yield, based on the phenanthroline, was 60–70%.

    76.0 mg substance gave 47.7 mg TlI;
    64.6 mg   "   "   51.9 mg AgCl;
    24.05 mg   "   "   1.10 ml N_2 at 24° and
                          761 mm Hg.

Found, %: Tl 38.70; Cl 19.88; N 5.39.

Calculated for $TlCl_3 \cdot p$-Ph.$2H_2O$, %: Tl 38.79; Cl 20.19; N 5.32.

† p-Ph represents 4,7- or $para$-phenanthroline.

After drying in a desiccator over $CaCl_2$, it was dried further at 105° and analysed again.

    78.7 mg substance gave 53.1 mg TlI;
    87.6 mg   "   "   76.7 mg AgCl;
    16.8 mg   "   "   0.822 ml N_2 at 24° and
                          761 mm Hg.

Found, %: Tl 41.62; Cl 21.67; N 5.63.

Calculated for $TlCl_3 \cdot p$-Ph, %: Tl 41.63; Cl 21.67; N 5.70.

To confirm the water in $TlCl_3 \cdot p$-Ph.$2H_2O$, the material dried at 105° was kept in a closed vessel over water, then dried again over $CaCl_2$ and, finally, at 105°. This was repeated many times, the specimen being weighed after each drying (Table 1). The change in weight corresponded to the removal and attachment of two molecules of water.

$TlCl_3 \cdot p$-Ph and $TlCl_3 \cdot p$-Ph.$2H_2O$ are pale yellow (almost white) crystals, moderately soluble in alcohol, ether, acetone, dioxan, and glacial acetic acid, sparingly soluble in chloroform and nitrobenzene, and almost insoluble in benzene and carbon tetrachloride. They are decomposed by water with the formation of thallium(III) oxide.

Preparation of $TlCl_3 \cdot 2(p$-Ph)

21–22 g 0.5 M alcoholic 4,7-phenanthroline were added to 10 ml 0.5 M $TlCl_3$ in anhydrous methanol. The precipitate was filtered off, washed with alcohol, dried at 105°, and analysed; the yield, based on the thallium, was 60–70%.

    98.1 mg and 79.8 mg substance gave 48.2 mg and
                                   39.0 mg TlI;
    70.3 mg and 73.7 mg   "   "   45.2 mg and
                                   47.2 mg AgCl;
    12.00 mg   "   "   0.865 ml N_2 at 24°
                                 and 760 mm Hg.

Found, %: Tl 30.31, 30.15; Cl 15.91, 15.87; N 8.28.

Calculated for $TlCl_3 \cdot 2(p$-Ph), %: Tl 30.46; Cl 15.85; N 8.35.

The solubility and physical properties of $TlCl_3 \cdot 2(p$-Ph) are similar to those of the compound with one molecule of 4,7-phenanthroline.

Preparation of $TlBr_3 \cdot p$-Ph and $TlBr_3 \cdot p$-Ph.$2H_2O$

Different weights of thallium(I) bromide were brominated in anhydrous methanol, the excess of free Br_2 was removed with phenol, and the thallium(III) bromide solutions were

TABLE 1. Drying of $TlCl_3 \cdot p$-Ph.$2H_2O$.

Weight of $TlCl_3 \cdot p$-Ph.$2H_2O$, mg	Loss in weight after drying at 105°, mg	Water lost, %		Weight of $TlCl_3 \cdot p$-Ph.$2H_2O$, mg, after storage in a desiccator over water followed by drying over $CaCl_2$	Loss in weight after repeat drying at 105°, mg
		found	calc.		
72.6	4.7	6.46	6.82	72.6 72.4	4.5 4.5
100.6	6.4	6.39	6.82	100.5 100.3	6.1 6.3