

REPORT OF THE PROJECT PROPOSAL SANCTIONED UNDER RUSA 2.0

TITLE: Synthesis, Structural Elucidation and Applications of Substituted Diphenyldithiophosphate Complexes of Some Transition and Non-Transition Elements

NAME OF THE TEACHER: Prof. Sushil K. Pandey

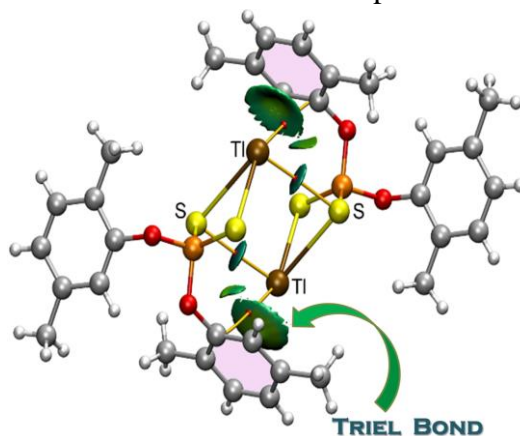
DEPARTMENT: Chemistry

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Publications in peer-reviewed journals:

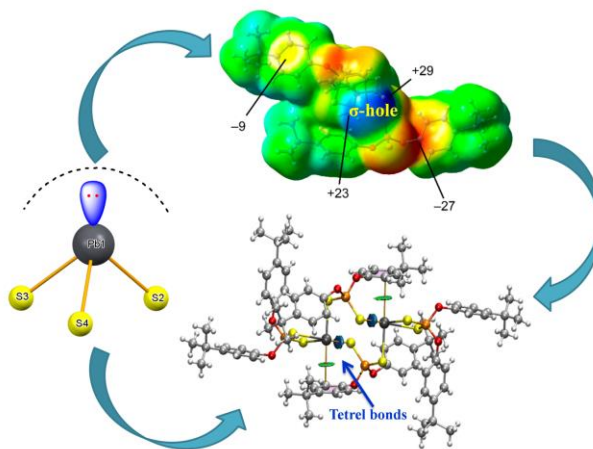
1. Tahira Firdoos, Pretam Kumar, Nipunn Sharma, Rosa M. Gomila, Antonio Frontera, Puneet Sood and **Sushil K. Pandey**. *Thallium(I)phosphorodithioates containing intra- and intermolecular π -hole triel bonds*. **CrystEngComm**, 2023, **25**, 3777-3789.

Abstract: Thallium compounds, *i.e.* $\text{Tl}^+[\text{S}_2\text{P}\{\text{OC}_6\text{H}_3(2,5\text{-(CH}_3)_2)\}_2]^-$ (**1**) and $\text{Tl}^+[\text{S}_2\text{P}\{\text{OC}_6\text{H}_3(3,5\text{-(CH}_3)_2)\}_2]^-$ (**2**), stabilized by intra- and intermolecular triel bonds were isolated and characterized by FT-IR, NMR (^{31}P , ^1H and ^{13}C) spectroscopy, and SC-XRD analysis. The crystal structures of **1** and **2** belong to monoclinic crystal systems with the space group $\text{C}2/c$ and $\text{P}2_1/n$, respectively. Interestingly, the positively charged Tl atom is bonded attractively with the π -holes of the 1,1-dithioate moiety. These compounds exist in ionic form and exhibit $\text{Tl}\cdots\text{S}$ and $\text{Tl}\cdots\pi$ contacts (TrBs), which assist the formation of unique supramolecular polymeric architectures owing to the stereochemically active lone pair of electrons and hemi-directed coordination sphere around thallium. A differentiating feature in compound **2** is the formation of a unique $\text{Tl}\cdots\pi/\pi\cdots\pi/\text{Tl}\cdots\pi$ self-assembly. The attractive nature of TrB was further confirmed by DFT calculations using the quantum theory of atoms-in-molecules (QTAIM) and non-covalent interaction plot (NCIPlot) index methods. A systematic Hirshfeld surfaces analysis was also carried out to compare the intermolecular interactions.



2. Pretam Kumar, Tahira Firdoos, Rosa M. Gomila, Antonio Frontera and **Sushil K. Pandey**. *Experimental and theoretical study of tetrel bonding and non-covalent interactions in hemidirected lead(II) phosphorodithioates: an implication on crystal engineering*. **Crystal Growth & Design**, 2023, **23**, 2138-2154.

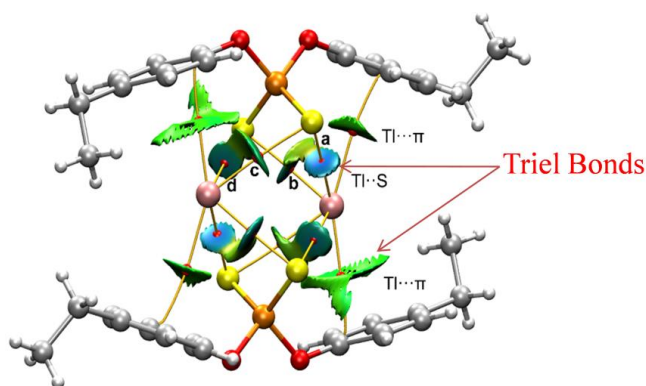
Abstract: The importance of tetrel bonds (TtBs) in spontaneous selfassembly has been highlighted in two new lead(II) complexes: i.e. $\text{Pb}[\text{S}_2\text{P}\{\text{OC}_6\text{H}_4(4\text{-C}(\text{CH}_3)_3)\}_2]_2$ (**1**) and $\text{Pb}[\text{S}_2\text{P}\{\text{OC}_6\text{H}_4(4\text{-C}_2\text{H}_5)\}_2]_2$ (**2**), which were successfully isolated and characterized by FT-IR, UV-vis and multinuclear NMR (^{31}P , ^1H and ^{13}C) spectroscopy. The structures of both complexes have been confirmed by single-crystal X-ray diffraction analyses. Interestingly, lead is coordinated by three sulfur atoms in **1** but by four sulfur atoms in **2**, due to stereochemically active lone pair electrons, thus leading to trigonal-pyramidal and tetragonal-pyramidal geometries, respectively. Complex **1** is the first example of a lead(II) dithiophosphate wherein the lead(II) center is coordinated to three S atoms. These complexes are stabilized at a lower coordination number and display hemidirected structures that allow forming σ -hole bonds. The lead(II) center establishes short contacts with sulfur atoms to form $\text{Pb}\cdots\text{S}$ TtBs that contribute to the construction of a self-assembled dimer in **1** but to a supramolecular polymer in **2**. The supramolecular assemblies are further stabilized by $\text{Pb}\cdots\pi$ TtB interactions. The attractive nature of TtBs has been studied by DFT calculations and characterized using a combination of Bader's quantum theory of atoms-in-molecules (QTAIM) and noncovalent interaction plot (NCI plot) index based on a reduced density gradient (NCI-RDG) analysis. A systematic Hirshfeld surface analysis facilitates a comparison of intermolecular interactions such as $\text{C-H}\cdots\pi$, $\pi\cdots\pi$, $\text{Pb}\cdots\text{S}$, and $\text{Pb}\cdots\pi$ in both complexes, which play a crucial role in the crystal engineering.



3. Tahira Firdoos, Pretam Kumar, Anu Radha, Rosa M. Gomila, Antonio Frontera, Puneet Sood and **Sushil K. Pandey**. *An insight into triel bonds in O,O'-diarylphosphorodithioates of thallium(I): experimental and theoretical investigations*. **New Journal of Chemistry**, 2022, **46**, 832-843.

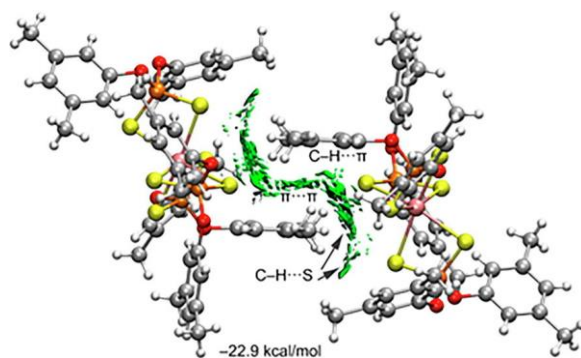
Abstract: Two new thallium compounds i.e. $\text{Tl}^+\{[(4\text{-C}_2\text{H}_5)\text{C}_6\text{H}_4\text{O}]_2\text{PS}_2\}_2^-$ (**1**) and $\text{Tl}^+\{[(4\text{-}(\text{CH})\text{CH}_3)_2\text{C}_6\text{H}_4\text{O}]_2\text{PS}_2\}_2^-$ (**2**). These new compounds have been characterized by elemental and spectral analyses. The crystal structure of **1** (Fig. a) and **2** (Fig. b) belongs to monoclinic

and triclinic system with space group $P2_1/c$ and $P\bar{1}$, respectively. Interestingly, compound **1** exists in ionic form and stabilized through intramolecular $Tl\cdots S$ (TrBs) interactions wherein thallium atom is symmetrically positioned in the cleft of ligand with longer $Tl-S$ distances. In compound **2**, the thallium atom is coordinated to one sulfur atom and other sulfur atom participates in TrB interactions. Both the compounds also exhibit intermolecular $Tl\cdots S$ and $Tl\cdots\pi$ contacts (TrBs) which assist to form unique supramolecular architectures owing to large size as well as coordinative unsaturation on the thallium. These non-covalent TrB interactions were authenticated by Hirshfeld surface analysis (HSA) and Density functional theory (DFT) calculations using the quantum theory of atoms-in-molecules (QTAIM) and non-covalent interaction plot (NCI Plot) index methods. TrBs involving Tl have been scarcely described in the literature; therefore this manuscript provides valuable insight into the importance of these unprecedented TrBs in the solid state.



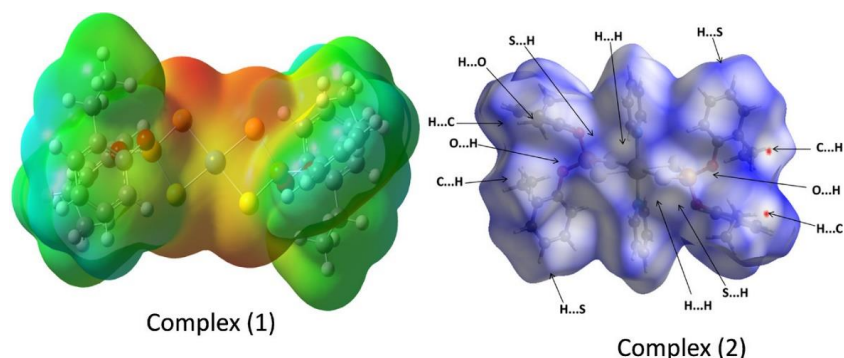
4. Tahira Firdoos, Pretam Kumar, Rosa M. Gomila, Antonio Frontera, Kamal and **Sushil K. Pandey**. *New complexes of indium(III) diaryldithiophosphates: Structural characterization and insight into supramolecular interactions*. **Polyhedron**, 2022, **226**, 116094.

Abstract: Mononuclear aryldithiophosphates of indium(III), $In[S_2P\{OAr\}_2]_3$; Ar = (3,5- CH_3) $2C_6H_3$ (**1**), (3,4- CH_3) $2C_6H_3$ (**2**), (2,5- CH_3) $2C_6H_3$ (**3**) and (2,4- CH_3) $2C_6H_3$ (**4**), have been synthesized and characterized by elemental analysis, NMR and FT-IR spectroscopy. Single crystal X-ray crystallography reveals that complex **1** belongs to the monoclinic crystal system with the space group $P2_1/c$, wherein the indium ion is six fold coordinated with sulfur atoms of the dithiophosphate moiety resulting in a distorted octahedral geometry. Complex **1** contains intermolecular $C\cdots H$, $C-H\cdots S$, $C-H\cdots\pi$ and $\pi\cdots\pi$ non-covalent interactions that help in attaining the stability of the molecule. A thorough Hirshfeld surface analysis (HSA) has also been carried out to scrutinize the intermolecular non-covalent interactions present within the molecule and the energetic features are evaluated using density functional theory (DFT) calculations. The non-covalent interaction plot (NCI Plot) index and molecular electrostatic potential (MEP) surfaces have also been used to characterize and rationalize the non-covalent $C-H\cdots S$, $C-H\cdots\pi$ and $\pi\cdots\pi$ interactions.



5. Deepika Sharma, Tahira Firdoos, Anu Radha, Sandeep Kumar, Sonam Shakya, Amanpreet K. Jassal and **Sushil K. Pandey**. *Synthesis, experimental and theoretical analyses of bis(2-ethylphenyl)phosphorodithioates of nickel(II)*. **Journal of Molecular Structure**, 2022, **1263**, 133166.

Abstract: Bis(2-ethylphenyl)dithiophosphates of nickel(II) of the composition $[(2-C_2H_5)C_6H_4O]_2PS_2]_2Ni$ (**1**) and $[(2-C_2H_5)C_6H_4O]_2PS_2(C_5H_5N)]_2Ni$ (**2**) were isolated successfully and characterized by experimental and theoretical analyses. Single crystal X-ray diffraction analysis of the complex (**2**) exhibits that nickel atom is hexa-coordinated with four sulfur atoms of dithio moiety at the equatorial position and two nitrogen atoms of pyridine on axial position. In addition, several non-covalent interactions were also observed that assist to form supramolecular architecture. An exhaustive investigation of the Hirshfeld surface (HS) analysis enables contributions to the crystal packing of the complex (**2**). The non-covalent interactions were identified using HSA and two dimensional finger print plot analysis. DFT/TD-DFT studies were also used to provide comparable theoretical data along with MEP map and electronic energy gap of HOMO→LUMO.



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Thallium(I)phosphorodithioates containing intra- and intermolecular π -hole triel bonds†

 Tahira Firdoos,^a Pretam Kumar,^a ^a Nipunn Sharma,^a Rosa M. Gomila,^b ^b Antonio Frontera,^b ^b Puneet Sood^c and Sushil K. Pandey ^{*a}

Thallium compounds, *i.e.* $\text{Tl}^+[\text{S}_2\text{P}(\text{OC}_6\text{H}_3(2,5\text{-(CH}_3)_2)_2)]^-$ (**1**) and $\text{Tl}^+[\text{S}_2\text{P}(\text{OC}_6\text{H}_3(3,5\text{-(CH}_3)_2)_2)]^-$ (**2**), stabilized by intra- and intermolecular triel bonds were isolated and characterized by FT-IR, NMR (³¹P, ¹H and ¹³C) spectroscopy, and SC-XRD analysis. The crystal structures of **1** and **2** belong to monoclinic crystal systems with the space group *C2/c* and *P2₁/n*, respectively. Interestingly, the positively charged Tl atom is bonded attractively with the π -holes of the 1,1-dithioate moiety. These compounds exist in ionic form and exhibit $\text{Tl}\cdots\text{S}$ and $\text{Tl}\cdots\pi$ contacts (TrBs), which assist the formation of unique supramolecular polymeric architectures owing to the stereochemically active lone pair of electrons and hemi-directed coordination sphere around thallium. A differentiating feature in compound **2** is the formation of a unique $\text{Tl}\cdots\pi/\pi\cdots\pi/\text{Tl}\cdots\pi$ self-assembly. The attractive nature of TrB was further confirmed by DFT calculations using the quantum theory of atoms-in-molecules (QTAIM) and non-covalent interaction plot (NCIPlot) index methods. A systematic Hirshfeld surfaces analysis was also carried out to compare the intermolecular interactions.

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Introduction

Thallium salts of more or less weakly coordinating anions are widely employed in ligand-exchange reactions to generate coordinately unsaturated metal compounds.¹ In modern coordination chemistry, the role of the majority of metals as clustering centers for ligands appears to be predictable. The coordination number and geometry can be extrapolated for most of the metal/ligand combinations by taking into account the size and the electronic configuration of the ligand function. However, the situation is quite challenging for main group metals in their low oxidation states in which they are to be assigned lone pairs of electrons.² Thallium(I) center has a strong tendency to achieve a higher coordination number due to its large size and unusual coordination pattern to form quasicyclic structures. Due to its low electrical charge and relativistically contracted valence shell, the Tl^+ cation has an intermediate character between a hard and soft character and

has affinity for both hard and soft donor atoms.³ There has been a phenomenal growth in the field of metal dithiolate chemistry in the past few decades, especially in terms of coordination chemistry and their applications.^{4–10} However, in comparison to transition metal dithiophosphates, the main group counterparts, especially thallium(I), did not receive much attention owing to the complexity of their coordination numbers and different geometries, which are influenced by the relativistic effect of the stereochemically active $6s^2$ lone pair electrons.^{2,11–13} Thallium is a toxic metal and utmost care should be taken with its use, but on the other hand, Tl(I) provides a unique opportunity as a ligand-directing center with closed-shell d10 metals, thereby contracting the $6s$ orbital, which makes the metal ion more electronegative, and therefore, more likely to induce metal-assisted interactions that may enhance the luminescent properties of the complexes.¹⁴ Although one of the larger cations, it often shows low coordination numbers in geometries, which leaves a large portion of the coordination sphere seemingly unoccupied.^{15–17}

Metal-directed self-assembly mediated by hydrogen bonding and other non-covalent interactions has emerged as one of the most prudent strategies to generate fascinating supramolecular dimeric and polymeric architectures with distinctive properties.^{18–20} These non-covalent contacts are weak compared to covalent bonds; however, they have shown wonderful advances in the field of supramolecular chemistry.^{21–23} Recently, interest in other non-covalent

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† Electronic supplementary information (ESI) available. CCDC 2255337 and 2255338. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3ce00396e>

Experimental and Theoretical Study of Tetrel Bonding and Noncovalent Interactions in Hemidirected Lead(II) Phosphorodithioates: An Implication on Crystal Engineering

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Pretam Kumar, Tahira Firdoos, Rosa M. Gomila, Antonio Frontera, and Sushil K. Pandey*



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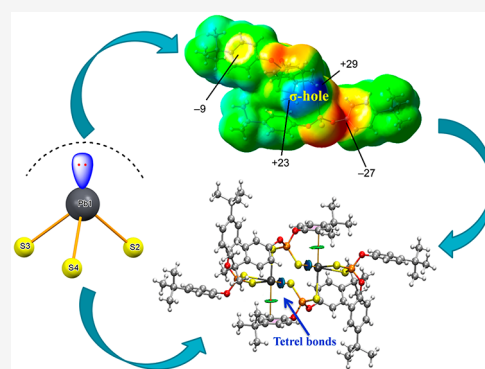


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Supporting Information

ABSTRACT: The importance of tetrel bonds (TtBs) in spontaneous self-assembly has been highlighted in two new lead(II) complexes: i.e. $\text{Pb}[\text{S}_2\text{P}\{\text{OC}_6\text{H}_4(4\text{-C}(\text{CH}_3)_3)\}_2]_2$ (**1**) and $\text{Pb}[\text{S}_2\text{P}\{\text{OC}_6\text{H}_4(4\text{-C}_2\text{H}_5)\}_2]_2$ (**2**), which were successfully isolated and characterized by FT-IR, UV-vis and multinuclear NMR (^{31}P , ^1H and ^{13}C) spectroscopy. The structures of both complexes have been confirmed by single-crystal X-ray diffraction analyses. Interestingly, lead is coordinated by three sulfur atoms in **1** but by four sulfur atoms in **2**, due to stereochemically active lone pair electrons, thus leading to trigonal-pyramidal and tetragonal-pyramidal geometries, respectively. Complex **1** is the first example of a lead(II) dithiophosphate wherein the lead(II) center is coordinated to three S atoms. These complexes are stabilized at a lower coordination number and display hemidirected structures that allow forming σ -hole bonds. The lead(II) center establishes short contacts with sulfur atoms to form $\text{Pb}\cdots\text{S}$ TtBs that contribute to the construction of a self-assembled dimer in **1** but to a supramolecular polymer in **2**. The supramolecular assemblies are further stabilized by $\text{Pb}\cdots\pi$ TtB interactions. The attractive nature of TtBs has been studied by DFT calculations and characterized using a combination of Bader's quantum theory of atoms-in-molecules (QTAIM) and noncovalent interaction plot (NCI plot) index based on a reduced density gradient (NCI-RDG) analysis. A systematic Hirshfeld surface analysis facilitates a comparison of intermolecular interactions such as $\text{C}\cdots\text{H}\cdots\pi$, $\pi\cdots\pi$, $\text{Pb}\cdots\text{S}$, and $\text{Pb}\cdots\pi$ in both complexes, which play a crucial role in the crystal engineering.



INTRODUCTION

The versatility in coordination chemistry of lead is mainly due to its large size, soft nature, and ability to adopt a broad range of coordination numbers,^{1–6} which leads to the formation of a wide variety of hybrid complexes and polymers.⁷ The chemistry of lead has attracted researchers in the search for lead(II) compounds having different molecular and supramolecular architectures.^{8–11} The development of new ligands capable of trapping Pb(II) from the human body or removal of lead from paints and drinking water is of continuing interest.^{12–16} Pb(II) is known to play an important role in biological systems, as it binds favorably with thiol and phosphate groups in proteins, nucleic acids, and cell membranes.^{17,18} Lead complexes with sulfur and selenium donor ligands have produced semiconductor materials.^{19–24} A distinct feature of Pb(II) complexes is displaying either holodirected or hemidirected structures owing to the stereochemically active or inactive 6s lone-pair electrons. In the case where lone-pair electrons on Pb(II) are stereochemically inactive with uniform stretching of metal–ligand bonds around

the Pb(II) ion, the complex is termed as holodirected; otherwise, it is termed as hemidirected.^{25–27} The hemidirected complexes can form supramolecular structures through secondary bonds like $\text{Pb}\cdots\text{N}$, $\text{Pb}\cdots\text{O}$, $\text{Pb}\cdots\text{S}$, $\text{Pb}\cdots\text{Cl}$, and $\text{Pb}\cdots\pi$ interactions. The presence of secondary bonds or noncovalent interactions is usually established in the hemidirected complexes of Pb(II) comprising wide structural diversities and properties.^{28–32}

Though noncovalent interactions were first documented by van der Waals in his doctoral thesis (1873),³³ this area has experienced dynamic growth in recent years.^{34–39} Now, noncovalent interactions have proven to be prominent tools

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An insight into triel bonds in *O,O'*-diarylphosphorodithioates of thallium(I): experimental and theoretical investigations†

Tahira Firdoos,^a Pretam Kumar,^a  Anu Radha,^a Rosa M. Gomila,^b 
Antonio Frontera,^b  Puneet Sood^c and Sushil K. Pandey^b *^a 

The vital role of triel bonding (TrB) has been highlighted in two new thallium compounds *i.e.* $\text{Tl}^+[(4\text{-C}_2\text{H}_5\text{C}_6\text{H}_4\text{O})_2\text{PS}_2]_2^-$ (**1**) and $\text{Tl}\{[(4\text{-CH}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{O})_2\text{PS}_2]_2\}$ (**2**). These new compounds have been characterized by elemental and spectral analyses. The crystal structures of **1** and **2** belong to the monoclinic and triclinic systems with space groups $P21/c$ and $P\bar{1}$, respectively. Interestingly, compound **1** exists in ionic form and is stabilized through intramolecular $\text{Tl}\cdots\text{S}$ (TrBs) interactions wherein the thallium atom is symmetrically positioned in the cleft of the ligand with longer $\text{Tl}\cdots\text{S}$ distances. In compound **2**, the thallium atom is coordinated to one sulfur atom and the other sulfur atom participates in TrB interaction. Both compounds also exhibit intermolecular $\text{Tl}\cdots\text{S}$, $\text{Tl}\cdots\pi$ (TrBs), and $\text{C}\cdots\text{H}\cdots\text{Tl}$ (anagostic) interactions, which assist to form unique supramolecular architectures owing to large size as well as coordinative unsaturation on the thallium. These non-covalent TrB interactions were authenticated by Hirshfeld surface analysis (HSA) and density functional theory (DFT) calculations using the quantum theory of atoms-in-molecules (QTAIM) and non-covalent interaction plot (NCI Plot) index methods. TrBs involving Tl have been scarcely described in the literature; therefore this work provides valuable insight into the importance of these unprecedented TrBs in the solid state.

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Introduction

Considerable attention has been focused on the field of metal dithiolates in the last few decades.^{1–5} Thallium is known to have a large radius and being a soft acid favors interactions with sulfur, nitrogen, and oxygen in decreasing affinity order (HSAB theory) and forms stable thallium(I)–sulfur compounds.⁶ Thallium compounds with sulfur donor ligands have found myriad applications such as analytical reagents,⁷ heavy metal biomethylation,⁸ optical glasses, and high-temperature superconductors.⁹ Recently, thallium compounds were used in medical technologies such as single photon emission computed tomography (SPECT) and thallium auto metallography (TIAMG).¹⁰

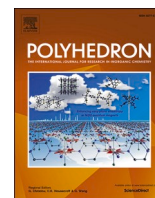
Supramolecular chemistry has monopolized the attention of researchers and is still a growing field.^{11–13} The syntheses as well as the design of molecular architectures with a low degree of covalency significantly impact the Lewis acidity of the metal.¹⁴ The non-covalent interactions are weak as compared to covalent interactions, however, they show magnificent advances in the field of supramolecular chemistry.^{15–17} These non-covalent forces control biological systems as these are specific without conferring as much severity as covalent forces¹⁸ and also allow for fine tuning of desirable electronic and optical properties. It is revealed from the literature that the nature of anagostic interactions has been less explored so far compared to agostic interactions. Both the agostic and anagostic $\text{C}\cdots\text{H}\cdots\text{M}$ interactions between the ligand and metal centres are well established,^{19,20} however, less commonly observed in organometallic complexes.^{21–23} The $\text{C}\cdots\text{H}\cdots\text{M}$ interactions have a marked effect on the molecular and electronic structure and hence on the reactivity of the molecule.²¹ These metal-mediated interactions are of significant importance due to their possible implications in the activation of $\text{C}\cdots\text{H}$ bonds.²⁴ Recently, investigations on other non-covalent contacts like σ -hole and π -hole interactions, in particular, of main group elements are growing rapidly and have proven to be a prominent tool in supramolecular chemistry.^{25–27} The term triel bond (TrB) is used

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† Electronic supplementary information (ESI) available. CCDC 2109341 and 2109342. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1nj04852j



New complexes of indium(III) diaryldithiophosphates: Structural characterization and insight into supramolecular interactions

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ABSTRACT

Mononuclear aryldithiophosphates of indium(III), $\text{In}[\text{S}_2\text{P}\{\text{OAr}\}_2]_3$; Ar = (3,5- CH_3) $_2\text{C}_6\text{H}_3$ (1), (3,4- CH_3) $_2\text{C}_6\text{H}_3$ (2), (2,5- CH_3) $_2\text{C}_6\text{H}_3$ (3) and (2,4- CH_3) $_2\text{C}_6\text{H}_3$ (4), have been synthesized and characterized by elemental analysis, NMR and FT-IR spectroscopy. Single crystal X-ray crystallography reveals that complex 1 belongs to the monoclinic crystal system with the space group $\text{P}2_1/\text{c}$, wherein the indium ion is six fold coordinated with sulfur atoms of the dithiophosphate moiety resulting in a distorted octahedral geometry. Complex 1 contains intermolecular $\text{C}\cdots\text{H}$, $\text{C}\cdots\text{H}\cdots\text{S}$, $\text{C}\cdots\text{H}\cdots\pi$ and $\pi\cdots\pi$ non-covalent interactions that help in attaining the stability of the molecule. A thorough Hirshfeld surface analysis (HSA) has also been carried out to scrutinize the intermolecular non-covalent interactions present within the molecule and the energetic features are evaluated using density functional theory (DFT) calculations. The non-covalent interaction plot (NCI Plot) index and molecular electrostatic potential (MEP) surfaces have also been used to characterize and rationalize the non covalent $\text{C}\cdots\text{H}$, $\text{C}\cdots\text{H}\cdots\pi$ and $\pi\cdots\pi$ interactions.

1. Introduction

The coordination chemistry of indium compounds derived from thiophosphorous ligands has been a prominent research area for a few decades due to various obvious reasons [1–4]. The inorganic complexes as well as organometallic compounds of indium with 1,1-dithiolate ligands, *i.e.* $\text{In}(\text{S}\cap\text{S})_3$, $[\text{RIn}(\text{S}\cap\text{S})_2]$ and $[\text{R}_2\text{In}(\text{S}\cap\text{S})]$ (where R = Me, Et; $\text{S}\cap\text{S} = \text{RCS}_2$, ROCS_2 , R_2NCS_2 and $(\text{RO})_2\text{PS}_2$), have been reported [2,5–10], which exist as discrete monomers having distorted geometries. The sustained research interest in the chemistry of indium compounds stems from their structural diversity and potential applications as solvent extraction reagents [11] and catalysts [12] as well as their cytotoxicity [13] and other interesting photophysical properties [14–16]. In-S compounds have been used as molecular precursors to develop thin films of indium sulphide [2,5]. However, due to the low volatility of dithiophosphates in comparison to dithiocarbamate complexes, they can have more use as precursors for the growth of In-S nanocrystalline materials by thermolysis in the compound tri-*o*-cetylphosphine oxide (TOPO) [9]. Recently, organo-indium complexes

have shown promising applications in C–C coupling reactions [17]. In the recent past, group 13 metal chelates have been used for the design and development of compounds with high luminous efficiency, since the discovery of the group 13 aluminium complex tris(8-hydroxyquinolinolato) aluminium(III) (AlQ) as an electro-luminescent material used in organic light-emitting diodes (OLEDs) [18]. Inspired by the parent molecule (AlQ₃), sterically bulky ligands have been used to stabilize group 13 metal complexes and enhance the luminescence efficiency [19].

It is revealed that supramolecular non-covalent interactions, such as H-bonds, $\text{CH}\cdots\pi$ and $\pi\cdots\pi$ stacking interactions, engaged in coordination procedures boost the stability of structures [20–22]. Complexes with oxygen and sulfur donor ligands show a remarkable tendency to self-assemble in the solid-state structures through non-covalent bonds, resulting in supramolecular associations [23–28]. Generally, non-covalent (secondary bonds) interactions are not strong enough to survive in the solution phase, but they show remarkable effects in crystal engineering [29–30]. These interactions play an important role in biological systems as they are specific without conferring as much rigidity

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Synthesis, experimental and theoretical analyses of bis(2-ethylphenyl)phosphorodithioates of nickel(II)

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ABSTRACT

Bis(2-ethylphenyl)dithiophosphates of nickel(II) of the composition $[(2-C_2H_5)_6C_6H_4O)_2PS_2]_2Ni$ (1) and $[(2-C_2H_5)_6C_6H_4O)_2PS_2(C_5H_5N)]_2Ni$ (2) were isolated successfully and characterized by experimental and theoretical analyses. Single crystal X-ray diffraction analysis of the complex (2) exhibits that nickel atom is hexa-coordinated with four sulfur atoms of dithio moiety at the equatorial position and two nitrogen atoms of pyridine on axial position. In addition, several non-covalent interactions were also observed that assist to form supramolecular architecture. An exhaustive investigation of the Hirshfeld surface (HS) analysis enables contributions to the crystal packing of the complex (2). The non-covalent interactions were identified using HS and two dimensional finger print plot (2D-FP) analysis. DFT/TD-DFT studies were also used to provide comparable theoretical data along with MEP map and electronic energy gap of HOMO→LUMO.

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1. Introduction

The chemistry of dithiophosphate complexes has a remarkable deal of interest over the past decades. In the realm of synthesis of coordination compounds, dithiophosphates have gained much attention in recent years due to their interesting network architecture, easy synthetic route and the versatile ability to form coordination complexes [1–5]. More recently, dithiophosphate complexes of Zn(II), Cd(II), Hg(II), Ni(II), Co(II), As(III) and Sb(III) have been reported that revealed many interesting bonding possibilities and interesting structural features to the coordination chemist [1–3,6–8]. Dithiophosphates shows wide range of applications such as additives in lubrication oils [9], in agriculture as acaricides or herbicides, insecticides and pesticides [10,11], as fabrication of nanoclusters [12], as rubber vulcanizers [13], and as antiwear and antioxidant additives in motor oils [14]. The resonance between the sulfur atoms assists these ligands to adopt various coordination modes with the metal centres. Because of the versatile ligand binding ability of nickel towards dithio ligands, low toxicity and its availability, the chemistry of nickel(II) dithiophosphates like $Ni[S_2P(OR)_2]_2 \cdot 2L$, (L = 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline), $Ni((RO)_2PS_2)_2$ (R = 2-chloroethyl,

cyclohexyl, 1,1-pentafluorophenylethyl), $Ni[S_2P(C_2H_5)_2]_2 \cdot NC_9H_7$, $Ni[S_2P(OCH_3)_2]_2 \cdot N_2H_8C_{12}$, $Ni[S_2P(OCH_3)_2]_2 \cdot N_2H_{12}C_{14}$ and $Ni((C_2H_5O)_2PS_2)_2 \cdot P(C_6H_5)_3$ etc. have been investigated and broadly studied [15–18]. These compounds are attractive and possess remarkable industrial applications [19]. The research work on coordination compounds, especially nickel is inspired by manifold potential applications such as its role as antioxidants in polyolefin [20], in the field of material science as hydrodesulfurization catalyst and electrochemical activation [21], as longer lasting antistatic agents [22], catalytically active for proton reduction [23], homopolymerization of ethylene [24] and in electronic and magnetic devices [25].

In the context of crystal packing, wider range of intermolecular interactions such as hydrogen bonding, $\pi \cdots \pi$ stacking, cation $\cdots\pi$, anion $\cdots\pi$ and CH \cdots X (X = O, N, S, F, Cl, Br, I) interactions are crucial as these are responsible for stabilizing structure of macromolecules. Among these, hydrogen bonding and $\pi \cdots \pi$ interactions are most important because of their strength and directionality. Although, these interactions are considerably weak but play a decisive role in the chemistry of crystal design and other areas of the molecular science [1,6,26,27]. Supramolecular associations involving π electron system have received great interest due to their pivotal role in the development of functional materials [28]. These interactions play an important role not only in industry but also in the design of homogeneous catalysis and in the construction of

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