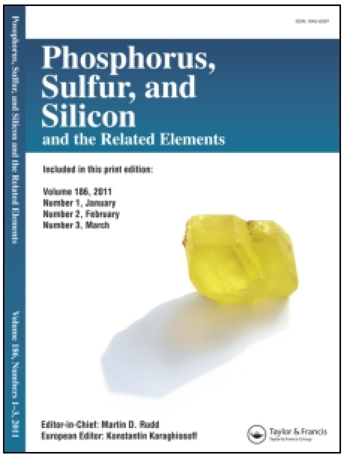

Phosphorus, Sulfur, and Silicon and the Related Elements

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Monomeric, Dimeric, and Trimeric Triselenometaphosphate

KONSTANTIN KARAGHIOSOFF and MICHAEL SCHUSTER

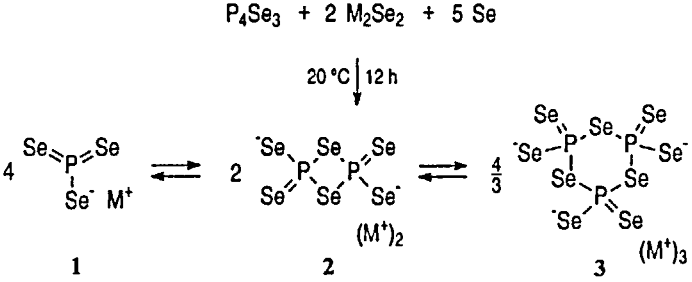
Department Chemie, Ludwig-Maximilians Universität München, Butenandtstr. 5–13 (Haus D), D-81377 München, Germany

Monomeric triselenometaphosphate PSe_3^- (**1**), its dimer (**2**) and trimer (**3**) are obtained for the first time in solution by oxidation of P_4Se_3 with M_2Se_2 (M = Li, Na) and elemental selenium and are fully characterized by ^{31}P and ^{77}Se NMR. The equilibrium between **1**, **2** and **3** depends strongly on the solvent and is shifted to the side of PSe_3^- in HMPA or DMPU. Monomeric trithiometaphosphate PS_3^- (**4**) is obtained by the analogous reaction of P_4S_3 with Li_2S_2 and elemental sulfur. **1** reacts with Se_2^{2-} and with P_4Se_3 to give the new selenophosphates $P_2Se_8^{4-}$ and $P_4Se_7^{2-}$, respectively. Further reaction of $P_4Se_7^{2-}$ with P_4Se_3 yields the new anion $P_9Se_{14}^{3-}$; its structure in the Bu_4P^+ salt is determined by X-ray crystallography.

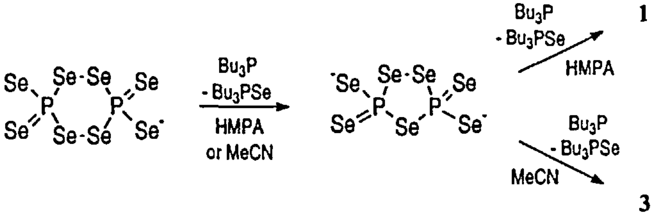
Keywords: selenophosphates; triselenometaphosphate; trithiometaphosphate; ^{31}P and ^{77}Se NMR; X-ray structure determination

The metaphosphate anions PO_3^- and PS_3^- are, in contrast to the nitrogen homologues NO_3^- and NS_3^-, not stable as monomers and form rings or infinite chains $(PCh_3)_n^{n-}$ (Ch = O, S).[1,2] Monomeric PO_3^- is described in the literature only as a reactive intermediate in solution and in the gas phase.[3] Evidence for monomeric PS_3^- in the solid state has been reported, however.[4]

Of the phosphorus chalcogen anions with the heavier chalcogens, only a few selenophosphates[5] and no tellurophosphate are described in the literature. Most of the selenophosphates are known only in the solid state. We find, that the oxidation of P_4Se_3 with an alkali metal diselenide M_2Se_2 (M = Li, Na) and grey selenium provides a general route to selenophosphates $P_nSe_m^{x-}$ in solution. Reaction of the three components in a 1 : 2 : 5 molar ratio results in the formation of triselenometaphosphate PSe_3^- (1) in equilibrium with its dimer $P_2Se_6^{2-}$ (2) and trimer $P_3Se_9^{3-}$ (3):

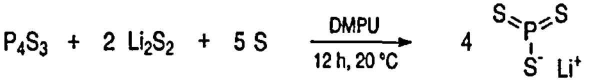


This equilibrium is strongly influenced by the solvent. Aprotic polar solvents like HMPA (hexamethyl phosphoric acid trisamide) or DMPU (dimethyl propylene urea), capable to coordinate to the alkali metal cations, shift the equilibrium to the side of monomeric PSe_3^-. The dimer **2** is observed only in DMPU in small amount (5%). In THF and acetonitrile the equilibrium is shifted mainly (70%) or completely to the side of the trimer **3**. The structures of both **2** (with a diselenadiphosphetane ring) and **3** (with a triselenatriphosphinane ring) are analogous to those of the corresponding thiophosphates $P_2S_6^{2-}$ and $P_3S_9^{3-}$.



An alternative route to triselenometaphosphates is represented by the deselenation of $P_2Se_8^{2-}$ [6] with tributylphosphane and demonstrates again the solvent dependency of the equilibrium between **1**, **2** and **3**. The first step yields regardless of the solvent used the new selenophosphate $P_2Se_7^{2-}$ with a triselenadiphospholane ring. The product of the second step, depends on the solvent: in acetonitrile only the trimer **3** is observed while in HMPA only PSe_3^- (**1**) is obtained.

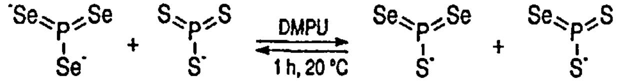
Following the synthesis of PSe_3^-, monomeric trithiometaphosphate PS_3^- (**4**) is obtained when P_4S_3 is oxidized with Li_2S_2 and elemental sulfur in DMPU as solvent:



4

$\delta^{31}P = +300$

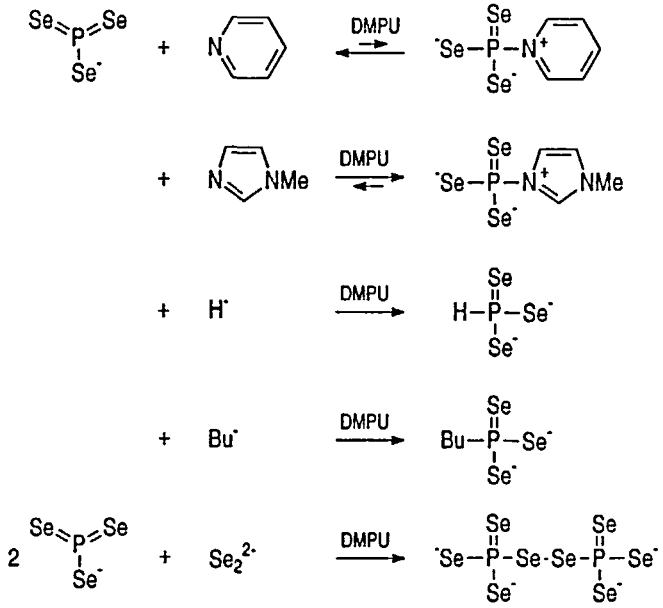
Reaction of PSe_3^- with PS_3^- results in a Se/S-exchange at phosphorus and yields the thioselenometaphosphates PSe_2S^- and $PSeS_2^-$:



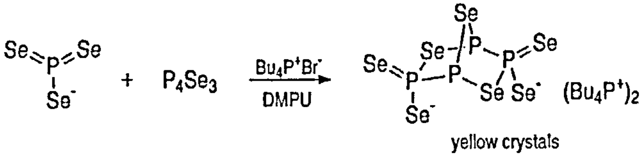
$\delta^{31}P$	+212	+300	+245	+273
$\delta^{77}Se$	+1252		+1101	+945
$^1J(Se,P)$ [Hz]	(-)788		(-)811	(-)833

Characteristic for all four metaphosphate anions of the series $PSe_{3-n}S_n^-$ (n = 0 - 3) is a ^{31}P chemical shift at low field, comparable to that of the threecoordinate pentavalent phosphorus in diselenoxo- and dithioxophosphoranes $RPCh_2$ (Ch = S, Se, $\delta^{31}P = 213 - 296$). Remarkable is the unusual ^{77}Se chemical shift, which is found at extremely low field compared to that of phosphane selenides ($\delta^{77}Se = +149$ to -497). The values observed for ^1J(Se,P) are typical for a one-coordinate selenium atom bonded to phosphorus.

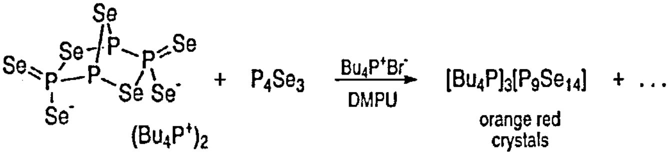
The acidity of the $\sigma^3\lambda^5$-phosphorus in PSe_3^- is remarkably low for a phosphorus atom in this bonding situation. It nevertheless governs the reactivity of the anion. PSe_3^- forms with pyridine and *N*-methyl imidazole 1:1 adducts; according to variable temperature ^{31}P NMR studies in the case of the pyridine the equilibrium is shifted at ambient temperature almost completely to the side of free PSe_3^- and in the case of the more basic *N*-methyl imidazole to the side of the adduct. Other nucleophiles like H^-, Bu^- and Se_2^{2-} also attack 1 at phosphorus and give the new selenophosphonate anions $HPSe_3^{2-}$ and $BuPSe_3^{2-}$ and the selenophosphate anion $P_2Se_8^{4-}$, respectively:



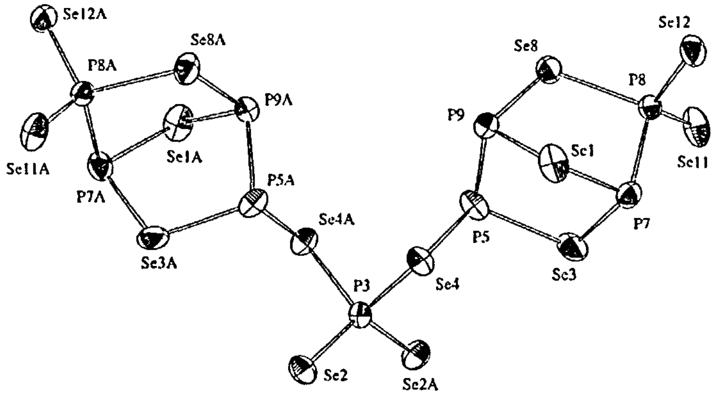
Remarkable is the reaction of PSe_3^- with P_4Se_3, which opens a route for the selective synthesis of polycyclic selenophosphates. It yields the new selenophosphate $P_4Se_7^{2-}$ which is isolated as the Bu_4P^+-salt. According to the ^{31}P and ^{77}Se NMR spectra $P_4Se_7^{2-}$ has the heteronorbornane structure shown below, analogous to that of α-$P_4Se_3I_2$.



Reaction of $P_4Se_7^{2-}$ with more P_4Se_3 results in the formation of the new selenophosphate anion $P_9Se_{14}^{3-}$. It is isolated as the Bu_4P^+ salt in form of orange red crystals.



According to the result of a single crystal X-ray structure determination the anion $P_9Se_{14}^{3-}$ consists of two heteronorbornane units, like those observed in *catena*-P_4Se_4 [7], which are bridged by a PSe_4 unit.



References

[1] A. Durif, in *The Chemistry of Inorganic Homo- and Heterocycles*, Vol. 2, Academic Press, London (1987), Chap. 22.

[2] M. Evain, R. Brec, G. Ouvrard, J. Rouxel, *Mater. Res. Bull.* **19**, 42 (1984).

[3] M. Meisel, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, M. Regitz, O.-J. Scherer eds., Thieme, Stuttgart, 1990, 415.

[4] H.-W. Roesky, R. Ahlrichs, S. Brode, *Angew. Chem.* **98**, 91 (1986); *Angew. Chem. Int. Ed. Engl.* **25**, 82 (1986).

[5] M. Kanatzidis, *Solid State & Material Science* **2**, 139 (1997).

[6] J. Zhao, W. T. Pennington, J. W. Kolis, *J. Chem. Soc., Chem. Commun.* 265 (1992).

[7] M. Ruck, *Z. Anorg. Allg. Chem.* **620**, 1832 (1994).