band at 1100 cm.$^{-1}$ to bridging ester groups. This is in contrast to assignments made in previous work.[9,10] Absorption bands in the 1000 to 1150 cm.$^{-1}$ region are found at 1137, 1106, 1067, and 1045 cm.$^{-1}$. In this study, the intensity of the 1045 cm.$^{-1}$ band is found to be concentration dependent and practically disappears in dilute solution where the principal species is monomer. When wet solvent is employed the 1100 cm.$^{-1}$ band disappears. This finding supports the assignment of the 1045 cm.$^{-1}$ band to bridging ester groups. The infrared spectrum of the monofluoride, $TiF(OC_2H_5)_3$, also contained a band around 1045 cm.$^{-1}$ which disappeared on dilution. The solid, Nujol mull of $TiF_2(OC_2H_5)_2$ had a band at 1045 cm.$^{-1}$ but the spectrum of the solid compound $TiF_3OC_2H_5$ did not. The latter compound is probably completely fluorine-bridged.

There are a great number of structures which can be drawn for these compounds which preserve octahedral coordination about the titanium and allow a preference for fluorine *vs.* ethoxyl bridges. No conclusions regarding structure can be drawn.

Acknowledgment.—The authors wish to acknowledge the generous support of this research by the Titanium Division of The National Lead Corporation.

---

[9] H. Kriegsmann and K. Licht, *Z. Elektrochem.*, **62**, 1163 (1958).

[10] T. Takatani, Y. Yoshimoto, and Y. Maskiko, *Kogyo Kagaku Zasshi*, **60**, 1382 (1957).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CONNECTICUT, STORRS, CONNECTICUT

Compounds of Post-Transition Elements with the Ordered Perovskite Structure[1]

BY ARTHUR W. SLEIGHT AND ROLAND WARD

Received August 23, 1963

The preparation and characterization of numerous compounds of the formula $A_2BB'O_6$ having the ordered perovskite structure have been described in previous publications.[2-8] Since A is an alkaline earth cation, the sum of the oxidation states of B and B′ must be eight.

Except for Pb, Bi, Sn, and the group IIIb elements, post-transition elements have not been found in the perovskite structure as cations. Ordered perovskites containing Sb, Te, I, and Tl have now been prepared and are listed in Table I. Furthermore, the compound Ba_2AgIO_6 represents the first instance of Ag as a B cation in the perovskite structure. The color of Ba_2InSbO_6 suggests that this compound may be oxygen-deficient. It is assumed that many other analogous compounds may exist, but attempts to prepare compounds containing Br^{VII}, Se^{VI}, or As^{V} as B cations were not successful.

TABLE I

$A_2BB'O_6$ TYPE COMPOUNDS

Compound	Lattice constants a, Å.	 c, Å.	Color
Ba_2ScSbO_6	8.197		White
Ba_2InSbO_6	8.269		Black
Sr_2CrSbO_6	7.862		Brown
Sr_2FeSbO_6	7.916		Pale green
Sr_2GaSbO_6	7.84	7.91 (tet.)	White
Ba_2MgTeO_6	8.13		Yellow
Ba_2CaTeO_6	8.393		Yellow
Ba_2NaIO_6	8.33		White
Ba_2AgIO_6	8.46		Brown
Ba_2TlTaO_6	8.42		Black

Experimental

Most of the reagents have been previously described.[3,6] $HIO_4 \cdot 2H_2O$, $NaIO_4$, Sb_2O_3, and TeO_2 were C.P. or reagent grade. Tl_2O_3 (99.2%) was obtained from K and K Laboratories, Inc. Ag_2O was obtained from Merck and Co., Inc. In general, high temperature solid state reactions, indicated by the following equations, were used to prepare these compounds. The reactants were intimately mixed and fired in air.

$$4BaO_2 + B_2O_3 + Sb_2O_3 \xrightarrow{1100°} 2Ba_2BSbO_6 + O_2$$

$$B = \text{Sc or In}$$

$$4SrO + B_2O_3 + Sb_2O_3 + O_2 \xrightarrow{1100°} 2Sr_2BSbO_6$$

$$B = \text{Cr, Fe or Ga}$$

$$2BaO_2 + BO + TeO_2 \xrightarrow{1100°} Ba_2BTeO_6 + {}^1/_2O_2$$

$$B = \text{Mg or Ca}$$

$$2BaO + NaIO_4 \xrightarrow{400°} Ba_2NaIO_6$$

$$4BaO_2 + Tl_2O_3 + Ta_2O_5 \xrightarrow{1000°} 2Ba_2TlTaO_6 + 2O_2$$

Ba_2NaIO_6 could also be precipitated from a solution of $NaIO_4$ upon the addition of a $Ba(OH)_2$ solution. Ba_2AgIO_6 was prepared in a similar manner. A solution of $Ba(OH)_2$ was added to a slurry of Ag_2O in a solution of periodic acid. All the ingredients were in stoichiometric proportions. The resulting slurry was digested on a steam bath for 12 hr. The product was filtered off and dried at 90°. Ba_2AgIO_6 could not be prepared by high temperature reactions due to the reduction of Ag^{I} to Ag metal.

Analysis of these compounds was not carried out since no purification procedure was found. The diffraction patterns of the final products, however, were completely indexable on the basis of the parameters listed in Table I. The relative intensities of the reflections corresponded to the expected values for the ordered perovskite structure and in all cases the (111), (311), and (331) reflections due to the ordered structure were prominent.

---

[1] Taken from the Ph.D. thesis submitted by Arthur W. Sleight to The University of Connecticut, 1963.

[2] S. G. Steward and H. P. Rooksby, *Acta Cryst.*, **4**, 503 (1951).

[3] E. J. Fresia, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **81**, 4783 (1959).

[4] A. W. Sleight and R. Ward, *ibid.*, **83**, 1088 (1961).

[5] J. Longo and R. Ward, *ibid.*, **83**, 2816 (1961).

[6] A. W. Sleight, J. Longo, and R. Ward, *Inorg. Chem.*, **1**, 245 (1962).

[7] A. W. Sleight and R. Ward, *ibid.*, **1**, 790 (1962).

[8] F. Patterson, C. Moeller, and R. Ward, *ibid.*, **2**, 196 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA

Reactions of Some Chlorophosphines with Tributylphosphine

BY S. E. FRAZIER, R. P. NIELSEN, AND H. H. SISLER

Received September 23, 1963

We wish to report three interesting reactions in which tri-*n*-butylphosphine extracts chlorine atoms from various chlorophosphines to form products containing P–P bonds. It is known[1] that triphenylphosphine is also capable of accepting chlorine atoms in the course of prolonged heating with chlorides of trivalent phosphorus, antimony, arsenic, and bismuth. The work reported herein expands the range of this reaction to include alkyl phosphines.[2]

Tributylphosphine, more easily oxidized than triphenylphosphine, reacts exothermally when mixed with phosphorus trichloride. A red-yellow, flocculent precipitate containing 80–90% phosphorus forms almost immediately. From X-ray powder diffraction analysis, this material appears to be amorphous. It is insoluble in water, acetone, alcohols, benzene, ether, and carbon disulfide. In addition to phosphorus, the substance contains some carbon, hydrogen, and chlorine; the analyses vary from sample to sample. One might reasonably assume that the product consists of a three-dimensional network of phosphorus atoms end-stopped with alkyl groups and chlorine atoms.

If the original reaction mixture is extracted with dry benzene a second product, tributyldichlorophosphorane, can be isolated; the reaction may therefore, be represented as shown below.

$$3(C_4H_9)_3P + 2PCl_3 \longrightarrow 3(C_4H_9)_3PCl_2 + 2P$$

When mixed with phenyldichlorophosphine, tributylphosphine reacts exothermally to give a white, crystalline mass. From this mass one can separate two crystalline solids, tributyldichlorophosphorane and a substance which is identical with tetraphenylcyclotetraphosphine reported first by Michaelis and Kohler[3] and later by Kuchen and Buchwald.[4]

$$4(C_4H_9)_3P + 4C_6H_5PCl_2 \longrightarrow 4(C_4H_9)_3PCl_2 + (C_6H_5P)_4$$

Likewise, a mixture of diphenylchlorophosphine and tributylphosphine solidifies after standing for several hours. Tetraphenylbiphosphine[5] was isolated in modest yield from the reaction mixture.

$$(C_4H_9)_3P + 2(C_6H_5)_2PCl \longrightarrow (C_4H_9)_3PCl_2 + (C_6H_5)_2P{-}P(C_6H_5)_2$$

These reactions provide quick, simple preparations of compounds containing phosphorus–phosphorus bonds using generally available chemicals.

Experimental[6]

Tributylphosphine was obtained from Food Machinery and Chemical Corporation and the fraction boiling at 60–61° (1.20 mm.) was used. Phosphorus trichloride was obtained from J. T. Baker Chemical Co. and used as obtained. Phenyldichlorophosphine and diphenylchlorophosphine were obtained from Victor Chemical Works and the fractions boiling at 91–93° (3.2 mm.) and 126° (1.0 mm.), respectively, were used. All organophosphorus compounds were handled in an atmosphere of dry nitrogen.

TABLE I

	Found				
	% C	% H	% Cl	% P	Yield, g.
Expt. 1	14.70	3.08	2.44	80.44	1.10 (86% of theory)
Expt. 2	5.22	1.23	0.49	88.90	0.91 (88% of theory)

Reaction of Phosphorus Trichloride with Tributylphosphine.—Tri-*n*-butylphosphine (0.080 mole) was added dropwise with stirring to a solution of 0.033 mole of phosphorus trichloride in 50 ml. of benzene. The exothermic reaction immediately produced a red-yellow, flocculent precipitate. This material was washed with dry benzene and the benzene solution and washings were removed by filtration. It was then washed in boiling acetone, filtered, and dried under vacuum. No melting point was observed up to 350°; the substance reacts violently with concentrated nitric acid, but is affected by the atmosphere only after long exposure. The analyses varied as illustrated in Table I.

The benzene solution and washings from the reaction were evaporated under vacuum, care being taken to avoid exposure to the atmosphere. A highly hygroscopic, white, crystalline material was obtained which was purified by sublimation at 120° under high vacuum; m.p. 134–137° (closed tube). *Anal.* Calcd. for $(C_4H_9)_3PCl_2$: Cl, 25.95. Found: Cl, 26.3.

Reinecke's Salt Derivative of $(C_4H_9)_3PCl_2$.[7]—An alcohol solution of Reinecke's salt,[8] $NH_4[Cr(SCN)_4(NH_3)_2]$, was added to an alcohol solution of the compound suspected to be tributyldichlorophosphorane. Upon addition of water a pink, crystalline material precipitated which was filtered by suction and dried under vacuum; m.p. 121–123° dec. The temperature of decomposition reported in the literature[6] is 124–126°. *Anal.* Calcd. for $(C_4H_9)_3PO \cdot H[Cr(SCN)_4(NH_3)_2]$: N, 15.63. Found: N, 15.57.

Reaction of $C_6H_5PCl_2$ and $(C_4H_9)_3P$.—Phenyldichlorophosphine (0.037 mole) was mixed with 0.037 mole of tributylphosphine. An exothermic reaction ensued, resulting in the formation of a solid, crystalline mass in a few seconds. The reaction mixture was sublimed at 120° under high vacuum and 6.7 g. (68% of theory) of $(C_4H_9)_3PCl_2$ was obtained on the cold finger. It melted at 134–137°. *Anal.* Calcd. for $(C_4H_9)_3PCl_2$: Cl, 25.95. Found: Cl, 26.29. Further identification was provided by the formation of the Reinecke's salt derivative.

The residue from the sublimation was washed with several portions of absolute alcohol, filtered, and dried under vacuum, care being taken to avoid its exposure to the atmosphere. The resulting yellowish powder melted at 147–150° in a sealed tube (lit. 150.5°). Its infrared spectrum was identical with that of tetraphenylcyclotetraphosphine[4]; yield 1.2 g. (30% of theory). *Anal.* Calcd. for $(C_6H_5P)_4$: C, 66.67; H, 4.66; P, 28.66. Found: C, 66.33; H, 4.86; P, 28.32.

Reaction of $(C_6H_5)_2PCl$ and $(C_4H_9)_3P$.—Diphenylchlorophosphine (0.027 mole) was mixed with 0.014 mole of tributylphosphine. The exothermic reaction resulted in a thick, homogeneous oil which slowly solidified to a crystalline mass. The presence of tributyldichlorophosphorane in this mixture was demonstrated by extracting the crystalline mass with two 25-ml. portions of alcohol. From this alcohol solution, the Reinecke's salt derivative, $(C_4H_9)_3PO \cdot H[Cr(SCN)_4(NH_3)_2]$ (dec. 121–123°), was precipitated as described above.

The remaining, crystalline material was extracted several times with freshly boiled, distilled water and dried under vacuum, care being taken to avoid exposure to atmospheric oxygen. The dry powder gave a cloudy melt at 119–120° in a sealed tube (lit. 120.5°). The infrared spectrum was identical with that reported for tetraphenylbiphosphine.[5]

---

(1) F. Challenger and F. Pritchard, *J. Chem. Soc.*, **125**, 864 (1924).

(2) One of the referees has called our attention to the exothermic reaction of phenyldichlorophosphine and the alkylarylphosphine, dimethylphenylphosphine, observed first by H. Kohler and A. Michaelis [*Ber.*, **10**, 814 (1877)] and later by J. Meisenheimer, *et al.* [*Ann. Chem.*, **449**, 228 (1926)]. This reaction is, no doubt, quite analogous to those reported herein. However, in both cases the products were described incorrectly.

(3) A. Michaelis and H. Kohler, *Ber.*, **10**, 807 (1877).

(4) W. Kuchen and H. Buchwald, *ibid.*, **91**, 2296 (1958).

(5) W. Kuchen and H. Buchwald, *ibid.*, **91**, 2871 (1958).

(6) Analyses by Mr. Wade Renn of the University of Florida; Galbraith Laboratories, Inc., Knoxville, Tenn.; and the author.

(7) K. Issleib and W. Seidel, *Z. anorg. allgem. Chem.*, **288**, 201 (1956).

(8) W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, 1954.

Synthesis of $(C_6H_5)_2P(O)$–$P(O)(C_6H_5)_2$.—A sample of tetraphenylbiphosphine produced by the method outlined above was suspended in absolute toluene and cooled with an ice bath. Dry air was passed through the suspension for several hours. The temperature was then raised to the boiling point of toluene, and the solids dissolved. Upon cooling to room temperature white crystals formed which were filtered and dried under vacuum; m.p. 166–167° (lit. 167°). *Anal.* Calcd. for $(C_6H_5)_2P(O)P(O)(C_6H_5)_2$: C, 71.64; H, 5.01. Found: C, 70.97; H, 5.00.

Acknowledgment.—The authors gratefully acknowledge the support of this work by W. R. Grace and Company through a contract with the University of Florida.

Contribution from the Department of
Inorganic and Analytical Chemistry,
The Hebrew University, Jerusalem, Israel,
and Argonne National Laboratory,
Argonne, Illinois

Difluorochlorinium Tetrafluoroborate

By Henry Selig[1] and Jacob Shamir

Received June 27, 1963

Seel[2,3] has demonstrated that AsF_5 and SbF_5 dissolve in ClF_3 to give products formulated as $[ClF_2]^+[AsF_6]^-$ and $[ClF_2]^+[SbF_6]^-$ on the basis of conductivity and infrared studies. An adduct of PtF_5 with ClF_3 has also been described.[4] In the present study it has been found that BF_3 also reacts with ClF_3 upon warming from −78° to room temperature according to the equation

$$BF_3(g) + ClF_3(g) \rightleftharpoons BClF_6(s) \qquad (1)$$

The compound $BClF_6$ is a colorless solid melting at 30°. The liquid has a marked tendency to supercool. The formula $[ClF_2]^+[BF_4]^-$ is consistent with conductivity and infrared data.

Vapor density measurements indicate that the compound is completely dissociated in the gas phase. The vapor pressure of $BClF_6(s)$ was measured over the range −30 to +20°. A plot of log *p vs.* 1/*T* gives the relation

$$\log p_{\rm mm} = \frac{-(2576 \pm 16)}{T} + (12.00 \pm 0.06) \qquad (2)$$

Experimental

Materials.—ClF_3 was obtained from the Matheson Co. and BF_3 from the Ohio Chemical and Mfg. Co. Both gases were purified by repeated low temperature sublimations.

Apparatus.—Preparation and purification were carried out in an all-nickel or Monel vacuum system similar to ones described elsewhere.[5] Pressure measurements were made with a Monel ACCO helicoid gage, 0–1500 mm. Temperatures above 0° were measured with a thermometer; below 0° constant temperature baths were used. Vapor density measurements were made in a thin-walled nickel weighing can fitted with a miniature brass Hoke valve. The melting point was determined in a thin-walled Kel-F tube.

Preparation of $BClF_6$.—The adduct was prepared by direct combination of the compounds between −78° and room temperature. Liquid ClF_3 at −78° rapidly absorbs BF_3 at first. The mixture begins to solidify as BF_3 is absorbed, slowing down additional absorption. It is preferable to warm a mixture of ClF_3 and excess BF_3 to room temperature in a closed nickel can. The mixture is then cooled to −78°, and the excess BF_3 is pumped off. The 1:1 adduct remaining behind can be easily sublimed and thus purified because of its high vapor pressure.

The apparent molecular weight of the gas determined by vapor density measurements was 81 ± 1. Since the expected molecular weight of an equimolar mixture of BF_3 and ClF_3 is 80.14, the compound appears to be totally dissociated in the gas phase.

Infrared Spectra.—Infrared spectra were obtained over the range 600–2000 cm.$^{-1}$ on a Perkin-Elmer Model 421 grating instrument. Vapor spectra were obtained in a 10-cm. nickel cell fitted with AgCl windows. The vapor spectra substantiated the conclusion obtained from vapor-density measurements that the compound was totally dissociated in the gas phase.

Solid spectra were obtained in a similar nickel cell fitted with an internal AgCl window which was an integral part of a liquid nitrogen reservoir. Spectra run with solid $BClF_6$ condensed on this window showed a broad peak centered at about 1030 cm.$^{-1}$. This band is characteristic of BF_4^-.[6] Spectra of solid BF_3 and ClF_3 run separately did not show this band.

Conductivity Measurements.—Measurements were carried out with a Model 216 B1 Industrial Instruments Co. conductivity bridge. The cell consisted of a Kel-F tee fitted with 0.25-in. platinum rods in the side arms. The other arm was connected *via* a 0.25-in. Kel-F U-tube to a Kel-F valve which was attached to the manifold. The compound, or a mixture of it with ClF_3, was condensed into the bottom of the U-tube and the valve was closed. The assembly was then detached from the manifold and immersed in a constant-temperature bath. After some time the assembly was inverted in such a way that the liquid flowed into the body of the cell so that conductivity measurements could be made.

Although ClF_3 did not attack the platinum electrodes, it was found that small amounts of platinum were dissolved off if in prolonged contact with $BClF_6$. After pumping off the compound, a small yellow residue, presumably PtF_4, remained in the U-tube. This residue dissolved in the solutions, but it had little effect on conductivity measurements as shown by the fact that when fresh ClF_3 was distilled into the cell, no increase in conductivity was detected.

Pure ClF_3 measured in our cell gave a specific conductance at 20° of $<10^{-6}$ ohm^{-1} cm.$^{-1}$. This is consistent with the value of $<10^{-9}$ ohm^{-1} cm.$^{-1}$ quoted in the literature.[7] Small amounts of BF_3 dissolved in ClF_3 raised the conductivity markedly. A 1 *M* solution of $BClF_6$ in ClF_3 possessed a specific conductance of 2.7×10^{-4} ohm^{-1} cm.$^{-1}$ at 20°. The specific conductance of molten $BClF_6$ at 31° was 1.5×10^{-2} ohm^{-1} cm.$^{-1}$. This remarkably high conductivity compares with the high values obtained with solutions of ClF_3–SbF_5 (6.65×10^{-3} ohm^{-1} cm.$^{-1}$ for a 0.564 *M* solution of ClF_3–SbF_5 in ClF_3 at 0°).

Acknowledgments.—H. S. wishes to thank the Israel Atomic Energy Commission for a fellowship grant under which this work was carried out, as well as the Hebrew University for providing laboratory facilities. We wish to thank Dr. Howard H. Claassen of Argonne National Laboratory for the use of the infrared cell for solids.

---

[1] Chemistry Division, Argonne National Laboratory, Argonne, Ill.

[2] F. Seel and O. Detmer, *Angew. Chem.*, **70**, 163 (1958).

[3] F. Seel and O. Detmer, *Z. anorg. allgem. Chem.*, **301**, 113 (1959).

[4] N. Bartlett and D. H. Lohman, *J. Chem. Soc.*, 5253 (1962).

[5] B. Weinstock and J. G. Malm, *J. Inorg. Nucl. Chem.*, **2**, 380 (1956).

[6] D. W. A. Sharp, "Advances in Fluorine Chemistry," Vol. 1, p. 79.

[7] A. A. Woolf and N. N. Greenwood, *J. Chem. Soc.*, 2200 (1950).