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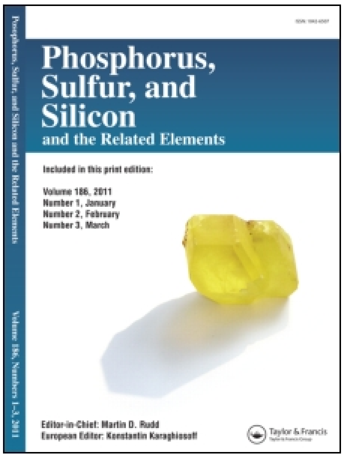

Phosphorus, Sulfur, and Silicon and the Related Elements

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Structural Diversity in Molecular Structures of MP(H)R Species (M = K, Rb, Cs)

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The molecular structures of the potassium, rubidium, and cesium derivatives of two different primary phosphanes, namely 2,4,6-tri-t-butylphenylphosphane and 2,6-dimesityl-phenylphosphane, are discussed.

Keywords: alkali metals; phosphides; phosphanes

INTRODUCTION

Alkali metal salts of phosphorus containing compounds are of interest because of their synthetic value as transfer reagents and the structural diversity of their solid-state structures. Among the alkali metal derivatives of phosphides of the general formula M[PR_2] and M[PRH], the lithium derivatives represent the vast majority of characterized species. Only a very limited number of heavier alkali metal congeners of *molecular* sodium and potassium phosphide derivatives has been structurally characterized so far. However, heavier alkali metal salts of phosphanes are of importance due to their enhanced reactivity compared with their lithium counterparts and also with respect to the structural diversity found in their solid-state structures.

Results and Discussion

Recently, we have focused our interest on the heavier congeners of alkali metal salts of two sterically demanding primary phosphanes, namely 2,4,6-tri-t-butylphenylphosphane ("supermesitylphosphane" = Mes^*PH_2) and 2,6-dimesitylphenylphosphane ($DmpPH_2$). The focus of our interest is to examine structural changes that might result from alkali metal cations larger than potassium and, additionally, to study the influence of donor solvent effects on the molecular structures.

The molecular structure of the base-free alkali metal derivatives (M = K, Rb, Cs) of supermesitylphosphane are of general composition $[MP(H)Mes^*]_x$[1, 2], exhibiting parallel extensions of infinitely extended, centrosymmetric M-P ladder structures with each supermesityl ring coordinated to an adjacent alkali metal cation. Surprisingly, no donor solvents are coordinated to the metal atoms of the potassium and rubidium derivative, although crystals were grown in the presence of a donor solvent (e.g. tetrahydrofuran, pyridine).

However, we were able to demonstate that in the case of the cesium derivative different base adducts showing a manifold of geometric variations of the polymeric Cs-P ladder framework can be obtained, depending on the donor ligand employed in the crystallization process. A common feature of these polymeric systems is a π coordination mode of each supermesityl ring to an adjacent alkali metal cation.

E.g., the solid-state structure of the pyridine adduct exhibits a novel and rather peculiar asymmetric polymeric structure that is found to be quite different from the molecular structures observed for the donor solvent-free alkali metal derivatives of the general formula $[MP(H)Mes^*]_x$ (M = K - Cs) as well as the tetrahydrofuran adduct $\{[CsP(H)Mes^*]_2(\mu\text{-THF})_{0.9}\cdot\text{toluene}\}_x$[2].

The extended structure of the pyridine adduct consists of a polymeric ladder framework of cesium and phosphorus atoms with additional coordination of one bridging donor solvent molecule (pyridine) per two cesium cations (Fig. 1). In contrast to the infinitely extended parallel polymers of the general formula $[MP(H)Mes^{*}]_{x}$ as well as the molecular structure of the tetrahydrofuran adduct, a twist is observed in the infinitely extended ladder of the pyridine adduct.

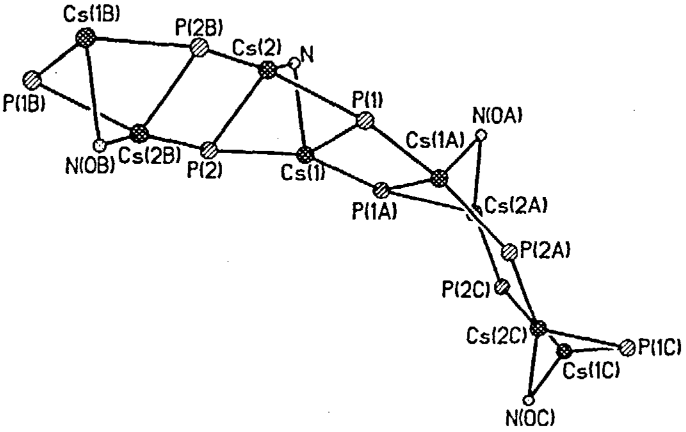

FIGURE 1 Ladder framework of the pyridine adduct

We continued our studies by employing the sterically demanding terphenyl ligand Dmp as a substituent on phosphorus. Our efforts produced crystal structure determinations of the potassium, rubidium and cesium derivative of 2,6-dimesitylphenylphosphane[3]. While the molecular structure of the potassium derivative features a four step K-P ladder-type structure, the rubidium derivative exhibits a cubic arrangement composed of four rubidium atoms and four DmpP(H)- ligands (Fig. 2). Contrarily, the cesium derivative is composed of a cation/anion pair $Cs^{+}Cs_{2}[P(H)Dmp]_{3}^{-}$, which results in formation of an infinitely extended polymeric two-dimensional network.

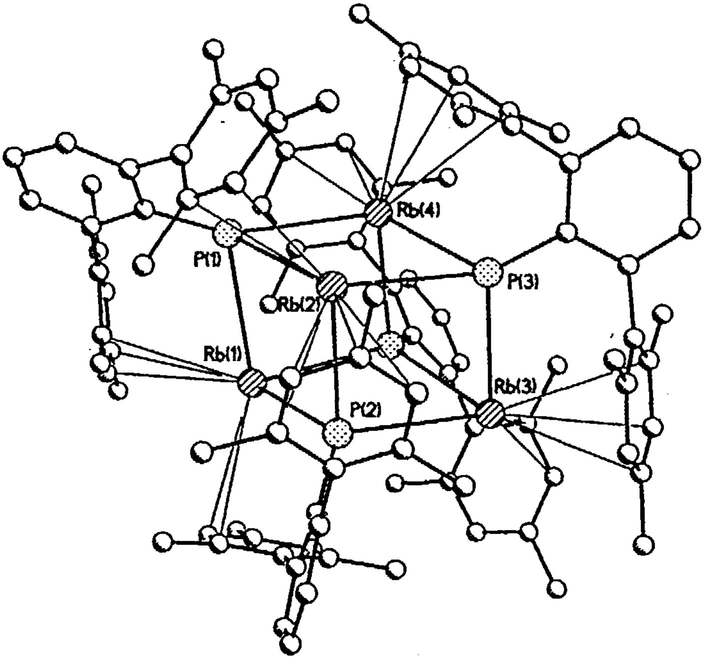

FIGURE 2 Molecular structure of [RbP(H)Dmp]4

Acknowledgments

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