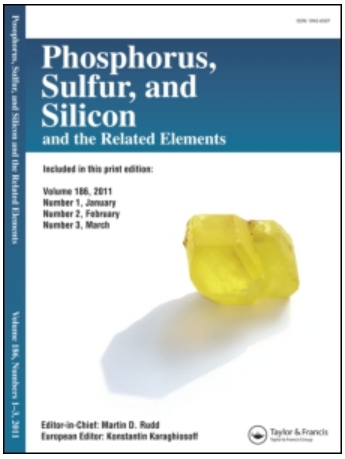

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P-Analog of Carbamic Acid: Crystal Structure of $(CO)_5CRH_2P$-COOH and *Ab Initio* Calculations

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P-ANALOG OF CARBAMIC ACID: CRYSTAL STRUCTURE OF $(CO)_5CRH_2P$-COOH AND *AB INITIO* CALCULATIONS

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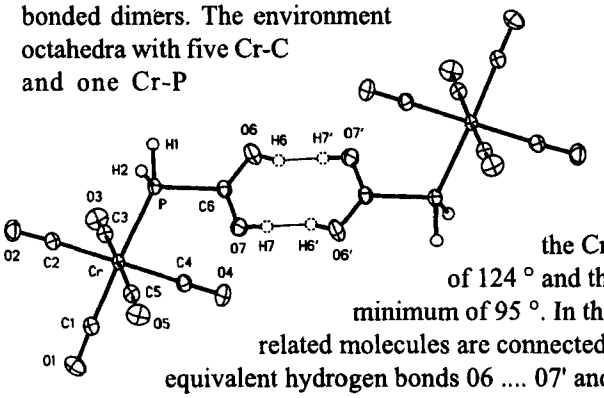
Phosphinoformic acid is unstable like the N-analogue carbamic acid. We found however that the acid can be stabilized by coordination via P to a $(CO)_5Cr$-moiety [1]. In accordance with the conclusions of Leiserowitz [2] about solid carboxylic acids the **crystal structure** of complex-stabilized phosphinoformic acid consists of hydrogen bonded dimers. The environment of the Cr atom is a distorted octahedra with five Cr-C bonds between 1.881 and 1.928 Å and one Cr-P bond of 2.335 Å. The angular distortion is small as shown by a maximum deviation of about 2.3 ° from the ideal geometry. At the P atom all bonding angles involving the Cr atom are widened to a maximum of 124 ° and the other ones are reduced to a minimum of 95 °. In the crystal structure two symmetry-related molecules are connected to each other by means of two equivalent hydrogen bonds 06 .... 07' and 07 .... 06' of 2.660 ç length between the carboxylic groups. Because of a twofold disorder along the bond P-C6, proven by bond lengths of 1.269(2) Å for C6-06 and 1.264(2) Å for C6-07 as well as by the localization and refinement of two H atoms with an occupancy factor of 0.5 bonded to each of the O atoms, no distinction can be made between the C=O double and the C-O single bond.



ab initio The structures were optimized without symmetry constraints [3]. The harmonic vibration frequencies were calculated analytically at the HF/3-21G* level of theory in order to characterize the stationary point on the potential hypersurface as a minimum. The calculation clearly shows that the hydrogen bonded dimer is energetically favoured by 63 kJ/mol at the HF/6-31G** level over two distinct monomers in the gas phase. This value is in the typical range for conventional acids (formic acid: 59 kJ/mol). Considering the bond lengths it can be stated that dimerization does not effect the P-C-bond length (186.0 pm HF/6-31G** level). However, the C-O bond lengths change significantly: the C-O double bond stretches (119.9 pm vs. 118.5 pm in the monomer), while the single bond shortens (130.5 vs. 132.8 pm). The O-H-O bridge is 278.7 pm long.

References

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