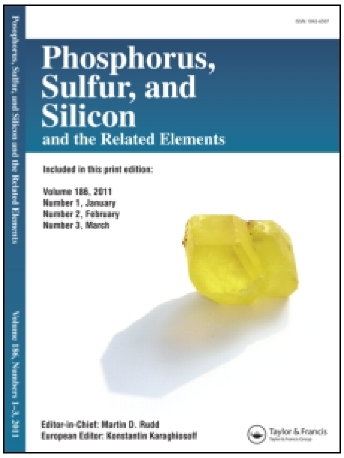

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Donorstabilized Monometaphosphates and Phosphonates- Structure, Bonding, and Reactivity

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Donorstabilized Monometaphosphates and Phosphonates- Structure, Bonding, and Reactivity

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Previously we reported on the preparative use of donorstabilized monometaphosphates, $Py.PO_2Cl$ and $Py.PS_2Cl$ [1]. ^{31}P MAS investigations as well as X-ray single crystal analysis have been carried out. The isotropic chemical shift of the sulfur compound shows the typical downfield shift (106 ppm) with respect to the oxygen compound. The chemical shift anisotropy gives additional information. The relative large spans Ω ($Py.PO_2Cl$: 401 ppm, $Py.PS_2Cl$: 461 ppm) [2] reveal strong deviations from tetrahedral symmetry ($\Omega = 0$ ppm) in agreement with the structural data. The values of the skew parameters κ (0.64 and 0.71 resp.) reflect the trend to axial symmetry ($\kappa = \pm 1$). X-ray diffraction and NMR data suggest a structural model corresponding to a concentration of double bond character on the two P-X bonds. This model is consistent with the extremely short P-X bond length (1.449 Å and 1.921 Å resp.) as well as the large P-X-P bond angles (126.4° and 123.7° resp.).

In order to study the influence of the character of the donor as a next step we studied $DMAPy.PO_2Cl$ and $DMAPy.PS_2Cl$. The enhancement of basicity on going from Py to DMAPy leads to a significant reduction of the spans to 309 ppm and 405 ppm resp. This goes conform with shortening of the P-N bond lengths by ca. 0.035 Å.

Now we extend our investigations to include monometaphosphonates with alkyl and aryl as ligands with the aim to obtain information on relationships between reactivity and bonding state at these molecules. The ^{31}P MAS NMR spectrum of $DMAPy.PO_2Ph$ shows three ^{31}P chemical shift tensors (intensity ratio 1:1:1) consistent with the crystal structure. The averaged spans and skews are similar to the corresponding parameters of $DMAPy.PO_2Cl$. Obviously, substitution of a chloride unit by a phenyl group does not affect the chemical shift tensor.

The ^{31}P MAS NMR spectrum of $DMAPy.PO_2$*t*-Bu shows two chemical shift tensors (intensity ratio 2:1). By future CP MAS experiments probably the more intense component will be resolved giving two 1:1 lines. Therefore the spectral information indicates at least two (probably three) different phosphorus sites, as has been found for the phenyl compound. This result is, however, in contradiction with the X-ray analysis, which has found only one phosphorus atom. The averaged span has a value of about 220 ppm. The value for skew is near zero. This is the maximum deviation from axial symmetry. Probably the high sterical demand is the reason therefore.

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