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.

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

BY ARTHUR W. SLEIGHT AND ROLAND WARD

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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.

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Reactions of Some Chlorophosphines with Tributylphosphine

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We wish to report three interesting reactions in which tri-*n*-butylphosphine extracts chlorine atoms from various chlorophosphines to form products con-