Phosphorous bonding in PCl$_3$:H$_2$O adducts: A matrix isolation infrared and *ab initio* computational studies

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ABSTRACT

Non-covalent interaction between PCl$_3$ and H$_2$O was studied using matrix isolation infrared spectroscopy and *ab initio* computations. Computations indicated that the adducts are stabilized through novel P···O type phosphorus bonding and conventional P—Cl···H type hydrogen bonding interactions, where the former adduct is the global minimum. Experimentally, the P···O phosphorus bonded adduct was identified in N$_2$ matrix, which was evidenced from the shifts in the vibrational wavenumbers of the modes involving PCl$_3$ and H$_2$O sub-molecules. Atoms in Molecules and Natural Bond Orbital analyses have been performed to understand the nature of interactions in the phosphorus and hydrogen bonded adducts. Interestingly, experimental evidence for the formation of higher PCl$_3$—H$_2$O adduct was also observed in N$_2$ matrix.

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1. Introduction

Phosphorus is the fifth most important biogenic element after carbon, hydrogen, oxygen, and nitrogen in terms of mass [1]. The P—O bond (especially in phosphate esters) is the fundamental unit present in DNA, RNA, and ATP systems and thus have significant role in the structure, metabolism and replication in living systems [2]. In the nuclear industry in particular, the PCl$_3$ molecule assumes significance as a precursor for the synthesis of phosphonates. The study of phosphorous containing molecules, involving non-covalent interactions would be helpful to gain more insight into the nature of weak bonding existing between phosphorus centered molecules with foreign reagents.

Studies on non-covalent interaction have been carried out since last century and in this regard hydrogen bonding interaction was well established experimentally as well as theoretically [3–6]. After conventional H-bonding interaction, halogen bonding was the most widely explored interaction wherein high anisotropic electrostatic potential seems to be responsible for interaction between two electronegative atoms [7–10]. In the recent past, non-covalent interactions involving oxygen and sulfur atoms referred as chalcogen bonding have been reported [11–13]. Recently, computational studies revealed a new type of bonding known as pnicogen bonding [14] in which interaction between a pnicogen atom such as N, P, As, Sb and Bi atoms of Lewis acid is

present [15]. Solimannejad et al. observed this kind of interactions computationally while studying the HSN and PH$_3$ system [16]. In their study H—P···N interaction was found to be more stable compared to the generally expected P—H···N interaction. Scheiner et al. further elaborated this unusual evidence by examining simple PH$_3$—NH$_3$ system and noticed that H—P···N interaction was twice more stable than the P—H···N interaction [17]. The stability of pnicogen bond was probed further by replacing one of the H atom of PH$_3$ by more electron withdrawing groups such as Cl or carbon chains [18–20]. Furthermore, the abilities of different donor atoms on the strength of pnicogen bonding were studied and revealed the following trend P···N > P···O > P···S > P···π [21,22]. Del Bene et al. performed quantum chemical studies to understand various parameters such as structure, binding energy, spin-spin coupling constant and NMR properties of pnicogen bonding [23–26]. Although, initial studies were focused on P···N and P···P interactions, extension of pnicogen bond to E···E′ bonding where interactions between other elements of group Va such as N···N, P···As or As—As were available in various literatures [27–29]. The study of pnicogen-bonded anionic adducts, bonds involving sp^2 hybridized phosphorous atom (in (H$_2$C = PX$_2$)), single pnicogen bonded adducts, intramolecular pnicogen interactions such as in PHF—(CH$_2$)$_n$—PHF system, and pnicogen-hydride interaction in complexes such as XH$_2$P···HBeY have been reported [30–34]. Detailed comparison between pnicogen bonding and hydrogen or halogen bonding was also the topic of several studies. Additionally, latest computational studies in this aspect claimed that vibrational spec-

troscopy would be a promising tool for investigation of this kind of new bonding [35,36].

In spite of numerous computational studies, experimental investigations are very much limited on this kind of interactions. Hill et al. reported for the first time the possibility of stabilization of P⋯P type interaction using NMR spectroscopy during the characterization of carborane-phosphino derivative [37,38]. X-ray diffraction was used to provide evidence for existence of P⋯P interactions in anion-neutral molecule interactions, pentafluorophenyl substituted diphosphine, and aminotetra phospines [39–41] and P⋯N interaction in aminoalkylferrocenyldichlorophosphanes [42], As⋯As in cyclopentadienyl arsenic compounds and E⋯E interactions in dipnicogen dimer and their dichalcogen dimer [43,44]. Single crystal X-ray diffraction method was used by Sundberg et al. for analyzing P⋯P interaction in 1,2-dicarba-*closo*-dodecaboranes [45]. The indications of nonbonding P⋯P interaction was observed during the study of Bis(phosphanyl)carborane(12) derivatives where $^{13}C\{^{1}H\}$ NMR technique has been used by Hey Hawkins et al. [46,47]. However, the specific experimental study is still scanty and no attempt has been made in this regard. Very recently, we have experimentally confirmed the existence of the pnicogen bonded P⋯O and P⋯π interactions involving phosphorus acceptor at low temperatures in the PCl_3—CH_3OH and PCl_3—C_6H_6 adducts respectively using matrix isolation infrared spectroscopy [48,49]. We have introduced the specific terminology of '*phosphorus bonding*' in place of pnicogen bonding to experimentally highlight the 'phosphorus centric' interactions among the pnicogen group of atoms.

In the present study, the phosphorus bonding interaction in PCl_3—H_2O adducts is reported in N_2 matrix using matrix isolation infrared spectroscopy. Experimental results are supported with *ab initio* computational studies.

2. Experimental methods

A Leybold AG pulsed tube closed cycle helium compressor cooled cryostat was used to achieve the low temperature for matrix isolation experiments. A base pressure $<1 \times 10^{-6}$ mbar was obtained in the cryostat housed in an evacuated vacuum chamber.

Analytical grade PCl_3 (Merck, Purity: >99%) and Milli-Q ultra pure water were used in the experiment. The samples were subjected to freeze-pump-thaw cycles before use. Nitrogen (INOX) with a purity of 99.9995% was used as the matrix gas. PCl_3 and H_2O were deposited onto a KBr-substrate maintained at 12 K by streaming them separately through a effusive twin-jet-nozzle system. PCl_3 gas was mixed with nitrogen gas in a mixing chamber and the resultant mixture was allowed to stream through one nozzle with the flow being adjusted by a dosing valve. A second nozzle was utilized for the deposition of H_2O. Here, a bulb containing H_2O was maintained at different temperatures ranging from -55 to -80 °C to control the required vapor pressure and thereby the concentrations in the matrix. Typical sample to matrix ratio ranging from 1 to 3:1000 for PCl_3:N_2 and 0.5–1.25:1000 for H_2O:N_2 were used. A typical deposition lasted for about 75 min at a rate of ~3 mmol/h.

Infrared spectra of the matrix-isolated samples were recorded in transmission mode between 4000 and 400 cm^{-1} using a BOMEM MB 100 FTIR spectrometer with 1 cm^{-1} resolution. After deposition, the matrix was slowly warmed to 32 K, maintained at this temperature for 15 min and then re-cooled to 12 K. The spectra of the matrix thus annealed were recorded again. All the spectra reported here refer to samples annealed at 32 K unless otherwise specified.

3. Computational methods

Ab initio calculations were performed on the PCl_3—H_2O system using a Gaussian09 package [50]. Geometries of the monomer were first optimized at B3LYP and MP2 levels of theory using 6-311++G (d,p) and aug-cc-pVDZ basis sets. Starting from the optimized monomer geometries, the geometry of the 1:1, 1:2 and 2:1 adducts was then optimized without imposing any structural constraints. Interaction energies were computed for the adducts, corrected separately for the basis set superimposition errors (BSSE) using the method outlined by Boys and Bernadi [51] and the zero point energies (ZPE). Turi and Dannenberg showed that simultaneous application of both BSSE and ZPE corrections tend to underestimate the interaction energies, thus both these corrections were not applied together [52]. Vibrational wavenumber calculations were performed on the optimized geometries to enable us to characterize the nature of stationary points and also to assign the experimentally observed vibrational wavenumbers. Indeed, all the structures discussed in this work correspond to minima on the potential energy surface.

To understand the nature of interaction in the 1:1 adducts, the theory of Atoms In Molecules (AIM) proposed by Bader was applied [53]. A (3,−1) bond critical point (BCP) that could be associated with the intra and intermolecular interactions was searched between the PCl_3 and H_2O sub-molecules of the adducts. The
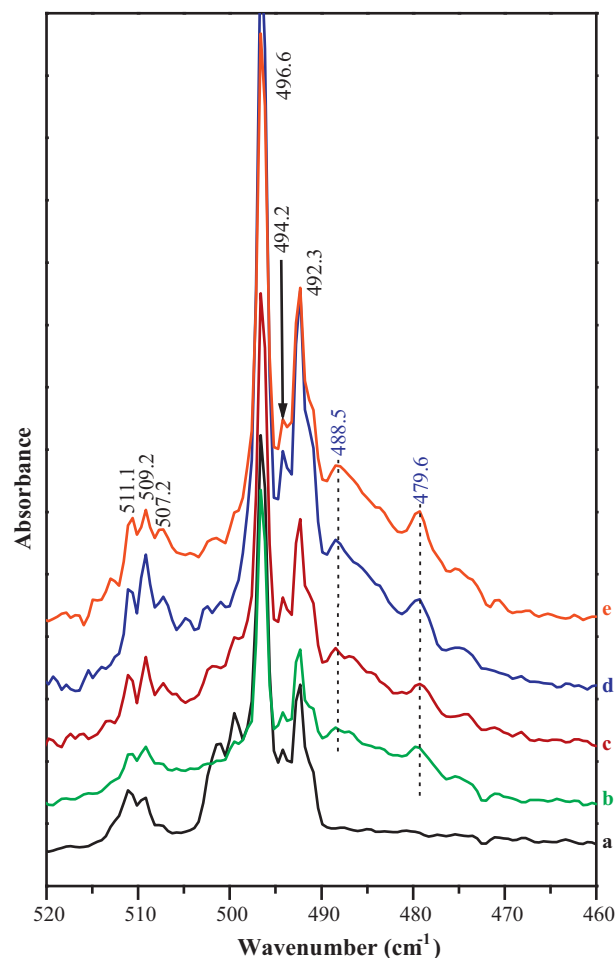
Fig. 1. Spectra of PCl_3—H_2O adducts in a N_2 matrix, spanning the region 520–460 cm^{-1}; matrix isolation spectra for various concentrations of $PCl_3/H_2O/N_2$, (a) 1/0/1000; (b) 1/1/1000; (c) 2/1/1000; (d) 3/1/1000 and (e) 3/1.25/1000. All spectra are recorded at 12 K after annealing at 32 K.