tained only from the P^{31} spectrum. It is interesting that a change in the dihedral angle formed by the P–O–C–H bonds from 180° in compounds IV–VI to 60° in the staggered configuration of compounds I–III causes a decrease in coupling constant by a factor of about three in the corresponding phosphites (I, IV), phosphates (III, VI), and thiophosphates (II, V). A similar relation for H–C–C–H systems has been treated by Karplus.[5] The increase in the value of $J_{\text{P-O-C-H}}$ for the series of compounds I–III and IV–VI is in accordance with the expectation that coupling is enhanced by increasingly electronegative substituents on the phosphorus atom.

Phosphorus chemical shifts in trivalent phosphorus compounds have been related with some success to X–P–X bond angles (X = H or halogen) by a consideration of the difference in electronegativity between X and P and the valence-electron imbalance on phosphorus.[4,6] It would seem that the relatively large difference (45 p.p.m.) in P^{31} chemical shift of the phosphites (I, IV) might be an indication of appreciably different O–P–O bond angles. Calculations based on the method of Parks,[6] however, yield O–P–O bond angles differing by less than 1°. This method involves solution of a quadratic equation giving alternative O–P–O bond angles of 93° 1′ and 104° 31′ for phosphite (I) and 93° 22′ and 103° 59′ for phosphite (IV). On the basis of scale models, the latter of the two values for each molecule is the more plausible. X-Ray analyses of these compounds and a number of metal complexes are in progress to explore O–P–O bond angles and their possible changes on coördination. The general trend in P^{31} chemical shifts from the trivalent phosphorus compounds (I, IV) to their corresponding pentavalent thiophosphate and phosphate derivatives parallels that observed for $(C_2H_5O)_3P$, $(C_2H_5O)_3PS$, and $(C_2H_5O)_3PO$.[7]

In contrast to acyclic compounds of comparable molecular weight, the rigidity of the polycyclic phosphites (I, IV) will minimize changes in O–P–O bond angle, conformational changes, and steric hindrance upon coördination to the chalcogens as well as to transition metals[8] and group III acids.[9] Hence the change in P^{31} resonance on coördination should more purely be due to the formation of the phosphorus to electron-acceptor bond.

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CONTRIBUTION FROM THE DIVISION OF CHEMICAL
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Crystallography of the Calcium Potassium Phosphate $CaK_3H(PO_4)_2$

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The crystallographic properties of the new salt $CaK_3H(PO_4)_2$ and some of the properties of the previously known[1] salt $MgNa_3H(PO_4)_2$ were determined by petrographic and X-ray techniques.

Experimental

Preparation of Crystals.—To a solution containing 115 g. of K_2HPO_4 and 10 g. of KOH in 144 ml. of H_2O was slowly added 50 ml. of 0.3 *M* calcium acetate. Rapid stirring during the addition promoted formation of a uniform, well dispersed gel, which crystallized after standing 1 to 3 hr. at room temperature. The crystals were collected on a suction filter, washed several times with small volumes of water, once with acetone, and dried at 105°. *Anal.* Calcd. for $CaK_3H(PO_4)_2$: Ca, 11.51; K, 33.67; P, 17.78; H_2O, 2.59. Found: Ca, 11.64; K, 33.5; P, 17.59; H_2O, 3.02. The crystals decompose slowly in water to form apatite pseudomorphs.

$MgNa_3H(PO_4)_2$ was prepared by the method of Bassett and Bedwell.[1] *Anal.* Calcd. for $MgNa_3H(PO_4)_2$: Mg, 8.56; Na, 24.26; P, 21.79; H_2O, 3.17. Found: Mg, 8.4; Na, 23.5; P, 21.6; H_2O, 4.9.

Results

Morphological and Optical Properties.—The salt $CaK_3H(PO_4)_2$ crystallizes as plates having monoclinic holohedral symmetry, class 2/m. The crystals are tabular on (001), which is also the composition plane of polysynthetic twins. Modifying forms, the sets {111} and {201}, impart a pronounced pseudo-hexagonal symmetry to the plate crystals and make them resemble truncated

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[1] H. Bassett and W. L. Bedwell, *J. Chem. Soc.*, 877 (1933).

rhombohedra whose dihedral angles on (001) deviate just perceptibly from 120°. Also, in many twinned crystals, successive layers united on (001) are rotated either 60 or 120° to adjacent layers, instead of 180° about c^*. The crystals tend to elongate along b. The density computed from refractive indexes and composition is 2.78 g./cc., and that measured pycnometrically is 2.77 g./cc.

The crystals are biaxial (+), $2V = 70°$ (calcd. $= 71.1°$), with $n_x = 1.538$, $n_y = 1.550$, $n_z = 1.575$. The OAP is (010), $n_y = b$, and $n_z \wedge a$ on $(010) = 31°$ in acute β; $\beta = 92.5°$. No dispersion was detected.

The morphology of untwinned crystals from about 20 preparations invariably indicated holohedral symmetry. (Twinned crystals resulting from oriented overgrowths at 120° may convey a false impression of hemimorphic character.)

The salt $MgNa_3H(PO_4)_3$ is reported[1] to crystallize as square or rectangular plates. The apparently orthorhombic plates of our preparations of this salt were penetration twins or, less frequently, contact twins of two thin lamellae. Coarse crystals were not perfectly rectangular but were mimetic twins of two thin lamellae that formed nearly perfect rectangular crystals. Occasionally the coarse crystals were three-membered penetration twins with hexagonal symmetry. On edge view the twinned units showed symmetrically opposed, steeply inclined extinction directions, indicating monoclinic or triclinic symmetry which is lower than that implied by the crystal habits. The crystals are optically (+). The maximum and minimum refractive indexes measured were $n_1 = 1.536$ and $n_2 = 1.568$; N_β was between 1.540 and 1.545. The density computed from refractive indexes and composition is 2.84 g./cc., and that measured pycnometrically is 2.82 g./cc.

X-Ray Diffraction.—Powder X-ray diffraction data for the two compounds are shown in Table I.

Rotation and Weissenberg photographs (CuKα radiation) show that the unit cell of $CaK_3H(PO_4)_2$ is monoclinic with $a = 9.93$ Å., $b = 5.72$ Å., $c = 7.44$ Å., and $\beta = 92.3°$. With two formula weights per unit cell, the calculated density, 2.72 g./cc., agrees closely with the optical and pycnometric values.

The observed reflections are (hkl) present when $h + k = 2n$, $(h0l)$ present when $h = 2n$, and $(0k0)$ present when $k = 2n$. The possible space groups are C_{2h}^3–C2/m, C_2^3–C2, and C_s^3–Cm. In accord with the apparent holohedral symmetry indicated by the crystal morphology, the most probable space group is C_{2h}^3–C2/m in which the calcium, potassium, hydrogen and phosphorus atoms must be in special positions. Any of these atoms, however, may occupy one of several possible sets of special positions.

TABLE I

POWDER X-RAY DIFFRACTION PATTERNS[a]

$CaK_3H(PO_4)_2$				$MgNa_3H(PO_4)_2$			
d, Å.	I/I_1	d, Å.	I/I_1	d Å	I/I_1	d, Å.	I/I_1
7.43	75	1.98	19	6.86	21	2.06	5
4.27	6	1.93	4	4.64	5	2.02	13
4.21	12	1.85	30	4.46	4	1.94	24
4.06	4	1.81	8	3.88	42	1.90	4
3.98	4	1.79	4	3.75	58	1.88	39
3.72	74	1.76	6	3.42	49	1.72	8
3.08	80	1.71	15	2.79	57	1.71	19
3.03	27	1.67	8	2.70	100	1.69	5
2.92	96	1.65	11	2.62	56	1.65	6
2.86	100	1.63	7	2.59	47	1.59	11
2.47	98	1.60	10	2.44	4	1.55	18
2.39	4	1.55	22	2.32	18	1.53	12
2.38	4	1.53	7	2.30	19	1.51	4
2.32	10	1.51	15	2.28	28	1.48	4
2.29	5	1.48	7	2.23	3	1.44	5
2.25	4	1.46	10	2.15	3	1.42	5
2.18	16	1.43	10	2.11	8	1.41	4
2.10	64	1.40	7	2.09	7		

[a] Patterns obtained with a Geiger counter X-ray diffractometer, CuKα radiation, $\lambda = 1.5405$ Å. The intensity values of each pattern were measured as peak heights above background and are expressed as percentages of the strongest line.

Weissenberg patterns from a c-axis setting show marked pseudo-hexagonal symmetry in the intensities of the reflections of the zero layer and pronounced pseudo-trigonal symmetry in the first and second layer lines. Morphological evidence of this pseudo-symmetry was noted above. Only one of the hexagonal space groups, D_{3d}^3–P$\bar{3}$m1, has symmetry elements and sites suitable for accommodation of one formula weight of $CaK_3H(PO_4)_2$. This space group is trigonal, in accord with the pseudo-symmetry of the higher layer lines. The $hk0$ reflections of the pseudo-trigonal cell are strong only when $h - k = 3n$. This suggests a smaller unit whose size is one-third that of the pseudo-hexagonal cell and whose corners are occupied by the heavy atoms. It appears that determination of the structure of $CaK_3H(PO_4)_2$ should not be difficult if crystals suitable for collection of intensity data can be prepared.

Discussion

The two salts, $CaK_3H(PO_4)_2$ and $MgNa_3H(PO_4)_2$, appear to be structurally related. Both are optically positive with similar birefringence, and both display twinning that causes the crystals to mimic hexagonal symmetry. The powder patterns for the two salts are dissimilar, but they both contain a prominent set of lines, which in $CaK_3H(PO_4)_2$ correspond to the first four orders of the 00*l* reflections. In the tracing for one preparation of $MgNa_3H(PO_4)_2$, all four of these reflections appeared with greatly enhanced intensities because of an orientation or particle size effect, showing that they were orders of the same plane. These spacings are 7.7% smaller in $MgNa_3H(PO_4)_2$ than in $CaK_3H(PO_4)_2$. A comparison of the densities of the two salts, along with the apparent decrease in the length of *c*, indicates that the *a* and *b* axes of $MgNa_3H(PO_4)_2$ are smaller by an average of 7%. When allowance is made for differences of this magnitude in the dimensions of the two cells, a similarity in groupings of lines in the two powder patterns is discernible.

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Preparation of Indium Antimonide and Gallium Arsenide Films

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This note describes a chemical method of making multicrystalline films of semiconductors such as InSb and GaAs which appears general for III–V compounds and which may also be useful in a modified form for compounds such as PbSe, HgSe, and Zn_3As_2. The basic approach is to form a film of a coördination compound containing elements from the IIIA and Va columns of the periodic table and to decompose this thermally into a film of the corresponding III–V semiconductor. The following equations for boron–antimony[2] and indium phosphide[3] summarize the more closely related past work on reactions of this type

$$Sb_2(CH_3)_4 + B_2H_6 \xrightarrow{100°} 2(CH_3)_2SbBH_2 + H_2 \quad (1)$$

$$(CH_3)_2SbBH_2 \xrightarrow{210°} SbB \text{ (black solid of this composition)} \quad (2)$$

$$In(CH_3)_3 + PH_3 \longrightarrow In(CH_3)_3PH_3 \quad (3)$$

$$In(CH_3)_3PH_3 \xrightarrow{-80°} (InCH_3PH)_x \quad (4)$$

$$(InCH_3PH)_x \xrightarrow{300°} InP \quad (5)$$

Experimental

Because of the inflammability of the compounds used and their reactivity with stopcock grease, most of the compounds were prepared and manipulated in a standard vacuum line equipped with mercury float valves and consisting of three main sections: (1) a storage system, (2) a tensimeter and measurement section, and (3) a reaction system.

Materials.—Stibine was prepared by the reaction of concentrated hydrochloric acid on a magnesium–antimony alloy, Mg_3Sb_2. The SbH_3 was purified by fractional distillation and condensation. The material which distilled through a trap at −139° and condensed in a trap at −159° was found to be tensimetrically homogeneous with a vapor pressure of 227 mm. at −45.2°. This is in agreement with the published value[4] of 224 mm. at the same temperature for SbH_3.

Trimethylindium was prepared by the reaction of dimethylmercury and indium metal in a sealed tube at 100°. The excess dimethylmercury was removed from the reaction product by fractional distillation. The trimethylindium condensed as large crystals, highly refractive to visible light, with a melting point of 88°, in good agreement with the published value[5] of 88.4°.

Trimethylstibine was prepared by the reaction of excess trimethylaluminum with SbF_3 at room temperature. The purified product had a vapor pressure of 30 mm. at 0°, which is in agreement with the literature value of 29.7 mm.[5]

Arsine was prepared in poor yield by the reaction of $LiBH_4$ with $AsCl_3$ in ether. Trimethylgallium was made by heating $Hg(CH_3)_2$ with Ga metal in a sealed tube at 130° for 1 week. The measured vapor pressure of the trimethylgallium was 65.0 mm. (lit. value[6] 64.5 mm.).

The Reaction of Stibine with Trimethylindium.—Stibine and trimethylindium were condensed at liquid nitrogen temperature in separate bulbs on each side of a U-tube connected to a mercury manometer. The SbH_3 bulb was brought to about −112° by means of a carbon disulfide slush bath, and the $In(CH_3)_3$ bulb was brought to room temperature. Thus, the $In(CH_3)_3$ sublimed through an atmosphere of about 2 mm. of SbH_3 at room temperature (26 to 28°) to the bulb at −112°. After three such passes a visible orange film formed on the U-tube between the bulbs, and an increase in the total pressure of the system was observed. Twelve or more passes were made to obtain films for tests. The orange film did not change in appearance when a boiling water bath was placed around

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