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Structure-Directing Interplay between Tetrel and Halogen Bonding in Co-Crystal of Lead(II) Diethyldithiocarbamate with Tetraiodoethylene

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Abstract: The co-crystallization of the lead(II) complex [Pb(S₂CNEt₂)₂] with tetraiodoethylene (C₂I₄) gave the co-crystal, [Pb(S₂CNEt₂)₂]·½C₂I₄, whose X-ray structure exhibits only a small change of the crystal parameters than those in the parent [Pb(S₂CNEt₂)₂]. The supramolecular organization of the co-crystal is largely determined by an interplay between Pb^{..}S tetrel bonding (TeB) and I^{..}S halogen bonding (HaB) with comparable contributions from these non-covalent contacts; the TeBs observed in the parent complex, [Pb(S₂CNEt₂)₂], remain unchanged in the co-crystal. An analysis of the theoretical calculation data, performed for the crystal and cluster models of [Pb(S₂CNEt₂)₂]·½C₂I₄, revealed the non-covalent nature of the Pb^{..}S TeB (-5.41 and -7.78 kcal/mol) and I^{..}S HaB (-7.26 and -11.37 kcal/mol) interactions and indicate that in the co-crystal these non-covalent forces are similar in energy.

Keywords: tetrel bonding; halogen bonding; non-covalent interactions; lead(II) dithicarbamates; QTAIM; NCI

1. Introduction

Non-covalent interactions [1–6] (NCIs) play a key role in the modulation of supramolecular organizations [7–14], which is useful for targeted crystal design [7–9,11,12,15– 19] and the fabrication of functional materials [20], as well as for enhancing catalytic activity [21,22] and reactivity [23–28]. All of these factors contributed to the motivation behind supramolecular chemistry studies utilizing a diversity of NCIs. The understanding of non-covalent forces is uneven with regards to the placement of the donor atoms in the periodic table. In this context, hydrogen- [29,30], halogen- [31–33], and chalcogen [34] bonds were widely studied (and obtained their IUPAC names [30,33,34]) in contrast to other types of non-covalent forces [4,7,35], such as tetrel bonding.

Tetrel bonding (abbreviated as TeB) belongs to the group of interactions that include Group 14 donors (namely, C/Si/Ge/Sn/Pb), whose understanding and applications are very far from exhaustive. Several reviews [35,36] considered the known examples of TeBs that occurred between a tetrel atom (functioning as a σ -hole donor) and a lone-pair possessing atom (acting as a nucleophilic component of the TeB linkage). Most of the recent reports on TeB have been focused on contacts involving carbon atom(s) [35,37–39] or silicon atom(s) [40,41], while TeB including σ -hole-donating tin [42] or lead sites [36,43–47] are still poorly investigated. Notably, before our decade, the ability of lead(II) to act as a

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Copyright: © 2022 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/). Lewis acid in intermolecular contacts was considered in the frameworks of additional coordination contacts, secondary bonding, or semi-coordination [36,48].

The coexistence and combined effects of two or more types of NCIs are important for the rational design of solid materials. Combinations of hydrogen and halogen bonds [49– 55], hydrogen and chalcogen bonds [56,57], and halogen and chalcogen bonds [25,58] in one system and their interplay have been verified, while the combined effects of TeB together with any other kind of NCI are, so far, little explored. In particular, several papers [59–62] outlined the coexistence of Pb···S(N) TeBs with π -stacking and/or hydrogen bonding in solid crystals. An interplay between TeB and hydrogen bonding was studied theoretically for the XCN/4-EF₃-pyridine (X = Cl, Br; E = C, Si, Ge) [63] and NH₃/EF₃X (E = C, Si, Ge, Sn; X = Cl, Br, I) systems [64].

Our recent reports verified various approaches for the supramolecular assembly of transition metal dithiocarbamates and -carbonates with halogen bond (abbreviated as HaB) donors [65–67]. In pursuit of that project, we turned to lead(II) species, where a positively-charged Pb^{II} site could function as a σ -hole-donating component of TeB [35]. The Cambridge Structural Database (CSD) search on the supramolecular organization of various homoleptic lead(II) dithiocarbamates revealed that Pb…S TeB is the main structure-directing interaction of these solid structures. We analyzed these TeB-based contacts in Section 2.1, whereupon in Section 2.2 and Section 2.3 we attempted to verify how another type of σ -hole interaction, namely HaB, affects the structural organization of the dithiocarbamates.

For this work, we used a combination of the lead(II) complex [Pb(S₂CNEt₂)₂] with strong (and potentially tetrafunctional) HaB donors, such as tetraiodoethylene (C₂I₄). The co-crystallization of [Pb(S₂CNEt₂)₂] with C₂I₄ gave the co-crystal, [Pb(S₂CNEt₂)₂]·½C₂I₄, in which, as we observed, the supramolecular organization of the X-ray solid-state structure is largely determined by an interplay between Pb^{...}S TeB and I^{...}S HaB. We found that despite a structure-directing contribution of HaB in the structure of [Pb(S₂CNEt₂)₂]·½C₂I₄, the TeBs from the parent complex, [Pb(S₂CNEt₂)₂], remain unchanged and the co-crystallization with the HaB donor provides only a small change in the crystal parameters. All our findings are consistently detailed in the following sections.

2. Results

2.1. CSD Search: Structural Features of Homoleptic Lead(II) Dithiocarbamates

The supramolecular structure of solid lead(II) dithiocarbamates is determined by the ability of lead(II) sites to form TeB(s). The CSD search revealed 19 structures of [Pb(S₂CNRR')₂], including 15 structures ($R_f \le 5.3\%$) exhibiting monomeric, oligomeric, and polymeric supramolecular motifs (Figure 1). Some complexes of the type [Pb(S₂CNRR')₂] (RR' = CH₂Ph/CH₂CH₂(thienyl-2) AGABOB, (CH₂Ph)₂ QECCAE, and QECCAE01) are monomeric (**A**) without noticeable Pb-involving contacts; in these cases, intermolecular Pb–S distances exceed 4.10 Å (higher than the Bondi radii [68] sum, Σ_{vdw} (Pb + S) = 3.82 Å).

We also identified two types of oligomeric structures. The structure of [Pb{S₂CN(Me)CH₂Ph}₂] (YEDQII) represents a TeB-based tetramer (Figure 1B), in which each of two central molecules are involved in four Pb^{...}S TeBs with two neighboring dithiocarbamate ligands. Another two peripheric molecules are involved in three contacts, each one with a neighboring molecule. A particular case is the structure of [Pb(S₂CNⁿPr₂)₂] (JADJIH), whose supramolecular aggregate consists of the molecular dimer, [Pb(S₂CNⁿPr₂)₂]₂, which exhibits inter- and intramolecular TeBs, and the two mononuclear [Pb(S₂CNⁿPr₂)₂] entities linked to the molecular dimer via four TeBs (Figure 1C).



Figure 1. Supramolecular organization of lead(II) dithiocarbamates: monomeric (**A**) and two tetrameric (**B**,**C**) forms. Hereinafter, short M^{...}S non-covalent contacts are shown by blue dotted lines, polymeric forms: two kind of chains, based on mutual Pb^{...}S contacts (**D**,**E**), 1D head-to-tail chain (**F**), and 1D head-to-tail chain involving Pb^{...}Pb interaction (**G**).

In the structure of [Pb(S₂CNCy₂)₂] (BEQWUQ), each metal atom forms only one Pb^{...} S TeB to give a 1D chain. However, if the other Pb^{...}S long contact (3.94 Å) (which exceeds Bondi Σ_{vdw} 3.82 Å) is taken into account, this pattern might be attributed to chains, where each of the two neighboring molecules forms two mutual Pb^{...}S contacts (Figure 1D). Another architecture of 1D chains (Figure 1E) was observed for [Pb(S₂CNRR')₂] (RR' = ^{*i*}Pr₂ IPTCPB01, Et/Pr NAYNUW and NAYNUW01, Et/Cy XAVYAU), where each complex forms two mutual contacts with the neighboring molecule, thus functioning as a TeB donor in one case and as a TeB acceptor in the other case.

The crystal structures of $[Pb(S_2CNRR')_2]$ (RR' = Me/CH₂Ph HABGAU, (CH₂)₅ JOR-RIU, Me₂ MTCBPB, and Et₂ PBETCA02) display 1D head-to-tail chains (Figure 1F). The 1D chains in the infinite polymeric structure of $[Pb{S_2CN(CH_2)_4}_2]$ (NINDUJ) are based on pentafurcated intermolecular contacts; each contact includes four Pb···S and one Pb^{···}Pb interaction (Figure 1G).

It is clear from the performed CSD search that the supramolecular organization of the crystal structures of lead(II) dithiocarbamates is greatly determined by Pb…S TeBs. These TeBs provide an assembly furnishing either tetrameric or polymeric structures. In some instances, Pb…S contacts are not formed, and the crystal structure motifs are determined by other non-covalent contacts, such as, for instance, H…S hydrogen bonds.

In the context of this study, we analyzed the structure of the parent complex $[Pb(S_2CNEt_2)_2]$ (PBETCA02, 1) employed for the co-crystallization (Section 2.2). This structure belongs to type F (Figure 1), where the complex forms 1D infinite chains determined by the Pb…S TeB. The coordination environment of the lead(II) ion exhibits 4-coordinated distorted pseudotrigonal pyramidal geometry. The Pb–S distances range from 2.7301(17) to 2.9050(13) Å, and the bite angles \angle S–Pb–S are 63.41(3) and 64.68(4)°; the interligand \angle S–Pb–S angles are in the range of 82.92(4)–135.90(5)°. The neighboring complexes are linked via Pb…S TeB [4] (Figure 2): each complex behaves as TeB donor toward two S atoms from a neighboring molecule (either from one or from different ligands), providing two σ -holes at the Pb^{II} center for two Pb…S contacts, and as a TeB acceptor toward another neighboring 1, thereby providing two σ -hole-accepting S atoms.



Figure 2. A fragment of the crystal packing of **1** (PBETCA02) showing Pb^{...}S TeB contacts (dotted lines).

2.2. Crystallizations and Structural Motifs of the XRD Structures

As a next step of our study, we performed the crystallization of **1** with different HaB donors: 1,2-diiodotetrafluorobenzene, 1,4-diiodotetrafluorobenzene, 1,3,5-triiodo-triafluorobenzene, and tetraiodoethylene (C2I4). However, only in the case of C2I4, we

obtained crystals suitable for XRD, namely $1.\frac{1}{2}C_2I_4$. This co-crystal was then studied by single-crystal XRD (see Sections 4.2 and 4.3 for details). The structure of $1.\frac{1}{2}C_2I_4$ is composed by one type of 1 and one type of C_2I_4 . Complex 1 exhibits a 4-coordinated distorted pseudotrigonal pyramidal geometry, which is rather typical for lead(II) dithiocarbamates [69,70]. The Pb–S distances are in the range of 2.7312(9)–3.0200(11) Å, while the bite angles \angle S–Pb–S are 62.04(3) and 66.10(3)°, and the interligand \angle S–Pb–S angles lie in a broad interval spanning from 81.89(3) to 140.23(3)°. The neighboring complexes are linked to each other via mutual Pb^{...}S TeB [4] (Figure 3).



Figure 3. A fragment of the crystal packing of 1.1/2C2I4 showing Pb. S TeB contacts (dotted lines).

Each metal center is involved in two TeBs with two different S sites (Table S2), thus accomplishing an infinite double zig-zag chain (Figure 4). Considering these TeBs, the coordination environment of each lead(II) is thus completed to a distorted octahedral. The S2 and S1 atoms are linked to C₂I₄ via HaB (Figure 5, Table S2). All four iodine atoms of C₂I₄ form HaBs and these contacts join TeB-based zig-zag chains to give a 3D structure.



Figure 4. Intermolecular Pb \cdot S TeB contacts-based double zig-zag chain in the crystal structure of $1 \cdot \frac{1}{2}$ C₂I₄.



Figure 5. A fragment of crystal packing of 1.1/2C2I4 showing I.S HaB contacts (dotted lines).

The search of CSD revealed only one structure of **1** with $R_w < 5\%$ (CSD refcode: PBETCA02; $R_w = 1.75\%$). In PBETCA02, similar to the structure of **1**·½C2I4, the lead(II) site exhibits a 4-coordinated distorted pseudotrigonal pyramidal geometry. The other geometric parameters are also very similar: the Pb–S distances are in the range of 2.7301(17)–2.9050(13) Å, the bite angles \angle S–Pb–S are 63.41(3) and 64.68(4)°, and the interligand \angle S–Pb–S angles span from 82.92(4) to 135.90(5)°. Each metal center forms two Pb[…]S TeBs with the neighboring **1**. Although the 1D chains are the main structural motives of both **1** and **1**·½C2I4, their architectures are different (Figure 6).



Figure 6. Pb…S-based supramolecular organization in the structures of **1** (PBETCA02, left panel) and **1**·½C2I4 (right panel). Short M…S TeB contacts are shown by blue dotted lines.

We performed the Hirshfeld surface analysis [71] for the XRD structures of **1** (PBETCA02) and co-crystal $1 \cdot \frac{1}{2}C_2I_4$ to verify what kind of intermolecular contacts provide the largest contributions to the crystal packing for both structures. For the visualization, we used a mapping of the normalized contact distance (d_{norm}); its negative value enables the identification of molecular regions (red circle areas) of substantial importance for the recognition of short contacts (Figure 7). For both structures, the shortest contacts are represented by Pb^{...}S TeBs, while $1 \cdot \frac{1}{2}C_2I_4$ I^{...}S HaB contacts are also clearly visible, and they provide a substantial contribution.





2.3. Theoretical Calculations

The calculated (PBE [72] -D3 [73]/def2-TZVP [74,75]) electrostatic surface (q = 0.001 e/bohr³) [76] potentials [77–79] for **1** and C₂I₄ are based on the experimentally obtained coordinates and these potentials are positive for the Pb^{II} site and all I atoms (Figure 8), which exhibit σ -holes; the maximum σ -hole potential on the iodine atoms of C₂I₄ is larger than that on the Pb atom in **1** (27.0 vs. 9.8–13.4 kcal/mol).



Figure 8. Electrostatic surface ($\rho = 0.001 \text{ e/bohr}^3$) potentials calculated for 1 (left) and C₂I₄ (right) molecules.

To get a deeper insight into the nature of non-covalent interactions in co-crystal $1.1/2C_{2}I_{4}$, we additionally performed two types of calculations. To model the whole system, the calculations under periodic boundary conditions (*crystal* model) were carried out in

CP2K [80–86] using a PBE [72]-D3 [87] functional and jorge-DZP-DKH [88–91] full-electron basis set with the Douglas–Kroll–Hess 2nd-order scalar relativistic calculations requesting relativistic core Hamiltonian [92,93]. Concurrently, for a more detailed analysis, the *cluster* models were calculated in Gaussian09 [94] using the same PBE [72]-D3 [73] functional and def2-TZVP [75,75] basis set, which contain two molecules of **1** only (two types of clusters accordingly to these TeBs) or the system **1** plus C₂I₄ (also two types of clusters). Both *crystal* and cluster models were based on the experimentally determined coordinates. For a more detailed description, see Computational (Section 4.4).

The QTAIM analysis [95–97] performed for the crystal and cluster models demonstrated the presence of bond critical points (3, –1) (abbreviated as BCP) between the I and S atoms as well as BCPs corresponding to the Pb^{...}S TeB interactions (Table 1). Consideration of the negative and small values of the BCP sign(λ_2)Q(**r**) values indicated the attractive and non-covalent nature of the Pb^{...}S and I^{...}S interactions [98]. The conclusion on the noncovalent nature is based on their close to zero positive energy density (0.000–0.001 hartrees/bohr³) and the balance of the Lagrangian kinetic energy G(**r**) and the potential energy density V(**r**) (–G(**r**)/V(**r**) ≥ 1) on the corresponding BCPs [97]. The same topological parameters (Table S3, the ESI) were found for the Pb^{...}S interactions in crystal and cluster models of **1** and [Pb(S₂CNⁿPr₂)₂] of the CSD PBETCA02 and IPTCPB01 structures, respectively. According to the performed NCI analysis, the surfaces of the reduced density gradient (RDG) [98] with a 0.35 e^{-½} value with assigned negative sign(λ_2)Q(**r**) values on them surround both BCPs of the I^{...}S (Figure 9) and Pb^{...}S (Figure 10) interactions. Hence, the existence of the non-covalent interactions was confirmed by NCI analysis.

Table 1. Parameters in (3, -1) bond critical points (the electron density with sign of $\lambda_2 \operatorname{sign}(\lambda_2)\varrho(\mathbf{r})$ in e/bohr³, Laplacian of electron density $\nabla^2 \varrho(\mathbf{r})$ in e/bohr⁵, the local electronic energy density H_b, local electronic potential energy density V(\mathbf{r}), and local electronic kinetic energy density G(\mathbf{r}) in hartrees/bohr³) corresponding I^{...}S HaBs and Pb^{...}S TeBs in both crystal and cluster models as well as Wiberg bond indexes (WBI) calculated for the cluster model.

	Bond	Model	$sign(\lambda_2)\varrho(r)$	∇²ϱ(r)	G(r)	V(r)	Hь	WBI
	C1S-I1S-S1	crystal	-0.016	0.043	0.010	-0.009	0.001	
_		cluster	-0.016	0.038	0.009	-0.008	0.001	0.08
	C1S-I2SS2	crystal	-0.019	0.046	0.011	-0.011	0.000	
		cluster	-0.018	0.042	0.010	-0.009	0.001	0.10
	S3–Pb1 S1	crystal	-0.019	0.039	0.010	-0.009	0.001	
		cluster	-0.019	0.038	0.010	-0.010	0.000	0.14
	S1–Pb1 S3	crystal	-0.016	0.032	0.008	-0.007	0.001	
		cluster	-0.016	0.032	0.008	-0.008	0.000	0.09



Figure 9. Visualization of QTAIM topological and NCI analyses for the model clusters (1)·(C2I4) with two different I··S HaBs. Blue dots correspond to (3; –1) bond critical points, orange dots to (3; +1) ring critical points, and bond paths are shown as black lines. For non-covalent interactions, RDG = 0.35 e^{-1/3} half-transparent surfaces are colored from blue (sign(λ_2) $\varrho(\mathbf{r}) = -0.015$ e/bohr³) to red (sign(λ_2) $\varrho(\mathbf{r}) = +0.015$ e/bohr³) through white.





Figure 10. Visualization of QTAIM topological and NCI analyses for the model clusters (1)₂ exhibiting two different Pb^{...}S TeBs. Blue dots correspond to (3; –1) bond critical points, orange dots to (3; +1) ring critical points, and bond paths are shown as black lines. For non-covalent interactions, RDG = 0.35 e^{-1/3} half-transparent surfaces are colored from blue (sign(λ_2) ϱ (**r**) = –0.015 e/bohr³) to red (sign(λ_2) ϱ (**r**) = +0.015 e/bohr³) through white.

Wiberg bond indexes [99–101], which were calculated for the I^{...}S HaBs and Pb^{...}S TeBs in the cluster model in the natural atomic partitioning scheme [102,103], are within the 0.08–0.14 range (Table 1). These values are lower than the typical values for coordinative bonds [104,105], but still show some covalent contributions, which are especially noticeable for the S3–Pb1^{...}S1 interactions.

The charge transfer from **1** to C_{2I_4} was evaluated by calculation of the sums of the natural population analysis (NPA) [102,103] atomic charges in the model clusters (**1**)·(C_{2I_4}) (Figure 9), which correspond to two different interactions, where the C_{2I_4} sums are -0.069 and -0.084 e for the C1S-I1S^{...}S1 and C1S-I2S^{...}S2 interactions, respectively.

The electron localization function (ELF) [106–108] projections (useful for the location of shared and lone pair areas), along with QTAIM bond critical points and paths [65,67,109–111] can be employed to reveal electron donating/accepting roles of atoms involved in non-covalent interactions. The projections for the I \cdot S HaBs carried out in the crystal and cluster models (Figure 11) show that the I \cdot S bond paths go through S lone pair areas (with high ELF values; orange zones) and also between I lone pair areas (with low ELF areas; green zones). Thus, the S atoms are electron donating partners toward iodine σ -holes. Correspondingly, the I \cdot S interactions can be treated as HaBs, according to the IUPAC recommendations for the identification of HaB [33].

The same projections (Figure 12) obtained for the Pb^{...}S interactions also demonstrate the Pb^{...}S bond paths lie on the S lone pair areas and far from the Pb lone pair areas. Since TeBs in many respects are analogous to HaBs [112] and Pb atoms behave as an electron acceptor toward sulfur, the Pb^{...}S interactions can be attributed to TeBs.



Figure 11. ELF projections through the Pb–S[…]I planes for the cluster (left) and crystal (right) models. QTAIM Q(**r**) topological pale brown nuclear (3, –3), blue bond (3, –1), and orange ring (3, +1) critical points are drawn with white bond paths and black interatomic zero-flux paths.





The strength of the I^{...}S and Pb^{...}S interactions were calculated as a difference between the energy of a cluster and a sum of the monomer's energies, thereby taking into account the basis set superposition error (BSSE) [113] using a counterpoise procedure. The energies (Table 2) were calculated for the model clusters (1)·(C₂I₄) with the C–I^{...}S interactions or for the (1)₂ clusters with the S–Pb^{...}S TBs. Notably, the TeB energies are comparable with those calculated for the model (1)₂ (–6.90 kcal/mol) and ([Pb(S₂CN[#]Pr₂)₂])₂ (–5.48 kcal/mol) clusters (Figure S1, the ESI) of the CSD PBETCA02 and IPTCPB01 structures, respectively. Notably, the geometrical parameters of non-covalent contacts and energies of HaB and TeB demonstrate a certain relationship. Thus, the normalized contact distances for Pb^{...}S and I^{...}S are comparable and fall into the 0.85–0.88 range, which corresponds to the close dimerization energies spanning from –5.41 to –11.37 kcal/mol.

Cluster Type	Bond	ΔE
(1) (C-L)	I1S S1	-11.37
$(1) \cdot (C_{214})$	I2SS2	-7.26
(1)	Pb1···S1	-7.78 a
(1)2	Pb1···S3	-5.41 a

Table 2. BSSE-corrected dimerization energies ΔE (kcal/mol) for the (1)·(C₂I₄) and (1)₂ heterodimers of two types.

^a—is $\Delta E/2$ values since two Pb^{...}S interactions dissociated from cluster to two monomers.

In summary, the results of the performed theoretical calculations confirmed the existence and the non-covalent nature of the I^{...}S HaB and Pb^{...}S TeB interactions for the crystal and cluster models of 1.1/2C₂I₄. We also revealed the electron donating/accepting roles of the interacting atoms from the ELF and NPA calculations. This attribution is in agreement with the experimental angle parameters of the corresponding interactions. The energies of the I^{...}S HaB and Pb^{...}S TeB interactions span the range from -5.41 to -11.37kcal/mol.

3. Discussion

The results of this study can be considered from at least two perspectives. In a narrow sense, we established that a common feature of the structure of $1 \cdot \frac{1}{2}$ C2I4 is the coexistence and interplay of Pb. S TeBs and I. S HaBs structure-directing interactions. The incorporation of the HaB donor in the crystal structure of 1 to give 1.1/2C2I4 pro-vides, only slightly, an F-to-E type (Figure 6) change of the parent TeB-based supramo-lecular motifs. Regardless of the structural changes that occurred during the co-crystallization, the structure of 1.½C2I4 preserves the Pb^{...}S TeB interactions. The number of Pb^{...}S contacts involving each molecule of 1 and the coordination geometry of the complex remain intact, while the interaction with the HaB donor gives an addi-tional supramolecular motif (Figure 13). As can be inferred from the examination of our results, the TeB bond determines both the structure of the homoleptic lead dithio-carbamate and the co-crystal, and the effects of TeB and HaB are comparable. An analysis of the theoretical calculation data, which were performed for the crystal and cluster models of 1.1/2C2I4 and confirms the non-covalent nature of both Pb. S TeB (-5.41 and -7.78 kcal/mol) and I. S HaB (-7.26 and -11.37 kcal/mol) interactions, as well as indicating that these non-covalent forces are comparable in their energies - while very different in regard to their physical natures.



Figure 13. Changes in the supramolecular organization of 1 occurred by the incorporation of the HaB donor. The Pb^{...}S contacts are shown by blue dotted lines, I^{...}S HaBs are given as black dotted lines.

The results of this work are consistent with those recently reported [69]. In the latter work, we found that the co-crystallization of $[Ni(S_2COEt)_2]$ with 1,4-

diiodotetrafluorobenzene (1,4-FIB) and 1,3,5-triiodotrifluorobenzene (1,3,5-FIB)—to give the co-crystals [Ni(S₂COEt)₂]·2(1,4-FIB) and [Ni(S₂COEt)₂]·2(1,3,5-FIB)—leads to a change in the geometry of the Ni…S contacts, but not to their disappearance. In both cases—adducts of nickel(II) dithiocarbonate and lead(II) dithiocarbamate—correlate with the high thiophilicity of these two metals, which is indirectly manifested in the pronounced ability of nickel and lead to form sulfides.

In a broader sense, our experimental observations and obtained computational data agree well with our recent studies that focused on the various approaches of HaB-involving supramolecular assembly of transition metal dithiocarbamates and -carbonates. These works [68–70] utilized square-planar late transition metal(II) complexes, which can act as dz^2 -orbital nucleophilic components of non-covalent interactions (Figure 14).



Figure 14. Comparison of [M(S₂CNEt₂)₂] (M = Ni, Pd, Pt) and [Pb(S₂CNEt₂)₂] as potential partners of NCIs.

Although the non-transition metal(II) ion in $[Pb(S_2CNEt_2)_2]$ forms four coordination bonds and exhibits a 2+ oxidation state, it is different from the square-planar late transition metal(II) dithiocarbamates. The choice of another metal center, namely Pb^{II} instead of the *d*⁸-metals, affects the types of non-covalent interactions involved in the assembly: a positively-charged lead(II) center behaves as a σ -hole donor and functions as a component of TeB.

From the viewpoint of NCI-based assembly, $[Pb(S_2CNEt_2)_2]$ bears four σ -hole-accepting centers at the S-atoms of the two dithiocarbamate ligands, and in this regard, the lead(II) site is similar to the platinum group metal(II) dithiocarbamates (Figure 14). At the same time, the distinction between the geometries of $[Pb(S_2CNEt_2)_2]$ and $[M(S_2CNEt_2)_2]$ (M = Ni, Pd, Pt) can result in different HaBs distribution, thus providing different supramolecular assembly patterns. The consideration of the structures of the transition and nontransition complexes demonstrated how the identity of metal centers affects the geometry and composition on NCI-based supramolecular assembly of dithiocarbamate or -carbonate complexes.

4. Materials and Methods

4.1. Materials and Instrumentation

Complex **1** was prepared according to the published procedure [69]. Other reagents and solvents were obtained from commercial sources and used as received. The Cambridge Structural Database search was performed by using ConQuest software [114] (version 2022.1.0; access date: 15 March 2022).

4.2. Co-Crystallization

A mixture of $[Pb(S_2CNEt_2)_2]$ (10.0 mg, 0.020 mmol) and C_2I_4 (5.3 mg, 0.010 mmol) was dissolved in dichloromethane (3 mL) under ultrasonic treatment and filtered off through a PTFE syringe filter (0.45 µm) from minor, solid impurities. The reaction mixture was then left to stand at room temperature for slow evaporation. Pale yellow crystals of $1.\frac{1}{2}C_2I_4$, suitable for XRD, were obtained after 4–5 days.

4.3. X-ray Structure Determination

Suitable single-crystals of $1 \cdot \frac{1}{2}C_2I_4$ were fixed on micro-mounts, placed on an Xcalibur, Eos diffractometer (monochromated Mo K α radiation, $\lambda = 0.71073$), and measured at 100(2) K using. Using Olex2 [115], the structure was solved with the ShelXT [116] (structure solution program using Intrinsic Phasing) and refined with the ShelXL [117] refinement package using Least Squares minimization. Supplementary crystallographic data for this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC 2205815) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, accessed on 7 September 2022. The table with the crystal data and structure refinement for $1 \cdot \frac{1}{2}C_2I_4$ can be found in the ESI.

4.4. Computational Details

Single-point DFT calculations based on experimentally determined coordinates with periodic boundary conditions using the Gaussian/augmented plane wave (GAPW) [118] basis set with a 350 Ry and a 50 Ry relative plane-wave cut-offs for the auxiliary grid, the PBE [72]-D3 [73,87] functional, and full-electron jorge-DZP-DKH [88-91] basis for crystal $(1 \times 1 \times 1 \text{ cell})$ models of $1 \cdot \frac{1}{2} C2I_4$, 1 (structure PBETCA02), and [Pb(S₂CN²Pr₂)₂] (structure IPTCPB01) were performed in the CP2K-8.1 program [80–86] with the Douglas-Kroll-Hess 2nd-order scalar relativistic calculations requested relativistic core Hamiltonian [92,93]. The 0.500 r_{loc} parameter was applied for Pb atoms. The 1.0 \times 10⁻⁶ Hartree convergence was achieved for the self-consistent field cycle in the Γ -point approximation. The analogous methodology was previously used for the investigation of the related halogenbonded systems [119]. The gas-phase study for cluster models was performed in the same PBE-D3 level of theory in Gaussian-09 [94] with the def2-TZVP [74,75] basis set. The basis set superposition error (BSSE) for the calculation of interaction energies has been corrected using the counterpoise method [113]. Electron localization function (ELF) [106–108] projection analysis and Bader [95–97] Atoms-In-Molecules topological analysis of electron density (QTAIM) were performed and visualized in Multiwfn 3.8 [120]. A non-covalent interactions (NCI) [101] analysis of the reduced density gradient (RDG) as well as the analysis of the electrostatic surface ($\varrho = 0.001 \text{ e/bohr}^3$) [76] potentials [77–79] (ESP) were carried out in Multiwfn 3.8 and visualized in VMD 1.9.3 [121]. Wiberg bond indexes (WBI) [99–101] in natural atomic partitioning scheme and natural population analysis (NPA) [102,103] atomic charges were calculated for cluster models using GENNBO utility in NBO 7.0 [122] based on 0.47 files generated in Multiwfn 3.8. At the preliminary stage of our work, we conducted several calculations using various functionals. An inspection of our results indicates that the change of functional does not affect the results and it is clear that PBE-D3 is a suitable functional, which is conventionally used in many studies of noncovalent interactions [119,123]

4.5. Details of the Hirshfeld Surface Analysis

HSA was carried out using the CrystalExplorer program [71,124–125]. The contact distances (d_{norm}) [126], based on Bondi vdW radii [68,127], were mapped on the Hirshfeld surface (Figure S2). In the color scale, the negative values of d_{norm} were visualized by red color, thereby indicating the contacts that were shorter than Σ_{vdW} . The values represented in white denote the intermolecular distances that are close to the vdW contacts with d_{norm} equal to zero. In turn, the contacts longer than ΣR_{vdW} with positive d_{norm} values were colored in blue.

5. Conclusions

We found that the co-crystallization of [Pb(S₂CNEt₂)₂] with C₂I₄ gave the co-crystal, [Pb(S₂CNEt₂)₂]-½C₂I₄, in which the supramolecular organization of the X-ray solid-state structure is largely determined by an interplay between Pb^{...}S TeB and I^{...}S HaB. Despite a structure-directing contribution of HaB in the structure of the co-crystal, the TeBs from

the parent complex, [Pb(S₂CNEt₂)₂], remain unchanged and the co-crystallization with the HaB donor provides only a small change of the crystal parameters. An analysis of the theoretical calculation data, performed for the crystal and cluster models of $[Pb(S_2CNEt_2)_2]\cdot^{1}/_{2}C_{2}I_{4}$, revealed the non-covalent nature of the Pb^{...}S TeB (-5.41 and -7.78 kcal/mol) and I^{...}S HaB (-7.26 and -11.37 kcal/mol) interactions and indicated that in the co-crystal, these non-covalent forces are similar in energy. Our experimental observations and appropriate computational data agree well with those reported in our recent studies that focused on the various approaches of HaB-involving supramolecular assembly of square-planar late transition metal dithiocarbamates and -carbonates [65–67]. The consideration of the structures of the transition and non-transition complexes demonstrated how the identity of metal centers affects the geometry and composition of NCI-based supramolecular assembly of dithiocarbamate or -carbonate complexes.

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