ate, a study was made of other boron halide–phosphorus halide (iodine, bromine, chlorine) complexes. The results of this study are discussed in this paper. Comparison is also made to the results of other workers for compounds of this series which have been previously reported in the literature.

Experimental Methods and Results

The complexes were formed by adding approximately 0.1 mole of the phosphorus halide to approximately 0.1 mole of the boron halide dissolved in 100 ml of carbon disulfide cooled to $-40°$. Carbon disulfide is used since the complexes are relatively insoluble in this solvent while the boron and phosphorus halides are soluble in carbon disulfide. Thus excess reagents can be removed by simple washing in carbon disulfide. The carbon disulfide was cooled to determine if some of the complexes might be stable at lower temperatures but unstable at room temperatures. Since the complexes are sensitive to moisture, and oxygen (to some extent), all operations were performed in a dry helium or argon stream.

Standard reagent grade starting materials were used except for boron triiodide which was prepared and purified by the authors.[2]

The boron content was determined by the quinalizarin method[3] and the phosphorus was determined as magnesium ammonium phosphate.[4]

For halide analysis, the complexes were weighed and transferred to a separatory funnel containing trichloroethylene and ether. A very dilute HNO_3 solution was added to hydrolyze the sample. The reduced halides were extracted and determined as the silver salt. Where two halides were involved, it was assumed that both halides were present in equimolar amounts.

Anal. Calcd for $I_3B{=}PI_3$: B, 1.34; P, 3.86; I, 97.4. Found: B, 1.33; P, 3.83; I, 97.4.

Anal. Calcd for $I_3B{=}PBr_3$: B, 1.5; P, 4.7; I, 57.6; Br, 36.3. Found: B, 1.6; P, 7.2; I, 47.7; Br, 30.1.

Anal. Calcd for $I_3B{=}PCl_3$: B, 1.9; P, 5.9; I, 72.1; Cl, 20.1. Found: B, 1.2; P, 4.8; I, 67.1; Cl, 21.0.

Anal. Calcd for $Br_3B{=}PI_3$: B, 1.5; P, 4.5; I, 57.6; Br, 36.3. Found: B, 1.8; P, 5.8; I, 50.2; Br, 24.9.

Anal. Calcd for $Br_3B{=}PBr_3$: B, 2.1; P, 5.9; Br, 92.0. Found: B, 2.0; P, 5.4; Br, 89.9.

In this study six complexes were formed. These complexes are all the boron triiodide and boron tribromide adducts with the three phosphorus halides. No boron trichloride complexes were detected even at $-40°$.

$I_3B{=}PI_3$ is an orange solid, stable under vacuum, and sublimes slowly at 100°. This complex forms easily at room temperature.

$I_3B{=}PBr_3$, also orange colored, is stable under vacuum to about 80°. It sublimes slowly at about 65°. It also can be formed at room temperature. $I_3B{=}PCl_3$ is a yellow-white solid which undergoes halogen exchange at 35°. $Br_3B{=}PI_3$ is also a yellow solid which decomposes near 50°; it can be formed at room temperature. $Br_3B{=}PCl_3$ is a white solid which decomposes on standing at 0°.

Discussion

Cross halogenation (exchange of halogens between boron and phosphorus) occurs in the phosphorus trichloride compounds with both boron bromide and boron triiodide, resulting in the formation of boron trichloride. The boron bromide–phosphorus chloride converted overnight at 0°, while the boron triiodide–phosphorus trichloride was stable at room temperature for several weeks, but cross halogenated rapidly when heated to 35°. However, $I_3B{=}PBr_3$ and $Br_3B{=}PI_3$ did not appear to be cross-halogenated even after heating at 100° (15 min). In an infrared study Cowley and Cohen[5] were also unable to detect cross halogenation in $Br_3B{=}PI_3$.

The order of stability of the complexes is $BI_3 > BBr_3 > BCl_3$, in agreement with Cook,[6] who investigated boron halide complexes with xanthone. For the phosphorus halides, the order of stability is $PI_3 > PBr_3 > PCl_3$. Cook also reports the relative stability of BBr_3 and BI_3 complexes is very close, which is probably the reason no exchange is found between $Br_3B{=}PI_3$ and $I_3B{=}PBr_3$.

The results for the boron trichloride–phosphorus trichloride complex are in agreement with Holmes,[7] who found no compound formed, but disagree with Steiber,[8] who did report a compound between these reagents which was not stable above 0°. Neither of these workers employed a solvent in their reactions, but used direct mixing of the reagents. The authors also made several attempts to produce this complex using no solvent and were unsuccessful in all attempts. No previous work on other boron chloride compounds with phosphorus tribromide or triiodide could be found. $PI_3{=}BBr_3$ was recently reported by Cowley and Cohen[5] using a technique similar to that employed in this work. Holmes[7] also reported synthesizing $Br_3B{=}PBr_3$ with a melting point of 61°, similar to the value reported in this study.

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CONTRIBUTION FROM AEROSPACE CORPORATION,
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Data for $LaTaO_4$ and $PrTaO_4$, a New Structure Type, and a Series of New Rare Earth Compounds, $K_{0.5}Ln_{0.5}Ta_2O_6$, with the $PbNb_2O_6$ Structure

BY G. M. WOLTEN AND A. B. CHASE

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Several authors, by comparing unpublished powder patterns, have concluded[1–4] that $LaTaO_4$, $CeTaO_4$, and $PrTaO_4$ do not have the fergusonite structure ($YNbO_4$) assumed by the remaining rare earth orthotantalates and all the rare earth orthoniobates.

It proved easy to prepare single crystals of $LaTaO_4$

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and $PrTaO_4$ which are suitable for a structure determination. We are confining ourselves here to reporting the lattice parameters and the space group, because the work disclosed the necessity of redetermining the fergusonite structure, a task to which we are assigning priority. Unexpectedly, three members of a new series of mixed metatantalates were also obtained, namely $K_{0.5}Ln_{0.5}Ta_2O_6$, where Ln is Ce, Pr, or Nd. No further work is planned for these, and we wish to report such data as were obtained. (Indexed powder patterns for all five compounds are being submitted to the ASTM X-ray powder diffraction file.)

Experimental Section

All compounds were crystallized from a melt containing 80 mole % KF, 10 mole % Ta_2O_5, and 10 mole % La_2O_3, Ce_2O_3, Pr_6O_{11}, or Nd_2O_3. The mixtures were held for about 5 hr at 1250° in covered platinum crucibles, then cooled to 1000° at a rate of approximately 2°/hr and removed from the furnace. Solvent and unreacted starting materials were removed by digesting the solidified mass with hot water and nitric acid. The products that were obtained are shown in Table I. In the case of the praseodymium compounds where both a simple orthotantalate and a mixed metatantalate were obtained, the proportion of the simple orthotantalate seemed to increase when the rare earth oxide was increased to 15 mole % and the cooling rate to approximately 5°/hr. (Note: Pr_6O_{11} was calculated as the Pr_2O_3 equivalent.)

TABLE I

TANTALATES OBTAINED FROM MOLTEN KF AT 1250°

Rare earth	Product 1	Product 2	Product 3
La	$LaTaO_4$	...	...
Ce	...	$K_{0.5}Ce_{0.5}Ta_2O_6$	...
Pr	$PrTaO_4$	$K_{0.5}Pr_{0.5}Ta_2O_6$	...
Nd (run A)	...	$K_{0.5}Nd_{0.5}Ta_2O_6$	$KTaO_3$
Nd (run B)	...	...	[a]

[a] Probably a solid solution of $KNdF_4$ and KF.

Results for Orthotantalates

The lattice parameters of $LaTaO_4$ and $PrTaO_4$ were measured on single crystals in a GE goniostat, using Cu Kα_1 radiation. Systematic absences were deduced from precession photographs taken with Ag Kα radiation. The results are tabulated in Table II.

TABLE II[a]

Compound	$LaTaO_4$	$PrTaO_4$
Space group	$P2_1/n$	$P2_1/n$
Z	4	4
a_0, A	15.02	15.03
b_0, A	5.59	5.50
c_0, A	3.91	3.86
β, deg	93.3	94.2
Color	White	Green
Habit	(100), (001), (110) elongated along [010] and [001]	(001), (100), striated on (100), elongated along [010]
Occasional twinning on	(100)	(001)

[a] No phase transformations were observed at elevated temperatures up to 1850° nor at high pressures up to 62 kbars.

Discussion of Orthotantalates

The results of Table II suggest a new structure type. A determination of the structure is planned for the future.

Results for Metatantalates

The new mixed metatantalates are isomorphous with the high-temperature (paraelectric) phase of $PbNb_2O_6$, as shown by the close resemblance of the powder patterns and lattice parameters. Table III lists the lattice parameters and compares them with those of the prototype and several other related compounds.[5-7]

TABLE III

Compound	Cation radius, A	a_0, A	c_0, A	Ref
$BaTa_2O_6$	1.34	12.59	3.92	5
$SrTa_2O_6$	1.12	12.45	3.85	5
$PbNb_2O_6$ (>560°)	1.20	12.56	3.925	6
$PbTa_2O_6$ (>260°)	1.20	12.507	3.893	5
$Ba_6Ti_2Nb_8O_{30}$	...	12.54	4.01	7
$K_{0.5}Ce_{0.5}Ta_2O_6$	1.20 (mean)	12.56	3.92	This work
$K_{0.5}Pr_{0.5}Ta_2O_6$	1.195	12.55	3.91	This work
$K_{0.5}Nd_{0.5}Ta_2O_6$	1.185	12.61	3.96	This work

The data taken from ref 5 have been transformed from a quadruple cell. The extinctions ($k = 2n$ for $0kl$) allow three space groups, P4/mbm, $P\bar{4}b2$, and P4bm. A full structure determination has been reported only for the barium titanium niobate,[7] and its space group is P4bm.

Discussion of Metatantalates

The lattice parameters of the neodymium compound appear too large when compared to other members of the series. The optical behavior of the crystals suggested that they may have been highly strained, and the strained nature of the material may have introduced errors in the measurements of lattice parameters. The crystals were large white blocks, up to 2 mm in size, bounded by (001) and $\{310\}$ faces. This habit probably expresses the pseudo-cubic character of the lattice. The spacing $d_{(310)}$ is within 1 or 2% of the value for c_0, and it is also equal to a_0 of the cubic perovskite $KTaO_3$. According to Francombe and Lewis,[8] the $PbNb_2O_6$ structure is related to certain tetragonal tungsten bronzes and consists of linked perovskite residues.

Although the potassium cerium and potassium praseodymium metatantalates are isostructural with the neodymium compound, their habits were entirely different. This may be due to their association with different side products in the preparation (see Table I). The cerium and praseodymium compounds were tangles of single-crystal fibers, 0.5 to 2 mm long parallel to the c axis and only 1 to 2 μ thick, the aggregate having the appearance and consistency of cotton. The fibers were too thin to support their own weight and thus could not be mounted for single-crystal work, but small wads of the materials stuffed into 0.3 mm i.d. capillaries gave excellent powder patterns. The neodymium compound was unsuitable for single-crystal work because of the strain mentioned, and a powder pattern was obtained from a ground-up crystal. The

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praseodymium compound was white, but the cerium compound was yellow. This would indicate oxidation of some Ce(III) to Ce(IV). Since in these structures the cations are located in only partially filled tunnels or cages formed by TaO_6 octahedra,[8] charge compensation is most likely achieved by an increase in cation vacancies, either K(I) or Ce(III). However, the deficiency was less than the precision (about 5%) of our fluorescence analysis,[9] which gave a 1:1:4 ratio for K:Ce:Ta.

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(9) We wish to thank Mr. J. H. Richardson of this organization for carrying out our quantitative X-ray fluorescence analyses.

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The Mechanism of the Reaction of Carbonatopentaamminecobalt(III) with Divalent Ions

BY R. B. JORDAN, A. M. SARGESON, AND H. TAUBE

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The investigation to be described arose from the observation that the reaction of $(NH_3)_5CoCO_3^+$ with $Pb^{2+}(aq)$ or $Hg^{2+}(aq)$ gives an almost immediate precipitate of the metal ion carbonate leaving $(NH_3)_5CoOH_2^{3+}$ in solution, while the reaction with $Ba^{2+}(aq)$

$$(NH_3)_5CoCO_3^+ + M^{2+} + H_2O \longrightarrow (NH_3)_5CoOH_2^{3+} + MCO_3 \quad (1)$$

is at least one hundred times slower. Of interest in these systems is the position of bond rupture—a question that can be settled by oxygen tracer experiments—and the difference in rates for different ions—a question that is not at all easily settled.

Experimental Section

(1) Tracer Studies on the Position of Bond Rupture.—The reactant solutions made up in O^{18}-enriched water were initially ~0.1 *M* in $(NH_3)_5CoCO_3NO_3$[1] and with $Hg(OAc)_2$, $Pb(NO_3)_2$, or $Ba(NO_3)_2$ at equivalent concentrations. The reaction time, 4 min for the first two reagents, was sufficient to ensure complete reaction in these cases. In the case of Ba^{2+} as reactant the reaction time was 2 hr and the reaction was only 30% complete in this time.

After reaction, the carbonates (in the case of Hg^{2+} as reactant, the product was probably the basic carbonate) were separated by filtration; the precipitates were washed lightly with water, then with methanol, and dried in a vacuum desiccator for 2 days. The precipitates were then treated with acid, the CO_2 formed being flushed out with He. Under these conditions very little exchange with the solvent takes place.

The filtrates resulting from the separation of the insoluble carbonates were immediately acidified with excess cold concentrated HBr; the solid aquo bromide was collected, washed with a small amount of water, then with methanol, and dried for 12 hr in a vacuum desiccator. The contained water was liberated by heating the solid. The water-oxygen was converted to CO_2 following the Anbar–Gutman[2] procedure, and the resulting CO_2 was purified by gas chromatography.

It should be recognized that the HBr treatment converts $(NH_3)_5CoCO_3^+$ to $(NH_3)_5CoOH_2^{3+}$. Thus in the case of the Ba^{2+} system, 70% of the aquo bromide results from the release by acid of CO_2 from the unreacted carbonato complex. The reaction of the carbonato complex with acid is known[3] to take place leaving the bridging oxygen in the aquo product. To determine the isotopic composition only of the aquo product resulting from the reaction of the complex ion with Ba^{2+}, an aliquot of the filtrate was taken and treated with LiBr. This treatment leaves $(NH_3)_5CoCO_3^+$ intact and in solution.

(2) Exchange of Oxygen between $(NH_3)_5CoCO_3^+$ and H_2O.—The reaction of $(NH_3)_5CoCO_3^+$ with Ba^{2+} is so slow that exchange of oxygen between the complex and solvent may affect the results. An experiment was undertaken to measure the rate of exchange, mildly alkaline conditions being chosen to avoid a contribution to the reaction by a hydrogen ion catalyzed path. The reactant solution, 0.10 *M* $(NH_3)_5CoCO_3^+$, was made up in O^{18}-enriched water, and the pH was adjusted to 9.6 using NaOH. Aliquots were taken at intervals and treated with cold concentrated HBr. The CO_2 was collected using a continuous stream of He, and the aquo complex formed was treated as described above.

For all experiments the isotopic composition of the solvent was determined by equilibrating it with CO_2; all isotopic compositions were determined by readings on CO_2 using an Atlas M 86 mass spectrometer; the temperature was 25°.

Results

The results of the tracer experiments are summarized in Table I, and of the exchange experiment in Table II.

TABLE I

TRACER RESULTS ON THE REACTION OF Hg^{2+}, Pb^{2+}, AND Ba^{2+} WITH $(NH_3)_5CoCO_3^+$

(Complex of normal isotopic composition)

	Enrichment ratio[a]			% oxygen from solvent in	
Ion	Solvent	MCO_3	$(NH_3)_5$-$CoOH_2^{3+}$	MCO_3	$(NH_3)_5$-$CoOH_2^{3+}$
Hg^{2+}	8.85	3.67	1.57	34	7.3
Pb^{2+}	7.40	2.90	1.02	30	0.3
Ba^{2+}	7.41	3.52	1.52[b]	39	8.0
			3.06[c]	39	32

[a] Isotopic ratio compared to that of a standard sample of CO_2. [b] Aquo derived by treating product solution with HBr. [c] Aquo precipitated with LiBr.

TABLE II

OXYGEN EXCHANGE BETWEEN SOLVENT AND $(NH_3)_5CoCO_3^+$ (pH 9.6; 25°)

	% exchange	
Time, min	CO_2[a]	$(NH_3)_5CoOH_2^{3+}$[b]
15	9.8	0
45	13.9	0
75	20.1	0
200	31.2	0.3
1080	68.2	3.3

[a] As found in the CO_2 formed when the reactant solution was treated with HBr. [b] As found in the aquo formed on treatment as above.

Discussion

Two facts emerge from the results for the Hg^{2+} and Pb^{2+} reactions: there is little or no enrichment in the

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