$(CN)_8^{4-}$, $Mo(C_2O_4)_4^{4-}$, and $Mo(CO_3)_4^{4-}$. Each has been shown to be diamagnetic, indicative of d^4sp^3 bonding.[7-9]

The physical properties of $MoCl_4 \cdot 4(C_6H_5)_3AsO$ suggest that it is the first example of a neutral octacoördinate Mo(IV) complex. Uncomplexed $MoCl_4$ is extremely sensitive to oxidation and hydrolysis, but the present complex is unaffected by boiling in water for 15 min., and by subsequent prolonged standing in water at room temperature. $MoCl_4$ is highly colored; the complex is white. The presence of eight ligands, coupled with the conductance data, can only be accounted for by octacoördination.

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Phosphorus Nuclear Magnetic Resonance Spectra of Polycyclic Phosphorus Compounds

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The chemical shifts of phosphorus in the polycyclic compounds I-III[1] and IV-VI[2] have been investigated.

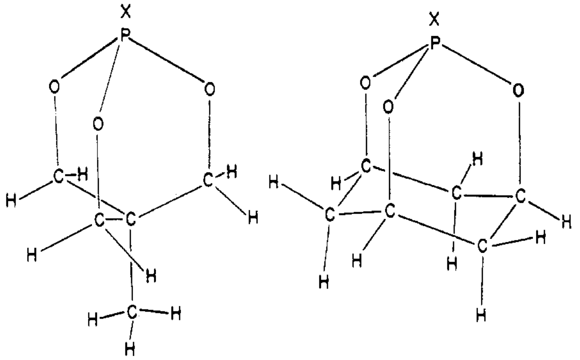
To ensure adequate signal strength, phosphorus spectra were obtained at 24.3 Mc./sec. on at least 1 *M* solutions. Where different solvents were used for the same compound, no significant difference in shift was observed.[3,4] Phosphorus chemical shifts are recorded in Table I in p.p.m. from external 85% phosphoric acid. The positive and negative signs refer to upfield and downfield values, respectively. Proton shifts were measured at 60 Mc./sec. and are recorded in p.p.m. downfield from tetramethylsilane in deuteriochloroform solutions at least 5% by weight in polycyclic compound.

TABLE I

PHOSPHORUS AND PROTON N.M.R. ABSORPTIONS

Compound	$\delta(P^{31})$	$J_{P-O-C-H}$ (c.p.s.)	$\delta(H^1)^d$ $C\beta$		
			$C\beta$	$C\gamma^e$	$C\delta$
I	$-91.5^{a,b}$	2	3.93		0.72
II	-57.4^c	6	4.48		.87
III	$+7.97^c$	7	4.48		.90
IV	$-137^{a,c}$	6	4.32	3.03, 1.87	
V	-64.0^c	19	4.97	2.73, 1.85	
VI	$+10.4^c$	20	5.05	2.82, 1.83	

[a] In chloroform. [b] In acetonitrile. [c] In dimethyl sulfoxide. [d] Greek subscripts refer to the position of the proton-bearing carbon atom with respect to phosphorus. [e] The difference in the chemical shifts of these protons is due to the chemically different axial and equatorial positions they occupy.



(I) (X = none)
(II) (X = sulfur)
(III) (X = oxygen)

(IV) (X = none)
(V) (X = sulfur)
(VI) (X = oxygen)

Figure 1.

Theoretically, the threefold axial symmetry of these molecules requires that phosphorus coupling with the nearest hydrogen atoms in the molecule yield a P^{31} septet in compounds I-III and a quartet in compounds IV-VI. The theoretical number of peaks was observed in the spectra of compounds IV-VI but spectra of compounds I-III revealed only five peaks; the outer two of theoretical intensity 5% of that of the center peak being lost in the noise. Phosphorus-proton coupling constants, $J_{P-O-C-H}$, obtained from H^1 resonance spectra, were substantiated by values obtained from P^{31} resonance spectra. The only H^1 spectrum which did not afford a value for this coupling was that of compound IV where the more complicated proton-proton coupling caused broadening of the absorptions so that the relatively small phosphorus-proton coupling was unobservable. The value for this constant was ob-

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(2) H. Stetter and K. Steinancker, *Ber.*, **85**, 451 (1952). Compound names: 2,8,9-trioxa-1-phospha-adamantane (IV), its 1-sulfide (V), and 1-oxide (VI).

(3) R. A. Y. Jones and A. R. Katritzky, *Angew. Chem.*, **1**, 32 (1962).

(4) N. Muller, P. Lauterbur, and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3557 (1956).

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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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).