Tweaking the Charge Transfer: Bonding Analysis of Bismuth(III) Complexes with a Flexidentate Phosphane Ligand

Réka Mokrái, Jamie Barrett, David C. Apperley, Zoltán Benkő,* and Dominikus Heift*

ABSTRACT: To account for the charge transfer and covalent character in bonding between P and Bi centers, the electronic structures of \([\text{P(C}_6\text{H}_4-\text{o-CH}_2\text{SCH}_3)_2\text{BiCl}]^{(3-\delta)+}\) \((n = 0-3)\) model species have been investigated computationally. On the basis of this survey a synthetic target compound with a dative \(P\rightarrow\text{Bi}\) bond has been selected. Consecutively, the highly reactive bismuth cage \([\text{P(C}_6\text{H}_4-\text{o-CH}_2\text{SCH}_3)_2\text{Bi}]^{3-}\) has been accessed experimentally and characterized. Importantly, our experiments (single-crystal X-ray diffraction and solid-state NMR spectroscopy) and computations (NBO and AIM analysis) reveal that the \(P\cdots\text{Bi}\) bonding in this trication can be described as a dative bond. Here we have shown that our accordion-like molecular framework allows for tuning of the interaction between \(P\) and \(\text{Bi}\) centers.

1. INTRODUCTION

The hundred years old concept of coordinative covalent or dative bonding has evolved from a fundamental physical theory\(^{1,2}\) to cornerstones of undergraduate chemical education. In contrast to electron-sharing covalent bonding, dative bonding arises between two closed-shell systems, an electron pair donor (Lewis base) and an electron pair acceptor (Lewis acid), and significant electron density is transferred from the donor to the acceptor (charge transfer). More recently, the concept of \(\sigma\)-hole interactions introduced just a decade ago\(^3,4\) has gained increasing attention\(^5\) (note that some examples such as hydrogen bonds and halogen bonds have been known for much longer\(^6\)). \(\sigma\)-Hole interactions, similarly to dative bonds, also arise between two closed-shell entities, but they are regarded as noncovalent in nature. A relatively new congener of noncovalent interactions is the pnictogen bond (PnB),\(^7\) which (in analogy with the IUPAC definition of a halogen bond\(^8\)) can be defined as an attractive interaction between the electron-deficient region of a pnictogen (group 15 element) called a pnictogen bond donor and a Lewis base (pnictogen bond acceptor, acting as an electron pair donor).\(^9,10\) In the past few years, the potential of PnB in structural assembly, supramolecular architecture, anion sensing, (organo)catalysis, and molecular recognition has also been highlighted.\(^5,11\) On the basis of thorough computational studies,\(^5,12,13\) pnictogen bonding is chiefly electrostatic in nature (attraction between the oppositely charged regions around the two centers). Moreover, charge transfer effects (donation from the lone pair of the Lewis base into the \(\sigma^*\)-antibonding orbitals at the pnictogen center) may also contribute, though to a much lesser extent. This also means that the charge transfer and thus the covalent character in pnictogen bonding are rather low. Importantly, the strength of a pnictogen interaction can be comparable to that of a hydrogen bond. However, the experimental observation is still challenging, especially with spectroscopic methods such as NMR spectroscopy.\(^3,13,14,45\)

Even though the concepts of both dative bonds and \(\sigma\)-hole interactions are well-known, to our knowledge the relationship and connectivity between them has not yet been explored experimentally. In the present study we aim to investigate the bonding situation in \(P/\text{Bi}\) complexes. Due to its highest polarizability among the group 15 elements, bismuth has the strongest ability to form complexes with conventional dative bonds. On the other hand, phosphorus stands out because of its excellent NMR properties (broad chemical shift range, 100% natural abundance) and can be employed as a sensor to detect delicate structural changes.

Several prototype donor–acceptor complexes are known in the literature exhibiting \(P\cdots\text{Bi}\) distances described as dative bonds such as the peri-substituted acenaphthyl derivative A \((2.7696(8)\ \text{Å})\)\(^{46}\) and other recently reported congeners of this family\(^47\) and the monocation B shown in Figure 1 \((2.6883(14)\ \text{and}\ 2.6750(13)\ \text{Å})\).\(^48\) Similarly, a dative bond was reported for a phosphane coordinated diphenylbismuth-
nium cation (see C 2.6672(19) Å). In contrast, significantly longer P–Bi distances of 2.968(3) and 2.937(3) Å were observed for the related complex $D$, in which two phosphane ligands coordinate to the bismuthenium cation. These bonds were described rather as an electrostatic, induced dipole–ion attraction than a conventional dative bond. $E$ The Bi–P distance can be stretched further as in the geminally substituted tris(acenaphthyl) bismuthine (3.218(3)–3.279(4) Å), in which only weak interactions between the P and Bi centers were found. Recently we have reported a series of phosphane–trihalobismuth complexes (PS$_3$BiX$_3$, X = Cl, Br, I), featuring even longer P–Bi distances (in the range of 3.365(1)–3.792(9) Å). The interactions between the P and Bi centers in these PS$_3$BiX$_3$ compounds exhibit a remarkable strength of 7.1–8.8 kcal mol$^{-1}$.52

The goal of the present study is to gain more insight into the bonding situation in bismuth(III) complexes with the PS$_3$ ligand. Although other multidentate ligand systems are known in the literature,53–64 due to their accordion-like structural flexibility the molecular skeleton of type PS$_3$BiX$_3$ seems to be suitable for experimental investigations. First, we aim to predict computationally how the pnictogen interaction between the bridgehead atoms P and Bi observed in the neutral PS$_3$BiCl$_3$ can be shifted into a dative (covalent) regime, and subsequently, we provide experimental evidence based on X-ray crystallography and NMR studies.

2. RESULTS AND DISCUSSION

2.1. Computational Considerations. To search for possible candidates in which the interaction between the P and Bi can be described with dative bonding, first we investigated a series of species related to PS$_3$BiX$_3$. As the P–Bi atom distance in PS$_3$BiX$_3$ depends on the halide substituent on the bismuth and decreases in the order I > Br > Cl,52 an obvious choice could be the complex of $P$ (C$_6$H$_4$-tricat) bismuthine (3.218(3)–3.279(4) Å), in which only weak interactions between the P and Bi centers were found. Recently we have reported a series of phosphane–trihalobismuth complexes (PS$_3$BiX$_3$, X = Cl, Br, I), featuring even longer P–Bi distances (in the range of 3.365(1)–3.792(9) Å). The interactions between the P and Bi centers in these PS$_3$BiX$_3$ compounds exhibit a remarkable strength of 7.1–8.8 kcal mol$^{-1}$.52

The goal of the present study is to gain more insight into the bonding situation in bismuth(III) complexes with the PS$_3$ ligand. Although other multidentate ligand systems are known in the literature,53–64 due to their accordion-like structural flexibility the molecular skeleton of type PS$_3$BiX$_3$ seems to be suitable for experimental investigations. First, we aim to predict computationally how the pnictogen interaction between the bridgehead atoms P and Bi observed in the neutral PS$_3$BiCl$_3$ can be shifted into a dative (covalent) regime, and subsequently, we provide experimental evidence based on X-ray crystallography and NMR studies.

The computations were performed using the BLYP-D3/cc-pVDZ(-PP) level, see the Supporting Information. Herein, we present the results obtained at the oB97XD/cc-pVDZ(-PP) level, which was successfully employed for similar systems.52 Furthermore, the solvent effects were simulated with the polarized continuum model (PCM), employing acetonitrile as solvent. On the optimized structures bond valences have been obtained according to the method described by Brown,65 employing the data set reported by Brese and O’Keeffe.66 Furthermore, NBO (natural bonding orbital) computations delivering the Wiberg bond indices as well as atoms in molecules (AIM) analyses58 have been carried out and the results are collected in Table 1. The NPA (natural population analysis) charges show the same tendencies as the AIM charges and, therefore, they can be found in Table S5 in the Supporting Information.

The P–Bi atom distance decreases systematically upon abstraction of the chlorides in the row of PS$_3$BiCl$_3$ → [PS$_3$Bi]$^{3+}$, both in the gas-phase calculations and with the PCM solvent model. If these two data sets (without and with solvent model) are compared, the largest difference (0.154 Å) is observed for the neutral PS$_3$BiCl$_3$, while the deviation is significantly smaller for the other species. The PCM model results in somewhat shorter P–Bi distances in the case of the neutral PS$_3$BiCl$_3$ and the monocationic [PS$_3$BiCl$_3$]$^+$, whereas it results in slightly longer distances for the di- and trications. Altogether, the differences between the results obtained with or without the solvent model are much smaller than those resulting from the change in the substituents/charge. Therefore, the general tendencies among the different species are not affected, and in the following we only discuss the parameters computed using the solvent model.

Importantly, the shortest P–Bi distance is found in the trication [PS$_3$Bi]$^{3+}$ (2.743 Å), being clearly in the range of dative bonds reported for compounds such as $A$, $B$, and $C$ (see Figure 1). As the direct coordination of solvent molecules to the bismuth center may have an effect on the interaction between the P and Bi centers, we have also computed the model species [PS$_3$Bi(ACN)]$^{3+}$. As expected, the competition between the donor atoms around the Bi center leads to an elongation of the P–Bi distance (2.849 Å in [PS$_3$Bi(ACN)]$^{3+}$). This bond, however, is significantly shorter than that in the dication (2.923 Å in [PS$_3$BiCl]$^{2+}$), and thus the effect of three coordinating solvent molecules is inferior to that of one chloride anion.

![Figure 1. Selected examples of P–Bi distances determined by X-ray crystallography. For B, C and D the counteranions are not shown. $\sum_{\text{covalent}}$ and $\sum_{\text{vdW}}$ denote the sum of covalent53 and van der Waals54 radii, respectively, for the P Bi couple.](https://dx.doi.org/10.1021/acs.inorgchem.0c00734)
The strengthening of the interaction between the P and Bi centers in the sequence of $\text{PS}_3\text{BiCl}_3$, $[\text{PS}_3\text{BiCl}_2]^{+}$, $[\text{PS}_3\text{BiCl}]^{2+}$, and $[\text{PS}_3\text{Bi}(\text{ACN})_3]^{3+}$ is also reflected in the increasing bond valence values ($s$) and Wiberg bond indices (WBI). These two nicely correlating parameter sets indicate a tendentious rise in covalent character on going from the neutral to the tricationic species. Surprisingly, the AIM charge at the bismuth center shows a decreasing trend upon abstraction of the chlorides, which is moderate if the solvent model is employed and is more pronounced in the gas-phase calculations. This descending charge can be explained by substantial charge transfer from the $\text{PS}_3$ ligand toward the bismuth center reaching $\Delta q = 1.875 \text{ e}$ in the gas phase ($\Delta q = 1.663 \text{ e}$ with the PCM solvent model) for $[\text{PS}_3\text{Bi}]^{3+}$. The intensification of the charge transfer is also nicely visible on the AIM charges at the phosphorus centers, which gradually grow from the neutral $\text{PS}_3\text{BiCl}_3$ ($q(\text{P}) = 1.695 \text{ e}$ in the gas phase, 1.693 e with PCM) to the trionic $[\text{PS}_3\text{Bi}]^{3+}$ ($q(\text{P}) = 1.924 \text{ e}$ in the gas phase, 1.867 e with PCM).

The results of the NBO investigations and partial charges are further bolstered by an atoms in molecules (AIM) analysis$^6$ of the electron density, which located bond critical points (bcp) between the P and Bi nuclei in each of the complexes. The trend of the electron density at the bond critical points ($\rho_{\text{bcp}}$) again indicates gradual strengthening of the interaction between the P and Bi atoms from $\text{PS}_3\text{BiCl}_3$ to $[\text{PS}_3\text{Bi}]^{3+}$. The Laplacian of the electron density at the P···Bi bcp ($\nabla^2 \rho_{\text{bcp}}$) is positive for each of these complexes, which suggests closed-shell interactions (dative, ionic, or $\sigma$-hole interaction). The electron density and its Laplacian at the bcp of the Bi···P bond in the tricationic $[\text{PS}_3\text{Bi}]^{3+}$ ($0.424 \text{ e/Å}^3$ and 0.697 e/Å$^5$, respectively) are similar to those reported for the acenaphthyl...
The trichloride bond valences (for details see Table S7 in the Supporting Information) initiates reorganization to reach a new equilibrium structure. These characteristics show that the P⁻⁻Bi interaction frees up a coordination site by 0.663 vu (taken as the least simple model based on the competing e⁻⁻ff interactions in the same direction).

On the basis of the computations above, all three cationic species seem to be suitable for experimental detection of a dative interaction between the P and Bi centers. However, to target the strongest possible P⁻⁻Bi interaction, we chose the trication [PS₃Bi]³⁺ with weakly coordinating anions as the best candidate for our experimental study.

2.3. Experimental Validation. In order to access the aimed tricationic coordination compound [PS₃Bi]³⁺, we decided to employ trifluoromethanesulfonate (triflate) as a counteranion for two reasons: the triflate anion is reasonably weakly coordinating, and bismuth triflate is an easily accessible metal salt, which is also widely used as a catalyst in various organic syntheses.

To form the target complex, the ligand P(C₆H₄-ortho-CH₂SCH₃)₃ (PS₃) and 1 equiv of commercially available bismuth trifluoromethanesulfonate Bi[OTf]₃(H₂O), n ≈ 14 according to a TGA measurement) were reacted in acetonitrile at room temperature. In the $^{31}P${H} NMR spectrum of this reaction mixture only a singlet at −22.0 ppm was observed, which appears in the $^{31}P$ NMR spectrum as a doublet with $J_{PH} = 535.0$ Hz, indicating protonation at the phosphorus center. This phosphorus-containing product was unambiguously identified by $^{31}P$, $^{1}H$, and $^{13}C$ NMR spectroscopy and a single-crystal X-ray diffraction study as the phosphonium salt [HPC₆H₄-ortho-CH₂SCH₃]₃[^{1}OTf]− (see Figure S7 in the Supporting Information). Note that bismuth salts in general are prone to hydrolysis in the presence of water and in this case the hydrolysis of bismuth triflate resulted in the formation of triflic acid, which as a strong acid can protonate the phosphate ligand PS₃.

According to the literature it is practically impossible to obtain strictly anhydrous bismuth triflate.$^{74,75}$ To decrease the possibility of hydrolysis, we dried Bi[OTf]₃ for 10 days at 160 °C under a dynamic vacuum, which resulted in a solid with the formula of Bi[OTf]₃(H₂O), n ≈ 2.8, on the basis of elemental analysis. We repeated the reaction described above employing Bi[OTf]₃(H₂O), n ≈ 2.8 in toluene instead of acetonitrile, which resulted in the formation of a yellow precipitate. On the basis of its solid-state $^{31}P$ CP-MAS NMR spectrum this material is a mixture of products. However, recrystallization from acetonitrile delivered yellow crystals isolated in a low yield (15%). These crystals were also suitable for single-crystal X-ray diffraction analysis (see below), showing that their composition is [PS₃Bi]₂[Bi₂O₄(OH)₄[OTf]₁₂](H₂O)(CH₃CN)₆, which was also confirmed by elemental analysis of the isolated product. [PS₃Bi]₂[Bi₂O₄(OH)₄[OTf]₁₂](H₂O)(CH₃CN)₆ is in the following abbreviated as [PS₃Bi]₂[BOT]⁶⁻, in which the “bismuth oxo triflate” cluster hexaanion [BOT]⁶⁻ stands for [Bi₂O₄(OH)₄[OTf]₁₂]⁻ (Figure 2). This compound is only stable in the solid state and was further characterized by CP-MAS $^{31}P$, $^{1}H$, $^{13}C$, and $^{31}F$ NMR spectroscopy (for details see section 2.5 and Figure 4). The low yield is attributed to the observation that [PS₃Bi]₂[BOT] decomposes in solution. Indeed, when crystals of [PS₃Bi]₂[BOT] are dissolved in dry acetonitrile, the $^{31}P$ NMR spectrum of the solution (see Figure S2) shows two resonances: a very small singlet resonance at δ +67.6 ppm is observed (likely indicating the [PS₃Bi]³⁺ species) while the larger doublet resonance at δ −22.0 ppm with the coupling constant $J_{PH} = 535.0$ Hz again indicates the
Figure 2. Schematic depiction of [PS₃]⁺[OTf]⁻ as a decomposition product.

2.4. Structural Studies. We suggest describing the compound [PS₃]²⁺[BOT] as an assembly of two tricationic [PS₃]³⁺ units and a central [Bi₆O₄(OH)₄]₆⁺ cluster anion (Figure 3a), on the basis of the analogy of the latter to known cluster anions such as [Bi₆O₄(OH)₄]₂⁺[F₃CCO₂]⁻[26–27]. Alternatively, [PS₃]²⁺[BOT] could also be considered as [[PS₃]⁺[BOT]⁺][Bi₆O₄(OH)₄]⁺[OTf]⁻ with two neutral capping {PS₃}⁺{Bi₆O₄(OH)₄}⁺{OTf}⁻ moieties and a central neutral {Bi₆O₄(OH)₄}⁺{OTf}⁻ cluster.

The so far unknown {Bi₆O₄(OH)₄}⁺{OTf}⁻ cluster hexaanion formally consists of a cationic [Bi₃(μ₃-O₂H₁)₃(μ₃-OH)]⁺ core surrounded by 12 triflate anions. In the core, which is a common motif in hydrolysis products of bismuth salts, the three Bi(III) centers are equidistant from the center of the ring and are connected by hydrogen bonds (Figure 3b). The additional (2 times 3) triflate anions bridge the central core with one of the two tricationic [PS₃]⁺ moieties on the two sides of the structure (Figure 3a).

The bismuth centers of these [PS₃]⁺ fragments are coordinated by three triflate anions as well as the three sulfur and the phosphorus centers of ligand PS₃; the C₆ symmetry around the bismuth centers suggests stereochemical inactivity of their lone pairs. The Bi–S atom distances of 2.749(9) Å reflect a dative bond between the sulfur donor and a Bi(III) cation (for example 2.6873(3)–3.013(2) Å in Bi(III) chalcogenone complexes). The Bi–O[triflate] distances (2.760(1) Å) are between the sum of the covalent and van der Waals radii of the respective elements (2.14 Å and 3.59 Å, respectively) and are in the range of those found in reported bismuth triflate compounds (2.836(11)–3.010(3) Å).

Most importantly, the P–Bi distance is 2.800(3) Å, which is only slightly longer than those in compounds A, B, and C in Figure 1 (from 2.6672(19) to 2.7696(8) Å); however, it is significantly shorter than the “pnictogen-bonded” P–Bi distances in PS₃BiX₃ (3.365(1)–3.792(9) Å). The corresponding bond valences have also been calculated (vide supra)(see Table S8 in the Supporting Information) and show that the P–Bi bond in [PS₃]²⁺[BOT] (s = 0.632 vu) is remarkably stronger than those in PS₃BiX₃ (s = 0.137, 0.047, and 0.043 vu for X = Cl, Br, I, respectively). The sum of the bond valences at the bismuth center indicates that the Bi in [PS₃]²⁺[BOT] (Σₖ = 2.874 vu) is undercoordinated in comparison to the halide analogues PS₃BiX₃ (Σₖ = 3.233, 3.217, and 3.191 vu for X = Cl, Br, I, respectively), which is in accord with the observations discussed for the gas-phase structures (vide supra).

We also compared the solid-state structure of [PS₃]²⁺[BOT] to the gas-phase structure of the tricationic adduct [PS₃]³⁺ obtained by DFT computations (vide supra). The structure corresponding to the energy minimum (in the gas phase) is not symmetrical and shows a stereochemically active lone pair at the bismuth center. Furthermore, a structure with a constrained C₆ symmetry was also obtained (as a second-order saddle point) lying only 3.7 kcal/mol higher in energy. This indicates that the coordination geometry around the bismuth is very flexible and, thus, the difference between the gas-phase and solid-state structures is most likely caused by crystal-packing effects. Nevertheless, the computed P–Bi distances in the gas phase (2.697 Å for the minimum and 2.715 Å for the C₆-symmetric structure) are similar but somewhat shorter than that in the solid-state structure (2.800(3) Å). We attribute this difference to weak coordination of the triflate anions in the solid state, transferring some electron density to the bismuth center and thus elongating the P–Bi atom distance.

2.5. Solid-State NMR Investigations. As ³¹P NMR spectroscopy is a useful tool in studying bonding situations, we investigated specifically the compound [PS₃]²⁺[BOT]. The chemical shifts obtained in both solid-state CP-MAS and solution ³¹P NMR spectra (+56.0 and +67.6 ppm, respectively) are similar to that of B, in which the phosphorus coordinates to a bismuth center (Figure 1, δ(³¹P) 50.8 ppm), confirming a remarkable change in the chemical environment around the phosphorus nucleus in comparison to the free ligand PS₃.
orcid.org/0000-

orcid.org/

the 31P and the quadrupolar 209Bi nuclei. However, since the J constant in the gas phase at the PBE1/TZ2P level with a assumption, we have simulated the spin–spin coupling mechanism in these compounds to be positive for the BPCl3, while it was negative for the compounds PS3BiCl3. The former is characteristic for a Mallory type through-space coupling mechanism resulting from the overlap of the Bi and P lone pairs, while we attribute the latter to a real through-bond coupling in line with the presence of a dative P Bi interaction.

3. SUMMARY AND CONCLUSIONS

In summary, it is demonstrated that a weak secondary pnictogen interaction previously reported for PS3BrX3 can be tuned into a dative bond employing the same molecular framework. On the basis of our DFT computations on the structures of [PS3BiCln]3+ (n = 0–3) and [PS3Bi(ACN)n]3+ model species, the increase in covalency and thus the shift toward dative bonding can be achieved by intensifying the charge transfer from the P to the Bi center already in the case of the monocation [PS3BiCl]3+. Experimentally this was realized by employing weakly coordinating triflate anions and a new coordination compound exhibiting a dative P Bi bond was synthesized and characterized, which shows marked contrast to pnictogen-bonded complexes PS3BiX3 described previously. Furthermore, our investigations reveal a connection between the nature of the P Bi interaction and the spin–spin coupling mechanism between the two nuclei involved, offering the possibility to distinguish between these two types of interactions. Our results also show that ligand P(C6H4-OCH2SCH3)3 is “flexidenate”, which means it can adopt different coordination modes and in these accordion-like complexes the distance between the bridgehead atoms may deviate by nearly 1 Å. Therefore, this system could also be of interest for the development of new catalytic systems: for example, with transition metals.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00734.

Description of experimental procedures, characterization of compounds, X-ray crystallographic studies, and computational details (PDF)

Accession Codes

CCDC 1941566 and 1941695 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

Zoltán Benkő – Budapest University of Technology and Economics, H-1111 Budapest, Hungary; orcid.org/0000-0001-6647-8320; Email: zbenko@mail.bme.hu

Dominikus Heift – Department of Chemistry, Durham University, DH1 3LE Durham, United Kingdom; orcid.org/0000-0002-6799-5052; Email: dominikus.heift@durham.ac.uk

Authors

Réka Mokrai – Budapest University of Technology and Economics, H-1111 Budapest, Hungary

Jamie Barrett – Department of Chemistry, Durham University, DH1 3LE Durham, United Kingdom

David C. Apperley – Department of Chemistry, Durham University, DH1 3LE Durham, United Kingdom

Complete contact information is available at:

https://dx.doi.org/10.1021/acs.inorgchem.0c00734

Inorg. Chem. XXXX, XXX, XXX–XXX

Figure 4. Room-temperature solid-state CP-MAS 31P NMR spectra of the adduct [PS3Bi]+[BOT], PS3BiI, PS3BiBr3, and PS3BiCl3 (at spinning rates of 8, 6, 6, and 10 kHz, respectively). For an easier comparison of the band widths, the resonances of [PS3Bi]+[BOT] and PS3BiXn (X = I, Br, Cl)52 have been centered at the same position. For all samples the line widths of the bands have been proven to be independent from the applied spinning rates. The symbols * and # indicate spinning side bands and [HPS3]+[OTf] impurity, respectively.
Notes
The authors declare no competing financial interest.

Acknowledgments
The authors thank Dr. P. W. Dyer, Dr. D. Yuft, Dr. A. Batsanov, and Dr. G. Müller for their help and acknowledge the support of a European Union COFUND/Durham Junior Research Fellowship under EU grant agreement number 609412, the ETH Zurich, a BME-Nanotechnology FKFP grant of EMMI (BME FKFP-NAT), NKFIH (PD 116329), a Janos Bolyai Research Scholarship, a UNKP-19-4-BME-422 grant, Varga József Alapítvány, and Pro Progressio Alapítvány.

Dedication
Dedicated to Prof. Magdolina Hargittai on the occasion of her 75th birthday.

References
(1) Lewis, G. N. The atom and the molecule. J. Am. Chem. Soc. 1916, 38 (4), 762–785.
(2) Nandi, A.; Kozuch, S. History and Future of Dative Bonds. Chem. - Eur. J. 2020, 26 (4), 759–772.
(3) Clark, T.; Hennemann, M.; Murray, J. S.; Politzer, P. Halogen bonding: the σ-hole. J. Mol. Model. 2007, 13 (2), 291–296.
(4) Politzer, P.; Murray, J. S.; Concha, M. C. Sigma-hole bonding between like atoms; a fallacy of atomic charges. J. Mol. Model. 2008, 14 (8), 659–665.
(5) Politzer, P.; Murray, J. S.; Clark, T. Halogen bonding and other σ-hole interactions: a perspective. Phys. Chem. Chem. Phys. 2013, 15 (27), 11178–11189.
(6) Kolář, M. H.; Hobza, P. Computer Modeling of Halogen Bonds and Other σ-Hole Interactions. Chem. Res. 2016, 116 (9), 5155–5187.
(7) Lim, J. Y. C.; Beer, P. D. Sigma-Hole Interactions in Anion Recognition. Chem. 2018, 4 (4), 731–783.
(8) Moilanen, J.; Ganesamoorthy, C.; Balakrishna, M. S.; Tuononen, H. M. Weak Interactions between Trivalent Pnicogen Centers: Computational Analysis of Bonding in Dimers X3E−EX3 (E = Pnicogen, X = Halogen). Inorg. Chem. 2009, 48 (14), 6740–6747.
(9) Zahn, S.; Frank, R.; Hey-Hawkins, E.; Kirchner, B. Pnicogen Bonds: A New Molecular Linker? Chem. - Eur. J. 2011, 17 (22), 6034–6038.
(10) Scheiner, S. The Pnicogen Bond: Its Relation to Hydrogen, Halogen, and Other Noncovalent Bonds. Acc. Chem. Res. 2013, 46 (2), 280–288.
(11) Desiraju, G. R.; Ho, P. S.; Kloo, L.; Legon, A. C.; Marquardt, R.; Metrangolo, P.; Politzer, P.; Resnati, G.; Rissanen, K. Definition of the halogen bond (IUPAC Recommendations 2013). Pure Appl. Chem. 2013, 85 (8), 1711–1713.
(12) Scheiner, S. Noncovalent forces; Springer International: Cham, Switzerland, 2015; online resource.
(13) Moaven, S.; Yu, J.; Vega, M.; Unruh, D. K.; Cozzolino, A. F. Self-assembled reversed bilayers directed by pnicogen bonding to form vesicles in solution. Chem. Commun. 2018, 54 (64), 8849–8852.
(14) Schmauck, J.; Breugst, M. The potential of pnicogen bonding for catalysis – a computational study. Org. Biomol. Chem. 2017, 15 (38), 8037–8045.
(15) Benz, S.; Poblador-Bahamonde, A. I.; Low-Ders, N.; Matile, S. Catalysis with Pnicogen, Chalcogen, and Halogen Bonds. Angew. Chem., Int. Ed. 2018, 57 (19), 5408–5412.
(16) Tang, Q. J.; Li, Q. Z. Enhancing effect of metal coordination interaction on pnicogen bonding. J. Mol. Model. 2016, 22 (3), 1–7.
(17) Mahmudov, K. T.; Gurbanov, A. V.; Guseinov, F. I.; da Silva, M. F. C. G. Noncovalent interactions in metal complex catalysis. Coord. Chem. Rev. 2019, 387, 32–46.
(18) Moaven, S.; Andrews, M. C.; Polaske, T. J.; Karl, B. M.; Unruh, D. K.; Bosch, E.; Bowling, N. P.; Cozzolino, A. F. Triple-Pnicogen Bonding as a Tool for Supramolecular Assembly. Inorg. Chem. 2019, 58 (23), 16227–16235.
(19) Sicibria, P.; Terraneo, G.; Daolio, A.; Baggioli, A.; Fumalari, A.; Leroy, C.; Bryce, D. L.; Resnati, G. 4,4’-Dipyridyl Dioxide-SbF3 CoCystal: Pnicogen Bond Prevails over Halogen and Hydrogen Bonds in Driving Self-Assembly. Cryst. Growth Des. 2020, 20 (2), 916–922.
(20) Lu, L.; Lu, Y.; Zhu, Z.; Liu, H. Pnicogen, chalcogen, and halogen bonds in catalytic systems: theoretical study and detailed comparison. J. Mol. Model. 2020, 26 (1), 16.
(21) Yang, M. X.; Hirai, M.; Gabbai, F. P. Phosphonium-stibonium and bis-stibonium cations as pnicogen-bonding catalysts for the transfer hydrogenation of quinolines. Dalton Trans. 2019, 48 (20), 6685–6689.
(22) Legon, A. C. Tetrel, pnicogen and chalcogen bonds identified in the gas phase before they had names: a systematic look at non-covalent interactions. Phys. Chem. Chem. Phys. 2017, 19 (23), 14884–14896.
(23) Klinkhammer, K. W.; Pyykko, P. Ab Initio Interpretation of the Closed-Shell Intermolecular E−E Attraction in Dipnicogen (H2E−EH2)2 and Dichalcogen (HE-EH)2 Hydride Model Dimers. Inorg. Chem. 1995, 34 (16), 4134–4138.
(24) Oliveira, V.; Kraka, E. Systematic Coupled Cluster Study of Noncovalent Interactions Involving Halogens, Chalcogens, and Pnicogens. J. Phys. Chem. A 2017, 121 (49), 9544–9556.
(25) Setiawan, D.; Kraka, E.; Cremer, D. Strength of the Pnicogen Bond in Complexes Involving Group Va Elements N, P, and As. J. Phys. Chem. A 2015, 119 (9), 1642–1656.
(26) Setiawan, D.; Kraka, E.; Cremer, D. Description of pnicogen bonding with the help of vibrational spectroscopy-The missing link between theory and experiment. Chem. Phys. Lett. 2014, 565, 134–142.
(27) Marin-Luna, M.; Alkorta, I.; Elguero, J. A computational study on [(PH2F)2(2)(+) homodimers involving intermolecular two-center three-electron bonds. Struct. Chem. 2016, 27 (3), 753–762.
(28) Roohi, H.; Tondro, T. Exploring the pnicogen bond non-covalent interactions in 4-PhNH2:PFnH3-n complexes (n = 1–3, X = H, F, OH, CHO, NH2, CH3, NO2 and OCH3). J. Fluorine Chem. 2017, 202, 19–33.
(29) Trubenstein, H. J.; Moaven, S.; Vega, M.; Unruh, D. K.; Cozzolino, A. F. Pnicogen bonding with alkoxide cages: which pnicogen is best? New J. Chem. 2019, 43 (36), 14305–14312.
(30) Radha, A.; Kumar, S.; Sharma, D.; Jassal, A. K.; Zareba, J. K.; Franconetti, A.; Frontera, A.; Sood, P.; Pandey, S. K. Indirect influence of alkyl substituent on sigma-hole interactions: The case study of antimony(III) diphenyldithiophosphates with covalent Sb-S and non-covalent Sb center dot center dot center dot S pnicogen bonds. Polyhedron 2019, 173, 114126.
(31) Tondro, T.; Roohi, H. Substituent effects on the halogen and pnicogen bonds characteristics in ternary complexes 4-PhNH2 · · · PH2F ... CIX (Y = H, F, CN, CHO, NH2, CH3, NO2 and OCH3, and X = F, OH, CN, NC, FCC and NO2): A theoretical study. J. Chem. Sci. 2020, 132 (1), 1–21.
(32) Shukla, R.; Chopra, D. Pnicogen bonds or “chalcogen bonds”: exploiting the effect of substitution on the formation of P−Se noncovalent bonds. Phys. Chem. Chem. Phys. 2016, 18 (20), 13820–13829.
(33) Wysokiński, R.; Zierkiewicz, W.; Michalczyk, M.; Scheiner, S. How Many Pnicogen Bonds can be Formed to a Central Atom Simultaneously? J. Phys. Chem. A 2020, 124, 2046.
(34) Zierkiewicz, W.; Michalczyk, M.; Wysokiński, R.; Scheiner, S. On the ability of pnicogen atoms to engage in both σ and σ-hole complexes. Heterodimers of Z(F(2)(C(6))H(S)(Z = P, As, Sb, Bi) and NH3. J. Mol. Model. 2019, 25 (6), 1–13.
(35) Esrafili, M. D.; Vakili, M.; Solimannejad, M. Cooperative effects in pnicogen bonding: (PH2F)2− and (PH2Cl)2− clusters. Chem. Phys. Lett. 2014, 609, 37–41.
(36) Adhikari, U.; Scheiner, S. Comparison of P−D (D = P,N) with other noncovalent bonds in molecular aggregates. J. Chem. Phys. 2011, 135 (18), 184306.

(37) Scheiner, S. Comparison of halide receptors based on H, halogen, chalcogen, pnicogen, and tetrrel bonds. Faraday Discuss. 2017, 203, 213–226.

(38) Scheiner, S.; Michalczyk, M.; Zierkiewicz, W. Structures of clusters surrounding ions stabilized by hydrogen, halogen, chalcogen, and pnicogen bonds. Chem. Phys. 2019, 524, 55–62.

(39) Scheiner, S.; Michalczyk, M.; Wysokinski, R.; Zierkiewicz, W. Structures and energetics of clusters surrounding diatomic anions stabilized by hydrogen, halogen, and other noncovalent bonds. Chem. Phys. 2020, 530, 110590.

(40) Scheiner, S. Effects of Substituents upon the P−N Noncovalent Interaction: The Limits of Its Strength. J. Phys. Chem. A 2011, 115 (41), 11202–11209.

(41) Buzsáki, D.; Kelemen, Z.; Nyulászi, L. Stretching the P−C Bond. Variations on Carbenes and Phosphenes. J. Phys. Chem. A 2020, 124, 2660.

(42) Joshi, P. R.; Ramanathan, N.; Sundararajan, K.; Sankaran, K. Phosphorous bonding in PC3H2: Adducts: A matrix isolation infrared and ab initio computational studies. J. Mol. Spectrosc. 2017, 331, 44–52.

(43) Zong, J.; Magné, J. T.; Kraml, C. M.; Pascal, R. A. A Congested Diphenyl-Arsenium, Diphosphine, and Diphosphine Ligands. Coordination Complexes of Bismuth Triflates with Tetrahydrofuran. Inorg. Chem. 1996, 35 (21), 6102–6107.

(44) Liu, X.; Bai, Y.; Verkade, J. G. Synthesis and structural features of new sterically hindered azaphosphatranes: ZP(RNCH2CH2)(3)N. J. Organomet. Chem. 1999, 582 (1), 16–24.

(45) Suter, R.; Swidan, A. a; Macdonald, C. L. B.; Burford, N. Oxidation of a germanium(II) dication to access cationic germanium(IV) fluorides. Chem. Commun. 2018, 54 (33), 4140–4143.

(46) Swidan, A.; Suter, R.; Macdonald, C. L. B.; Burford, N. Tris[benzimidazol]amine (L) complexes of pnictogen(III) and pnictogen(V) cations and assessment of the [LP]3+/[LPF2]3+ redox couple. Chem. Sci. 2018, 9 (26), 5837–5841.

(47) Riddlestone, I. M.; Kraft, A.; Schaefer, J.; Krossing, I. Taming Weak Pnictogen Bonds: New Opportunities for Luminescent Materials. Chem. Sci. 2019, 10 (49), 5468–5471.

(48) Kremliček, V.; Hydl, J.; Yoshida, W. Y.; Růžička, A.; Rheingold, A. L.; Turek, J.; Hughes, R. P.; Dostál, L.; Cain, M. P. Heterocycles Derived from Generating Monovalent Pnictogens within NCN Pincer and Bidentate NCN Complexes: Hypervalency versus Bell-Clappers versus Static Aromatics. Organometallics 2018, 37 (15), 2481–2490.

(49) Brown, I. D. VALENCE: A program for calculating bond valences. J. Appl. Crystallogr. 1996, 29, 479–480.

(50) Bres, N. E.; O’Keefe, M. Bond-Valence Parameters for Solids. Acta Crystallogr., Sect. B: Struct. Sci. 1991, 47, 192–197.

(51) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. NBO 5.0: Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 2001.

(52) Bader, R. F. W. A quantum theory of molecular structure and its applications. Chem. Rev. 1991, 91 (5), 893–928.

(53) Cremer, D.; Kraka, E. Chemical-Bonds without Bonding Electron-Density: Does the Difference Electron-Density Analysis Suffice for a Description of the Chemical-Bond. Angew. Chem., Int. Ed. 1984, 23 (8), 627–628.

(54) Cremer, D.; Kraka, E. A Description of the Chemical-Bond in Terms of Local Properties of Electron-Density and Energy. Croat. Chem. Acta 1984, 57 (6), 1259–1281.

(55) Riddlestone, I. M.; Kraft, A.; Schaefer, J.; Krossing, I. Taming the ‘Cationic Beast’: Novel Developments in the Synthesis and Application of Weakly Coordinating Anions. Angew. Chem., Int. Ed. 2012, 51 (17), 2740–2755.

(56) Ollevier, T. New trends in bismuth-catalyzed synthetic transformations. Org. Biomol. Chem. 2013, 11 (17), 2740–2755.

(57) Ollevier, T. Bismuth-Mediated Organic Reactions. Top. Curr. Chem. 2012, 311, 1–277.

(58) Labrouillere, M.; Le Roux, C.; Gaspard, H.; Laporterie, A.; Dubac, J.; Desmurs, J. R. An efficient method for the preparation of bismuth(III) trifluoromethanesulfonate. Tetrahedron Lett. 1999, 40 (2), 285–288.

(59) Gaspard-Illhomme, H.; Le Roux, C. Bismuth(III) triflate in organic synthesis. Eur. J. Org. Chem. 2004, 2004 (12), 2517–2532.

(60) Chitnis, S. S.; Vos, K. A.; Burford, N.; McDonald, R.; Ferguson, M. J. Distinction between coordination and phosphine ligand oxidation: interactions of di- and triphenylphosphines with Pn(3+) (Pn = P, As, Sb, Bi). Chem. Commun. 2016, 52 (4), 685–688.
(77) Loera Fernandez, I. I.; Donaldson, S. L.; Schipper, D. E.; Andleeb, S.; Whitmire, K. H. Anionic Bismuth-Oxido Carboxylate Clusters with Transition Metal Counterions. Inorg. Chem. 2016, 55 (21), 11560−11569.
(78) Dehnen, S.; Corrigan, J. F. Clusters - contemporary insight in structure and bonding; Springer International: Cham, Switzerland, 2017; p 379.
(79) Senevirathna, D. C.; Blair, V. L.; Werrett, M. V.; Andrews, P. C. Polynuclear Bismuth Oxido Sulfonato Clusters, Polymers, and Ion Pairs from Bi2O3 under Mild Conditions. Inorg. Chem. 2016, 55 (21), 11426−11433.
(80) Senevirathna, D. C.; Werrett, M. V.; Blair, V. L.; Mehring, M.; Andrews, P. C. 2D and 3D Coordination Networks of Polynuclear Bismuth Oxido/Hydroxido Sulfonato Clusters from Low Temperature Solid-State Metathesis Reactions. Chem. - Eur. J. 2018, 24 (26), 6722−6726.
(81) Rogow, D. L.; Fei, H. H.; Brennan, D. P.; Ikehata, M.; Zavali, P. Y.; Oliver, A. G.; Oliver, S. R. J. Hydrothermal Synthesis of Two Cationic Bismuthate Clusters: An Alkylendisulfonate Bridged Hexamer, [Bi6O4(OH)(4)(H2O)(2)][(CH2)(2)(SO3)(2)](3) and a Rare Nonamer Templated by Triflate, [Bi9O8(OH)(6)][CF3SO3] (5). Inorg. Chem. 2010, 49 (12), 5619−5624.
(82) Pye, C. C.; Gunasekara, C. M.; Rudolph, W. W. An ab initio investigation of bismuth hydration. Can. J. Chem. 2007, 85 (11), 945−950.
(83) Sundvall, B. Crystal and Molecular-Structure of Tetraoxotetrahydroxobismuth(III) Nitrate Monohydrate, Bi6O4-(NO3)3·H2O. Acta Chem. Scand. A 1979, 33 (3), 219−224.
(84) Sattler, D.; Schlesinger, M.; Mehring, M.; Schalley, C. A. Mass Spectrometry and Gas-Phase Chemistry of Bismuth-Oxido Clusters. ChemPlusChem 2013, 78 (9), 1005−1014.
(85) Srinivas, K.; Sathyarayana, A.; Babu, C. N.; Prabu, S.; Srinivas, S; Sundar, S.; Srinivas, K.; Babu, C. N.; Prabu, S. Structural characterization of bismuth(III) and antimony(III) chlorotriflates: Key intermediates in catalytic Friedel-Crafts transformations. Eur. J. Inorg. Chem. 2004, 2004 (14), 2823−2826.
(86) Mallory, F. B.; Luzik, E. D.; Mallory, C. W.; Carroll, P. J. Nuclear spin-spin coupling via nonbonded interactions. 7. Effects of molecular structure on nitrogen-fluorine coupling. J. Org. Chem. 1992, 57 (1), 366−370.
(87) Manatt, S. L.; Cooper, M. A.; Mallory, C. W.; Mallory, F. B. Evidence for a Steric Effect on Directly Bonded Carbon-Fluorine and Carbon-Proton Nuclear Magnetic-Resonance Couplings. J. Am. Chem. Soc. 1973, 95 (3), 975−977.
(88) Hierso, J.-C.; Fihri, A.; Ivanov, V. V.; Hanquet, B.; Pirio, N.; Donnadieu, B.; Rebière, B.; Amardeil, R.; Meunier, P. “Through-Space” Nuclear Spin−Spin JPP Coupling in Tetrabenzylferrocenyl Derivatives: A 31P NMR and X-ray Structure Correlation Study for Coordination Complexes. J. Am. Chem. Soc. 2004, 126 (35), 11077−11087.