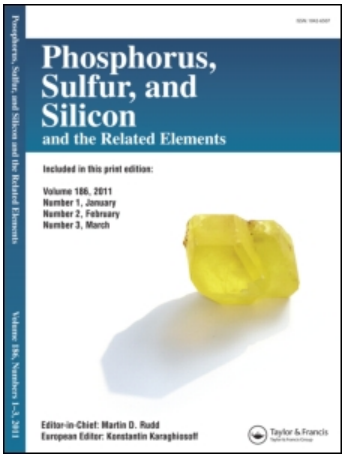

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Systematic Investigation of Tri- and Tetrametaphosphimates

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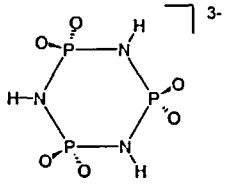
A systematic investigation of tri- and tetrametaphosphimates based on single-crystals is reviewed and results of a conformation analysis of the cyclic six- and eight-membered P-N rings of the $(PO_2NH)_3^{3-}$ and $(PO_2NH)_4^{4-}$ ions are given.

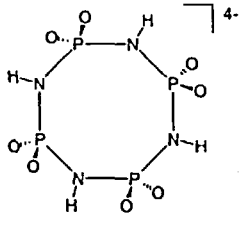
Keywords: Trimetaphosphimates; Tetrametaphosphimates; Conformation analysis; Puckering parameters; Crystal structures

INTRODUCTION

In order to synthesize oxonitridophosphates with framework structures, we are interested in precursor compounds containing P, O and N, e. g. tri- and tetrametaphosphimates. In contrast to the well investigated structural chemistry of tri- and tetrametaphosphates[1] only little is known about trimetaphosphimates (tri-μ-imidocyclotriphosphates) and

tetrametaphosphimates (tetra-μ-imidocyclotetraphosphates), although the first syntheses were already described in 1895.[2] These compounds were intensively investigated by IR spectroscopy and powder diffraction, but until recently only few crystal structures were known. Therefore we have started a systematic synthetic and structural investigation of tri- and tetrametaphosphimates.[3,4] These compounds contain six- and eight-membered ring anions $(PO_2NH)_3^{3-}$ and $(PO_2NH)_4^{4-}$:





SYNTHESIS

The starting material for the synthesis of tri- and tetrametaphosphimates are the cyclic chlorophosphazenes (Equ. (1)-(3), e. g. with M^I).

$$(PNCl_2)_3 + 9\ M(OOCCH_3) + 6\ H_2O \rightarrow M_3(PO_2NH)_3 + 6\ MCl + 9\ CH_3COOH \quad (1)$$

$$(PNCl_2)_4 + 8\ M(O_2CCH_3) + 8\ H_2O \rightarrow M_4(PO_2NH)_4 + 4\ MCl + 8\ CH_3CO_2H + 4\ HCl \quad (2)$$

$$(PNCl_2)_x + (2+2\ x)\ H_2O \rightarrow H_x(PO_2NH)_x{\cdot}2H_2O + 2\ x\ HCl \text{ (with } x = 3 \text{ or } 4) \quad (3)$$

Using the sodium salts or acids tri- and tetrametaphosphimates of

mono-, bi-, tri-, and tetravalent cations were obtained (e. g. Equ. (4)-(5)).

$$2\ Na_x(PO_2NH)_x \cdot yH_2O + x\ MCl_2 \rightarrow M_x[(PO_2NH)_x]_2 + 2\ x\ NaCl + y\ H_2O\ (e.\ g.\ M^{II})\ (4)$$

$$H_x(PO_2NH)_x \cdot 2H_2O + \tfrac{1}{2}\ x\ M_2CO_3 \rightarrow M_x(PO_2NH)_x + (2+\tfrac{1}{2}\ x)\ H_2O + \tfrac{1}{2}\ x\ CO_2\ (M^{I})\ (5)$$

Most of the reactions were conducted at RT in aqueous solution. Single-crystals were obtained by evaporation of the solvent or by diffusion controlled addition of ethanol or methanol to the mixture.

CONFORMATION ANALYSIS

For the detailed characterization and structural comparison of the cyclic P-N rings in tri- and tetrametaphosphimates a conformation analysis was carried out. Therefore, torsion angles,[5] displacement asymmetry parameters,[6] and puckering parameters[7] were calculated using the results of the single-crystal structure determinations. Especially the analysis of the puckering parameters is useful for the exact quantitative evaluation of the ring conformations. Whereas the puckering parameters for six-membered rings are well known, they had to be derived for eight-membered rings. The conformation analysis shows that the P_3N_3 rings in trimetaphosphimates often adopt a chair conformation. Nevertheless, in some cases a combination of twist boat and boat conformation is observed. The P_4N_4 rings in tetrametaphosphimates exhibit a twist boat, a saddle, or a chair conformation.

CRYSTAL STRUCTURES

The crystal structures of tri- and tetrametaphosphimates are manyfold and depend on the existing cations. In all structures N-H···O hydrogen bonds play a crucial role. In the materials with monovalent cations the N-H···O hydrogen bonds lead to the formation of pairs, double layers, or to a three-dimensional network of $(PO_2NH)_3^{3-}$ ions and to the formation of strings or columns of $(PO_2NH)_4^{4-}$ ions for tri- and tetrametaphosphimates, respectively. In the structures of transition metal trimetaphosphimates, the $(PO_2NH)_3^{3-}$ ions act as mono-, bi-, or tridentate ligands coordinating the transition metal ions (M). Thus, for example infinite double chains with alternating metal and $(PO_2NH)_3^{3-}$ ions, isolated ionic complexes $\{M[(PO_2NH)_3]_2\}^{x-}$, or complex anions $\{M_4(\mu_4\text{-}O)(\mu\text{-}OH)_6[(PO_2NH)_3]_4\}^{4-}$ are formed. These structure elements are interconnected in the crystal by N-H···O and O-H···O hydrogen bonds and by coordination to the alkaline metal cations.

References

[1] A. Durif, *Crystal Chemistry of Condensed Phosphates* (Plenum Press, New York, 1995).
[2] H. N. Stokes, *Ber. dtsch. chem. Ges.* **28**, 437 (1895).
[3] R. Marchand, W. Schnick, N. Stock, *Adv. Inorg. Chem.* **50**, 193 (2000).
[4] S. Correll, W. Schnick, unpublished.
[5] R. Bucourt, *Topics in Stereochemistry* **8**, 159 (1974).
[6] M. Nardelli, *Acta Crystallogr.* **C39**, 1141 (1983).
[7] D. Cremer, J. A. Pople, *J. Am. Chem. Soc.* **97**, 1354 (1975).